KINETICS OF OXIDATION OF SOME AROMATIC HYDROCARBONS BY QUINOLINIUM DICHROMATE

SUMMARY

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SUMMARY

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Hexavalent chromium compounds have been widely used as oxidizing agents, reacting with diverse kinds of organic substrates. The mechanism of oxidation varies with the nature of the chromium(VI) species and the solvent used. The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be a subject of interest. A number of novel chromium(VI) oxidizing agents have been introduced, especially for complex or highly sensitive substances where great selectivity and effectiveness, coupled with mildness of conditions, are prerequisites for success.

Some of the chromium(VI) reagents which have been used as efficient oxidizing agents are:

Chromium trioxide; chromyl chloride; Jones reagent — a solution of Cr(VI) oxide in concentrated sulfuric acid(1); Collins' reagent — dipyridinium Cr(VI) oxide in dichloromethane(2); Corey's reagent — pyridinium chlorochromate(3); pyridine oxodiperoxy chromium(VI) reagent(4); pyridinium dichromate(5); bis tetrabutylammonium dichromate(6); Chaudhuri's reagent — pyridinium fluorochromate(7); 4-(dimethylamino)-pyridinium chlorochromate(8); Cr(VI)

oxide diperoxide(9); Chlorotrimethylsilane-chromium trioxide(10); chromium peroxide complexes(11); imidazolium dichromate(12); pyridinium bromochromate(13); biphosphonium dichromate(14); and 3-carboxy pyridinium dichromate(15).

New procedures have been emerging involving non-aqueous chromium(VI) reagents with the general idea that anhydrous conditions are more conducive to mild oxidation.

The reagent employed in the present investigation, quinolinium dichromate(QDC), $(C_9H_7NH^+)_2Cr_2O_7^{2-}$, has emerged as a very useful and versatile oxidant(16), which is clearly deserving of widespread application.

CHAPTER-I Kinetics of Oxidation of Toluene and Substituted Toluenes

The kinetics of oxidation of toluene and substituted toluenes (xylenes, methoxytoluenes and nitrotoluenes) by quinolinium dichromate(QDC) has been studied in acid medium, using dimethyl formamide as the solvent, under a nitrogen atmosphere. The progress of the reaction was followed spectrophotometrically, by observing the disappearance of chromium(VI) at 440nm. A stoichiometric ratio , Δ[QDC]/ Δ[Substrate], of 1.09 indicated a two-electron transfer. The rate of the reaction was found to be dependent on the first powers of the concentrations of each reactant (substrate, oxidant and acid). The linear increase in the oxidation rate with acidity suggested the involvement of a protonated Cr(VI) species in the rate determining step.

The reaction has been found to be fastest in those solvent mixtures containing the largest proportions of dimethyl formamide. Plots of log k_1 (the pseudo-first-order rate constant) against the reciprocal of the dielectric constant were linear, with positive slopes, indicating an ion-dipole type of reaction. This was also in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated Cr(VI) species.

The effect of changes in temperature on the rate of the reaction has been studied, and the activation parameters have been evaluated. The reactions were characterized by negative entropies of activation. This would suggest an ordered transition state, relative to the reactants. The isokinetic temperature was 359K. Although current views do not attach much physical significance to isokinetic temperatures, a linear correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is usually a necessary condition for the validity of the Hammett equation. Further, the values of the free energies of activation were nearly constant, indicating that the same mechanism operated for the oxidation of all the substrates studied.

The kinetic rates of oxidation were in accordance with the theory of electronic substituent effects. It was found that electron-releasing groups caused an acceleration in the rate of the reaction, while electron-withdrawing groups caused a retardation in the rate of the reaction. A plot of log k_{rel} against σ^+ gave a value of $\rho = -0.20$. For most hydrogen abstraction reactions, the reaction constants (ρ) have small magnitudes.

A kinetic isotope effect, k_H/k_D, was observed in the range 5.0-5.3 for substituted toluenes, which indicated that the rate-determining step involved the cleavage of the carbon-hydrogen bond of the methyl group attached to the arene ring.

There was no induced polymerization of acrylonitrile or the reduction of mercuric chloride. No ESR signals could be detected. These results do not rule out free radical intermediates; they simply do not provide evidence that radicals are formed. This may be due to the high rate of oxidation of the free radicals.

Although the reaction did not give any ESR signals and there was no evidence for the induced polymerization of acrylonitrile or the reduction of mercuric chloride, the possibility of a hydrogen abstraction mechanism cannot be completely excluded. The radical formed initially would react rapidly with the Cr^{5+} species formed in the initial step. The transition state could be considered as involving a carbon atom which would exist with both, radical and carbonium ion character. This resonance hybrid would possess lower energy than either the radical or the carbonium ion, which would account for the stability of the intermediate. Efforts to isolate the possible intermediate, benzyl alcohol, were not successful. This indicated that the intermediate, formed in the slow step of the reaction, was converted rapidly to the product. The only isolable product, in each case, was the corresponding aldehyde, which was characterized as the respective 2,4-dinitrophenyl hydrazone derivative, obtained in good yields. Since drastic conditions of concentrations and temperatures were not employed in the present investigation, only one methyl group (in the case of xylenes) underwent oxidation to give the corresponding aldehyde. There was no formation of acid in any of these reactions, implying that the product (the corresponding aldehyde in each case) was stable, and did not undergo further oxidation, under the experimental conditions employed in this investigation.

CHAPTER 2 Kinetics of Oxidation of Diphenylmethane, Triphenylmethane and Fluorene

The kinetics of oxidation of diphenylmethane, triphenylmethane and fluorene by quinolinium dichromate(QDC) has been studied in acid medium, using dimethyl formamide as solvent, under a nitrogen atmosphere. The stoichiometry of the reaction was determined to be 1:2 (substrate: oxidant). The rate of the reaction showed a first order dependence on the concentrations of each reactant — substrate, oxidant and acid. The increase in the rate with acidity suggested the involvement of a protonated Cr(VI) species in the rate-determining step of the reaction.

With an increase in the dielectric constant of the medium, there was a decrease in the rate of the reaction, which was in consonance with the observation that the use of more polar solvents required larger reaction times.

The rate of the reaction was enhanced, with an increase in the temperature of the medium. The activation parameters have been evaluated.

Conjugation influences and resonance factors seem to play an important role in these oxidation reactions. The observed order of reactivity was:

Fluorene >triphenylmethane> diphenylmethane.
Fluorene was oxidized rapidly, owing to the labile nature of the 9-position. The electromeric effect would be higher in fluorene, which would contribute to a much higher rate of oxidation of fluorene over that for triphenylmethane and diphenylmethane. Steric hindrance due to the triarylmethane group would result in triphenylmethane being oxidized at a faster rate, compared to diphenylmethane.

Structure-reactivity correlations were obtained using the Hammett equation. Electron-releasing groups caused an increase in the rate of oxidation, whereas electron-withdrawing groups caused a retardation in the rate of the reaction. Plots of log k_{rel} against σ were linear, and the values of the reaction constants (ρ) were obtained as -1.50 (fluorenes) and -1.25 (diphenylmethanes). The values of the reaction constants (ρ) indicated that the initial reaction was the abstraction of a hydrogen atom, forming a radical intermediate in the rate-determining step of the reaction.

The kinetic isotope effect, $k_H/k_D=6.0$ for 9,9'-dideuterofluorene, indicated the cleavage of a carbon-hydrogen bond in the rate-determining step of the reaction, yielding a radical intermediate.

The presence of radical intermediates was detected by ESR spectroscopy and by the polymerization tests.

The mechanistic pathway of the reaction involved the formation of a radical intermediate in the slow step of the reaction. The conversion of the radical to the carbocation was rapid, and hence the formation of the carbocation could not be detected. The intermediates, benzhydrol and fluorenol (formed during the oxidations of diphenylmethane and fluorene, respectively) could not be isolated from the respective reaction mixtures. This indicated that the radical intermediate was converted, in rapid steps, to the products.

The major products obtained in these oxidation reactions, in good yields, were benzophenone (from diphenylmethane), triphenylcarbinol (from triphenylmethane), and fluorenone (from fluorene). These products were characterized by analytical and spectral methods.

CHAPTER 3 Kinetics of Oxidation of Polynuclear Aromatic Hydrocarbons

The kinetics of oxidation of polynuclear aromatic hydrocarbons (naphthalene and phenanthrene) by quinolinium dichromate (QDC) has been studied in acid medium, using dimethyl formamide as the solvent, under a nitrogen atmosphere. The stoichiometries of the reactions were determined. The rate of the reaction was dependent on the first powers of the concentrations of each reactant — substrate, oxidant and acid. The first order dependence of the rate on acid concentration indicated that a protonated Cr(VI) species was involved in the rate-determining step of the reaction.

The rate of the reaction was increased, with increasing proportions of dimethyl formamide. Plots of log k_1 against the reciprocal of the dielectric constant were linear, with positive slopes, suggesting an ion-dipole type of reaction.

Increasing the temperature of the reaction medium resulted in an increase in the rate of the reaction. The activation parameters have been evaluated.

Hammett plots of log k_{rel} against the σ values of substituents yielded values of the reaction constants (ρ)

of -1.30 (naphthalenes) and -1.79 (phenanthrenes), indicating the formation of a radical intermediate in the slow step of the reaction.

When the reaction was performed with naphthalene $-d_8$, the rate of the reaction showed a significant decrease, and the k_H/k_D value obtained was 5.80. This indicated a cleavage of the carbon-hydrogen bond in the rate-determining step of the reaction.

The reaction pathway involved a hydrogen abstraction process, resulting in the formation of a radical intermediate, which was detected by the polymerization of acrylonitrile and by the reduction of mercuric chloride.

The products obtained from the oxidation reactions, in good yields, were 1,4-naphthoquinone (from naphthalene), and 9,10-phenanthraquinone (from phenanthrene). These products were characterized by analytical and spectral methods.

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I certify that the thesis entitled "KINETICS OF OXIDATION OF SOME AROMATIC HYDROCARBONS BY QUINOLINIUM DICHROMATE" *submitted by MR. GIRISH CHANDRA SARMA for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the Award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.*

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TO

MY TWO DAUGHTERS

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Girish Chandra Sarma

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CONTENTS

INTRODUCTION

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Oxidation is an essential operation in organic syntheses and several reagents have been developed for a wide variety of transformations(1,2). Hexavalent chromium compounds have been widely used as oxidizing agents reacting with diverse kinds of organic substrates. In the course of these reactions, the Cr(VI) compounds are reduced to the Cr(III) species.

The earliest known Cr(VI) oxidants are chromium trioxide and chromyl chloride. Chromium trioxide has been used in various kinds of reaction media such as water, sulphuric acid, acetic anhydride, t-butyl alcohol and pyridine. Chromyl chloride has been generally used in carbon tetrachloride and carbon disulphide.

In the recent past, a large number of novel Cr(VI) oxidizing agents have been introduced, mostly in response to the needs of mildness and selectivity. The usefulness of "Jones reagent"(3) for the oxidation of organic compounds has been well established.

One of the earliest and most widely employed Cr(VI) oxidants was "Collins reagent" - dipyridinium-Cr(VI) oxide in dichlorometnane(4). The use of dichloromethane as the reaction medium constituted a major breakthrough in oxidation with dipyridinium-Cr(VI) oxide.

For oxidation purposes, the most widely used Cr(VI) complex with pyridine has been pyridinium chlorochromate(PCC) popularly known as "Corey's reagent"(5). Its principal advantage is that this reagent is not air or moisture sensitive, and oxidation with it does not involve handling a large volume of solvent. Studies on the kinetics of oxidation of primary alcohols by PCC have provided important information on the mechanism of the process(6). Involvement of protonated chromium species in the rate determining step was indicated by the catalysis of the reaction by acid, the acid catalysed reaction being first order. PCC does not polymerise acrylonitrile, and a hydrogen transfer hypothesis was thus not tenable. A substantial kinetic isotope effect, $k_H/k_D=5.71$, at 303K suggested a hydride transfer in the rate determining step. The transfer could occur directly between the alcohol and the protonated species or intramolecularly after the initial formation of a chromate ester. A few representative examples of oxidation of primary and secondary alcohols by PCC are given in Table 1.

Table 1. Oxidation of Primary and Secondary Alcohols by PCC (ref.5).

Alcohol	Product	% yield
1-Heptanol	Heptanal	78
1-Decanol	Decanal	92
1,6-Hexane diol	Hexandial	68
Oct-2-yn-1-ol	Oct-2-ynal	84
Citronellol	Citronellal	82
Benzhydrol	Benzophenone	100

The difficulties in handling Collins reagent and the problem arising out of the acidic nature of Corey's reagent were overcome by the use of pyridinium dichromate, $PyCr_2O_7$(PDC), which was recognised as a mild and selective oxidizing agent(7). This reagent is soluble in a number of solvents, though an aprotic medium is necessary for getting satisfactory results. PDC is generally used either in solution in DMF or as a suspension in dichloromethane. Anhydrous conditions were used during oxidation with PDC, and when the oxidation was performed in DMF, the carbonyl compounds were isolated by ether extraction after pouring the reaction mixture in water. PDC shows remarkable selectivity as an oxidizing agent. When dissolved in DMF, it clearly oxidizes allylic alcohols to the corresponding α,β-unsaturated aldehydes in excellent yields.

PDC in dichloromethane oxidized primary and secondary alcohols efficiently. The aldehydes obtained as products from primary alcohols do not undergo further oxidation.

Cr(VI) oxide-3,5-dimethyl pyrazole(8) is a Cr(VI) complex which has been used as an oxidant with mixed success. The reagent is presumed to form a cyclic chromate ester that generates the carbonyl compound through intramolecular elimination. Despite the high yields of some simple aldehydes and ketones from the corresponding alcohols and near quantitative oxidation of geraniol, this reagent proved to be unsatisfactory in a number of cases(9,10).

Pyridine oxodiperoxy chromium, $C_5H_5N:CrO_5$, a complex of chromium pentoxide with pyridine, has also been used for the oxidation of primary and secondary alcohols(11).

In order to protect acid sensitive functional groups during oxidation of alcohols with Cr(VI)oxide, various polar aprotic solvents have been used. At least three such solvents, namely DMF(12), hexamethyl phosphoramide or HMPT(13-15) and dimethyl sulphoxide(16), have been used with some success. A solution of Cr(VI) oxide in DMF containing a trace of concentrated sulfuric acid was able to oxidize alcohols containing acid sensitive protecting groups. The presence of catalytic amounts of sulfuric acid was essential, accompanied by the presence of an ice bath and an inert nitrogen atmosphere. Oxidation with Cr(VI) oxide in HMPT showed excellent selectivity. When a solution of Cr(VI) oxide was added to an equal volume of the substrate dissolved in HMPT, simple axial and equatorial hydroxyl functions were oxidized, the latter at a much faster rate(13). Under the same experimental conditions, Cr(VI)oxide in HMPT was found to oxidize allylic hydroxyl functions in preference to other alcoholic groups(13). A series of primary and secondary alcohols were oxidized in 80-90% yields by a solution of sodium dichromate dihydrate in concentrated sulfuric acid in DMSO at 70°C. DMSO acts as a solvent in these oxidations and not as an oxidant, as shown by the negligible oxidation of the substrate in the absence of dichromate.

The technique of using reagents intercalated in, or adsorbed on, a solid support(17) has also been exploited in oxidations with Cr(VI) oxidizing agents. The solid supports used have included graphite, silica, alumina, silica gel, celite and various reagents. As in the case of other Cr(VI) reagents, attempts were made to achieve mild reaction conditions, better selectivity and convenient isolation of the oxidation products. On heating with graphite under reduced pressure, Cr(VI)oxide was claimed to be uniformly intercalated and the resulting substance was found to oxidize primary alcohols to aldehydes in high yields(18). Later work showed that the oxidizing agent was a surface deposit of Cr(VI) oxide on graphite (19-20).

Chromyl chloride adsorbed on silica-alumina was found to be an effective oxidizing agent for primary and secondary alcohols under neutral non-aqueous conditions (21). It has been reported that chromic acid adsorbed on silica gel was able to bring about the instantaneous oxidation of primary and secondary alcohols(22). Collins reagent adsorbed on celite has been used to oxidize allylic alcohols to the corresponding aldehydes(23-24). Chromic acid supported on an ion-exchange resin has been used to oxidize primary and secondary alcohols(25). This polymer supported reagent is prepared by adding the chloride form of the resin to an aqueous solution of Cr(VI)oxide under stirring. PCC, adsorbed on alumina, has been claimed (26) to be a better oxidizing agent than in dichloromethane suspension. Better efficiency has also been claimed(27) for the oxidation of primary and secondary alcohols using PCC supported on polymer. The reagent, poly[Vinyl(pyridinium chlorochromate)], (PVPCC), is prepared by adding Cr(VI) oxide and concentrated hydrochloric acid to polyvinyl pyridine suspended in water.

Several facile oxidations of secondary alcohols with chromic acid in a two-phase system of ether and water have been reported (28-30). This method has proved particularly suitable for the synthesis of ketones, which are susceptible to epimerization under oxidizing conditions(28).

Cr(VI)oxide in a mixture of ether and dichloromethane oxidizes several secondary alcohols in the presence of celite(31).

There have been several reports on the oxidation of primary and secondary alcohols by Cr(VI) oxidants under phase transfer catalysis(32-36).

Allylic and benzylic alcohols were efficiently oxidized to the corresponding aldehydes with bis-tetrabutyl ammonium dichromate (TBADC) in refluxing dichloromethane(37).

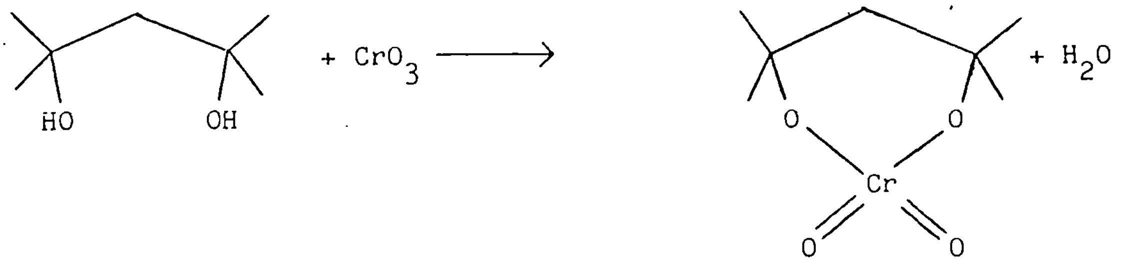
The 2,2'-bipyridine complex of chlorochromic acid is a useful oxidizing agent and the use of this reagent had resulted in simplified procedures for the purification of the resulting carbonyl compounds(38). The 2,2'-bipyridinium chloro chromate and the 2,2'-bipyridine-chromium trioxide complex have both proved to be specially useful in oxidations of compounds with acid-sensitive protecting groups, due to the internal buffering of the 2,2'-bipyridyl system. These results indicated that synthetically useful changes in the properties and reactivity of Cr(VI) reagents could be brought about by varying the amine ligand associated with chromium trioxides. Another Cr(VI) reagent which has proved useful as a mild selective reagent for the oxidation of complex allylic and benzylic alcohols to the corresponding carbonyl compounds was 4-(dimethylamino)pyridinium chlorochromate(39). Secondary alcohols proved to be more reactive towards this reagent than primary alcohols. The ready preparation of this oxidizing agent, its selectivity, and the ease of using this reagent indicated that it may prove to be a useful alternative to other reagents in the oxidation of complex allylic and benzylic alcohols.

Since the process of oxidation in organic chemistry is of great value as a fundamental process in a wide scope of chemical conversions, there has been considerable interest in the development of newer Cr(VI) reagents for the oxidation reactions. Since the appearance of pyridinium chlorochromate(5,40), other similar oxidizing agents have been developed varying the amine ligand associated with the chlorochromate anion.

A Cr(VI) reagent which was found to have certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, short reaction times, and high yield was pyridinium fluorochromate, PFC(41). In dichloromethane as solvent, PFC was found to oxidize primary and secondary alcohols to the corresponding aldehydes or ketones, and was also found to oxidize benzoin to benzil, as also anthracene and phenanthrene to their corresponding quinones(41).

A new class of Cr(VI) reagents derived from chromium trioxide and halosilanes has been developed(42). These reagents are highly efficient for the oxidation of alcohols to carbonyl compounds, for the oxidative coupling of mercaptans into disulphides and for a mild cleavage of oximes to carbonyl compounds. Chlorotrimethylsilane-chromium trioxide has been shown to be an efficient oxidizing agent for the conversion of arylmethanes to benzaldehyde, and for the oxidative cleavage of some benzyl esters(42).

The oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is most frequently accomplished in synthetic practice by the use of Cr(VI) reagents in amounts ranging from stoichiometric to large excess over stoichiometric(43). A new and highly effective reagent combination for the catalytic oxidation of secondary alcohols to ketones has been used(44). The reagent consisted of peroxy acetic acid as the stoichiometric oxidant and the Cr(VI) ester(1) as the catalyst with carbon tetrachloride-methylene chloride mixture as solvent. A solution of Cr(VI) ester(1) was prepared from 2-4 dimethylpentan-2,4-diol and CrO_3 in dry CCl_4.



(1)

The efficient oxidation of alcohols to carbonyl compounds under mild conditions has been a necessary theme in organic syntheses. An improved procedure was described for the extremely rapid and efficient oxidation of alcohols, by the addition of a small quantity of anhydrous acetic acid to pyridinium dichromate(PDC) and freshly activated molecular sieve powder in dichloromethane at room temperature(45).

Chromium peroxide complexes have been used as general oxidants in organic syntheses. 2,2'-bipyridyl chromium peroxide has been used to convert different classes of alcohols to the carbonyl compounds, for C-C bond cleavages in 1,2-diols, for the quantitative decarboxylation of α-hydroxy acids, for the conversion of oximes to their carbonyl compounds, thiols to disulphides, dihydroxy phenolic compounds to quinones, benzylamine to benzaldehyde, aromatic amines to their azo compounds, and for the conversion of anthracene and phenanthrene to their quinones(46). Pyridine chromium peroxide has been used to convert different classes of alcohols to the carbonyl compounds, thiols to disulphides, anthracene to anthraquinone, and for the decarboxylation of mandelic and benzylic acids(46). Chromium peroxide etherate has also been used as an effective reagent for the oxidation of different classes of alcohols to their carbonyl compounds(46).

Imidazolinium dichromate(IDC) has been shown to be very useful and reliable for the oxidation of allylic and benzylic alcohols to the corresponding carbonyl compounds in high yields under mild conditions(47).

The phase transfer catalysed oxidation of benzylic alcohols using benzyltriethylammonium chlorochromate has been reported(48).

Pyridinium bromochromate has been reported as an efficient oxidant for the oxidation of benzyl alcohols, fluorenols and benzoin, all these reactions being performed in chloroform(49).

The biphosphonium dichromate reagent, $(C_6H_5)_3\,P^+CH_2P^+(C_6H_5)_3Cr_2O_7{}^{2-}$, was a particularly mild and selective reagent for the oxidation of primary and secondary alcohols(50). The oxidation of primary alcohols to aldehydes occurs without further oxidation to acid, and without double bond isomerisation or migration for such alcohols as geraniol(50).

The oxidation kinetics of alcohols by pyridinium fluorochromate (PFC) indicated that PFC was an efficient two-electron oxidant which was capable of participating in oxygen-transfer oxidations(51).

3-Carboxy pyridinium dichromate(NDC), readily prepared from nicotinic acid and chromium trioxide, is an efficient reagent for the oxidation of alcohols to carbonyl compounds in the presence of pyridine(52). The optimum molar ratio of substrate:oxidant:pyridine to ensure complete oxidation of starting material in a short reaction time was found to be 1:2.5 : 20 respectively.

The Cr(VI)oxide diperoxide oxidation of organic sulphides(53) and of tertiary amines(54) have been reported. The rate law observed suggested a mechanism involving a preliminary coordination of the amine to the metal. The oxidation rate of the amines and organic sulphides indicated a mechanism having some single-electron-transfer (SET) character.

Quinolinium dichromate(QDC) having the structure, $(C_9H_7NH^+)_2Cr_2O_7^{2-}$, has been used for the oxidation of alcohols and aldehydes(55). QDC is a stable orange solid, which has been prepared by dissolving CrO_3 in water, adding quinoline and collecting the product. It has been shown that quinolinium dichromate(QDC) works as efficiently as Collins' reagent(4) and activated manganese dioxide(56). The data in Table 2 shows the details of the oxidation of some alcohols and aldehydes by QDC in dichloromethane and dimethyl formamide solvents.

Table 2. Oxidation of alcohols and aldehydes by QDC (ref.55)

Compound	Product	Yield (%) In CH_2Cl_2	Yield (%) In DMF
n-Butanol	n-Butanal	69	74
Benzyl alcohol	Benzaldehyde	45	45
Benzhydrol	Benzophenone	55	48
Benzaldehyde	Benzoic acid		55
Cinnamaldehyde	Cinnamic acid		52
Crotonaldehyde	Crotonic acid		85

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SCOPE OF THE PRESENT INVESTIGATION

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The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be a subject of interest. There exists a need for new methods, especially for complex or highly sensitive substances where selectivity and effectiveness, coupled with mildness of conditions, are prerequisites for success. New procedures are emerging, involving non-aqueous chromium(VI) reagents, with the general idea that anhydrous conditions are more conducive to mild oxidation. The reagent employed in this investigation, quinolinium dichromate(QDC), $(C_9H_7NH^+)_2Cr_2O_7^{2-}$, has emerged as a useful and versatile oxidant, which is clearly deserving of widespread application.

The present investigation is a detailed kinetic probe into the oxidation of various organic substrates by quinolinium dichromate (QDC), in acid medium, using dimethyl formamide solvent, under a nitrogen atmosphere. The purpose of this investigation has been to attempt to extend the scope of this oxidizing agent (QDC), in acid medium, and to explore and establish mechanistic pathways of reactions involving organic substrates hitherto not studied so far. The substrates chosen for this investigation have included the following hydrocarbons:

1. Toluene and substituted toluenes
2. Diphenylmethane, triphenylmethane and fluorene.
3. Polynuclear aromatic hydrocarbons (naphthalene and phenanthrene).

For each oxidation reaction, the stoichiometry of the reaction has been determined. The concentrations of substrate, oxidant and acid have been varied, and the effects of these variations on the reaction rates have been studied. The solvent composition has been varied, in order to study the effect of a change in the dielectric constant of the medium on the rate of the reaction. Changes in the temperature of the reaction medium have been made, and the activation parameters have been evaluated. The nature of the reactive species involved in the oxidation process has been suggested. For each reaction, the products have been isolated, and characterized by analytical and spectral methods. The presence of radical intermediates has been confirmed by ESR spectroscopy, polymerization reactions, the Hammett plots and kinetic isotope effects. Based on the observed experimental data, mechanistic pathways for the oxidation of the substrates by quinolinium dichromate(QDC), in acid medium, have been proposed.

EXPERIMENTAL

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Conductivity Water:

Conductivity water was prepared by the following method: tap water was distilled first with alkaline potassium permanganate and then redistilled with Merck "Pro Analysi" sulfuric acid from an all-glass vessel. This sample of double distilled water was further distilled from an all-quartz vessel (Sunvic, U.K.). The conductivity water thus prepared was utilised for the preparation of all the solutions used in the kinetic determinations.

Perchloric Acid:

"Baker Analysed" reagent was used.

N,N-Dimethyl formamide:

Dimethyl formamide was purified by the following method: Anhydrous copper sulphate was prepared by heating copper sulphate ($CuSO_4.5H_2O$) until it turned white. The complete removal of water molecules was checked by its constant weight after repeated heating. Anhydrous copper sulphate was mixed with dimethyl formamide (SDS, AR grade), and the mixture was allowed to stand for 24 hours. The solution was filtered and the filtrate was distilled under reduced pressure (b.p. 153°C). The distillate thus collected was used as the solvent.

Quinolinium dichromate $(C_9H_7NH^+)_2Cr_2O_7^{2-}$

To a stirred solution of CrO_3(100g) in water (100ml) cooled in ice, quinoline (86 ml) was added in small portions. The solution was diluted with acetone (400ml), cooled to -20°C, and the orange solid which separated out was filtered, washed with acetone, dried in vacuo and recrystallized from water (m.p. 160°C). The purity of the compound was further checked by spectral analysis. Infrared spectrum (KBr) exhibited bands at 930, 875, 765 and 730cm^{-1}, characteristic of the dichromate ion.

Substrates:

Toluene, xylenes, fluorene, substituted fluorenes, diphenylmethane, and triphenylmethane were E.Merck samples. Nitrotoluenes were obtained from Koch-Light Laboratories (U.K.). Naphthalene, substituted naphthalenes, phenanthrene and substituted phenanthrenes were BDH samples. All these substrates were purified by distillation or by repeated recrystallizations until their boiling points or melting points, respectively, were in agreement with literature values. The purity of each of the substrates was checked by spectral analysis.

The methoxy toluenes were prepared by the following method:

A solution of 20g of sodium hydroxide in 200ml water and 30g of o-cresol were taken in a 500ml round bottom flask fitted with a separating funnel. The mixture was stirred well and cooled by immersing in an ice bath. 30ml of dimethyl sulphate was taken in the separating funnel and was added to the mixture, dropwise, during one hour, while the mixture was stirred vigorously. The mixture was refluxed, with stirring, for about 2 hours in order to complete the methylation. The mixture was cooled, transferred to a separating funnel, and the lower layer was removed. The upper layer was washed once with water, twice with dilute sulfuric acid, and again with water until the washings were neutral to litmus. The mixture was dried over anhydrous magnesium sulphate and the contents were distilled. The distillate (o-methoxytoluene) was collected at 171°C. The other isomers were prepared by using p-cresol and m-cresol respectively (b.p. of p-methoxytoluene = 174°C; m-methoxytoluene =178°C). The purity of the three isomers was further checked by spectral analysis.

All ir spectra were recorded on an IR-297 (Perkin

Elmer) spectrophotometer, UV spectra on an UV-26 (Beckman) spectrophotometer and nmr spectra on an EM-390 (Varian) 90MHz NMR spectrometer.

The boiling points, melting points and the spectral data obtained for each of the substrates used, are summarized in Table 1.

TABLE 1

Substrate 1	Boiling points or melting points (°C) 2	UV (nm)* 3
Toluene	110	261(H)
p-xylene	137.5	268(H)
o-xylene	144	262(M/W)
m-xylene	139	264 (M/W)
p-methoxy tolune	174	224 (A)
o-methoxy tolune	171	227 (A)
m-methoxy tolune	178	222 (A)
p-nitrotoluene	54 (m.p.)	217,285(A)
o-nitrotoluene	221	202,266,325(W)
m-nitrotoluene	232	203,273,315 (W)
Diphenylmethane	264	260(A)
Benzhydrol	68.5(m.p)	259(CH)
Triphenyl methane	95 (m.p.)	262(A)
Fluorene	117.5 (m.p.)	206,260,301(A)
2-methoxyfluorene	108 (m.p.)	271,303(A)
2-methylfluorene	103 (m.p.)	265,305(A)
2-bromofluorene	114 (m.p.)	260, 290(A)

1	2	3
2-chlorofluorene	96(m.p.)	266,295(A)
2-nitrofluorene	157 (m.p.)	233 (A)
9-fluorenol	152 (m.p.)	270,305(A)
Naphthalene	358 (m.p.)	220,275,301(A)
1-methylnaphthalene	244	220,281(H)
1-methoxynaphthalene	269.5	231,293(cH)
1-nitronaphthalene	61 (m.p.)	333 (A)
phenanthrene	102 (m.p.)	250,293,346(A)
9-methylphenanthrene	90 (m.p.)	252,297,331(A)
9-bromophenanthrene	63 (m.p.)	256,302,334(cH)
9-nitrophenanthrene	116 (m.p.)	207,243,250(A)
9-methoxy phenanthrene	96 (m.p.)	247,274,305(A)

*A=alcohol; W=water; cH=cyclohexane; H=hexane; M/W=methanol-water mixture.

Deuterated Compounds:

All the deuterated compounds used were obtained from Isotopes Inc., USA.

(a) $ArCD_3$($Ar=X-Ph$, where X was $-CH_3$, $-OCH_3$, $-NO_2$). The nmr spectrum of each of the samples in CCl_4 did not show any absorption for the methyl protons.

(b) 9,9-dideuteriofluorene: the nmr spectrum of this sample in CCl_4 did not show the absorption for the protons at the 9-position.

(c) Naphthalene-d_8: nmr analysis did not show the absorption for the proton at the 8-position.

(d) Diphenylmethane-d_2 was prepared by the known method(1), and its purity was checked by nmr analysis.

Acrylonitrile

The monomer (BDH) was washed with 5% sodium hydroxide solution to remove the inhibitor (hydroquinone), and then with 3% orthophosphoric acid to remove any basic impurities. It was then washed with water, dried over anhydrous calcium chloride, and distilled under reduced pressure in an atmosphere of nitrogen. The middle fraction was collected (b.p. 77°C) and used.

Other reagents

All other reagents used were of Analar grade, and were purified before use, and their boiling points/ melting points were checked, and found to agree with those given in the literature.

Kinetic Method:

All the standard flasks and reaction vessels were of pyrex glass with well-ground stoppers. The reaction vessels used were stoppered conical flasks which were painted black on the outside to prevent any photochemical change. All the glass apparatus used were tested for loss of solvent, and the loss was found to be negligible. The standard flasks, reaction vessels and the pipettes used were standardised, using conductivity water, and the correction was found out and applied.

An electrically operated thermostatic water-bath was used. It was provided with sufficient thermal lagging, suitable heaters and stirrers with proper cooling arrangements for continuous work. A xylene-filled regulator, working in conjunction with an electronic relay, was used to maintain the required temperature accurately, with fluctuations of not more than ±0.1°C. The temperatures were recorded by means of an accurate sensitive thermometer, reading to tenths of a degree. The bath-liquid was water, covered with a layer of liquid paraffin to minimise evaporation of water and loss of heat due to radiation.

Spectrophotometers

For absorption measurements, the spectrophotometers used were: (a) Digital spectrophotometer Type 106 (Systronics), and (b) UV26 (Beckman) UV-Visible spectrophotometer.

(a) The Type 106 Digital spectrophotometer was a single beam spectrophotometer having a grating of

600 lines/mm, and a wave length range from 340nm to 960nm. The nominal spectral slit width was 20nm, constant over the entire range. The full scale deflection could be obtained over the wavelength range of 340nm to 600nm. By the addition of a red filter and interchanging of the phototube, the range could be extended to 960nm. In order to ensure maximum sensitivity of the instrument, and to minimize the errors in measurements of optical density due to fluctuations in voltage, the spectrophotometer was connected to the mains through an external voltage stabilizer. This was in addition to the in-built voltage stabilizer within the instrument itself. The light source was a 15 watt tungsten lamp operated by a regulated power supply. The instrument was calibrated, as specified in the instruction manual, over the range of concentrations of K_2CrO_4 in KOH solutions, so as to verify Beer's law at 370nm.

(b) The UV-26 (Beckman) UV-Visible spectrophotometer was a single monochromator, having a filter grating of 1200 lines/mm, and a wavelength range from 190nm to 900nm. This spectrophotometer had a thermostatic control arrangement and the absorbance value was displayed directly on the digital display and on the recorder. Photometric linearity was checked over the range of concentrations of K_2CrO_4 in KOH solutions, as specified in the instruction manual, so as to verify Beer's law at 370nm.

Absorption cells

The absorption cells were of 'Corning' glass and of 8ml capacity for the spectrophotometer Type 106 (Systronics). Quartz cells of 5ml capacity were used for spectral determinations with the UV-26 spectrophotometer (Beckman). All the cells were thoroughly cleaned by aqueous ethanol and acetone, and dried before they were used for the spectral measurements. After the transfer of the solution to the cell, care was taken to see that no solution adhered to the outer surface of the cell. During the measurements, the cells were covered.

Rate measurements

A known amount of the substrate was weighed accurately into a 10ml standard flask, dissolved and made up with the requisite quantities of dimethyl formamide, so as to make the solutions of the required molarity. Quinolinium dichromate was accurately weighed out into a 10ml standard flask, dissolved and made up in dimethyl formamide. Sufficient time was allowed to compensate for any change of heat during dilution. A known volume of perchloric acid was taken in a 10ml standard flask and made up with distilled water so as to make the solution of required strength. The three solutions were separately thermostated at the required temperature for 1 h, under a nitrogen atmosphere. Equal volumes of the two solutions of oxidant and perchloric acid were mixed. An equal volume of the substrate solution was then introduced, and the reaction mixture mixed well. The reaction mixture was homogeneous throughout the duration of the reaction.

The progress of the reaction was followed by observing the disappearance of Cr(VI). Readings were taken at regular intervals of time, by noting the decrease in optical density at 440nm, spectrophotometrically.

All the kinetic experiments were carried out in duplicate or in triplicate, and the rate constants which were determined were found to be reproducible to within ±3%. All reactions were performed under a nitrogen atmosphere. Since the reactions were performed at high concentrations of acid, the ionic strength was not maintained constant.

Calculations

(a) Rate constants:

For all the kinetic determinations, pseudo-first-order reaction conditions have been used, wherein the concentration of the substrate has been taken in a very large excess over that of the concentration of the oxidant.

The pseudo - first -order rate constant, k_1, expressed as sec^{-1}, were calculated from the equation(2):

$$k_1 = \frac{2.303}{t} \log \frac{D_o}{D_t} \qquad (1)$$

where D_o was the initial optical density of the reaction mixture, and D_t was the optical density at time t.

The logarithmic plots of optical density against time were linear, and extrapolation to zero time gave the values of D_o.

The values of the second order rate constant, k_2, expressed in $M^{-1}s^{-1}$, were computed by dividing the pseudo-first-order rate constant (k_1,s^{-1}) by the concentration of the substrate(M).

All values of rate constants were the average of two or more experiments, with agreement being within ±3%.

(b) Thermodynamic activation parameters:

These parameters were determined from a study of the effect of temperature on the rate of the reaction.

The various parameters have been calculated as follows:

(i) Activation energy(E):

From the linear plot of log k_1 against the reciprocal of temperature(T),

$$\text{Slope} = -\frac{E}{2.303\ R}$$

$$E = -\ \text{Slope} \times 2.303\ R \qquad (\text{kJ mol}^{-1})$$

(ii) Enthalpy of activation ($\Delta H^{\neq}$)

$$\Delta H^{\neq} = E - RT$$

(kJ mol^{-1})

(iii) Entropy of activation ($\Delta S^{\neq}$)

$$k_1 = \frac{kT}{h}\, e^{\Delta S^{\neq}/R} \cdot e^{-\Delta H^{\neq}/RT}$$

$$\Delta S^{\neq} = 2.303R\ [\log k_1 + \frac{\Delta H^{\neq}}{2.303\ RT} - \log \frac{kT}{h}]$$

$(\text{J.K}^{-1}\text{mol}^{-1})$

where k is the Boltzmann constant, h is the Planck's constant, and R is the gas constant.

(iv) Free energy of activation ($\Delta G^{\neq}$):

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

(kJmol^{-1})

Stoichiometry

The stoichiometric experiments were carried out under nitrogen at 313K, under the conditions of $[QDC]_o > [Substrate]_o$, at varying acid concentrations. The disappearance of Cr(VI) was followed, until the absorbance values became constant. The $[QDC]_\infty$ was estimated. The stoichiometric ratio, $\Delta[QDC]/\Delta[Substrate]$ was obtained, for each oxidation reaction studied. The individual stoichiometric equations have been shown along with the reactions of each of the substrates with the oxidant.

Product analysis

The reactions were carried out in a manner similar to the kinetic experiments (using an excess of the substrate) and were allowed to proceed to completion, keeping the reaction mixture for about 24 hours, in an atmosphere of nitrogen. The products obtained from the reaction of the various substrates with the oxidant were isolated as follows:

(a) Product from the oxidation of toluene, xylenes, methoxytoluenes, nitrotoluenes, diphenylmethane, triphenylmethane and fluorene:

At the end of the reaction, the reaction mixture was diluted with ice-water saturated with sodium chloride, neutralised with $NaHCO_3$, and was extracted several times with ether. The ether extract was washed with water, dried over anhydrous $MgSO_4$ and then concentrated. The characterization of the products was carried out as follows:

(i) Spotting on TLC plates showed two spots for the products obtained from the oxidation of toluene, xylenes, methoxy toluenes and nitrotoluenes. Separation was effected on an alumina column, using varying proportions (100:0 to 70:30, v/v) of hexane and chloroform as the eluant. The product obtained with lesser proportions of chloroform was tested for the aldehyde by TLC, in the case of toluene and all the substituted toluenes. One spot was obtained when the chromatogram was sprayed with 2,4-dinitrophenyl hydrazine. An aliquot (5ml) was pipetted into 50ml of 2N HCl saturated at 0°C with 2,4-dinitrophenyl hydrazine. The aldehyde was converted to the 2,4-dinitrophenyl hydrazone, which was filtered, washed, dried and weighed. The yields were calculated from the amounts of the 2,4-dinitrophenylhydrazone formed, and were found to vary between 75-85% for all the substrates. The melting points of the corresponding 2,4-dinitrophenylhydrazones were determined after one or more recrystallizations from ether. The corresponding m.p.'s of the 2,4-DNP derivatives thus prepared are shown in Table 2.

Table 2

Substrate	Oxidation product	Melting point (°C) of 2,4-DNP erivatives prepared
Toluene	Benzaldehyde	235
p-xylene	p-tolualdehyde	232
m-xylene	m-tolualdehyde	193
o-xylene	o-tolualdehyde	192
p-methoxytoluene	p-methoxy benzaldehyde	253
m-methoxytoluene	m-methoxy benzaldehyde	244
o-methoxy toluene	o-methoxy benzaldehyde	250
p-nitrotoluene	p-nitro benzaldehyde	318
m-nitrotoluene	m-nitro benzaldehyde	290
o-nitrotoluene	o-nitro benzaldehyde	264

Further proof for the formation of the corresponding aldehyde was obtained by isolating the aldehyde, using the standard method(3). IR analysis gave a sharp band at 1700cm^{-1}, which was characteristic of the carbonyl stretching for an aldehyde group attached to an aryl ring. Two weak bands at 2850cm^{-1} and 2750cm^{-1} were characteristic of the C-H stretching.

The second product, obtained in about 5-10% yield, was a polymeric material, which could not be characterized.

(ii) Spotting on TLC plates showed two spots for the product obtained from the oxidation of fluorene. The crude product was chromatographed on a silica gel column using varying proportions (100:0 to 70:30, v/v) of hexane and chloroform for elution. The product obtained with lesser proportions of chloroform was found to be identical with 9-fluorenone (m.p.=82°C), which was further characterized by IR (absorption at 1750cm^{-1}) and UV analyses (in cyclohexane, absorption at 257nm, 295nm and 378nm). The yield of the product, 9-fluorenone, was ~85%. The product obtained with higher proportions of chloroform was coloured, and could not be analyzed further, since it underwent polymerization. An analysis of the products of the reaction mixture did not show the presence of fluorenol or of any ketal.

(iii) Spotting on TLC plates showed one spot each for the products obtained from the oxidation of diphenylmethane and triphenylmethane.

Product from diphenylmethane: An aliquot (5ml) was pipetted into 50ml of 2N HCl saturated at 0°C with 2,4-DNP. The product was filtered, washed, dried and weighed. The yield was calculated from the amount of 2,4-dinitrophenylhydrazone formed. The melting point was taken after one or more recrystallizations from ether (m.p.=236°C). yield ~85%.

The remainder of the solution was taken in 20ml benzene. The benzene layer was separated, washed with 5% NaOH, then with water, and dried over anhydrous $MgSO_4$. The excess benzene was removed by distillation and the product was collected. On solidification, a white solid was obtained (m.p.=48°C). The IR spectrum exhibited a carbonyl band at $1670 cm^{-1}$ and certain other bands characteristic of benzophenone(4).

Product from triphenylmethane: This product was identified as the tertiary alcohol, triphenylcarbinol. The IR spectrum gave sharp bands, at $3620cm^{-1}$ (O-H stretching), $1360cm^{-1}$ (C-O stretching), and $1150cm^{-1}$(O-H bending), characteristic of triphenylcarbinol. Yield ~80%.

Product from the oxidation of Naphthalene

The reaction mixture was neutralized with $NaHCO_3$, extracted with chloroform, washed with water, dried over anhydrous $MgSO_4$ and concentrated. Spotting on TLC plates showed two spots. The crude product was chromatographed over a neutral alumina column, using hexane and benzene in varying proportions (100:0 to 70:30, v/v) as the eluant. The product obtained with increasing proportions of benzene was found to be identical with 1,4-naphthoquinone (m.p. = 124°C). IR analysis showed sharp bands at 1690 and $1680 cm^{-1}$, characteristic of the carbonyl stretching for polynuclear quinones. There was approximately 60-70% conversion of the naphthalene to the product. The second product was the starting naphthalene (~30%), indicating that the actual yield of the product was higher than the percent conversion.

Product from the oxidation of Phenanthrene

The reaction mixture was cooled, filtered, and washed with water. The solid obtained was suspended in ethanol, 20ml of sodium metabisulfite solution was added, and the mixture allowed to stand for 30 minutes. 50ml of water was added, and the mixture was filtered. To the filtrate, saturated sodium carbonate solution was added. The precipitate was stirred, filtered, and washed with water. The solid obtained (orange yellow needles) was dried over calcium chloride in a desiccator (yield ~60%, m.p.=209°C; product : 9,10-phenanthroquinone).

Tests for Radical formation

Many of the oxidation reactions investigated were observed to proceed via radical intermediates formed in the rate-determining step of these reactions. The presence of these radical intermediates was observed by the following tests:

(a) Reduction of inorganic ions,

$$R. + M^{(n+1)\cdot +} \longrightarrow R^{+} + M^{n+1} .$$

Mercuric chloride was easily reduced by these radicals to insoluble mercurous chloride, which was relatively inert towards reoxidation by the oxidant M^{n+}.

(b) Polymerization of an added olefinic monomer, such as acrylonitrile.

1ml acrylonitrile (0.02M) and 2ml of substrate solution (0.2M) in DMF and $HClO_4$(1.5M) were placed in the lower part of a Thunberg tube(5). 2ml of oxidant solution (0.02M) in DMF was placed in the upper part of the tube. The system was evacuated, and filled with dry nitrogen. The two solutions were mixed and allowed to stand at 313K for 30 minutes. There was the formation of a white opalescence indicating the formation of a polymer. Each experiment was accompanied by a blank control.

ESR measurements

The presence of radical intermediates formed in the slow step of the reaction was detected and confirmed by ESR measurements.

Using the requisite reaction conditions, the radicals were generated, in a flow system (E-4, Varian), by mixing the substrate and oxidant, by volume, in an esr sample tube just outside the cavity of the spectrometer. The mixture was placed under high vacuum, in order to expel dissolved oxygen and the sample tube was placed in the cavity of the spectrometer. The conditions for obtaining the spectrum at 77K were as follows:

Scan range 4000G, field set 3300G, modulation amplitude 6.3G, microwave frequency 9.45GHz, time constant 0.3 sec, scan time 4 minutes.

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DISCUSSION

KINETICS OF OXIDATION OF TOLUENE AND SUBSTITUTED TOLUENES

The oxidation of toluene and substituted toluenes has been studied by several workers, using a variety of oxidizing agents.

Chromium(VI)

Chromic acid has been used to oxidize toluene and substituted toluenes to the corresponding benzoic acids(1-3). The reactions were first order in substrate and second order in oxidant(2). Electron releasing groups favoured the reaction, whereas electron withdrawing groups were observed to retard the rate of the reaction(2,3). Chromic acid was used to convert xylenes to the dicarboxylic acids(4), while the halotoluenes and nitrotoluenes were oxidized to the corresponding acids(5-8). The oxidation of halotoluenes, nitrotoluenes and methoxytoluenes by aqueous sodium dichromate had resulted in the formation of the corresponding acids(9), the yield of the product being generally superior to that obtained with chromic acid. Chromyl acetate has been used to convert halotoluenes(10), nitrotoluenes(11), and xylenes(12) to the corresponding aldehyde acetates. The oxidation of toluenes and substituted toluenes by chromyl chloride had resulted in very high percent conversions of these substrates to the corresponding aldehydes(13-18). The kinetics of oxidation of toluene and substituted toluenes by chromic acid in acetic acid-water mixtures at varying acidities of $HClO_4$ has been reported(19); the ρ value of -1.3 had indicated a radical process, and the oxidation product was the corresponding aldehyde(19). A stepwise mechanism was proposed for the Cr(VI) oxidation of toluene and substituted toluenes, wherein electron withdrawing groups retarded the rate, and electron releasing groups accelerated the rate of the reaction(20).

Permanganate and Manganese(III)

The oxidation of toluene by $KMnO_4$ involved an attack mainly at the methyl group resulting in the formation of benzoic acid(21-22). The three isomeric chlorotoluenes were oxidized by $KMnO_4$ mainly to the benzoic acids in water or acetic acid solution(23), but were degraded to CO_2 in sulfuric acid solution(21). Mn(III) sulfate in sulfuric acid was used to oxidize toluene and p-xylene to benzaldehyde and p-methylbenzaldehyde respectively; no benzoic acid was produced(24). The oxidation of p-methoxytoluene by Mn(III) acetate in acetic acid involved an initial reversible electron transfer, yielding the cation radical(PMT)$^{\bullet +}$ the loss of proton in the slow step gave a radical which was rapidly oxidized to the product, anisyl acetate(25). When substituted toluenes were oxidized by Mn(III) acetate in acetic acid with KBr as catalyst, benzyl acetates were obtained as the products; this was a radical process(26). The kinetics of oxidation of toluene and substituted toluenes by $KMnO_4$, in aqueous acetic acid and phosphate buffer, has been reported; the mechanism involved the reaction of the substrate with MnO_4^- in the rate-determining step to yield the benzylic radical(27). The oxidation of p-methoxytoluene by Mn(III) acetate in acetic acid containing mineral acid, afforded biaryls as the main products(28).

Cobalt(III)

The oxidation of toluene by cobaltic perchlorate in 50% acetonitrile was first order in both reactants, yielding benzaldehyde and benzoic acid as the major products (29,30). In 70% acetonitrile, the oxidation of toluene under nitrogen at 15°C containing 0.77M $HClO_4$ gave benzaldehyde as the major product. p-Nitrotoluene was oxidized very slowly to the aldehyde(29,30). Cobalt(III) acetate in acetic acid has been employed for the oxidation of p-xylene(31,32).

Fe^{2+}/hydrogen peroxide

The oxidation of toluene by Fe^{2+}/hydrogen peroxide (Fenton's reagent) gave bibenzyl and the cresols as the major products(33). At pH 3.6, the corresponding adducts were oxidized to the cresols in 34% yield; at lower pH, the acid-catalyzed elimination of water from the cresols gave bibenzyl in 60% yield(33).

Vanadium(V)

The kinetics of oxidation of toluene and substituted toluenes by V(V) under conditions of high acidities of H_2SO_4, in aqueous acetic acid, was observed to be first order in both reactants(34). Electron withdrawing groups retarded the rate, while electron releasing groups accelerated the rate of the reaction. Structure, solvent and salt influences were taken into account, and a mechanism which involved a two-electron transfer was postulated(34).

Lead tetraacetate

The oxidation of toluene and substituted toluenes by lead tetraacetate gave the corresponding benzylacetates in varying yields(35-38).

Cerium(IV)

The oxidation of p-xylene by ceric sulfate was first order in each reactant, and involved a one-electron transfer to give a free radical and Ce(III) in the rate-determining step; the final product was the aldehyde(39). When toluene and substituted toluenes were oxidized by Ce(IV) in 50% acetic acid, the products were the aldehydes obtained in good yields. It was further postulated that this oxidation could involve either a one-electron step giving a benzylic radical, or a two-electron step giving a carbonium ion and a Ce(II) species(40). The specificity of Ce(IV) had been stressed in the oxidation of toluene and substituted toluenes in acid media, wherein quantitative yields of the respective aldehydes were obtained(41). The oxidation of toluene by ceric ammonium nitrate in dilute nitric acid had yielded benzyl nitrate, but this ester underwent rapid oxidation to the alcohol, and ultimately gave the aldehyde(42). The oxidation of toluene and substituted toluenes by Ce(IV) in acid media gave good yields of the corresponding aldehydes(43,44). The dualistic nature of Ce(IV) was observed in these reactions based on ρ values of -1.7 for electron withdrawing groups, and -4.3 for electron releasing groups(44). A correlation of reactivity with ionization potentials was observed in the oxidation of xylenes by Ce(IV) in acid media(45,46).

Potassium hexacyanoferrate(III)

The oxidation of toluene and substituted toluenes by potassium hexacyanoferrate(III) in acid media, was first order in each reactant (substrate, oxidant and acid), and involved a one-electron transfer to give a free radical, which was converted to the corresponding aldehyde(47).

PRESENT WORK

The present work is a detailed kinetic investigation of the oxidation of toluene and substituted toluenes (having electron-releasing groups and electron-withdrawing groups) by quinolinium dichromate (QDC) in acid medium, using dimethyl formamide as the solvent.

Stoichiometry (vide "Experimental"):

The stoichiometries of all the oxidation reactions were determined. A stoichiometric ratio, Δ[QDC]/Δ [Substrate], of 1.09 was obtained (Table 1).

Table 1. Stoichiometry of the oxidation of toluenes; [Substrate]0.005M, T313K

$[HClO_4]$(M)	0.10	0.20	0.25	0.50
10^2[QDC](M)	2.50	2.60	2.70	2.80
Δ[QDC]/Δ[Toluene]	1.10	1.04	1.14	1.04
Δ[QDC]/Δ[p-Methoxytoluene]	1.03	1.09	1.15	1.07
Δ[QDC]/Δ[p-Xylene]	1.18	1.06	1.10	1.02
Δ[QDC]/Δ[p-Nitrotoluene]	1.11	1.17	1.04	1.08

The stoichiometry conformed to the overall equation:

$$\text{X-Ph-CH}_3 + 2Cr^{6+} + H_2O \longrightarrow \text{X-Ph-CHO} + 2Cr^{4+} + 4H^+ \qquad (1)$$

(X=H, Me, OMe, NO_2)

This envisaged a two-electron transfer, in agreement with Brown's observations(48).

Effect of substrate and oxidant

The rate of the reaction was found to be dependent on the concentrations of both, substrate and oxidant. The order of the reaction with respect to substrate concentration was obtained by changing the substrate concentration and observing the effect on the rate, at constant [QDC] and $[H^+]$. The results have been recorded in Tables 2-4.

Table 2. Rate data for the oxidation of Xylenes in DMF.

[Substrate] (10^2 X M)	[QDC] (10^3 X M)	$10^4 \times k_1^{(s-1)}$			
		p-Xylene	o-Xylene	m-Xylene	toluene
1.0	1.0	3.8	3.5	3.2	3.0
2.5	1.0	9.2	8.8	8.0	7.3
5.0	1.0	18.5	18.0	16.2	14.8
7.5	1.0	27.0	26.5	23.0	21.7
10.0	1.0	38.0	35.0	32.5	30.0
20.0	1.0	75.0	70.0	64.0	60.0
1.0	0.75	3.9	3.4	3.3	3.0
1.0	0.50	3.8	3.5	3.3	3.0
1.0	0.25	3.8	3.5	3.2	3.1
1.0	0.10	3.9	3.5	3.3	3.0

$[HClO_4]$ = 0.75M, T313K.

Table 3. Rate data for the oxidation of methoxytoluenes in DMF.

[Substrate] (10^2xM)	[QDC] (10^3xM)	$10^4 \times k_1(s^{-1})$			
		p-methoxy-toluene	m-methoxy-toluene	o-methoxy toluene	toluene
1.0	1.0	4.4	4.1	3.9	3.0
2.5	1.0	11.0	10.2	9.8	7.3
5.0	1.0	22.5	20.3	19.4	14.8
7.5	1.0	33.2	30.5	29.2	21.7
10.0	1.0	44.0	41.0	39.0	30.0
20.0	1.0	89.0	81.0	77.0	60.0
1.0	0.75	4.3	4.2	3.8	3.0
1.0	0.50	4.2	4.0	3.7	3.0
1.0	0.25	4.0	4.1	3.9	3.1
1.0	0.10	4.4	4.0	3.7	3.0

$[HClO_4]$ = 0.75M, T=313K

Table 4. Rate data for the oxidation of nitrotoluenes in DMF.

[Substrate] 10^2 X M	[QDC] 10^3 XM	$10^4 \times k_1$ (s^{-1}) m-nitro-toluene	p-nitro-toluene	o-nitro-toluene	toluene
1.0	1.0	2.2	2.1	2.0	3.0
2.5	1.0	5.5	5.1	4.8	7.3
5.0	1.0	11.2	10.5	9.9	14.8
7.5	1.0	16.3	15.5	14.6	21.7
10.0	1.0	23.0	21.0	20.0	30.0
20.0	1.0	46.0	42.0	40.0	0.0
1.0	0.75	2.3	2.1	2.1	3.0
1.0	0.50	2.5	2.0	2.0	3.0
1.0	0.25	2.2	2.5	2.0	3.1
1.0	0.10	2.3	2.1	2.3	3.0

$[HClO_4]$ = 0.75M, T = 313K

Plots of k_1, the pseudo-first-order rate constant, against a twenty-fold range of concentration of substrate gave straight lines passing through the origin (Figs.1-3), indicating that the rate of oxidation was dependent on the first power of the concentration of the substrate. This was further seen by the constant values of k_2, the second order rate constant.

Under pseudo-first-order conditions, individual kinetic runs were first order with respect to the oxidant

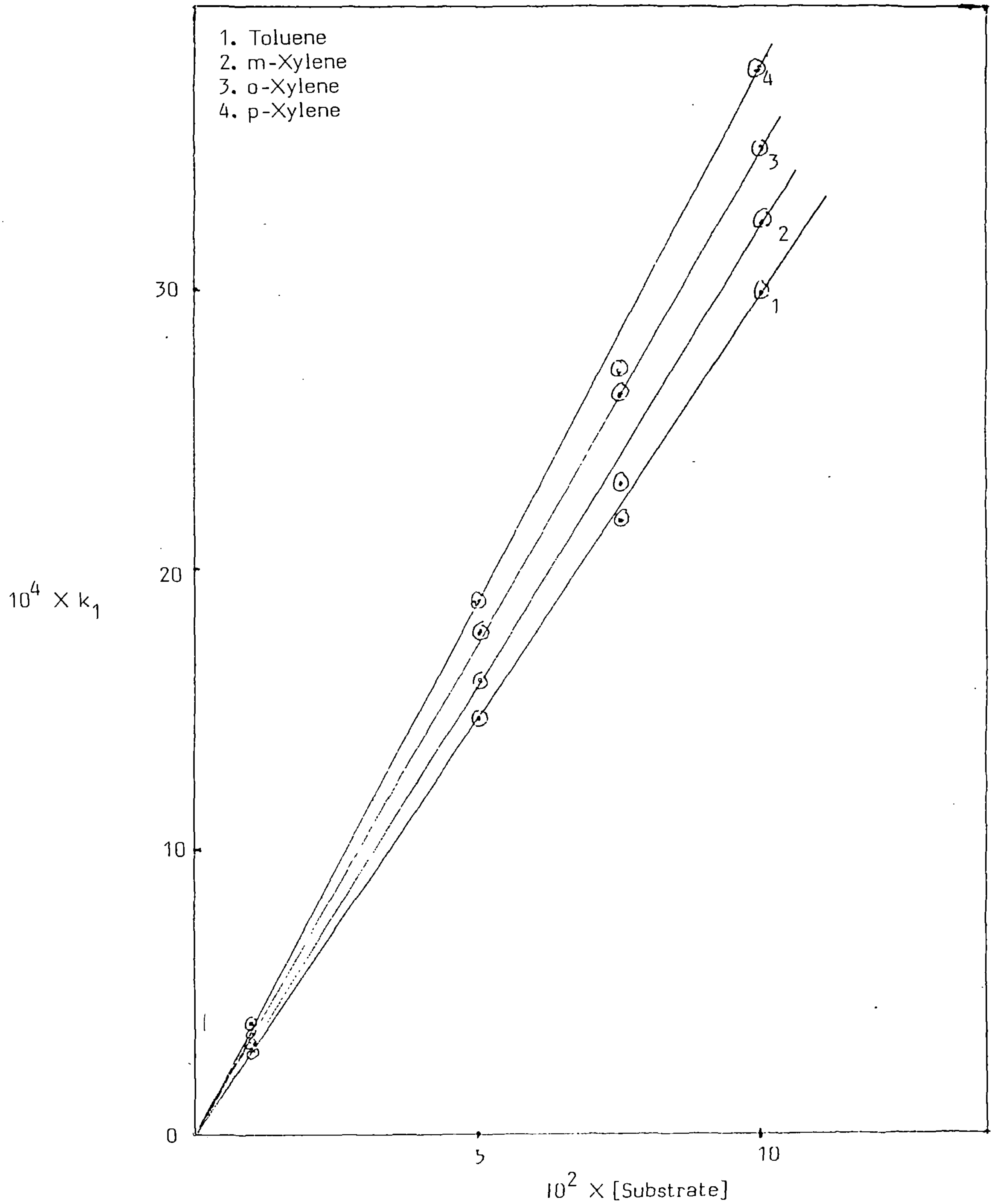


Fig. 1: Plot of log k_1 against substrate concentration (Xylenes).

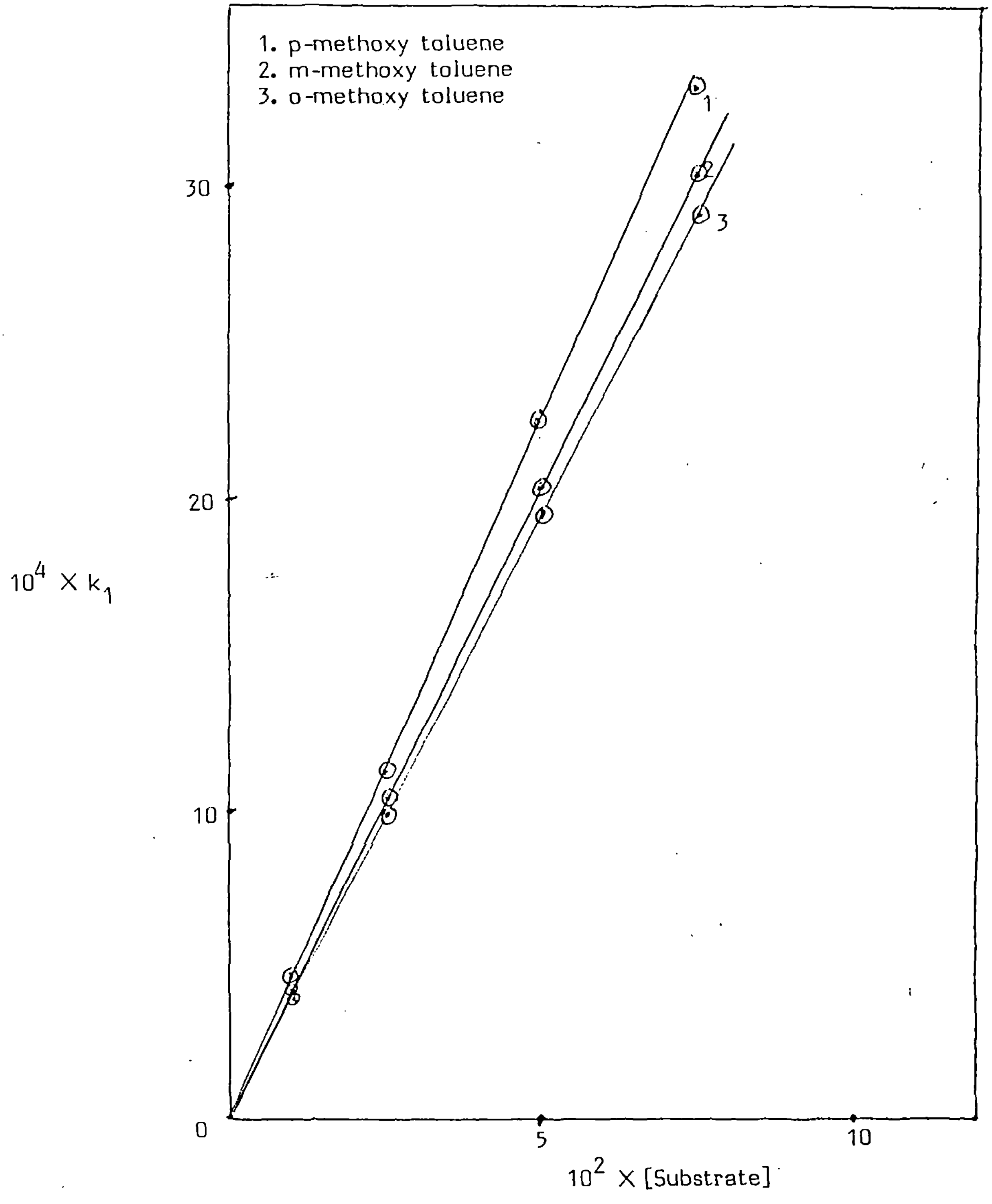


Fig.2: Plot of log k_1 against substrate concentration (Methoxytoluenes)

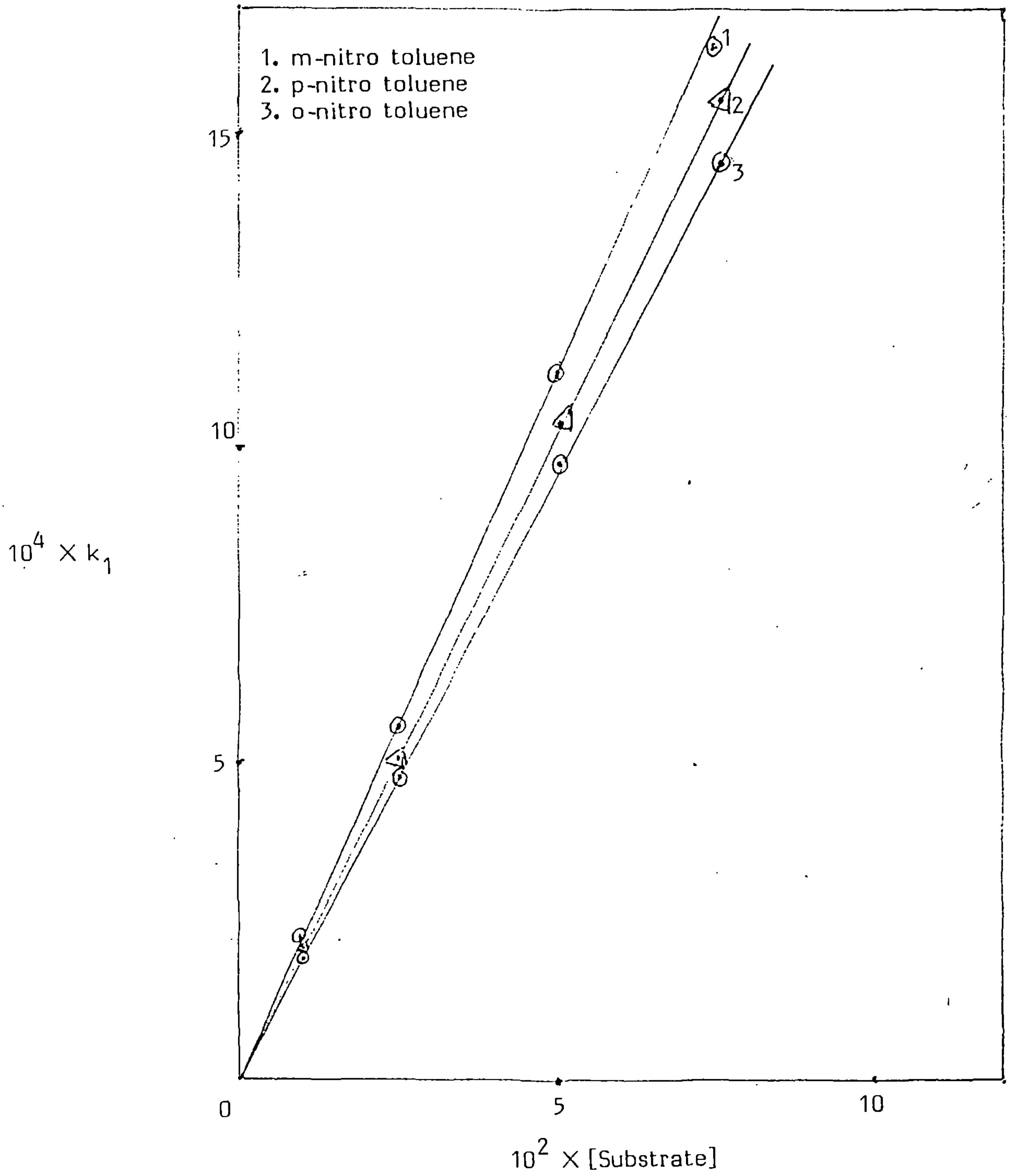


Fig. 3: Plot of log k_1 against substrate concentration (Nitrotoluenes)

(QDC). Further, the pseudo-first-order rate constants(k_1) were independent of the initial concentration of QDC. When a constant concentration of substrate (large excess) was used, k_1 did not show any appreciable variation with the change in concentration of the oxidant, indicating a first order dependence of the reaction on the concentration of the oxidant (Tables 2-4).

Effect of acid

The reaction was susceptible to changes in acid concentration, and the rate was observed to increase with an increase in concentration of the acid (Tables 5-7).

Table 5. Effect of acid on the oxidation of xylenes in DMF.

$[HClO_4]$ (M)	$10^4 \times k_1 (s^{-1})$			
	p-Xylene	o-xylene	m-Xylene	toluene
0.25	1.3	1.2	1.1	1.0
0.50	2.7	2.5	2.3	2.1
0.75	3.8	3.5	3.2	3.0
1.0	5.5	5.0	4.5	4.2
1.25	6.5	6.1	5.5	5.0

[Substrate] = 0.01M, [QDC] = 0.001M, T = 313K

Table 6. Effect of acid on the oxidation of methoxytoluenes in DMF

$[HClO_4]$ (M)	$10^4 \times k_1 (s^{-1})$ p-methoxy-toluene	m-methoxy-toluene	o-methoxy-toluene	toluene
0.25	1.5	1.4	1.3	1.0
0.50	3.0	2.8	2.6	2.1
0.75	4.4	4.1	3.9	3.0
1.0	6.1	5.5	5.1	4.2
1.25	7.6	6.9	6.5	5.0

[Substrate] = 0.01M; [QDC] = 0.001M; T = 313K

Table 7. Effect of acid on the oxidation of nitrotoluenes in DMF.

$[HClO_4]$ (M)	$10^4 \times k_1 (s^{-1})$ m-nitro-toluene	p-nitro-toluene	o-nitro toluene	toluene
0.25	0.8	0.7	0.6	1.0
0.50	1.6	1.4	1.2	2.1
0.75	2.2	2.1	2.0	3.0
1.0	3.3	2.7	2.4	4.2
1.25	4.3	3.4	3.0	5.0

[Substrate] = 0.01M; [QDC] = 0.001M; T = 313K.

Plots of log k_1 against $\log[H^+]$ were linear with slopes equal to unity (Figs.4-6), indicating that the rate of the reaction was dependent on the first power of the concentration of the acid.

The linear increase in the oxidation rate with acidity suggested the involvement of a protonated Cr(VI) species in the rate determining step. There have been earlier reports of the involvement of such Cr(VI) species in chromic acid oxidations (49a). Protonated Cr(VI) species have been observed in the presence of p-toluenesulfonic acid in nitrobenzene-dichloromethane mixtures(50).

Rate law

Under the present experimental conditions, wherein pseudo-first-order conditions have been used for all the kinetic runs, the observed rate law can be expressed as:

$$\text{Rate} = -\frac{d[\text{Cr(VI)}]}{dt} = k[\text{Substrate}]\,[\text{QDC}]\,[H^+] \; . \qquad (2)$$

Effect of solvent

Reactions involving an ionic reactant are susceptible to solvent influences. It is hence to be expected that in the present investigation, the solvent should

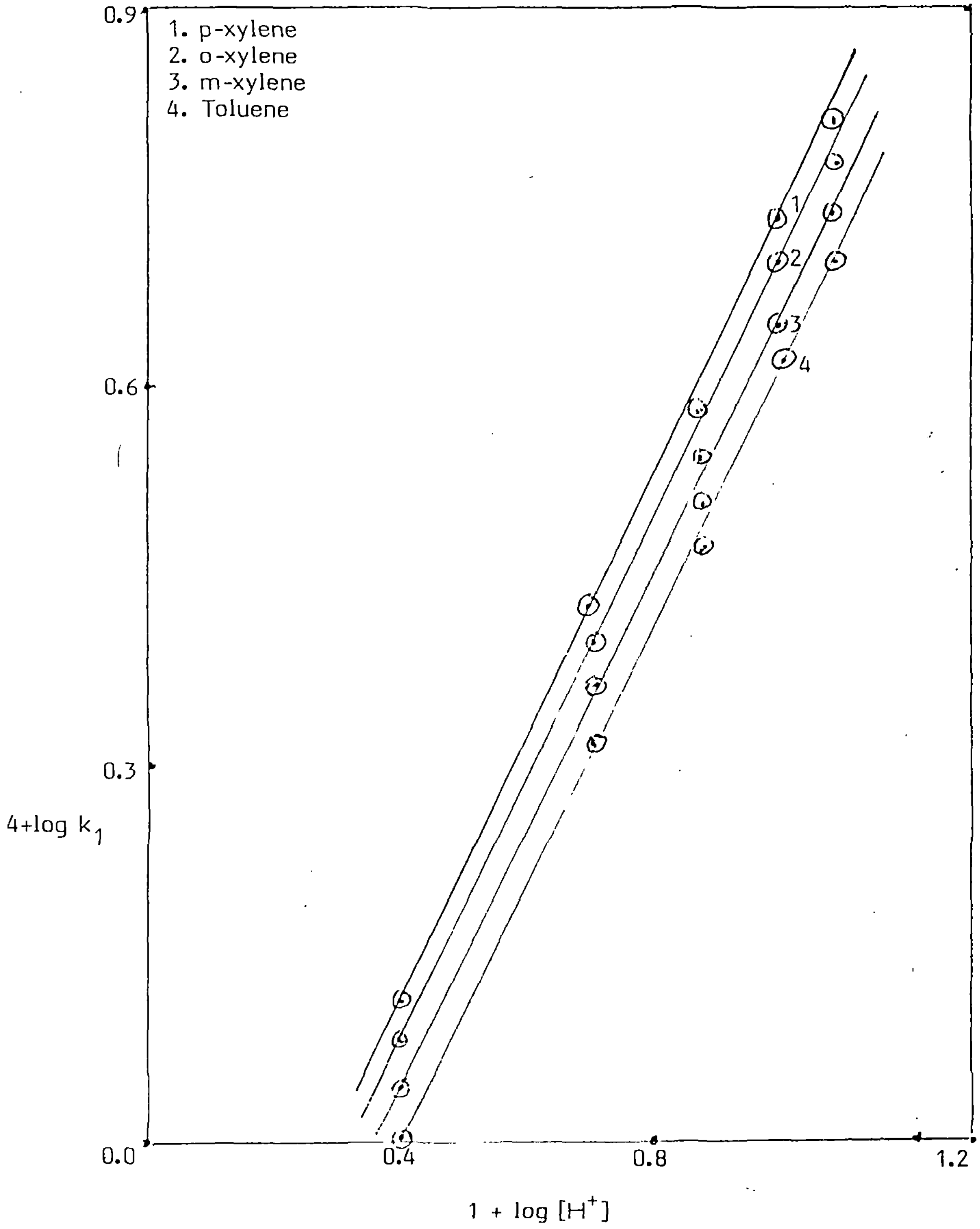


Fig.4: Plot of log k_1 against log$[H^+]$ (Xylenes)

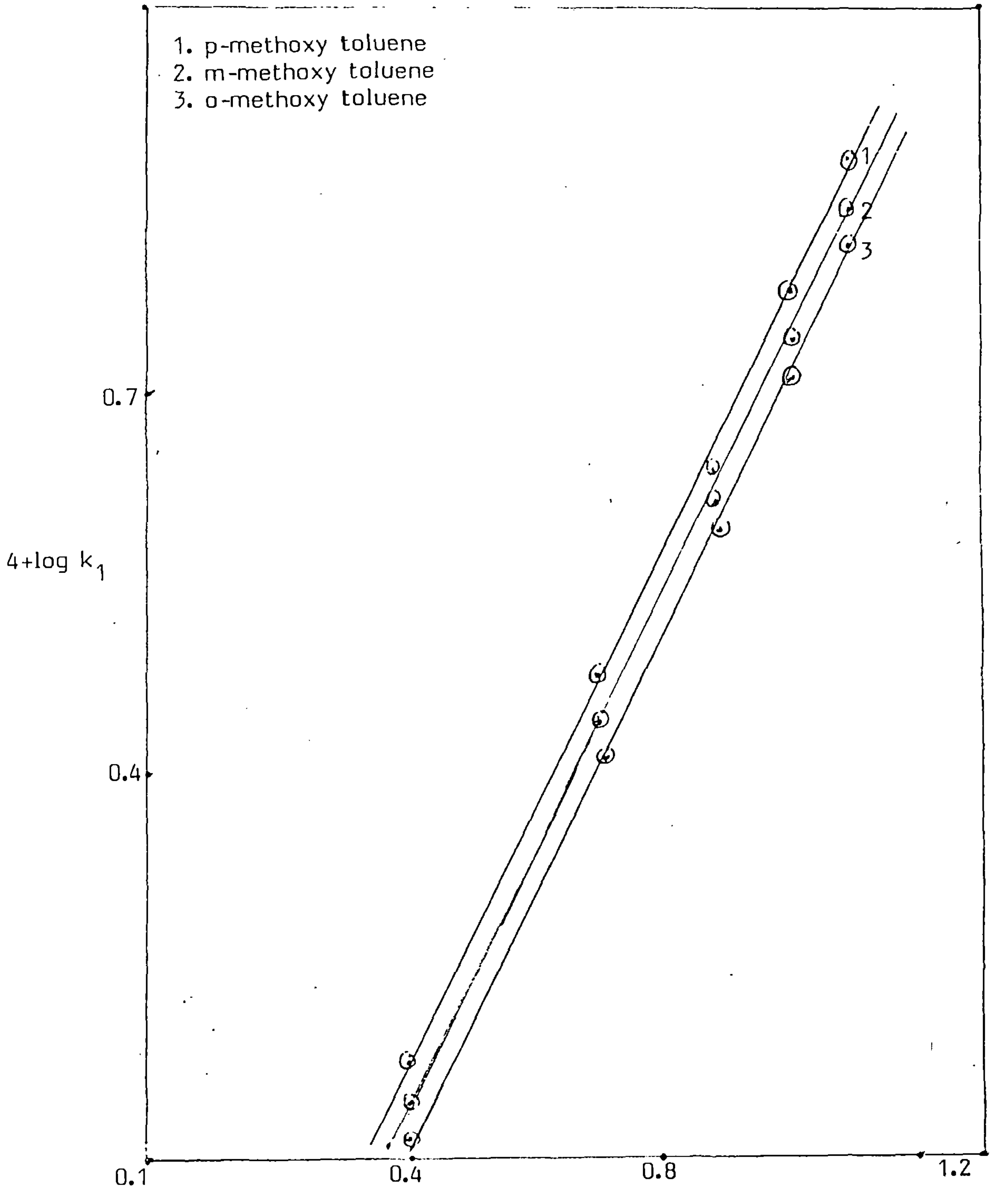


Fig.5: Plot of log k_1 against log [H^+] (Methoxytoluenes)

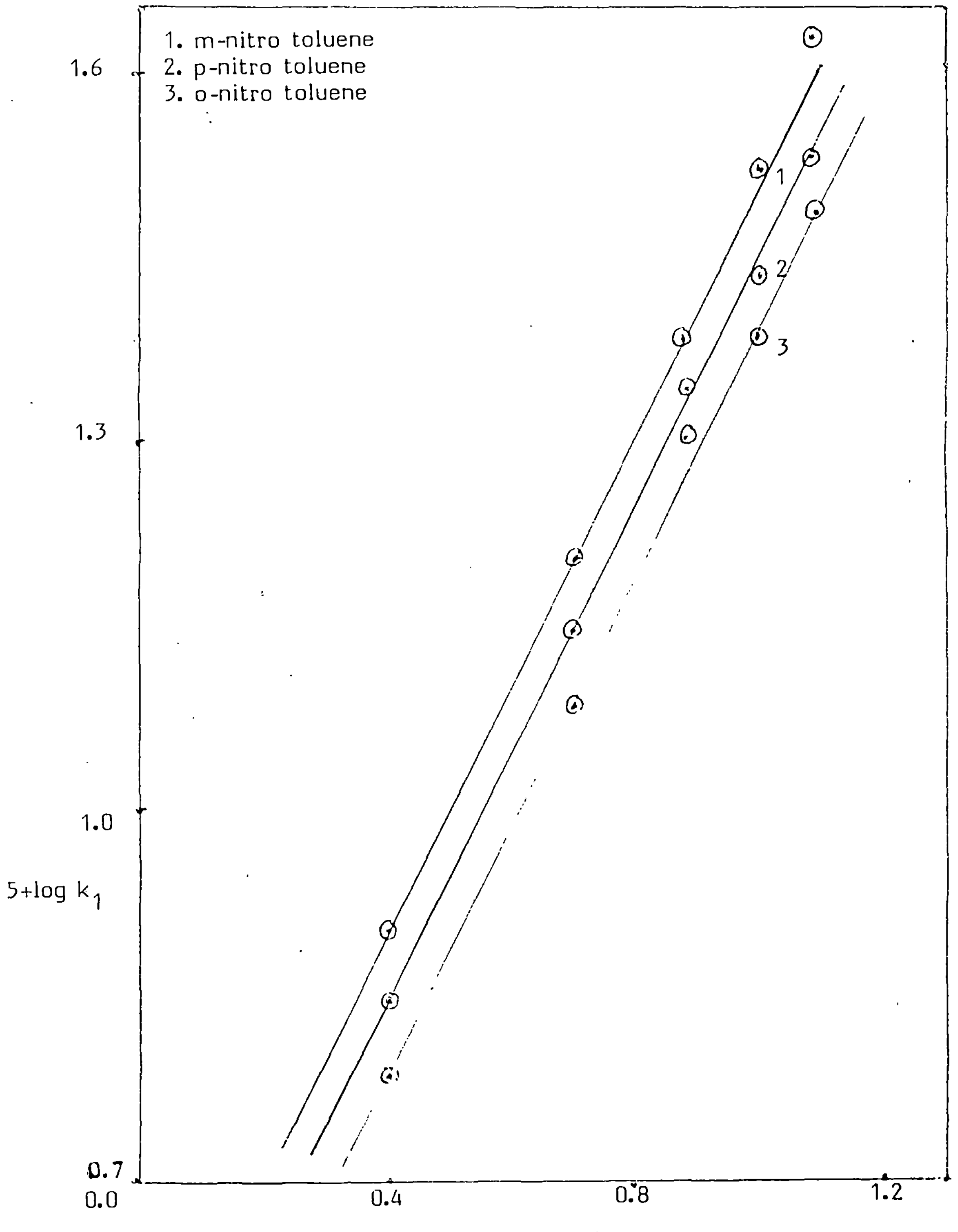


Fig.6: Plot of log k_1 against log $[H^+]$ (Nitrotoluenes)

be playing an important part. In the case of each of the substrates oxidized by quinolinium dichromate, the rate of oxidation was slowest in those solvent mixtures that contained the largest proportions of water, and *increasing proportions of dimethyl formamide resulted* in an increase in the rate of oxidation (Tables 8-10).

Table 8. Effect of solvent on the oxidation of xylenes.

DMF : H_2O (v/v)	$10^4 \times k_1(s^{-1})$			
	p-Xylene	o-xylene	m-xylene	toluene
100:0	3.8	3.5	3.2	3.0
95:5	3.5	2.6	2.4	2.3
90:10	3.0	2.2	2.0	1.9
85:15	2.4	1.9	1.8	1.7
80:20	2.2	1.7	1.6	1.5

[Substrate]=0.01M, [QDC]=0.001M, $[HClO_4]$=0.75M, T = 313K.

Table 9. Effect of solvent on the oxidation of methoxytoluenes.

DMF : H_2O (v/v)	$10^4 \times k_1(s^{-1})$			
	p-methoxy-toluene	m-methoxy-toluene	o-methoxy-toluene	toluene
100 : 0	4.4	4.1	3.9	3.0
95 : 5	3.9	3.4	2.9	2.3
90 : 10	3.5	2.9	2.4	1.9
85 : 15	3.1	2.5	2.0	1.7
80 : 20	2.8	2.3	1.8	1.5

[Substrate]=0.01M, [QDC]=0.001M, [$HClO_4$]=0.75M, T=313K

Table 10. Effect of solvent on the oxidation of nitrotoluenes.

DMF : H_2O (v/v)	$10^4 \times k_1(s^{-1})$			
	m-nitro-toluene	p-nitro-toluene	o-nitro-toluene	toluene
100 : 0	2.2	2.1	2.0	3.0
95 : 5	2.0	1.8	1.7	2.3
90 : 10	1.8	1.6	1.5	1.9
85 : 15	1.6	1.4	1.3	1.7
80 : 20	1.4	1.2	1.1	1.5

[Substrate]=0.01M, [QDC]=0.001M, [$HClO_4$]=0.75M, T=313K.

The dielectric constants for DMF-Water mixtures have been estimated from the dielectric constants of the pure solvents(51).

In the present investigation, in going from 80% DMF to 100% DMF, the polarity decreases. This decrease in the polarity of the medium caused an increase in the rate of the reaction (Tables 8-10). Plots of log k_1 against the reciprocal of the dielectric constant were linear (Figs.7-9), with positive slopes. This suggested an interaction between a positive ion and a dipole(52), and was in consonance with the observation that in the presence of an acid, the rate determining step involved a protonated Cr(VI) species.

On the basis of the solvating power of the solvent, a correct prediction of a qualitative nature can be made of the rate of the reaction in different solvent media. In the present investigation, the transition state is less polar than the initial state (reactants), because of the increased dispersal of charges in the transition state. This would indicate that the extent of solvation of the transition state was less than that for the reactants, thus agreeing with the assumptions of Hughes and Ingold(53). Therefore, the decrease in the rate of oxidation on the addition of a more polar

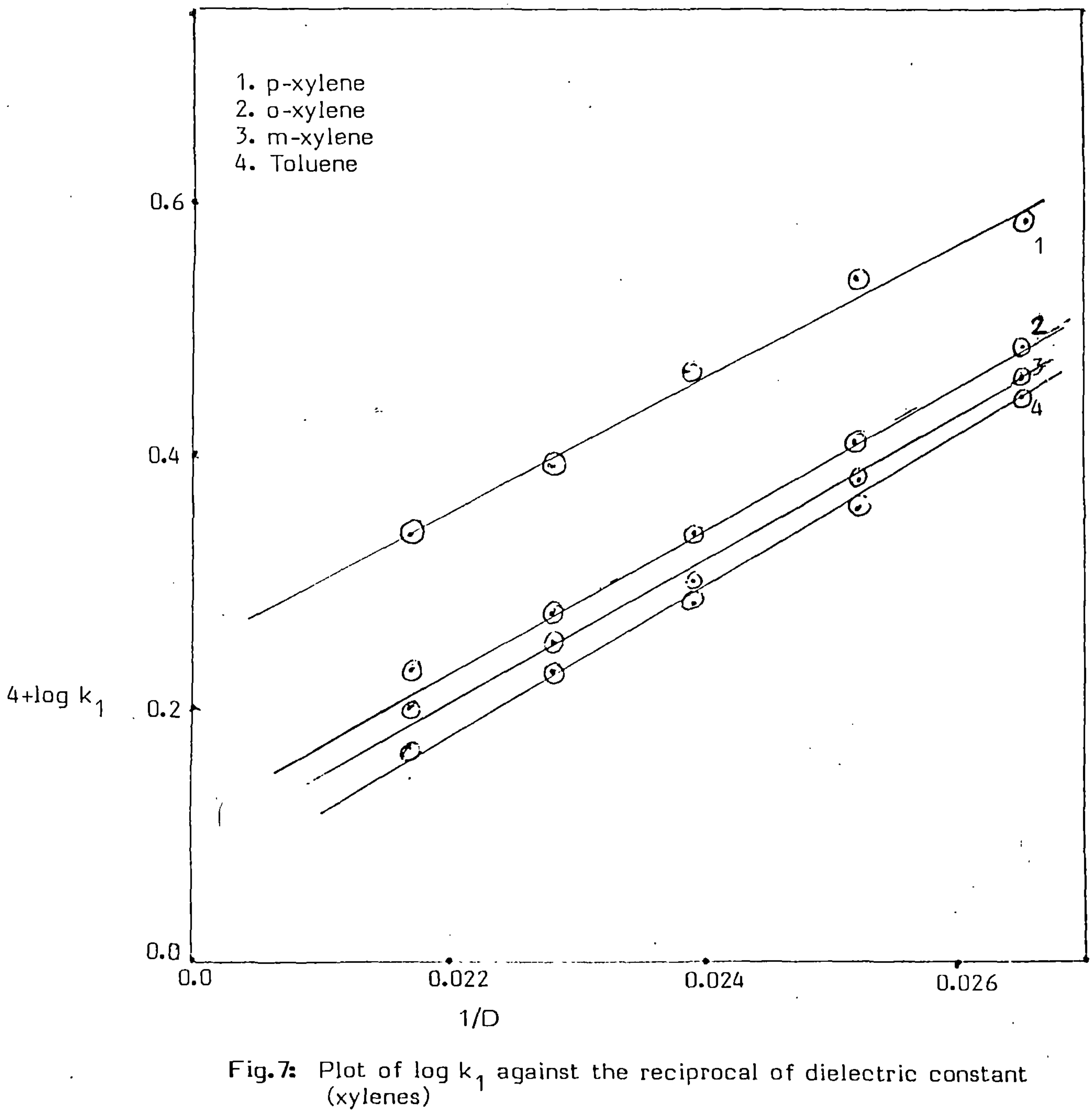


Fig.7: Plot of log k_1 against the reciprocal of dielectric constant (xylenes)

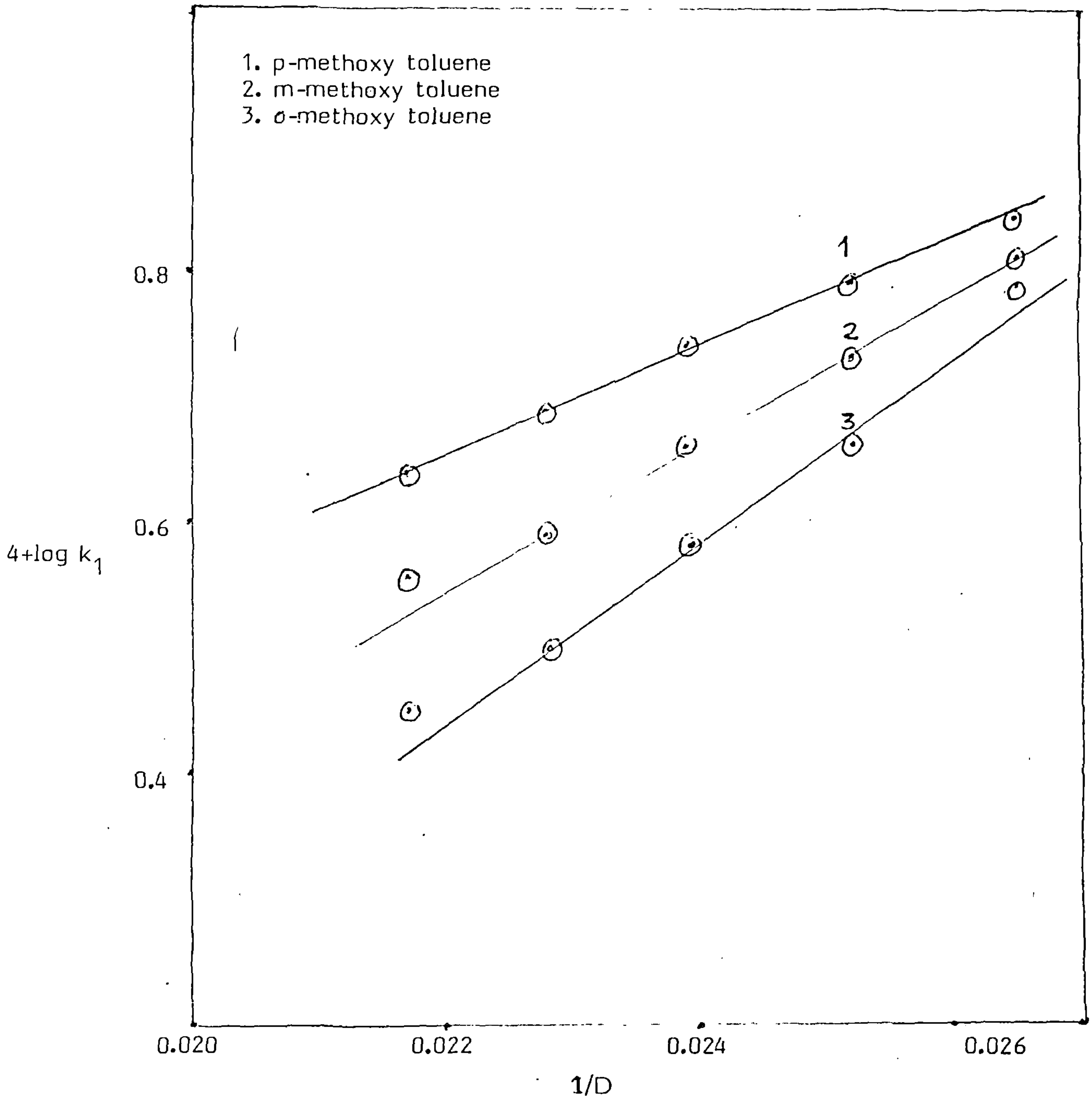


Fig.8: Plot of log k_1 against the reciprocal of dielectric constant. (Methoxy toluenes)

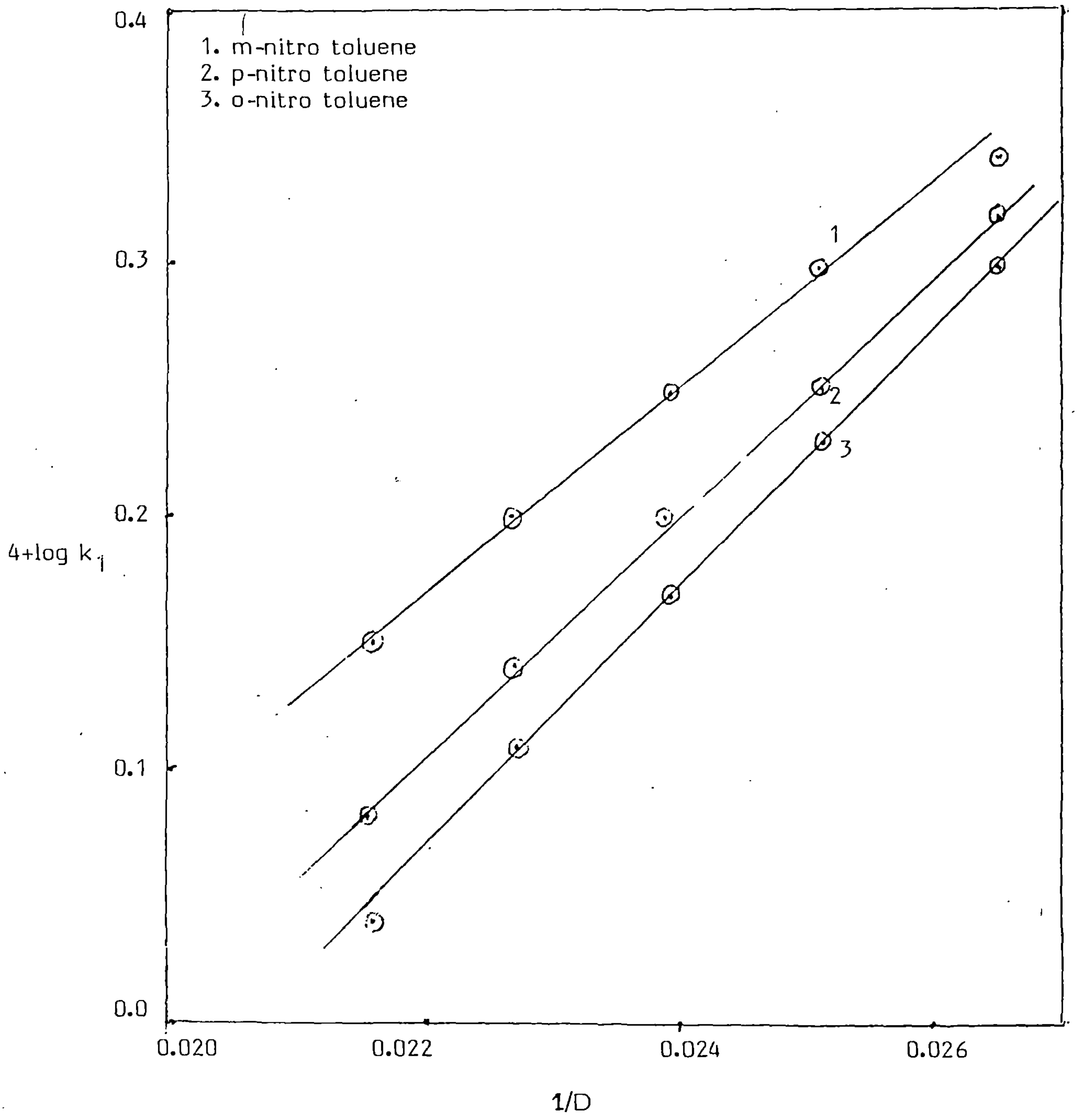


Fig.9: Plot of log k_1 against the reciprocal of dielectric constant (Nitro toluenes)

solvent, as in the present investigation, is a natural result of the progressive increase in solvation of the reactants more than that of the transition state. The effect of a change in the solvent composition on reaction rates would also depend on factors such as solvent-solute interactions(54,55), and on solvent structure.

Effect of Temperature

The rate of the reaction was influenced by changes in temperature (Tables 11-13).

Table 11. Effect of temperature on the oxidation of xylenes in DMF.

Temp [±0.1K).	$10^4 \times k_1(s^{-1})$ p-Xylene	o-xylene	m-xylene	toluene
303	1.9	1.5	1.3	1.1
308	2.9	2.6	2.4	2.1
313	3.8	3.5	3.2	3.0
318	5.4	4.8	4.4	4.5
323	8.0	7.2	6.7	6.7

[Substrate]=0.01M, [QDC]=0.001M, $[HClO_4]$=0.75M

Table 12. Effect of temperature on the oxidation of methoxytoluenes in DMF.

Temp (±0.1K)	$10^4 \times k_1(s^{-1})$			
	p-methoxy-toluene	m-methoxy-toluene	o-methoxy - toluene	toluene
303	2.1	1.8	1.7	1.1
308	3.0	2.8	2.6	2.1
313	4.4	4.1	3.9	3.0
318	5.9	5.3	5.1	4.5
323	8.2	7.9	7.7	6.7

[Substrate]=0.01M, [QDC]=0.001M, $[HClO_4]$=0.75 M

Table 13. Effect of temperature on the oxidation of nitrotoluenes in DMF.

Temp (±0.1K)	$10^4 \times k_1(s^{-1})$			
	m-nitro-toluene	p-nitro-toluene	o-nitro-toluene	toluene
303	0.8	0.7	0.5	1.1
308	1.4	1.3	1.2	2.1
313	2.2	2.1	2.0	3.0
318	3.5	3.3	3.1	4.5
323	5.2	4.9	4.7	6.7

[Substrate]=0.01M, [QDC]=0.001M, $[HClO_4]$=0.75M.

Plots of log k_1 against the reciprocal of temperature were linear (Figs.10-12), suggesting the validity of the Arrhenius equation. The slopes of the plots were used to calculate the activation energies of the reactions (vide 'Experimental':Calculations). The other activation parameters have been evaluated and have been shown in Table 14.

Table 14. Activation parameters.

Substrate	E (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1}mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
Toluene	67	64	-109	98
p-xylene	54	51	-149	98
o-xylene	62	59	-122	97
m-xylene	64	61	-117	98
p-methoxytoluene	51	48	-153	95
m-methoxytoluene	58	55	-132	96
o-methoxytoluene	60	57	-127	98
m-nitrotoluene	73	70	-94	99
p-nitrotoluene	75	72	-89	100
o-nitrotoluene	76	73	-85	100

Error limits $E \pm 2$ kJ mol^{-1}, $\Delta H^{\neq} \pm 2$ kJ mol^{-1}

$\Delta S^{\neq} \pm 3$ JK^{-1} mol^{-1}, $\Delta G^{\neq} \pm 2$ kJ mol^{-1}

The oxidations of all the substrates were characterized by negative entropies of activation. This would suggest an ordered transition state relative to the reactants(56).

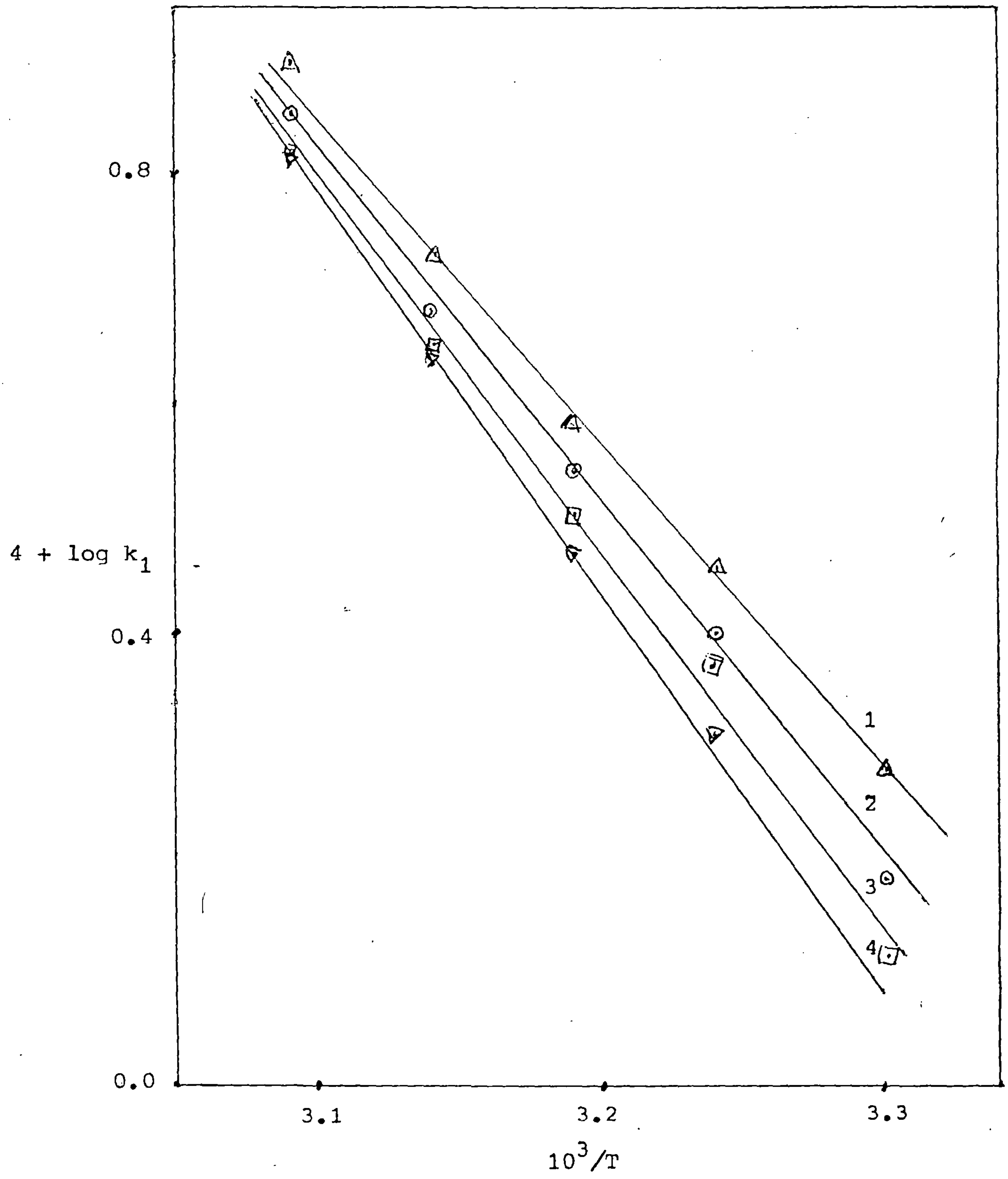


Fig. 10 - Plot of log k_1 versus inverse of temperature (1: p-xylene; 2: o-xylene; 3: m-xylene; 4: toluene)

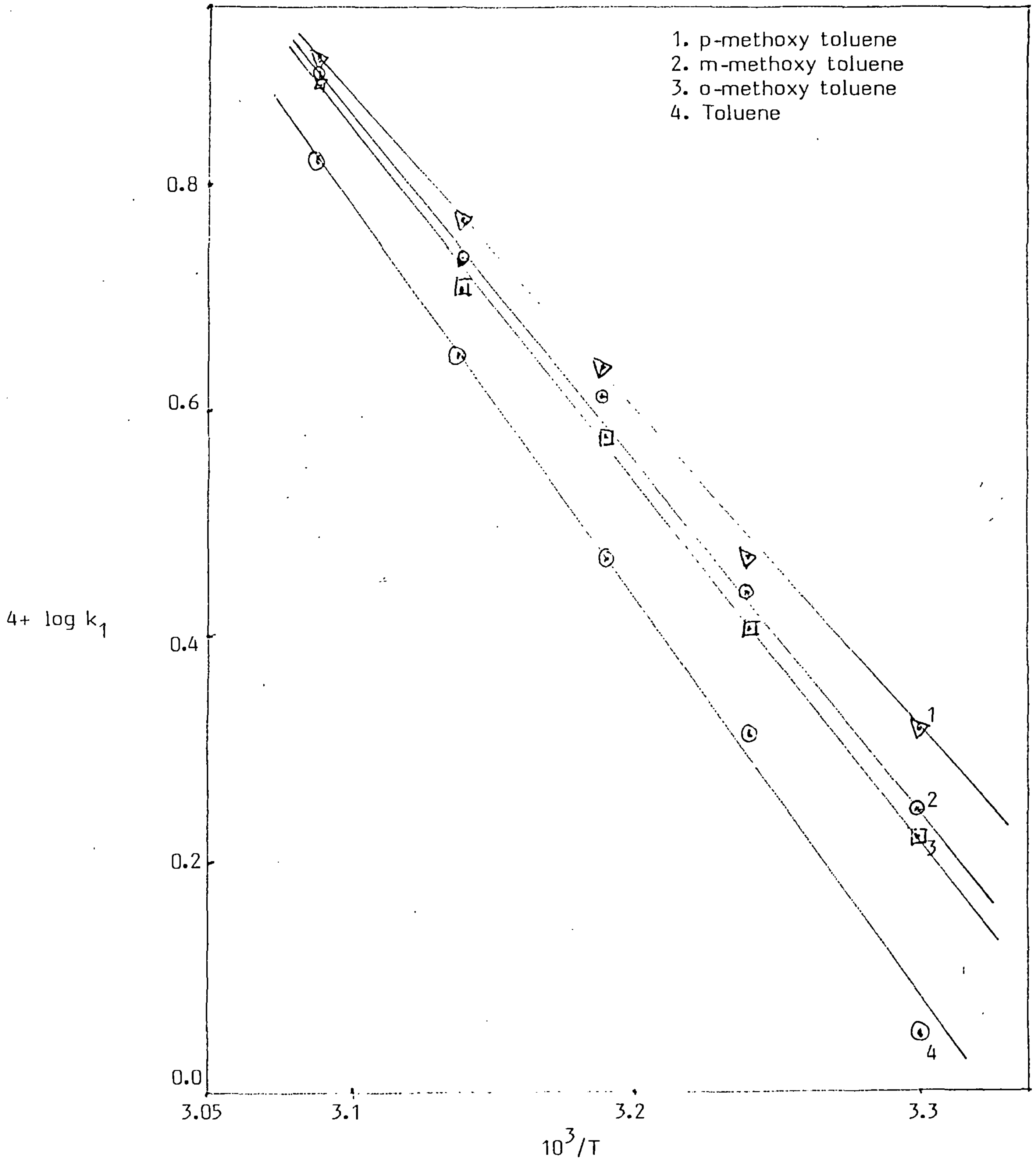


Fig.11: Plot of log k_1 against inverse of temperature (Methoxy toluenes).

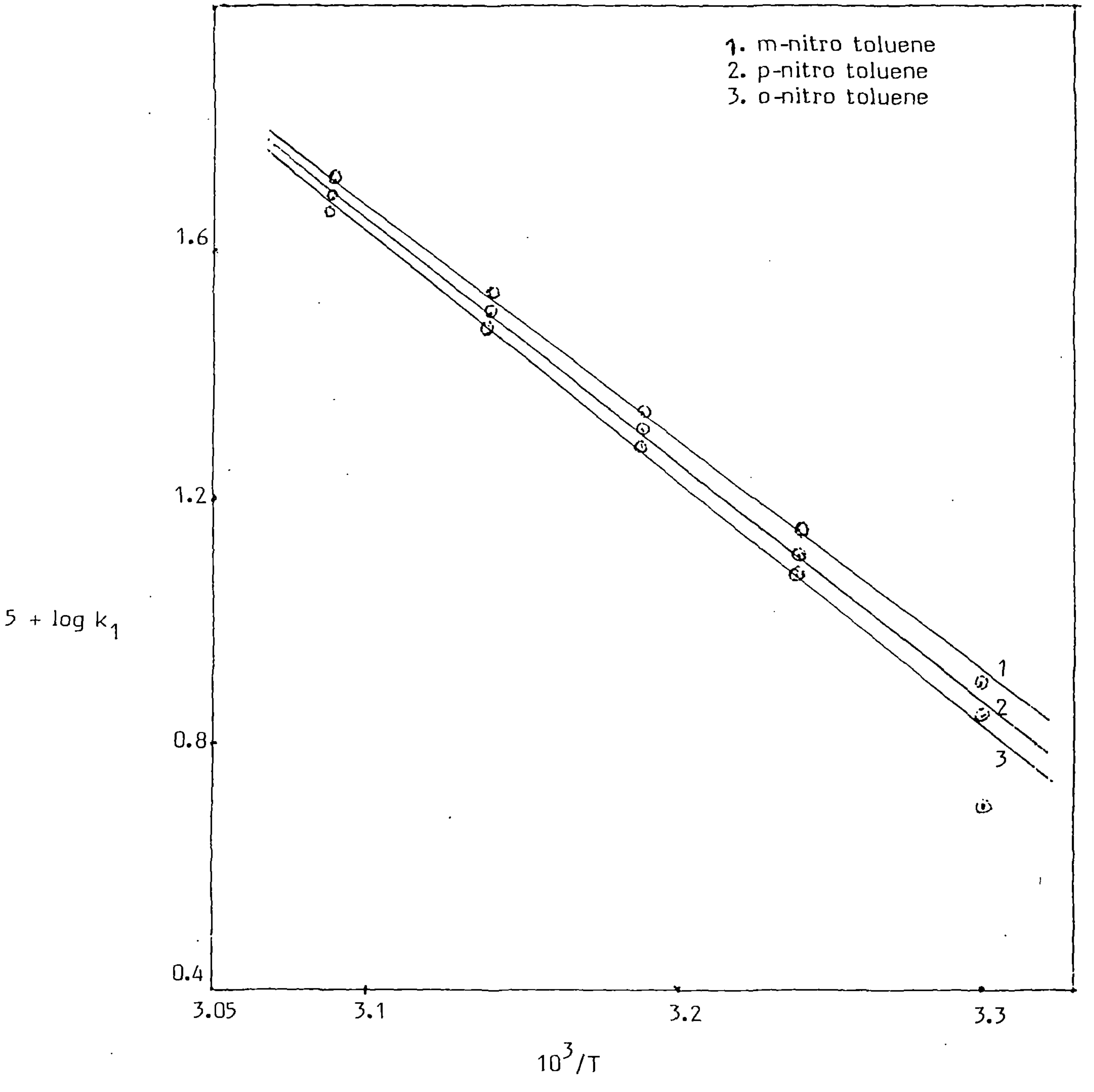


Fig.12. Plot of log k_1 against the reciprocal of temperature (Nitro toluenes).

Differences in solvation of substrates in the ground state and transition state might also contribute to some extent to the negative entropies of activation(57).

Isokinetic Relationship:

The enthalpies and entropies of activation for a reaction are linearly related by the equation

$$\Delta H^{\neq} = \Delta H_{o}^{\neq} + \beta \Delta S^{\neq} \qquad (3)$$

where β is the isokinetic temperature. For these oxidation reactions, the activation enthalpies and entropies were linearly related. The correlation was tested and found to be valid by applying Exner's criterion(58). The isokinetic temperature, obtained from the plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$, was 359K (Fig.13). Although current views do not attach much physical significance to isokinetic temperature(59), a linear correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is usually a necessary condition for the validity of the Hammett equation. Further, the values for the free energies of activation ($\Delta G^{\neq}$) were nearly constant, indicating that the same mechanism operated for the oxidation of all the substrates studied.

Structural influences on the rate of oxidation

Since structure-reactivity correlations give an

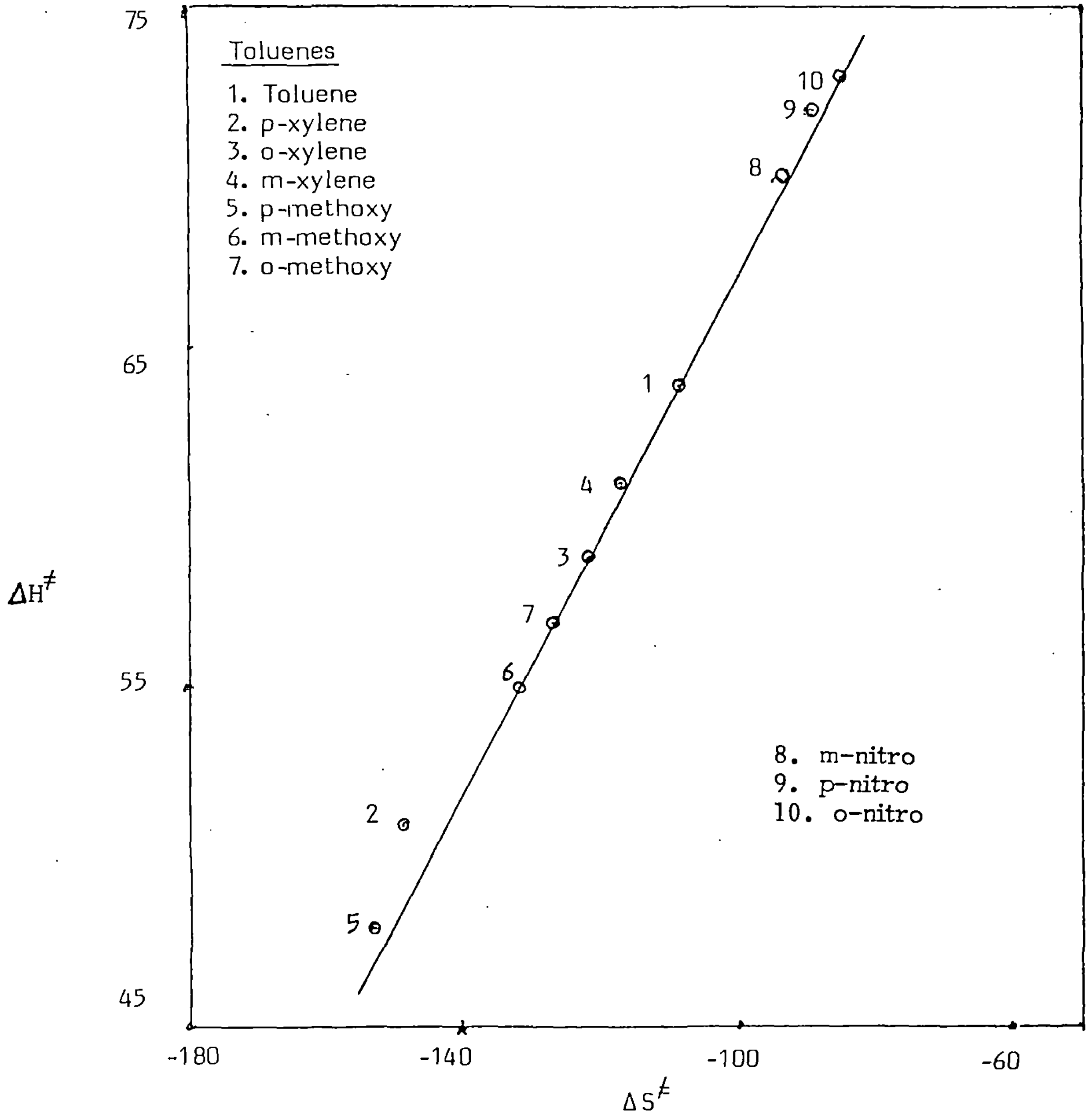


Fig.13: Isokinetic plot (Toluenes).

insight into the nature of the transition state and hence the mechanism of the reaction, an attempt was made to obtain a linear free energy relationship using the Hammett equation. It was observed that electron-releasing groups accelerated the rate of the reaction as compared to toluene, whereas electron-withdrawing groups exerted a deactivating influence on the rates of these reactions (Table 15).

Table 15. Effect of substituents on the rate of oxidation.

Substituted toluene	$10^4 \times k_1(s^{-1})$	Relative Rate
p-methoxy	4.4	1.47
m-methoxy	4.1	1.37
o-methoxy	3.9	1.30
p-methyl	3.8	1.27
o-methyl	3.5	1.17
m-methyl	3.2	1.07
H (toluene)	3.0	1.00
m-nitro	2.2	0.73
p-nitro	2.1	0.70
o-nitro	2.0	0.67

[Substrate]=0.01M, [QDC]=0.001M, $[HClO_4]$=0.75M, T=313K.

A plot of the logarithm of the relative rates of reactions against the Hammett substituent constants, σ values(60), was linear (Fig.14) and the value of

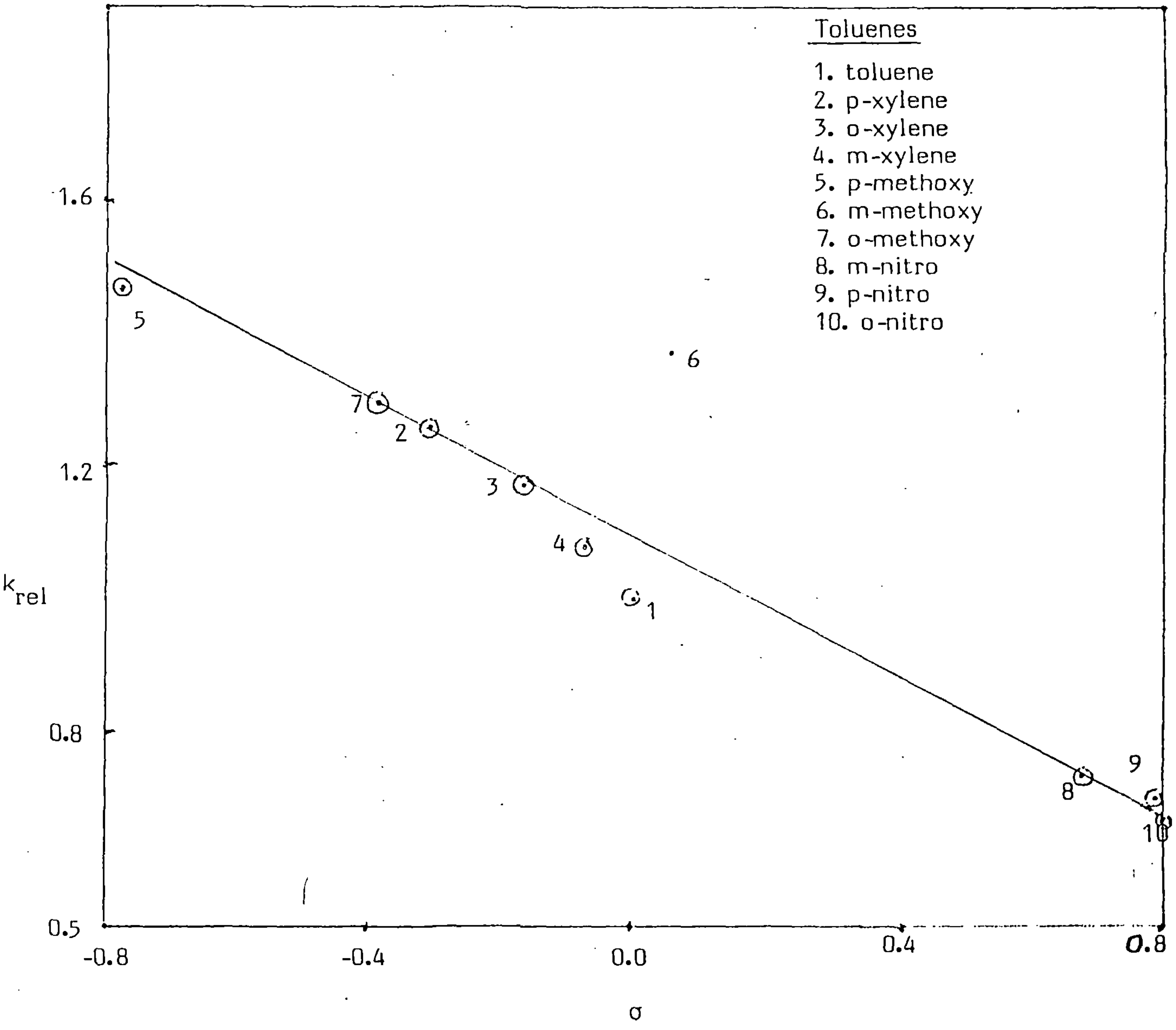


Fig.14: Hammett plot (Toluenes)

the reaction constant, ρ, was -0.20. For most hydrogen abstraction reactions, the reaction constants(ρ) have small magnitude(61).

The rate data for positionally substituted toluenes indicated virtually no difference between the isomers, as for example, the failure to observe any rate difference for ortho-substituted isomers (Table 15). Marginal effects were observed for the different isomers, and steric effects for ortho-substituted toluenes were not pronounced.

A correlation between rates of reactions and ionisation potentials would seem appropriate. The ionisation potential for the three isomers of xylene(62) for example, are quite close (p-xylene = 8.44 ev., o-xylene= m-xylene=8.56 ev, toluene=8.82 ev). Based on the ionisation potentials, the observed order of reactivity would be: p-xylene > o-xylene = m-xylene > toluene. This order of reactivity has been observed (Table 15). The same rationalization would be valid for the oxidation of methoxytoluenes and nitrotoluenes, with regard to their relative rates of reactivity.

Kinetic isotope effect

The kinetic isotope effect has been studied, in order to determine the nature of the intermediate formed in the rate-determining step of these oxidation reactions. In the case of the oxidation of substituted toluenes, a kinetic isotope effect, k_H/k_D, was observed in the range 5.0-5.3, which indicated that the rate-determining step involved the cleavage of the carbon-hydrogen bond of the methyl group attached to the arene ring. The results have been shown in Table 16.

Table 16. Kinetic isotope effects for the oxidation of toluenes.

Substrate (toluenes)	$10^4 \times k_1 (s^{-1})$ ArCH$_3$(k_H)	ArCD$_3$(k_D)	k_H/k_D
p-CH_3-C_6H_4-	3.8	0.73	5.2
o-CH_3-C_6H_4-	3.5	0.70	5.0
m-CH_3-C_6H_4-	3.2	0.62	5.2
p-OCH_3-C_6H_4-	4.4	0.85	5.2
m-OCH_3-C_6H_4-	4.1	0.80	5.1
o-OCH_3-C_6H_4-	3.9	0.75	5.2
m-NO_2-C_6H_4-	2.2	0.44	5.0
p-NO_2-C_6H_4-	2.1	0.41	5.1
o-NO_2-C_6H_4-	2.0	0.38	5.3

Similar k_H/K_D values have been obtained in the oxidation of various kinds of substrates, to suggest that the rate-determining step involved the cleavage of the C-H bond. The oxidation of deuteriated aldehydes by permanganate produced substantial isotope effects, suggesting that the rate-controlling step was the cleavage of the C-H bond(63). In the chromic acid oxidation of benzaldehyde, the kinetic isotope effect obtained indicated that C-H bond cleavage occurred in the rate-determining step(64). In the chromic acid oxidation of diphenylmethane, a k_H/k_D value of 6.4 had been observed, which indicated that the rate-determining step was the cleavage of the methylene carbon-hydrogen bond, yielding the benzhydryl radical(65). The deuterium isotope effect for the Cr(V) oxidation of benzhydrol in 65% acetic acid gave a value of k_H/k_D=5.9, showing that C-H bond cleavage was the rate-controlling step(49b).

Induced polymerization

Since all the reactions were performed under nitrogen, the possibility of induced polymerization was tested. It was seen that there was no induced polymerization of acrylonitrile or the reduction of mercuric chloride. Further, no ESR signals could be detected in each of the oxidation reactions studied (E-4, Varian). These results do not rule out free radical intermediates; they simply do not provide evidence that radicals are formed. This may be due to the high rate of oxidation of the free radicals. Control experiments were performed, in the absence of the substrate. The concentration of the oxidant, QDC, did not show any appreciable change.

Mechanism

Based on the stoichiometry of the oxidation reactions, and the observed experimental data, the mechanistic pathway of the reaction has to be considered. Some of the kinetic observations which must be taken into account are the following:

(a) The rate of the reaction showed a first order dependence on the concentration of the acid (Tables 5-7), indicating that the rate-determining step involved a reaction between a protonated Cr(VI) species and the substrate.

(b) A decrease in the polarity of the solvent medium resulted in an increase in the rate of the reaction (Tables 8-10). Linear plots of log k_1 against the reciprocal of the dielectric constant indicated an ion-dipole type of interaction (Figs.7-9). This was in accordance with the involvement of a protonated Cr(VI) species in the rate-determining step of the reaction.

(c) The value of the reaction constant (ρ) was -0.20. For most hydrogen abstraction reactions, the reaction constants (ρ) have small magnitudes(61).

(d) The kinetic isotope effect, k_H/k_D=5.0-5.3 (Table 16) demonstrated a cleavage of the carbon-hydrogen bond of the methyl group attached to the aryl ring.

(e) The near constancy of the free energies of activation (Table 14) showed that the same mechanism was operative in these oxidation processes.

Although the reaction did not give any ESR signals, and there was no evidence for the induced polymerization of acrylonitrile and the reduction of mercuric chloride, the possibility of a hydrogen abstraction mechanism cannot be completely excluded. The radical formed initially would react rapidly with the Cr^{5+} species formed in the initial step, similar to what has been observed in the oxidation of saturated hydrocarbons by Cr(VI) compounds (49c, 66). The significant kinetic isotope effect observed (k_H/k_D=5.0-5.3; Table 16), would suggest considerable carbonium ion character in the transition state. The transition state could be considered as involving a carbon atom which would exist with both, radical and carbonium ion character. Such types of intermediates have been reported in earlier investigations(77-80). This resonance hybrid would possess lower energy than either the radical or the carbonium ion, which would account for the stability of the intermediate.

In an earlier report on the oxidation of hydrocarbons by Cr(VI), a kinetic isotope effect, k_H/k_D, of 6.4 had demonstrated a cleavage of the carbon-hydrogen bond in the rate determining step(65). Further, the radical species, formed in the initial step, underwent rapid oxidation.

In the present investigation, the small difference in the rates of reactions between toluene and substituted toluenes (Table 15), and the small value of the reaction constant (ρ=-0.20) observed in the oxidation, clearly indicated the possibility of a hydrogen abstraction mechanism. A cleavage of the carbon-hydrogen bond, in the rate-determining step of the reaction, was supported by the observed kinetic isotope effect, k_H/k_D, in the range 5.0-5.3 (Table 16).

Under the experimental conditions employed in the present investigation, the only isolable product, in each case, was the corresponding aldehyde, which was characterized as the respective 2,4-dinitrophenylhydrazone derivative. Since drastic conditions of concentrations and temperature were not employed in the present study, only one methyl group (in the case of xylenes) underwent oxidation to give the corresponding aldehyde. It had been shown in an earlier investigation that the oxidation of xylenes by ceric ions(41) had resulted in the formation of the corresponding aldehyde, indicating that only one of the methyl groups in xylene was oxidized.

It has been well established that the first step in the oxidation of toluenes by ceric ions was a one-electron transfer to give a radical cation. This was rapidly followed by the loss of a proton to form a benzyl radical which was then oxidized to a benzyl cation(67-69). Ceric trifluoro-acetate in aqueous trifluoroacetic acid has been found to be effective for the oxidation of activated toluenes to the corresponding aldehydes(70). Various chromium(VI) reagents such as trimethylsilyl chlorochromate(71) and chromyl trifluoroacetate(72), have been employed for the oxidation of toluenes and substituted toluenes, the products being the corresponding aldehydes(71,72). During the flow reactor oxidation of toluene, radical atom and radical-radical reactions (Eq.4 and 5 respectively),

$$\mathrm{ArCH_2^{\bullet}} + \mathrm{O} \longrightarrow \mathrm{ArCHO} + \mathrm{H} \qquad (4)$$

$$\mathrm{ArCH_2^{\bullet}} + \mathrm{HO_2^{\bullet}} \longrightarrow \mathrm{ArCH_2O} + \mathrm{OH}$$

$$\longrightarrow \mathrm{ArCHO+H} \qquad (5)$$

were responsible for the conversion of toluene to benzaldehyde(73). The liquid-phase oxidation of substituted toluenes to the corresponding aldehydes has been investigated from an industrial point of view(74). The selective liquid-phase oxidations of substituted toluenes to the corresponding aldehydes have been reported, using various cobalt-based catalysts. For example, the catalyst $Co(OAc)_2$-$Ce(OAc)_3$-$Cr(OAc)_3$ in a mole ratio 3:1:2 was used to oxidize p-methoxytoluene to p-anisaldehyde in 76% yield(75). The catalyst, $Co(OAc)_2$-$Mn(OAc)_2$ in a mole ratio 3:1 was used to oxidize 3,4,5-trimethoxytoluene to 3,4,5-trimethoxybenzaldehyde in 91% yield(76). There was no formation of any acid in any of these liquid-phase oxidation reactions of substituted toluenes(75,76), indicating that there was no further oxidation of the product aldehyde, in all these cases.

No other intermediate product(s) could be isolated from the reaction mixture. Efforts to isolate the possible intermediate, benzyl alcohol, were not successful. Independent kinetic experiments were carried out on the oxidation of benzyl alcohol by QDC, in acid medium. It was observed that there was a rapid conversion to the aldehyde. The rate data for the oxidation of benzyl alcohol has been recorded in Table 17.

Table 17. Rate data for the oxidation of benzyl alcohol, in DMF.

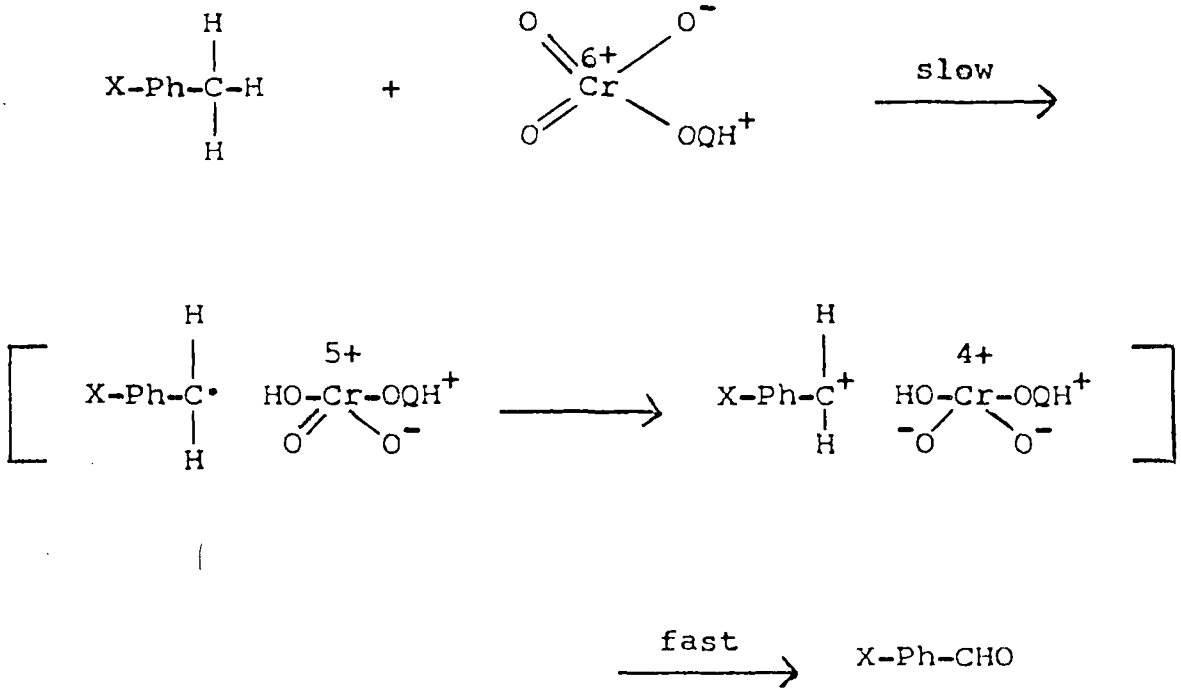
[Benzyl alcohol] (10^2 X M)	10^3 X k_1 (s^{-1})
1.0	2.5
5.0	12.0
10.0	26.0
20.0	51.0

[QDC] = 0.001M, $HClO_4$ = 0.75M, T313K.

Comparison of the rate data for the oxidation of benzyl alcohol (Table 17) with those for the oxidation of toluene and substituted toluenes (Tables 2-4) would indicate that benzyl alcohol, when formed as an intermediate in the oxidation of substituted toluenes by QDC, in acid medium, would undergo a rapid reaction to give the corresponding aldehyde. It would be pertinent to recall the earlier experimental observations wherein benzyl alcohol was rapidly oxidized to benzaldehyde in good yields when oxidized by t-butylchromate in petroleum ether(77), potassium dichromate in glacial acetic acid(78), V(V) in acid media(79), pyridine-CrO_3complex(80), Co(III) in perchloric acid(81), Ce(IV) in acid media(82), nitric acid(83), acid permanganate(84-85), lead tetraacetate(86), chloramine-T(87), ruthenium tetroxide(88-89), pyridine chlorochromate(90), sodium-N-chloro-p-toluene sulfonamide(91), and by sodium-chlorobenzene sulfonamide (92).

In the present investigation, all the substrates (toluene and substituted toluenes) were oxidized by quinolinium dichromate, in acid medium, to give the corresponding aldehyde, which has been characterized as the respective 2,4-dinitrophenylhydrazone derivative. *There was no formation of acid in any of these reactions,* implying that the product (the aldehyde in each case) was stable and did not undergo further oxidation, under the present experimental conditions.

SCHEME


X-Ph-C-H
6+
Cr
O
O
O⁻
OQH⁺
slow
X-Ph-C•
5+
HO-Cr-OQH⁺
X-Ph-C⁺
4+
HO-Cr-OQH⁺
fast
X-Ph-CHO

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KINETICS OF OXIDATION OF DIPHENYLMETHANE TRIPHENYLMETHANE AND FLUORENE

The oxidation of arylalkanes has been studied by various workers, using a variety of oxidizing agents.

Chromium(VI)

The reaction of arylalkanes with CrO_3 in glacial acetic acid was second order in CrO_3 and first order in substrate, and had involved the formation of transient Cr(IV) and Cr(V) complexes(1,2). Diphenylmethane gave mainly benzophenone ; no diphenylmethanol or its acetate were obtained. Triphenylmethane gave triphenylcarbinol(1,2), whereas fluorene was oxidized to fluorenone in greater than 90% yield(2). The chromic acid oxidation of triphenylmethane gave the corresponding tertiary alcohol initially, and more vigorous oxidation led to the breakdown of one aryl group, with the formation of a diaryl ketone(3,4). The CrO_3 oxidation of diphenylmethane and triphenylmethane was studied in acetic acid at 50°C, in the presence of azide ions; the intermediate carbonium ions formed were scavenged with azide ions(5). The chromic acid oxidation of hydrocarbons in 95% acetic acid, using an acid catalyst in large concentration compared with that of Cr(VI) yielded relative rates of oxidation, wherein the order of reactivity was observed to be fluorene >> triphenylmethane ≃ diphenylmethane > toluene (6). The chromyl chloride oxidation of diphenylmethane(7,8), and triphenylmethane(8,9) had yielded benzophenone and triphenylcarbinol respectively, in greater than 90% yields. Fluorene was converted to fluorenone in good yields when oxidized by aqueous sodium dichromate(10), and by chromyl chloride(11).

Cobalt(III)

The oxidation of diphenylmethane by cobalt(III) perchlorate in aqueous acetonitrile, had yielded benzophenone(12,13).

Cerium(IV)

Cerium(IV) has been used to oxidize diphenylmethane to benzophenone, triphenylmethane to triphenylcarbinol and fluorene to fluorenone in good yields(14).

Permanganate, Manganese(III) and Manganese(IV)

The kinetics of oxidation of diphenylmethane by $KMnO_4$ has been reported(15). The Mn(III) acetate oxidation of triphenylmethane had yielded triphenylcarbinol(16). The oxidation of diphenylmethane and triphenylmethane by MnO_2 dispersed in aromatic hydrocarbon solvents was observed to proceed via radical formation through hydrogen abstraction by the oxidant(17).

Nickel peroxide

Nickel peroxide has been used to oxidize diarylmethanes, in which the methylene group is doubly activated by the aromatic rings, to give the corresponding diaryl ketones in high yields(18). For example, fluorene gave fluorenone in 66 %. yield, and diphenylmethane gave benzophenone in 79% yield(18).

Lead tetraacetate

The lead tetraacetate oxidation of diphenylmethane(19-21) and triphenylmethane(20,21) had yielded the corresponding acetates. The kinetic aspects of the oxidation of arylakanes by lead tetraacetate have been reported(22).

Thallium(III), Vanadium(V) and Phenyl iodosoacetate

The kinetics of oxidation of fluorene by thallium(III) and vanadium(V) have been investigated(23,24). The kinetics of oxidation of arylalkanes by phenyl iodosoacetate, catalyzed by Ru(III), have been reported(25).

Potassium hexacyanoferrate(III)

The kinetics of oxidation of arylalkanes by potassium hexacyanoferrate(III), in acid media, have been reported(26). The oxidation of diphenylmethane and triphenylmethane gave good yields of benzophenone and triphenylcarbinol, respectively(26a), while the oxidation of fluorene gave fluorenone in good yields(26b).

PRESENT WORK

The kinetics of oxidation of arylalkanes by Cr(VI) reagents have not received adequate attention. The present work is an investigation of the kinetic features of the oxidation of arylalkanes (diphenylmethane, triphenylmethane and fluorene) by quinolinium dichromate in acid medium using dimethyl formamide as solvent.

Stoichiometry (vide 'Experimental'):

The stoichiometries of the reactions were determined to be 1:2 (substrate:oxidant) for all the substrates studied. The stoichiometric equations can be represented as follows:

(a) $Ph_2CH_2+2Cr^{VI}+H_2O \longrightarrow Ph_2CO+2Cr^{IV}+4H^+$ (1)
(Diphenylmethane)

(b) $Ph_3CH+Cr^{VI}+H_2O \longrightarrow Ph_3COH+Cr^{IV}+2H^+$ (2)
(Triphenylmethane)

(c) $C_{13}H_{10}+2Cr^{VI}+H_2O \longrightarrow C_{13}H_8O+2Cr^{IV}+4H^+$ (3)
(Fluorene)

Effect of substrate and oxidant

The rate of the reaction was observed to be dependent on the first powers of concentrations of both, substrate and oxidant (Tables 1-2).

Table 1. Rate data for the oxidation of diphenylmethane and triphenylmethane in DMF.

[Substrate] (10^2X M)	[QDC] (10^3 X M)	Diphenylmethane	Triphenylmethane
		10^4xk_1(s^{-1})	
1.0	1.0	3.68	4.45
2.5	1.0	9.05	11.23
5.0	1.0	18.40	22.10
7.5	1.0	27.10	33.72
10.0	1.0	36.25	45.05
20.0	1.0	72.15	90.15
1.0	0.75	3.56	4.50
1.0	0.50	3.73	4.37
1.0	0.25	3.65	4.31
1.0	0.10	3.62	4.48

$[HClO_4]$ = 1.0M, T = 313K.

Table 2. Rate data for the oxidation of fluorene in DMF.

[Fluorene] (10^2 x M)	[QDC] (10^3 x M)	10^3 x k_1 (s^{-1})
1.0	1.0	4.57
2.5	1.0	11.25
5.0	1.0	22.03
7.5	1.0	34.12
10.0	1.0	44.50
1.0	0.75	4.66
1.0	0.50	4.39
1.0	0.25	4.48
1.0	0.10	4.55

$[HClO_4]$ = 1.0M, T = 313K.

Plots of k_1 against the concentration of substrates were linear passing through the origin (Figs.1-2), indicating that the rate of oxidation was dependent on the first power of concentrations of substrates.

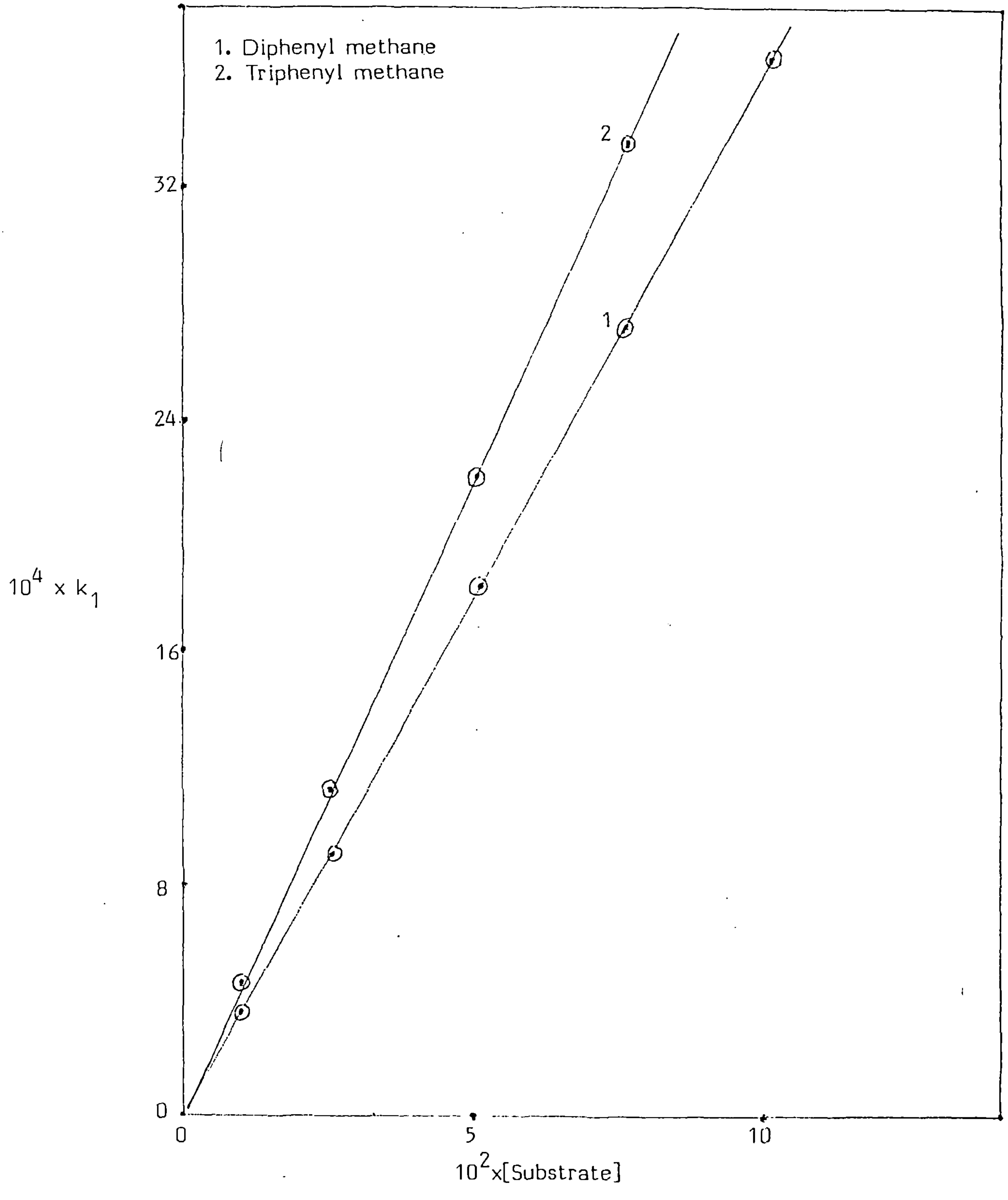


Fig.1: Plot of log k_1 against substrate concentration (Arylalkanes).

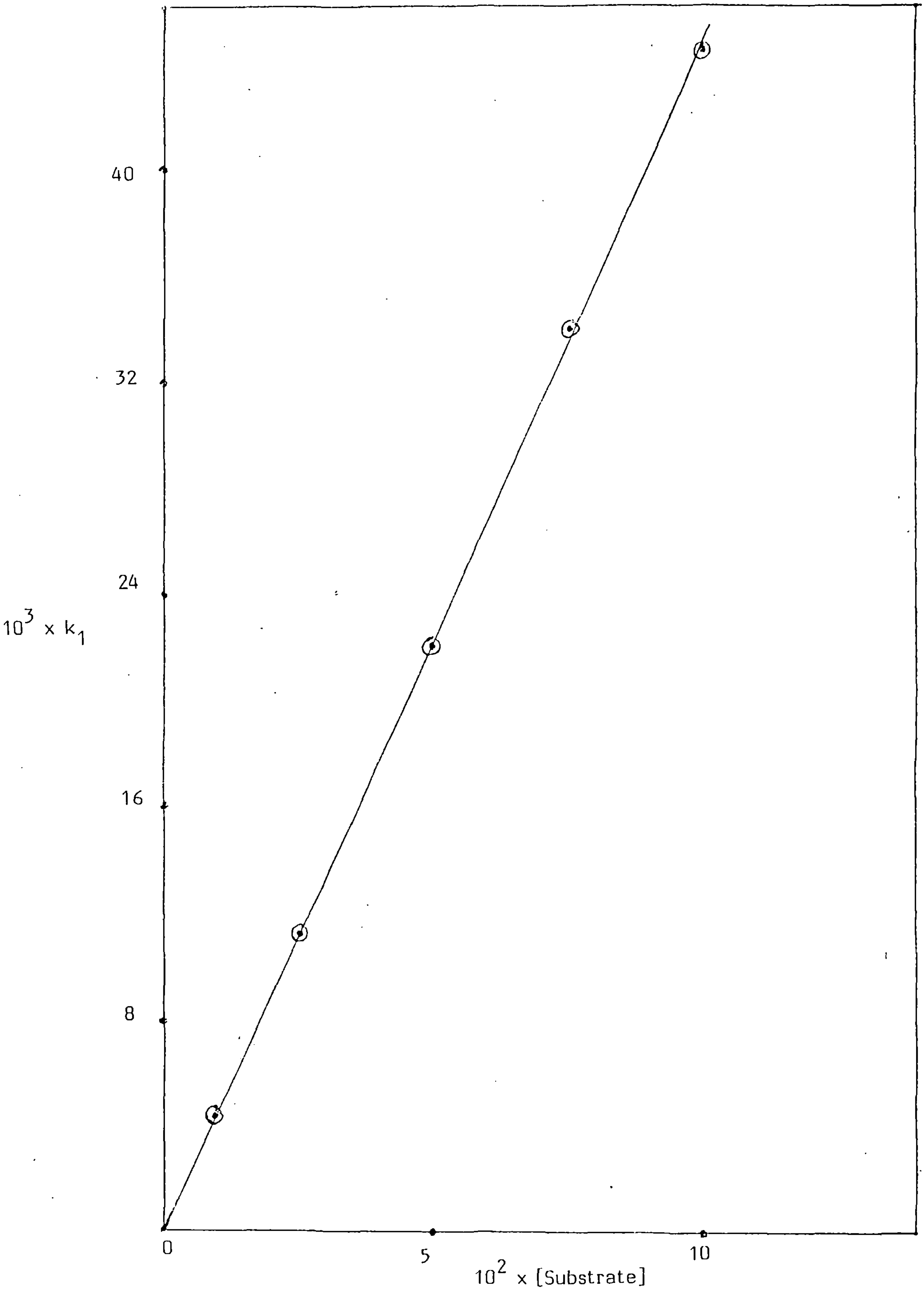


Fig.2: Plot of log k_1 against substrate concentration (Fluorene)

The values of k_2 (second order rate constant) were fairly constant, confirming the first order dependence of the rate on the concentrations of the substrates (Tables 1-2). When the concentration of the substrate was kept constant (taken in large excess), the pseudo-first-order rate constant (k_1) did not show any appreciable variation with changing concentrations of the oxidant (Tables 1-2), indicating that the rate of the reaction was dependent on the first power of the concentration of the oxidant.

Effect of acid

The rate of the reaction was observed to be dependent on the first power of the concentration of the acid (Table 3).

Table 3. Effect of acid on the oxidation of arylalkanes in DMF.

$[HClO_4]$ (M)	diphenylmethane	triphenylmethane	fluorene
	$10^4 \times k_1(s^{-1})$		$10^3 x k_1(s^{-1})$
1.5	5.25	7.15	6.80
1.0	3.68	4.45	4.57
0.75	2.58	3.57	3.38
0.50	1.80	2.25	2.30
0.25	0.87	1.20	1.12
0.10	0.36	0.45	0.46

[Substrate] = 0.01M, [QDC] = 0.001M, T = 313K.

Plots of log k_1 against log $[H^+]$ were linear, with unit slopes, showing that the reaction was dependent on the first power of the concentration of acid (Figs.3-4).

Rate law

The increase in the oxidation rate with acidity suggested the involvement of a protonated Cr(VI) species in the rate determining step. The involvement of such protonated species has been well established in chromic acid oxidations(27a).

Under the present experimental conditions, wherein pseudo-first order conditions have been employed for all the kinetic runs, the rate law can be expressed as:

$$\text{Rate} = -\frac{d[\text{Cr(VI)}]}{dt} = k[\text{Substrate}][\text{QDC}][H^+] \qquad (4)$$

Effect of solvent

The dielectric constants for DMF-water mixtures have been estimated from the dielectric constants of the pure solvents(28). The estimated dielectric constants of the solvent mixtures used have been shown in Tables 4-5.

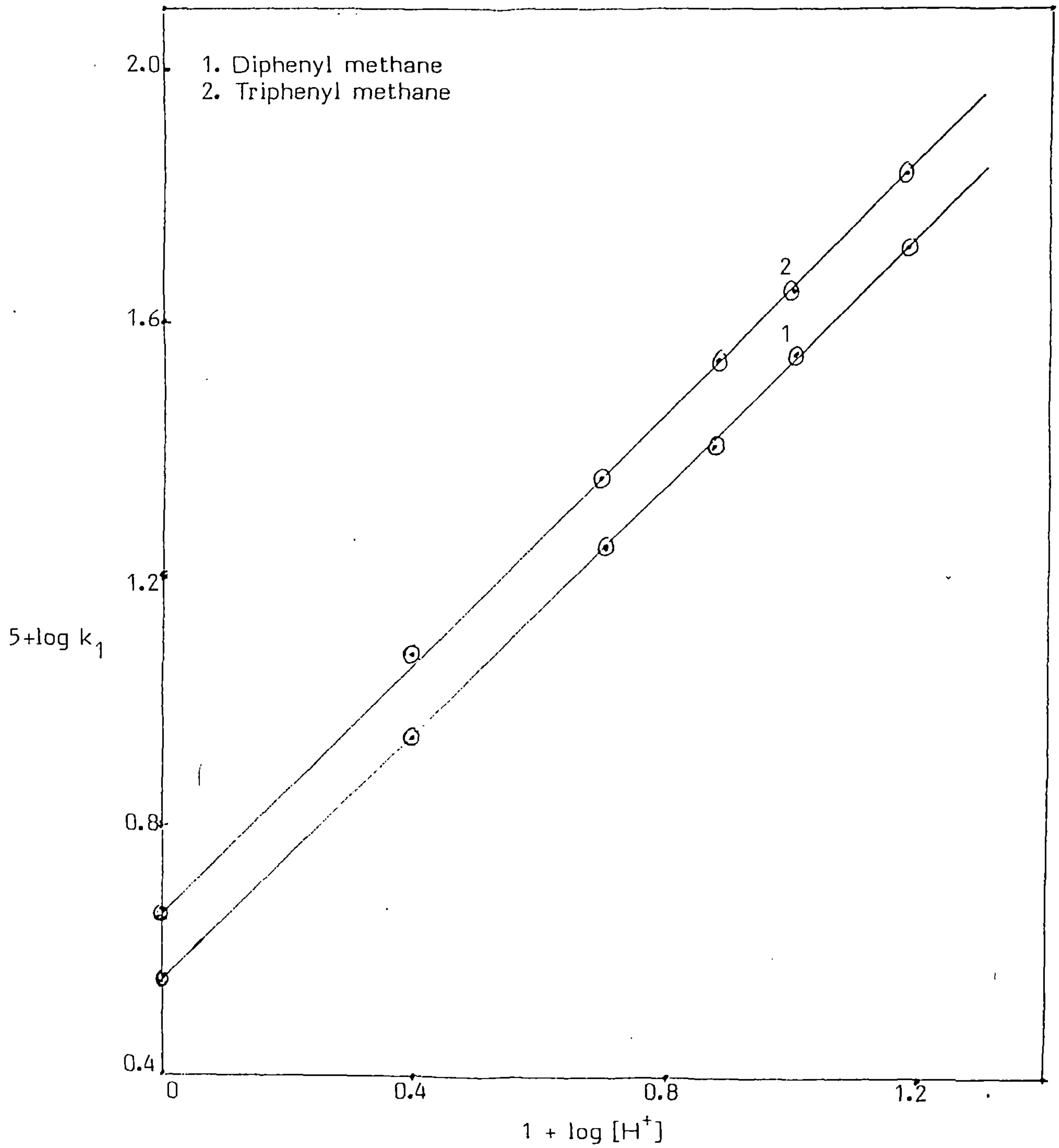


Fig.3: Plot of log k_1 against log $[H^+]$ (Arylalkanes)

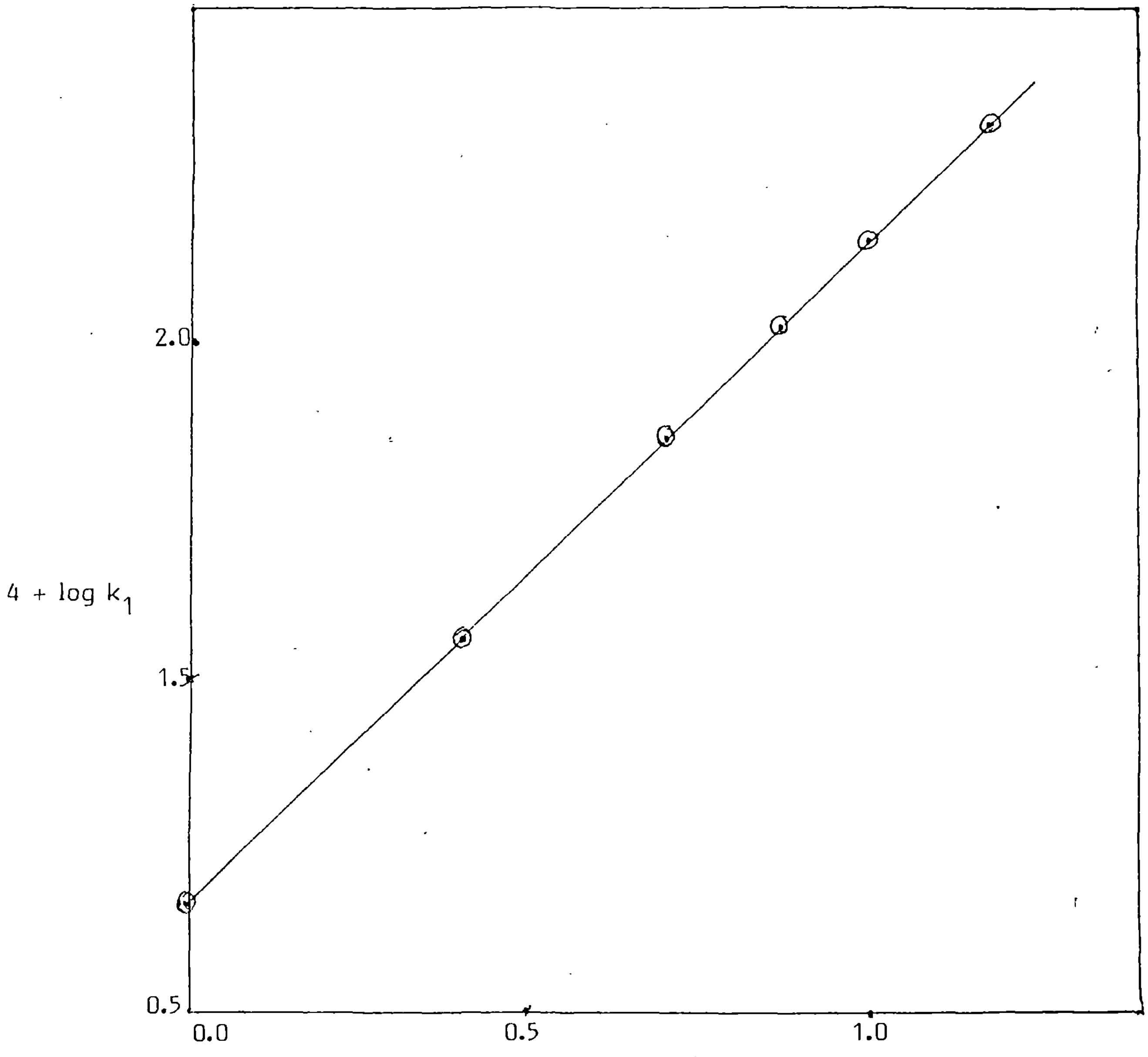


Fig.4: Plot of log k_1 against log [H^+] (Fluorene)

The rate of the reaction was susceptible to changes in the polarity of the solvent medium, with varying proportions of DMF-water. With an increase in the dielectric constant of the medium, there was a decrease in the rate of the reaction (Tables 4-5). This was in consonance with the observation that the use of more polar solvents required larger reaction times (29).

Table 4. Effect of solvent on the oxidation of diphenylmethane and triphenylmethane.

DMF : H_2O (% v/v)	D	Diphenylmethane	Triphenylmethane
		$10^4 \times k_1$ (s^{-1})	
100:0	37.6	3.68	4.45
95:5	39.7	1.63	3.02
90:10	41.8	1.48	2.51
85:15	43.9	1.34	2.09
80:20	46.1	1.23	1.70

[Substrate]=0.01M, [QDC] = 0.001M, [$HClO_4$] = 1.0 M T = 313K.

Table 5. Effect of solvent on the oxidation of fluorene.

$DMF:H_2O$ (% v/v)	D	$10^3 \times k_1$ (s^{-1})
100:0	37.6	4.57
95:5	39.7	3.41
90:10	41.8	2.95
85:15	43.9	2.50
80:20	46.1	2.18

[Fluorene] = 0.01M, [QDC] = 0.001M, $[HClO_4]$ = 1.0M, T = 313K.

Plots of log k_1 against the reciprocal of dielectric constants were linear with positive slopes (Figs.5-6). This suggested an interaction between a positive ion and a dipole(30), and confirmed that the rate-determining step, in the presence of acid, involved a protonated Cr(VI) species. The effect of a change in solvent composition on reaction rate would also depend on factors such as the solvating power of the solvents(31), solute-solvent interactions(32,33) and solvent structure.

Effect of temperature

The rates of the reactions were observed to be susceptible to changes in temperature (Tables 6-7).

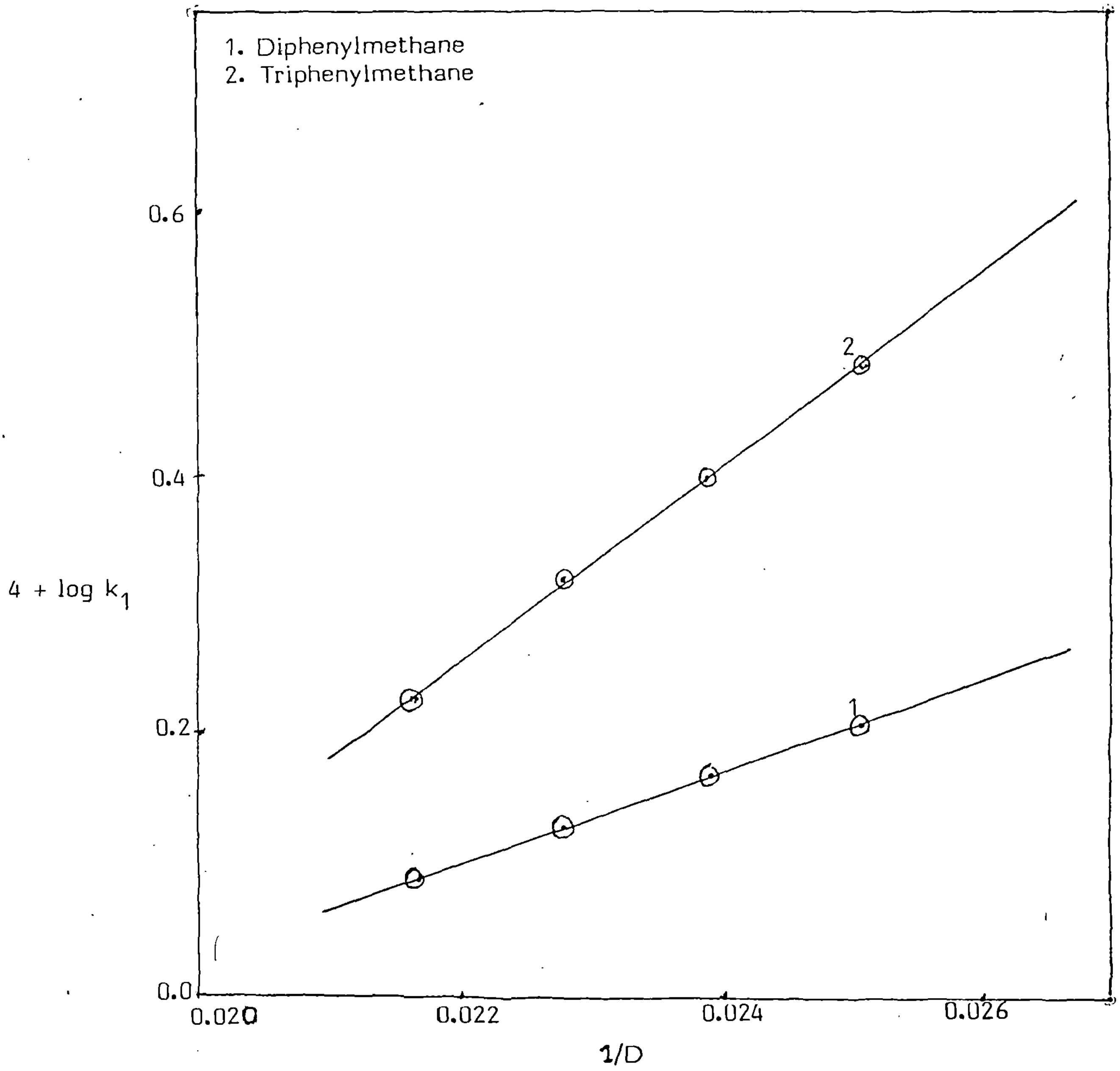


Fig.5: Plot of log k_1 against the reciprocal of dielectric constant (Arylalkanes)

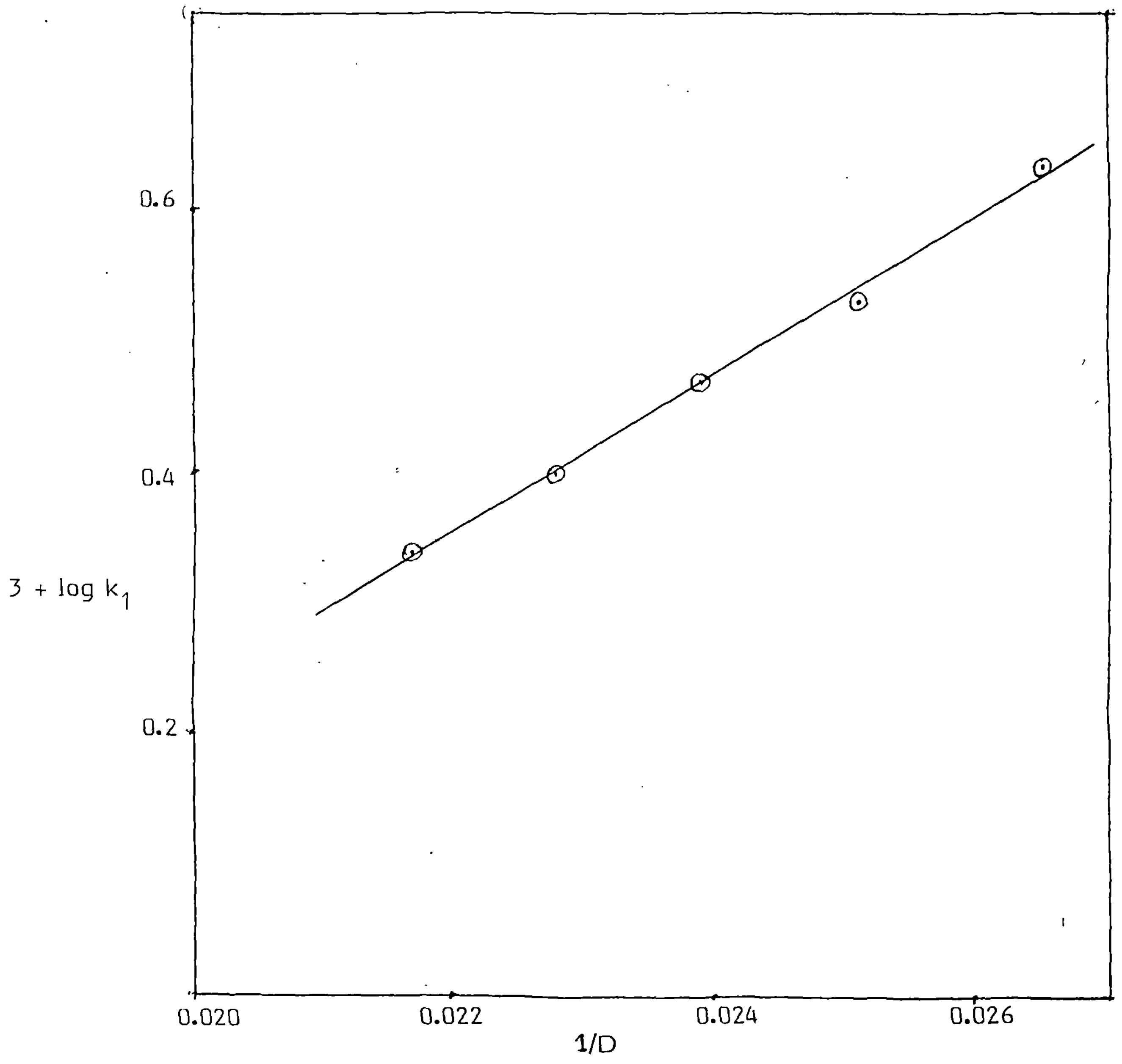


Fig.6: Plot of log k_1 against the reciprocal of dielectric constant (Fluorene)

Table 6. Effect of temperature on the oxidation of diphenylmethane and triphenylmethane in DMF.

Temp. (±0.1K)	10^2k ($M^{-2}s^{-1}$)	
	Diphenylmethane	Triphenylmethane
308	2.18	2.96
313	3.68	4.45
318	7.44	8.97
323	10.03	11.47
328	15.01	17.36

[Substrate] = 0.01M, [QDC] = 0.001M, [$HClO_4$] = 1.0M,
$k = k_1/[\text{Substrate}][H^+]$.

Table 7. Effect of temperature on the oxidation of fluorene in DMF.

Temp (±0.1K)	k ($M^{-2}s^{-1}$)
308	0.261
313	0.457
318	0.551
323	0.734
328	0.995

[Fluorene] = 0.01M, [QDC] = 0.001M, [$HClO_4$] = 1.0M,
$k = k_1/[\text{Substrate}][H^+]$

Plots of log k_1 against the reciprocal of temperature were linear (Figs. 7-8). The slopes of the plots were used to calculate the activation energies of the reactions. The other activation parameters were calculated and have been shown in Table 8.

Table 8. Activation parameters for diphenylmethane, triphenylmethane and fluorene.

Parmeters	Diphenyl-methane	Triphenyl-methane	Fluorene
E (kJ mol^{-1})	87±3	77±3	56±2
$\Delta H^{\neq}$(kJ mol^{-1})	84±3	74±3	53±2
$\Delta S^{\neq}$(JK^{-1} mol^{-1})	-68±3	-78±3	-121±3
$\Delta G^{\neq}$ (kJ mol^{-1})	105±3	97±3	91±3

Structural influences on the rate of reaction

Conjugation influences and resonance factors seem to play a prominent role in these reactions. In this series, fluorene was oxidized fastest since the 9-position of the fluorene molecule was particularly labile. The greater oxidation rate of fluorene over diphenylmethane and triphenylmethane (Tables 1-2), may be due to the electromeric effect, which would be expected to be higher in fluorene. Steric hindrance

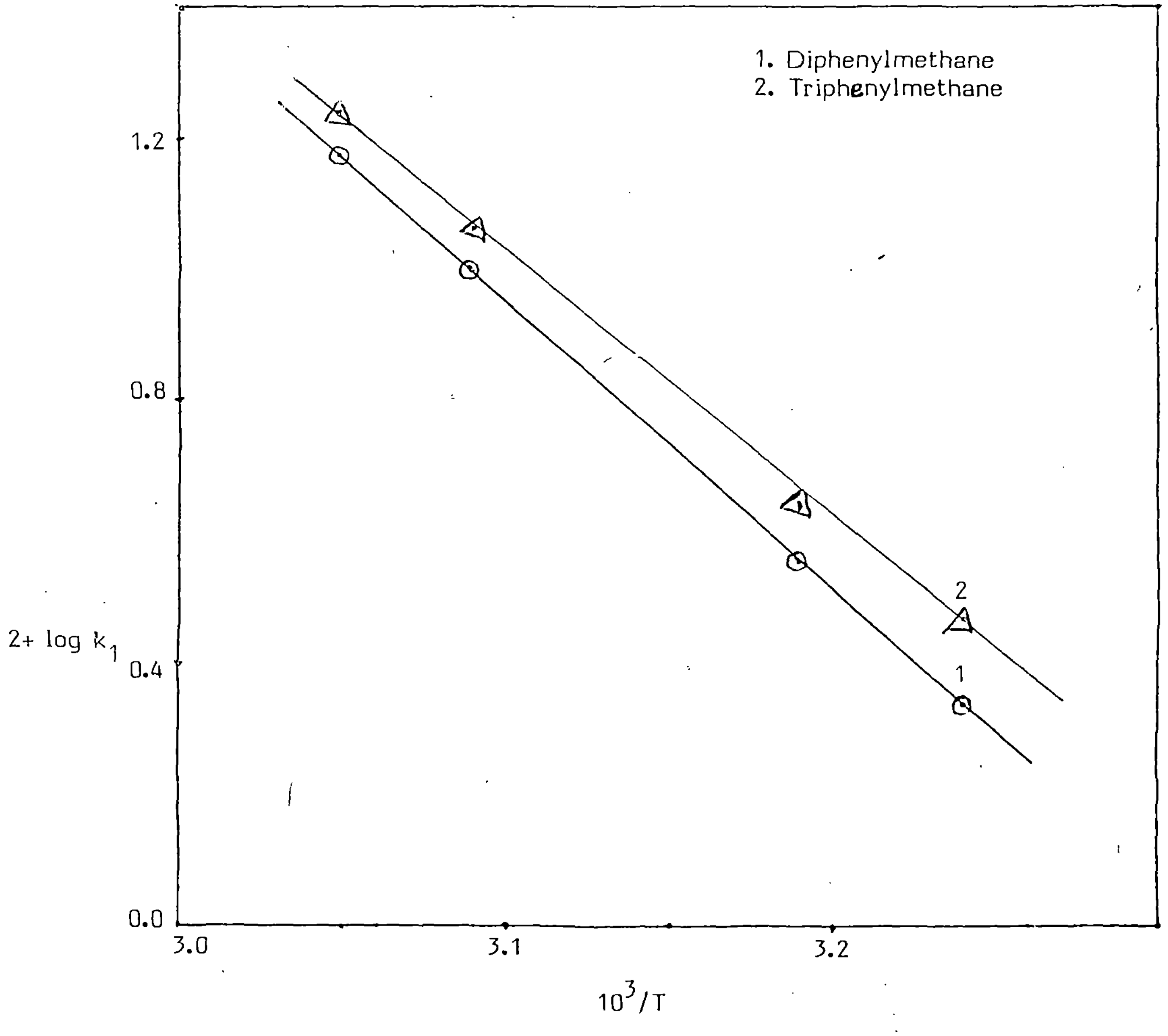


Fig.7: Plot of log k_1 against the reciprocal of temperature (Arylalkanes)

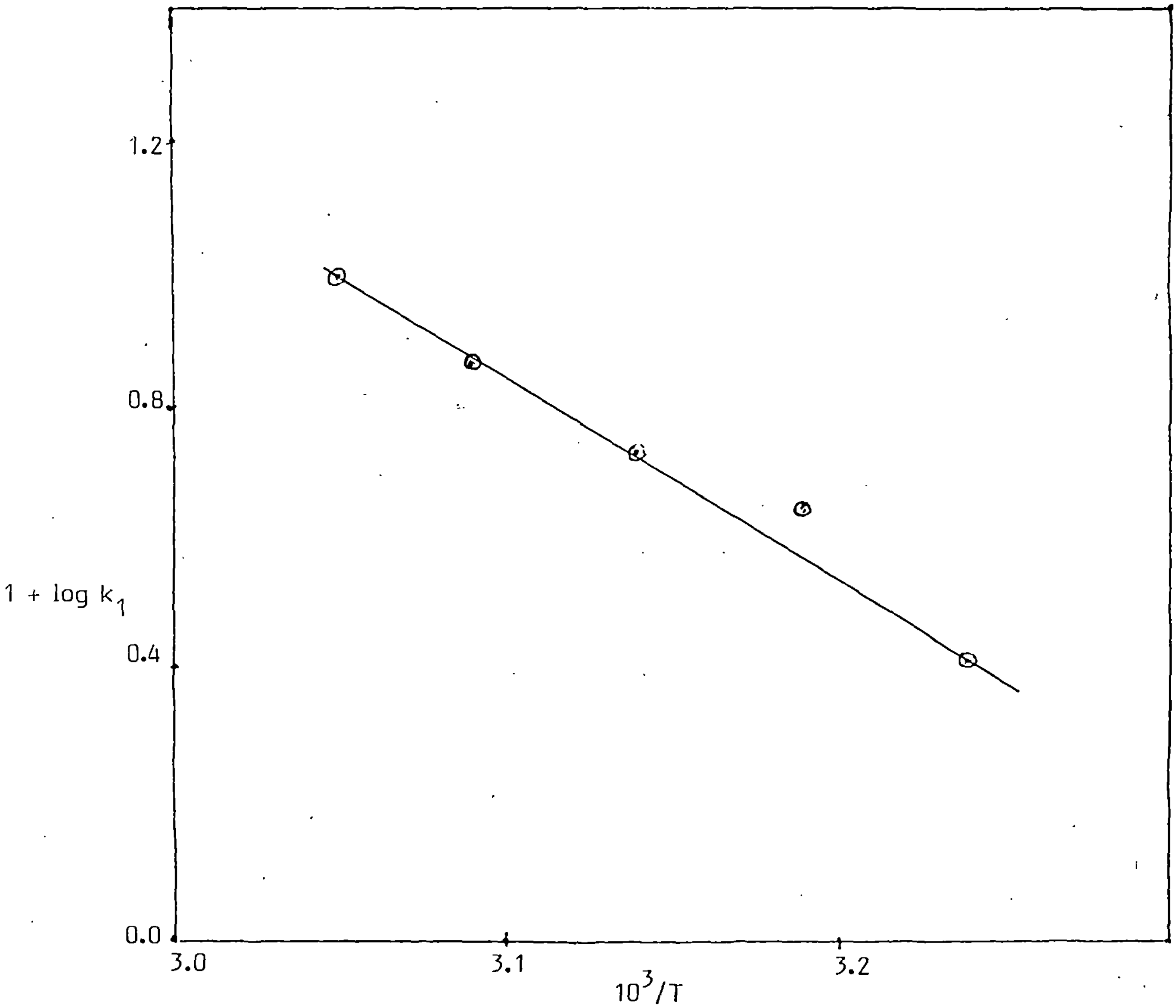


Fig. 8: Plot of log k_1 against the reciprocal of temperature (Fluorene)

due to the triarylmethane group would result in triphenylmethane being oxidized at a faster rate, compared to diphenylmethane.

Hammett plot

The effect of substituents was determined and it was observed that electron-releasing groups caused an increase in the rate of the reaction, whereas electron-withdrawing groups caused a retardation in the rate of the reaction (Tables 9-10).

Table 9. Effect of substituents on the oxidation of diphenylmethane in DMF.

Substituent	10^2k ($M^{-2}s^{-1}$)	k/k_H
p-Methoxy	32.75	8.9
p-Methyl	9.20	2.5
H	3.68	1.0
p-Cl	2.61	0.71
p-Br	2.32	0.63
m-Cl	1.14	0.32
m-Br	1.14	0.32

[Substrate]=0.01M, [QDC]=0.001M, [$HClO_4$]=1.0M, T=313K

Table 10. Effect of substituents on the oxidation of fluorene in DMF.

Substituent	k ($M^{-2}s^{-1}$)	k/k_H
2-methoxy	1.444	3.16
2-methyl	0.914	2.0
H (fluorene)	0.457	1.0
2-Br	0.416	0.91
2-Cl	0.407	0.89
2-NO_2	0.023	0.05

[Substrate]=0.01M, [QDC]=0.001M, [$HClO_4$]=1.0M, T=313K.

Structure-reactivity correlations were obtained using the Hammett equation. Plots of the logarithm of relative rates of reactions against σ (34) were linear (Figs.9-10) and the values of the reaction constants(ρ) were obtained as -1.50 (fluorenes) and -1.25 (diphenylmethanes). The values of the reaction constants (ρ) indicated that the initial reaction was the abstraction of a hydrogen atom, forming the radical intermediate in the rate determining step of the reactions. Earlier investigations had shown that hydrogen atom abstractions from toluene yielding a radical(35), gave ρ values between -0.75 and -1.50. In the oxidation of toluene by chromic acid, the effect of substituents had yielded a ρ value of

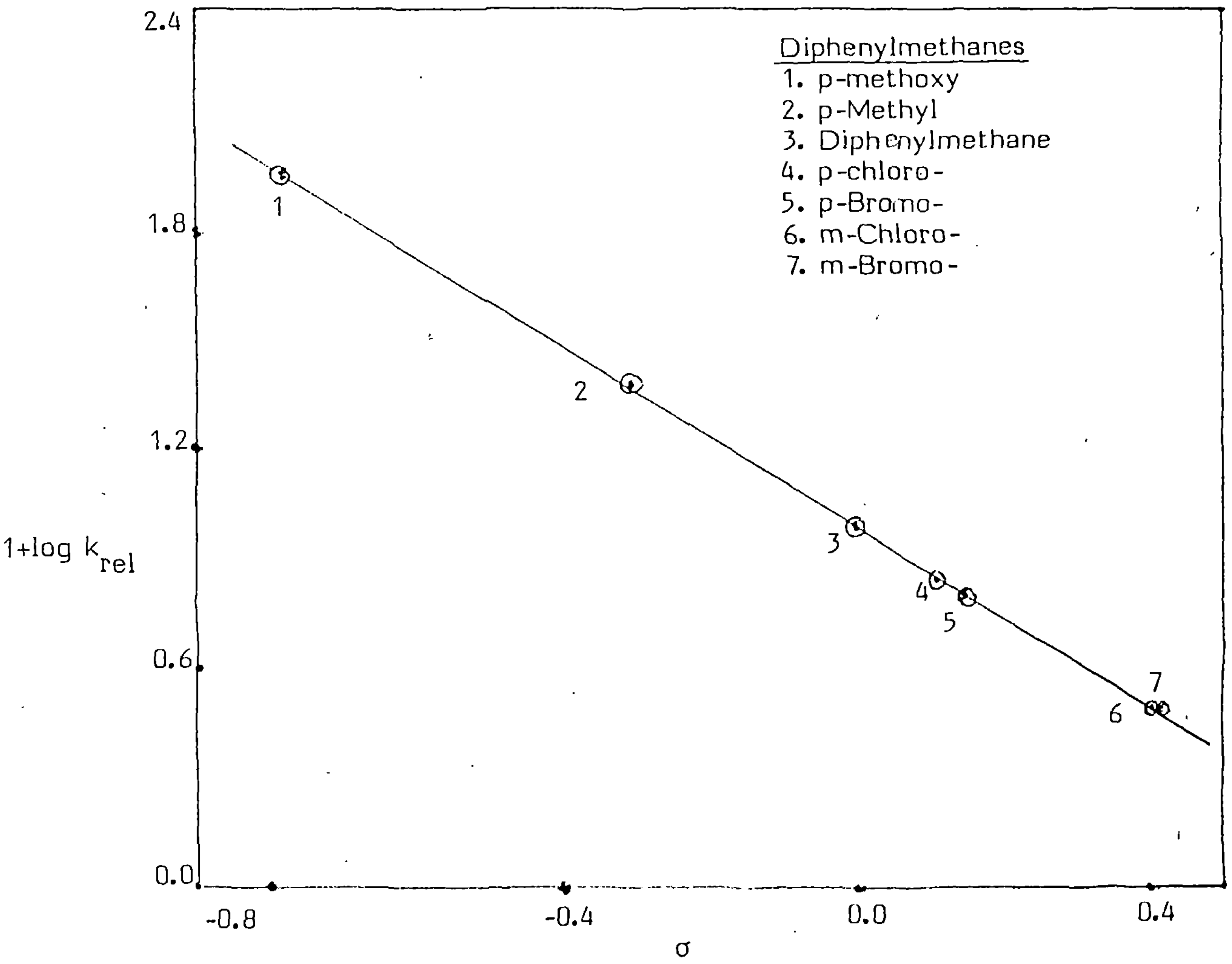


Fig.9: Hammett plot (Diphenylmethanes)

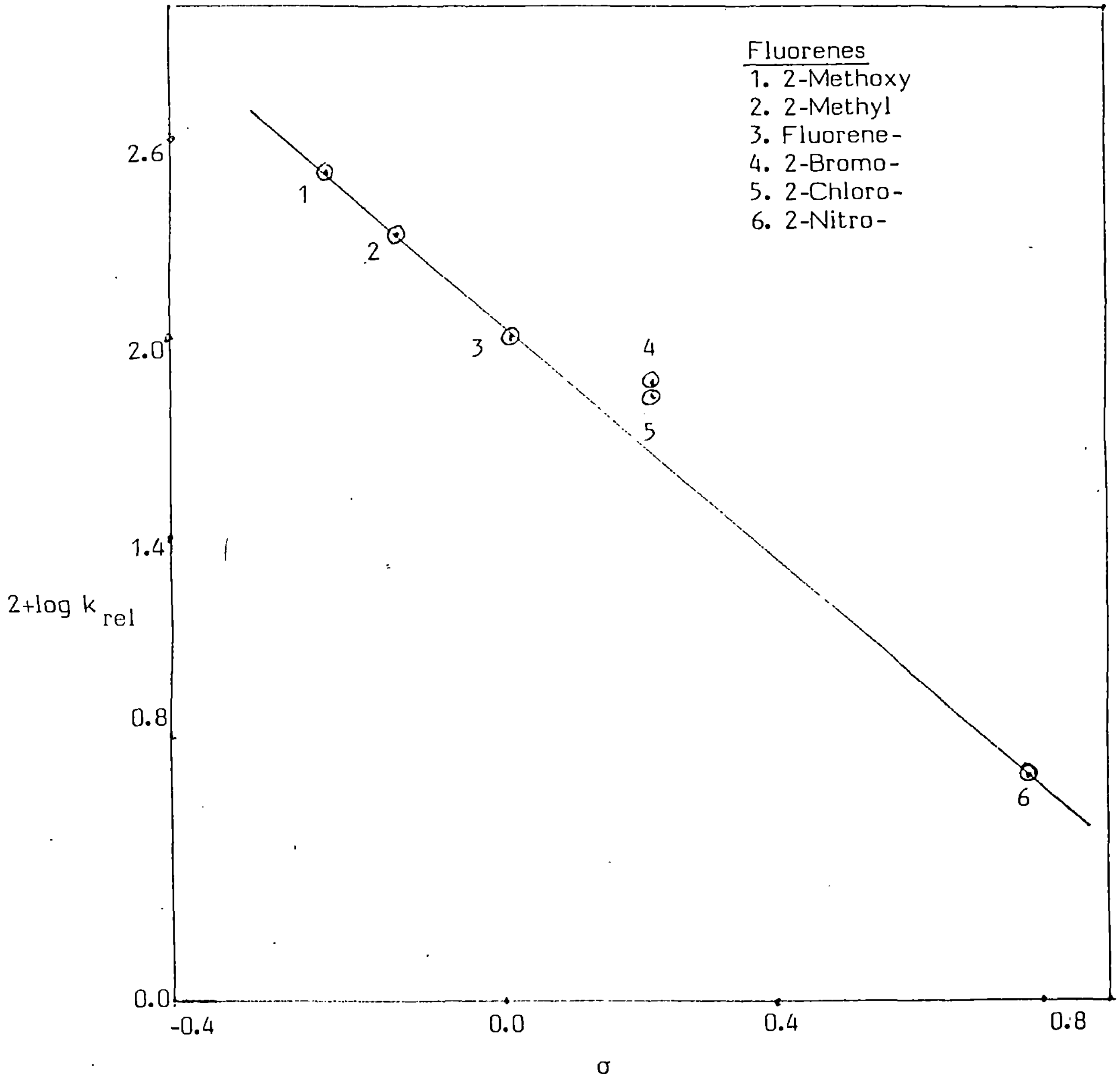


Fig.10: Hammett plot (Fluorenes)

-1.40(36). The effect of substituents was correlated with a reaction constant, ρ, of -1.40, in the oxidation of diphenylmethane by chromic acid(6). In the oxidation of fluorene by potassium hexacyanoferrate(III), the ρ value of -1.5 had demonstrated the formation of a radical intermediate in the rate determining step of the reaction(26b).

Kinetic isotope effect

When the reaction was carried out using 9,9-dideuterofluorene, the rate of the reaction was decreased by a factor of 6.0 at 313K (Table 11).

Table 11. Kinetic isotope effect at 313K.

[Substrate] (M)	Fluorene	9,9-dideutero-fluorene
	($10^3 \times k_1$, s^{-1})	
0.01	4.57	0.76
0.025	11.25	1.87
0.05	22.03	3.68
	0.449 (k_H) ($M^{-2}s^{-1}$)	0.075 (k_D) ($M^{-2}s^{-1}$)
k_H/k_D = 6.0		

[QDC] = 0.001M, $[H^+]$ = 1.0M, k_H and k_D = k_1/[Fluorene] $[H^+]$

The observation of such a kinetic isotope effect would indicate that there was the breaking of the carbon-hydrogen bond in the rate-determining step of the reaction, resulting in the formation of a radical intermediate. The chromic acid oxidation of diphenylmethane had demonstrated a k_H/k_D value of 6.4(6), wherein the rate determining step had been established as the cleavage of the methylene carbon-hydrogen bond, forming the benzhydryl radical.

ESR spectra of radical intermediates

The esr spectra of the corresponding radicals generated from the oxidation of each of the substrates were obtained (vide 'Experimental'). The spectrum of the radical obtained at room temperature from the oxidation of diphenylmethane gave 18 lines, that from the oxidation of triphenylmethane gave 25 lines with considerable overlap, while that from the oxidation of fluorene gave 9 lines. Such spectra have been analyzed in detail in earlier investigations(37-39). It can thus be concluded that the reaction pathway involved the formation of a radical intermediate, generated in the rate-determining step of the reaction.

The esr spectrum was further examined in order to establish the nature of the chromium intermediate species formed during the course of the reaction. One main peak with g=1.970±0.005 was obtained at 77K. This spectrum was observed to decrease with time, and could not be detected after about 30 minutes from the time of initiation of the reaction. This peak could not be due to Cr(III), since the concentration of Cr(III), and hence the intensity of the peak, would have increased with time. If a Cr(IV) intermediate were to be formed, then the presence of two unpaired electrons and S=1 would have shown a broad spectrum having two peaks of low intensity. No such species could be observed. With one unpaired electron and S=1/2, the Cr(V) species would give an esr spectrum with one main peak. A similar spectrum had been reported for the hypochromate ion, CrO_4^{-3}, with a value of g=1.97 (40). Further analysis of the spectrum, obtained in the present investigation, showed a dependence on temperature. Above 77K, the spectrum could not be obtained, owing to spin-orbit coupling which tends to broaden the spectrum at higher temperatures, thus vitiating the formation of an esr signal. It has been shown in an earlier investigation that for vanadium tetrachloride and other symmetrical V(IV) compounds (isoelectronic with Cr(V) species), no esr signals could be observed between 90K and 330K, whereas for unsymmetrical vanadium compounds, such as $VCl_2(OR)_2(ROH)$, (where R=n-butyl or t-butyl), esr spectra could be obtained at 330K(41). In the present study, the esr spectrum of the oxidation reaction mixture at 77K must be due to the formation of a Cr(V) species. It would be justified to postulate that the chromium species initially formed in the oxidation of all these substrates (diphenylmethane, triphenylmethane and fluorene) by QDC, at 77K, was Cr(V).

Mechanism

Based on the stoichiometry of the oxidation reactions and the observed experimental data, the mechanistic pathways of the reactions have to be considered. The kinetic observations which have to be taken into account while proposing the reaction pathway are the following:

(a) The rate of the reaction showed a first order dependence on the concentration of the acid (Table 3), indicating that the slow step of the reaction involved the reaction between the substrate and a protonated Cr(VI) species.

(b) A decrease in the polarity of the solvent medium had resulted in an enhancement in the rate of the reaction (Tables 4-5). Linearity in the plots of log k_1 against the inverse of the dielectric constant suggested an ion-dipole type of interaction (Figs.5-6). This was in consonance with the observation that the use of more polar solvents leads to greater reaction times(29). This also confirmed the involvement of a protonated Cr(VI) species in the rate determining step of the reaction.

(c) The values of the reaction constants (ρ) were -1.25 (for diphenylmethanes) and -1.50 (for fluorenes). The magnitude of the ρ values indicated the formation of a radical intermediate in the slow step of the reactions.

(d) The kinetic isotope effect, k_H/k_D = 6.0 (Table 11), indicated that the rate determining step involved a carbon-hydrogen bond cleavage from the methylene carbon atom.

The initial reaction between the substrate and the oxidant, in acid medium, was the abstraction of a hydrogen atom forming the radical intermediate. It can be postulated that the reaction pathway was via the formation of a radical intermediate generated in the rate determining step of the reaction. The initiation of the polymerisation of acrylonitrile and the induced reduction of $HgCl_2$ indicated the presence of a radical intermediate. ESR spectroscopy has confirmed the presence of the radical intermediate.

The observed increase in the rate of the reaction with a decrease in the polarity of the solvent medium (Tables 4-5) indicated that the transition state was much less polar than the reactants. This would contribute to the facile formation of a radical intermediate, rather than an ionic species, in the rate determining step of the reactions.

The radical intermediate underwent rapid conversion, in a series of steps, to give the product. The steps leading from the radical to the products (benzophenone and fluorenone from diphenylmethane and fluorene, respectively) could not readily be studied, since they followed the rate-determining step. No intermediate product(s) could be isolated from the reaction mixtures, in both these oxidation reactions. Efforts to isolate the intermediates, benzhydrol and fluorenol respectively, from the oxidations of diphenylmethane and fluorene, were not successful. Independent kinetic experiments conducted in this laboratory showed that both, benzhydrol and fluorenol, were oxidized very rapidly (Tables 12-13).

Table 12. Rate of oxidation of benzhydrol by QDC, in DMF.

[Benzhydrol] (10^2xM)	10^2 x k_1 (s^{-1})
1.0	14.0
5.0	73.0
10.0	150.0

[QDC] = 0.001M, $[H^+]$ = 1.0M, T = 313K

Table 13. Rate of oxidation of fluorenol by QDC, in DMF.

[Fluorenol] (10^2xM)	k_1 (s^{-1})
1.0	0.16
5.0	0.82
10.0	1.56

[QDC] = 0.001M, $[H^+]$ = 1.0M, T = 313K.

Comparison of the rate data of Tables 1-2 and Tables 12-13, would establish that if the respective alcohols, benzyhydrol and fluorenol, were to be formed as reaction intermediates, they would be rapidly oxidized to the respective products, benzophenone and fluorenone. Earlier work had shown that benzhydrol was rapidly oxidized to benzophenone in good yields when oxidized by chromic acid(6), alkaline permanganate(42), CrO_3-pyridine complex(43), and by N-bromo saccharin(45). Earlier investigations had shown that fluorenol was rapidly oxidized to fluorenone, when oxidizing agents such as V(V) in acid medium (46) and bromamine-T in acid medium(47) had been used.

Further evidence in support of the radical mechanism may be found in a comparison of the rates of hydrogen abstraction (from toluene, diphenylmethane, triphenylmethane and fluorene) and the rates of solvolysis of the corresponding chlorides (Table 14).

Table 14. Relative rates of oxidation, hydrogen abstraction and solvolysis.

Substrate	Relative rate of oxidation	Relative rate of hydrogen abstraction by CCl_3(a)	Relative rate of solvolysis by chlorides(b)
Toluene	1.0	1.0	1.0
Diphenylmethane	8.0	8.0	2×10^3
Triphenylmethane	12.0	16.7	1×10^7
Fluorene	130.0		

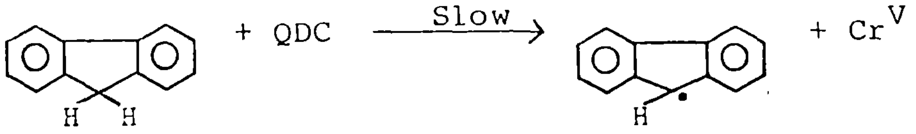
(a) ref. 48 ; (b) ref. 49.

The relative rates of oxidation were observed to be as follows: toluene = 1.0, diphenylmethane = 8.0, triphenylmethane = 12.0 and fluorene = 130 (Table 14). These relative rates appeared to be too small to be attributed to an ionic pathway. These relative rates of oxidation, by QDC, were comparable to those obtained in an earlier investigation wherein chromic acid in 95% acetic acid had been used as the oxidant(6). The data in Table 14 showed that there was agreement between the relative rates of oxidation and the rates of hydrogen atom removal, but the range of rates of solvolysis was much larger.

The observation of a kinetic isotope effect indicated that the cleavage of the carbon-hydrogen bond occurred in the rate-determining step. The small difference in the rates of reactions between the different substrates (toluene, diphenylmethane, triphenylmethane and fluorene) and the small values of ρ ($\rho = -1.25$ for diphenylmethanes, and $\rho = -1.50$ for fluorenes) obtained for these oxidation reactions suggested the possibility of mechanisms as follows:

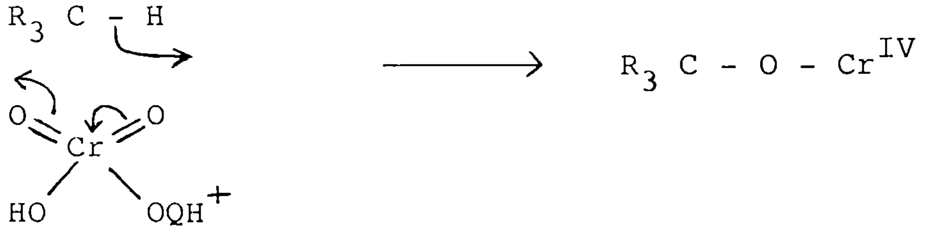
$$R_2CH_2 + QDC \xrightarrow{\text{Slow}} R_2\dot{C}H + Cr^{V} \qquad (5)$$

$$R_3CH + QDC \xrightarrow{\text{Slow}} R_3\dot{C} + Cr^{V} \qquad (6)$$



(7)

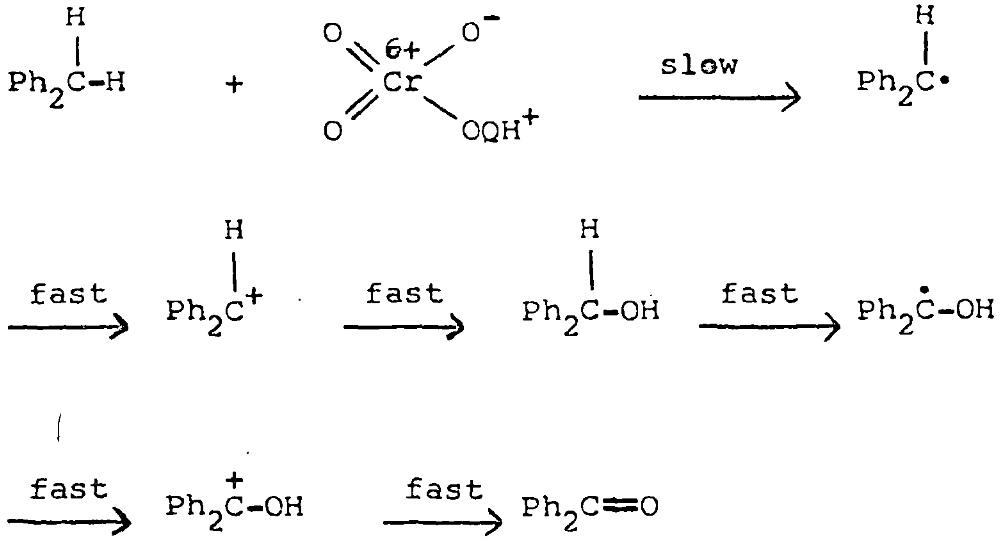
The radical intermediate formed was probably oxidized by one of the chromium species, possibly forming an ester such as:



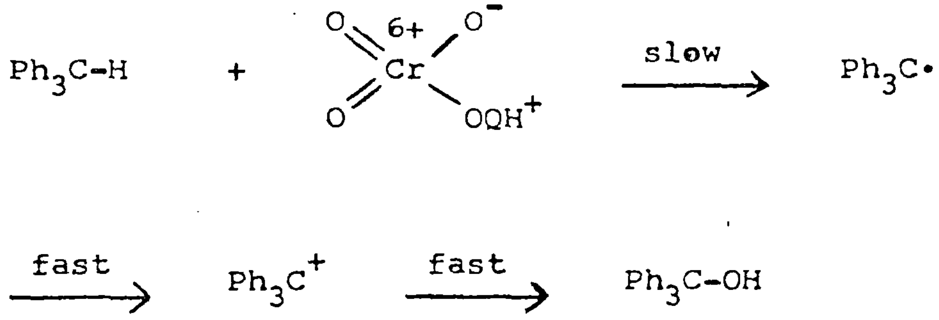
(8)

It can be postulated, therefore, that in the oxidation of these substrates (diphenylmethane, triphenylmethane and fluorene), the rate determining step was the abstraction of a hydrogen atom giving a radical. The subsequent conversion of the radical to the product, in all the cases, was rapid (Schemes 1-3). Resonance factors seem to be important in these reactions. The trend of observed reactivity (fluorene > triphenylmethane > diphenylmethane) is justifiable, on the basis of the stability of the products. In the case of fluorene and diphenylmethane, the products obtained were the ketones, which would be stabilized by conjugation influences more than the parent hydrocarbons. In the case of triphenylmethane, the presence of three bulky groups would facilitate the formation of the triphenylmethyl radical. The product, triphenyl carbinol, would be formed quite easily, even though this product would not have any carbonyl stabilisation with the pi-bonded aromatic system. This would account for the faster rate of oxidation for triphenylmethane over that for diphenylmethane. Under the present experimental conditions, no benzophenone could be isolated from the reaction mixture containing triphenylmethane and QDC in acid medium.

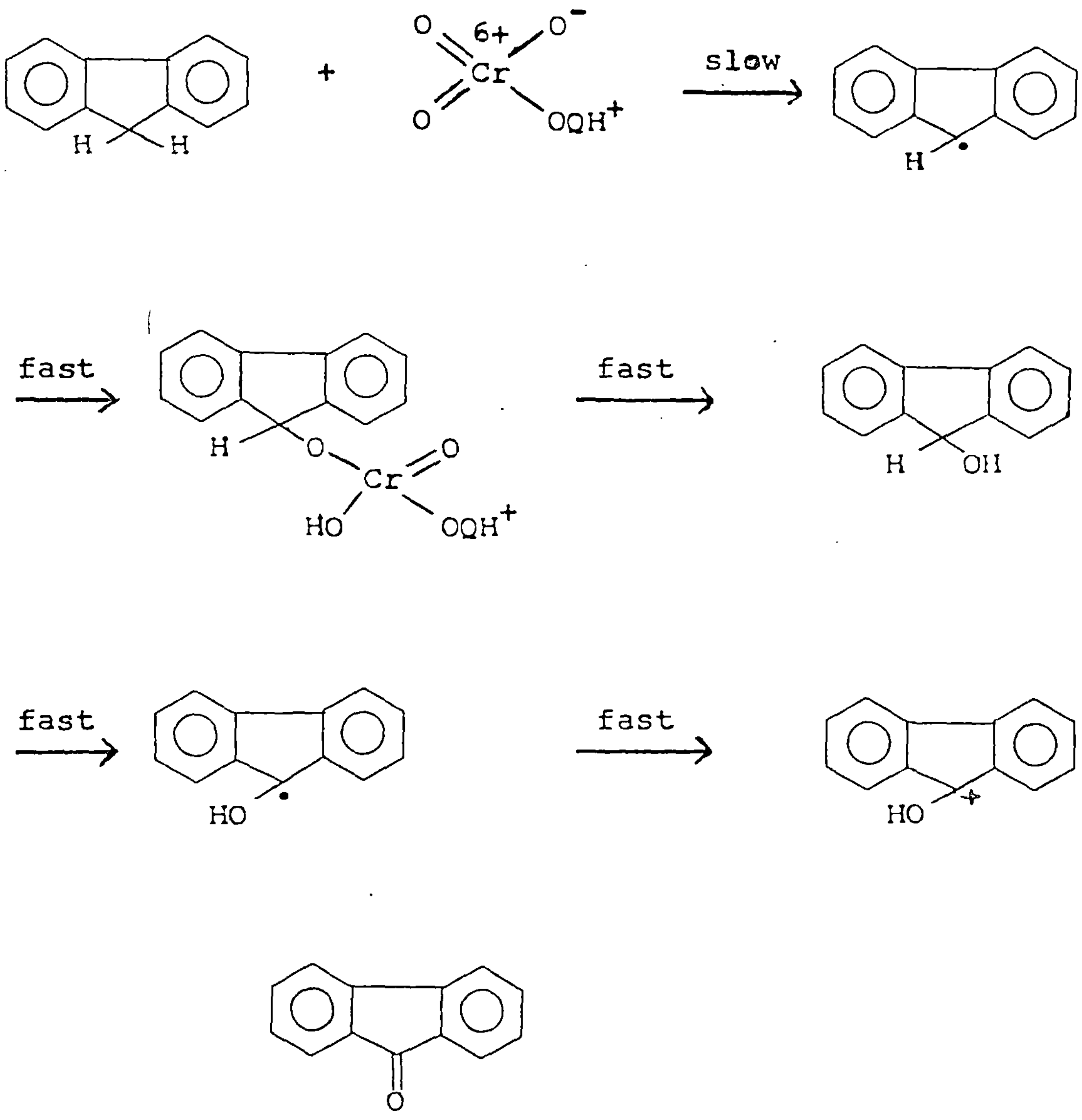
SCHEME 1



SCHEME 2



SCHEME 3



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H
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fast
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OOH⁺
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KINETICS OF OXIDATION OF POLYNUCLEAR AROMATIC HYDROCARBONS

1. Naphthalene

There has been a great deal of interest generated regarding the oxidation of naphthalene by various oxidizing agents. The ceric sulfate oxidation of naphthalene in aqueous acetic acid-sulfuric acid mixtures gave a first order dependence in each reactant(1). Chromic acid oxidation of polynuclear aromatic hydrocarbons generally resulted in nuclear oxidation. For example, (a) naphthalene gave 1,4-naphthoquinone and phthalic acid(2); (b) 2,3-dimethylnaphthalene gave 2,3-dimethyl-1,4-naphthoquinone(3); (c) 2-methylnaphthalene gave 2-methyl-1,4-naphthoquinone(4); and (d) 1-methylnaphthalene gave 5-methyl-1,4-naphthoquinone(5). With aqueous sodium dichromate, ring oxidation was made negligible under conditions which permitted side chain oxidation. Thus, methylnaphthalenes were oxidized to the corresponding naphthoic acids in about 95% yield(6). The chromic acid oxidation of 1,2,5-trimethylnaphthalene had resulted in the loss of an alkyl group, to yield 2,5-dimethyl-1,4-naphthoquinone(7). When heated with lead tetraacetate in acetic acid, napththalene gave 1-acetoxynaphthalene in 26% yield(8), but neither methylnaphthalenes nor products of their further conversion was detected. The oxidation of naphthalene by Milas's reagent(9) gave phthalic acid(10). The oxidation of naphthalene by peracetic acid had yield o- and p- quinones(11). Naphthalenes have been oxidized by aqueous $KMnO_4$(12,13) and by ruthenium tetroxide(14,15); the products in both these oxidations were the corresponding phthalic acids. The oxidation of naphthalene has been carried out by cobalt(III) perchlorate in aqueous acetonitrile(16), V(V) ions(17) and by periodic acid(18). The oxidation of naphthalene by potassium hexacyanoferrate(III) in acid media had yielded α-naphthol in approximately 35-45% conversion(19). A ρ value of -4.0 and the lack of a deuterium kinetic isotope effect suggested the formation of an aromatic cation radical in the rate-determining step of the reaction(19).

2. Phenanthrene

The chromic acid oxidation of phenanthrene(20,21) and 1-methylphenanthrene(22) had yielded phenanthraquinone and 1-methyl-9,10-phenanthraquinone, respectively. The chromic acid oxidation of 9-ethylphenanthrene had yielded phenanthraquinone(23), indicating the removal of an alkyl group during oxidation. The oxidation of methylphenanthrenes by aqueous sodium dichromate had given the corresponding phenanthroic acids in good yields(6). The oxidation of 9-methylphenanthrene by chromyl chloride had yielded 9-phenanthraldehyde in 30% yield and phenanthraquinone in 18% yield(24). The oxidation of phenanthrene by V(V) in 6N H_2SO_4 at 50°C had given phenanthraquinone in 38% yield(17). The oxidation of phenanthrene by Co(III) perchlorate in aqueous acetonitrile has been investigated(16). Ruthenium tetraoxide in CCl_4 has also been used for the oxidation of phenanthrene, the product being 9,10-phenanthraquinone in 28% yield(25). The oxidation of phenanthrene by potassium hexacyanoferrate(III)in acid medium had yielded 9-hydroxyphenanthrene in approximately 20-25% conversion(26).

PRESENT WORK

The present work is a kinetic investigation of the oxidation of polynuclear aromatic hydrocarbons (naphthalene and phenanthrene) by quinolinium dichromate, in acid medium, using dimethyl formamide as solvent.

Stoichiometry (vide "Experimental")

The stoichiometries of the reactions were determined and found to conform to the overall equations:

(a) $C_{10}H_8+3Cr^{VI}+2H_2O \longrightarrow C_{10}H_6O_2+3Cr^{IV}+6H^+$ (1)

(b) $C_{14}H_{10}+3Cr^{VI}+2H_2O \longrightarrow C_{14}H_8O_2+3Cr^{IV}+6H^+$ (2)

Effect of substrate and oxidant

Under pseudo-first-order conditions, the initial kinetic runs were first order with respect to the oxidant (QDC). Further, the rate constants were independent of the initial concentration of QDC (Tables 1-2).

Table 1. Rate data for the oxidation of naphthalene in DMF.

[Naphthalene] (10^2xM)	[QDC] (10^3xM)	10^4 x k_1 (s^{-1})	10^2 x k_2 ($M^{-1}s^{-1}$)
1.0	1.0	2.80	2.80
2.5	1.0	6.96	2.78
5.0	1.0	14.13	2.83
7.5	1.0	21.05	2.81
10.0	1.0	27.90	2.79
20.0	1.0	56.10	2.81
1.0	0.75	2.73	
1.0	0.50	2.69	
1.0	0.25	2.85	
1.0	0.10	2.91	
1.0	0.05	2.87	

$[HClO_4]$ = 0.5M, T = 313K.

Table 2. Rate data for the oxidation of phenanthrene in DMF.

[Phenanthrene] (10^2 x M)	[QDC] (10^3 x M)	10^4x k_1 (s^{-1})	10^2 x k_2 ($M^{-1}s^{-1}$)
1.0	1.0	1.80	1.80
5.0	1.0	9.0	1.80
7.5	1.0	14.2	1.89
10.0	1.0	18.5	1.85
20.0	1.0	37.3	1.87
1.0	0.75	1.7	
1.0	0.50	1.8	
1.0	0.10	1.6	

$[HClO_4]$ = 0.5M, T = 313K.

The order of the reaction with respect to substrate was determined by varying the concentrations of naphthalene and phenanthrene, respectively, over a twenty-fold range and observing the effect on the rate, at constant QDC and acid concentrations. The data have been recorded in Tables 1-2. It was observed that the reaction showed a first order dependence on the concentrations of the substrates. Plots of k_1 against the concentration of the substrate were linear passing through the origin (Figs.1-2), indicating a first order dependence of the reaction on the concentrations of the substrates. The second order rate constants(k_2) were found to remain constant as the concentrations of the substrate was increased, indicating that the reaction was first order with respect to the substrate concentration (Tables 1-2).

Effect of acid

The rate of the reaction showed an increase, with increasing concentrations of acid (Tables 3-4).

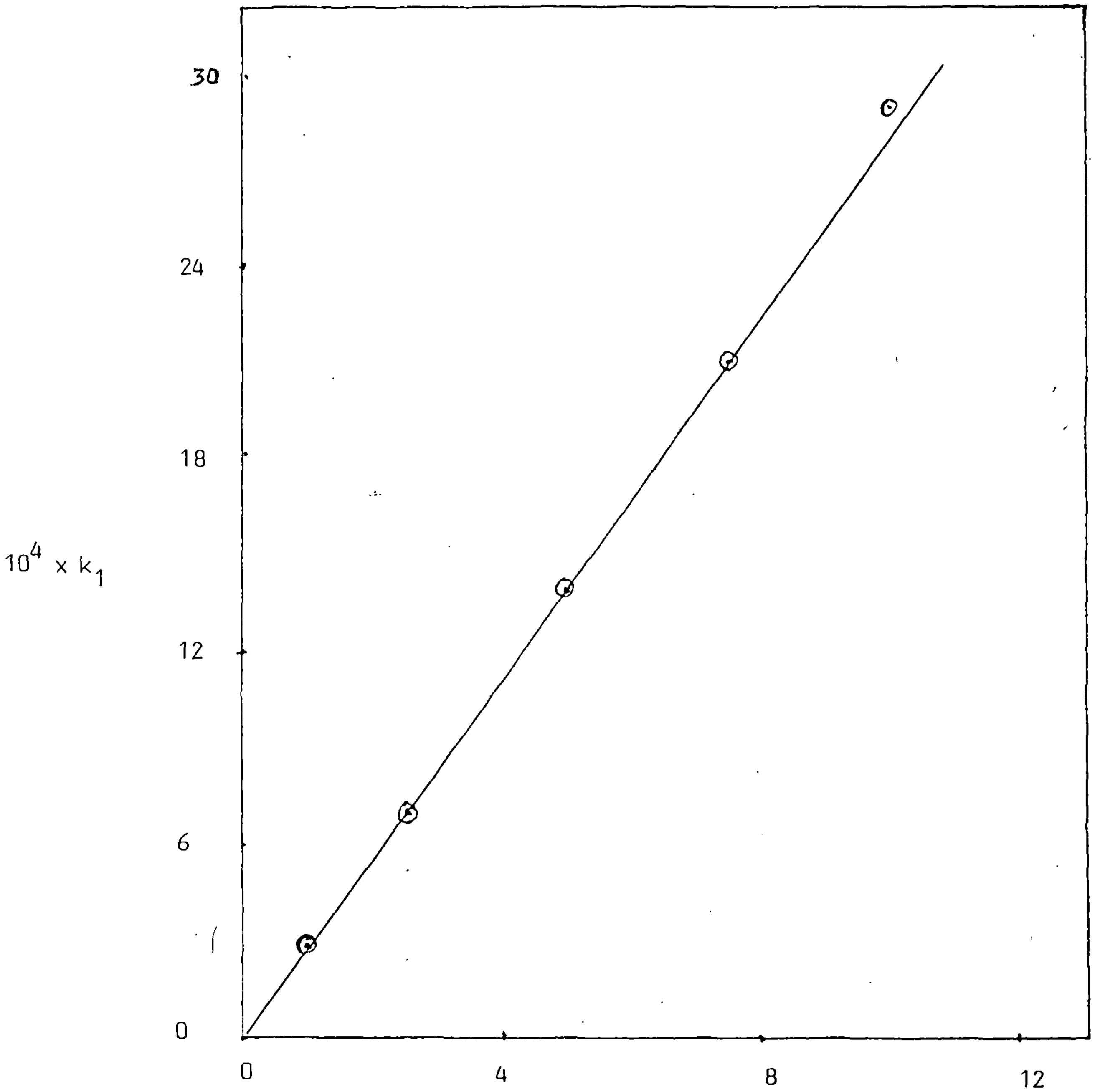


Fig.1: Plot of k_1 against substrate concentration (Naphthalene)

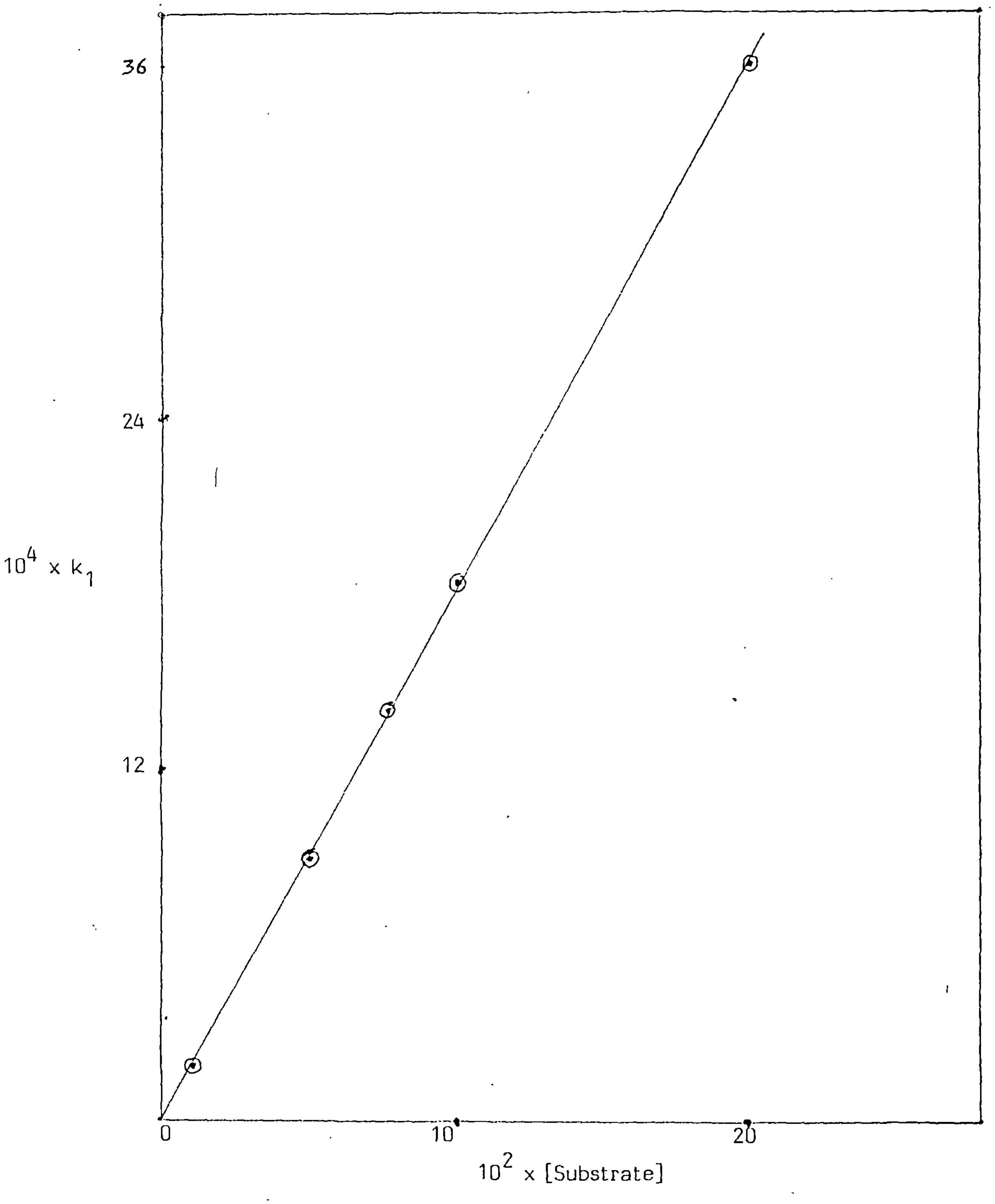


Fig.2: Plot of k_1 against substrate concentration (Phenanthrene)

Table 3. Effect of acid on the oxidation of naphthalene in DMF.

$[HClO_4]$ (M)	$10^4 \times k_1$ (s^{-1})	$10^4 k_1/[H^+]$
0.10	0.56	.60
0.25	.42	5.68
0.50	2.80	5.60
0.75	4.18	5.57
1.00	5.71	5.71

[Naphthalene]=0.01M, [QDC] = 0.001M, T = 313K.

Table 4. Effect of acid on the oxidation of phenanthrene in DMF.

$[HClO_4]$ (M)	$10^4 \times k_1$ (s^{-1})	$10^4 k_1/[H^+]$
0.25	0.9	3.60
0.50	1.8	3.60
0.75	2.6	3.47
1.0	3.7	3.70
1.25	4.6	3.68

[Phenanthrene]=0.01M, [QDC] = 0.001M, T = 313K.

Plots of log k_1 against $\log[H^+]$ were linear, with slopes equal to unity (Figs.3-4), indicating that the reaction was dependent on the first power of the concentration of acid. The increase in the rate of oxidation with acidity indicated the involvement of a protonated Cr(VI) species in the rate determining step. The involvement of such species is prevalent in chromic acid oxidation reactions(27a).

Rate law

Under the present experimental conditions, wherein pseudo-first-order conditions have been used for all the kinetic determinations, the rate law could be expressed as:

$$\text{Rate} = -\frac{d[\text{Cr(VI)}]}{dt} = k[\text{Substrate}][\text{QDC}][H^+] \qquad (3)$$

Effect of solvent

The dielectric constants for DMF-water mixtures have been estimated from the dielectric constants of pure solvents and have been recorded in Table 5.

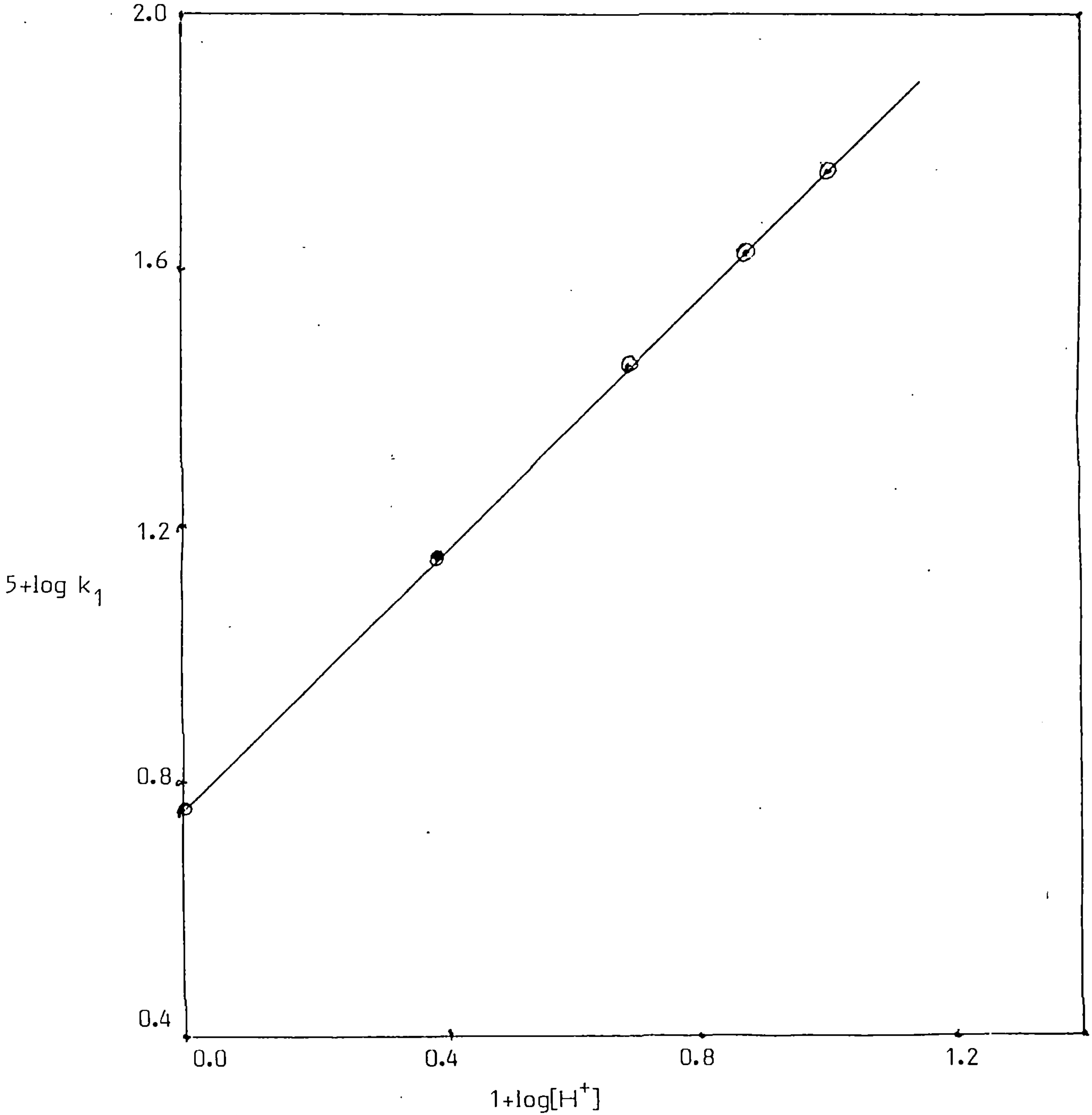


Fig.3: Plot of log k_1 against log [H^+] (Naphthalene)

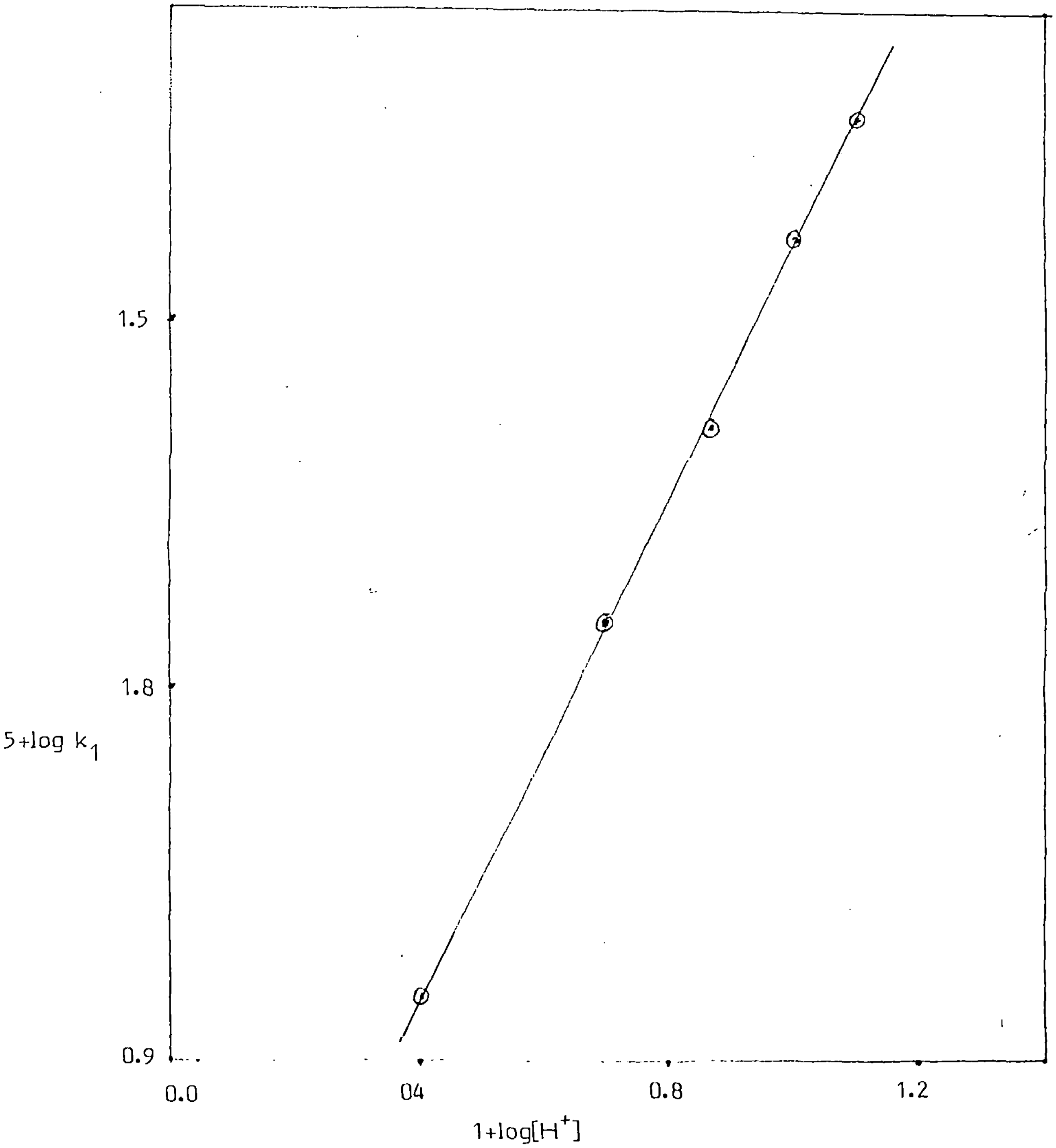


Fig.4: Plot of log k_1 against log[H$^+$] (Phenanthrene)

Table 5. Effect of solvent on the rates of oxidation for naphthalene and phenanthrene.

DMF : H_2O (%, v/v)	D	Naphthalene (10^4k_1, s^{-1})	Phenanthrene (10^4k_1, s^{-1})
100:0	37.6	2.80	1.8
95:5	39.7	2.42	1.4
90:10	41.8	2.22	1.1
85:15	43.9	2.05	0.9
80:20	46.1	1.71	0.7

[Substrate]=0.01M, [QDC] = 0.001M, [$HClO_4$]=0.5M, T = 313K.

Changes in the composition of the solvent mixtures affected the rates of these reactions. The essential features concerning the effect of solvent on the rate of oxidation of naphthalene and phenanthrene can be summarized as follows:

(a) Increasing propositions of dimethyl formamide resulted in an increase in the rate of the reaction (Table 5). This was in accordance with the observation that larger reaction times were required for more polar solvents(28). This was brought about by a lowering of the dielectric constant of the medium, which would result in a less polar transition state compared to more polar reactants.

(b) Plots of log k_1 against the reciprocal of dielectric constant were linear with positive slopes (Figs.5-6), ndicating that the reaction was of the ion-dipole type(29). This also confirmed the participation of a protonated Cr(VI) species in the rate determining step of the reaction.

(c) Solvent effects on the rates of reactions may also be due to factors such as the solvating power of solvents(30), solute-solvent interaction(31,32) and solvent structures.

Effect of temperature

The rates of reactions were increased with an increase in the temperature (Table 6).

Table 6. Effect of temperature on the oxidation of naphthalene and phenanthrene in DMF.

Temp. (±0.1K)	Naphthalene	Phenanthrene
	(10^4 x k_1, s^{-1})	
303	1.91	1.2
308	2.31	1.4
313	2.80	1.8
318	3.13	2.2
323	3.90	2.8

[Substrate] = 0.01M, [QDC] = 0.001M, [$HClO_4$] = 0.5M.

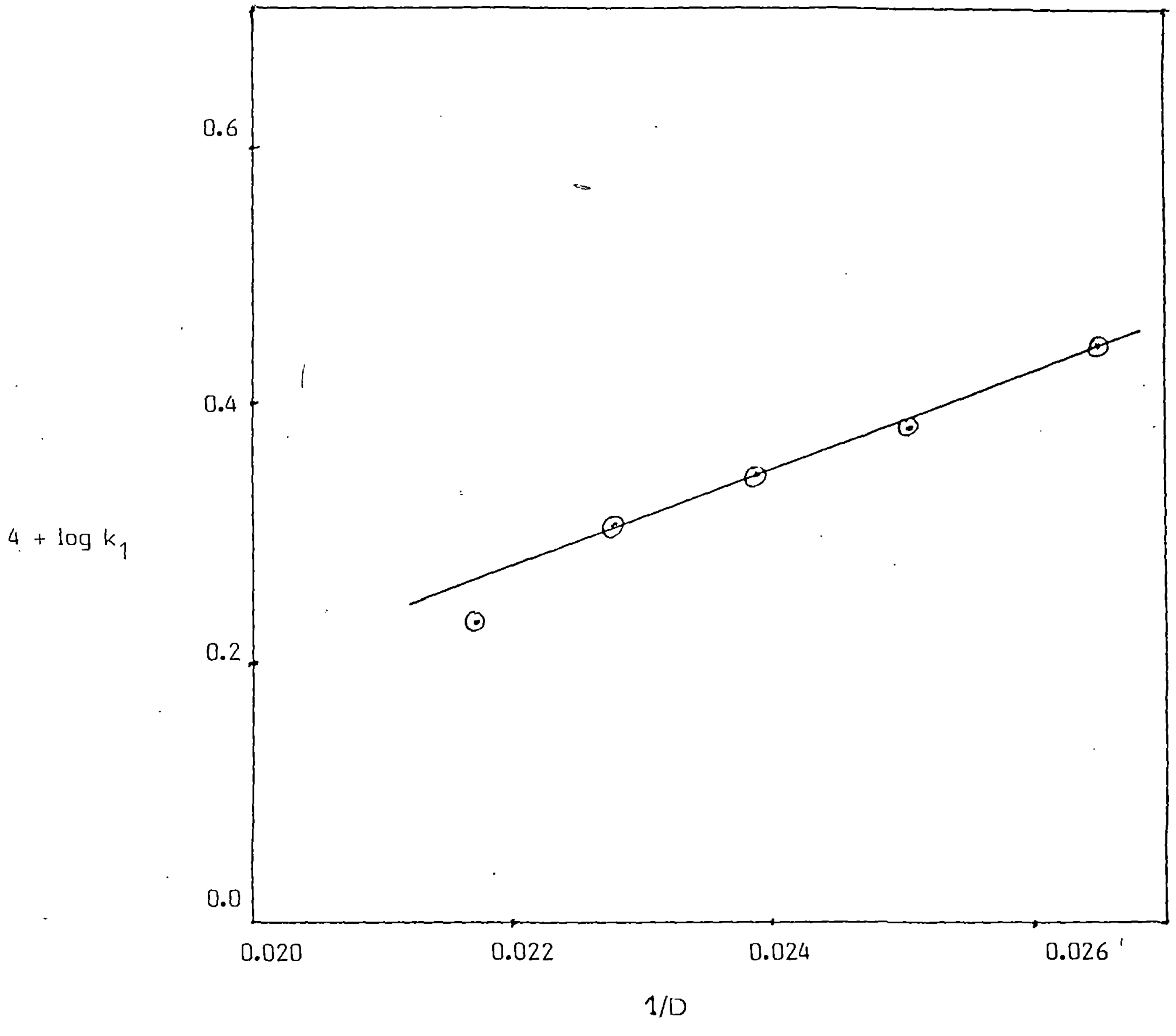


Fig.5: Plot of log k_1 against the reciprocal of dielectric constant (Naphthalenes)

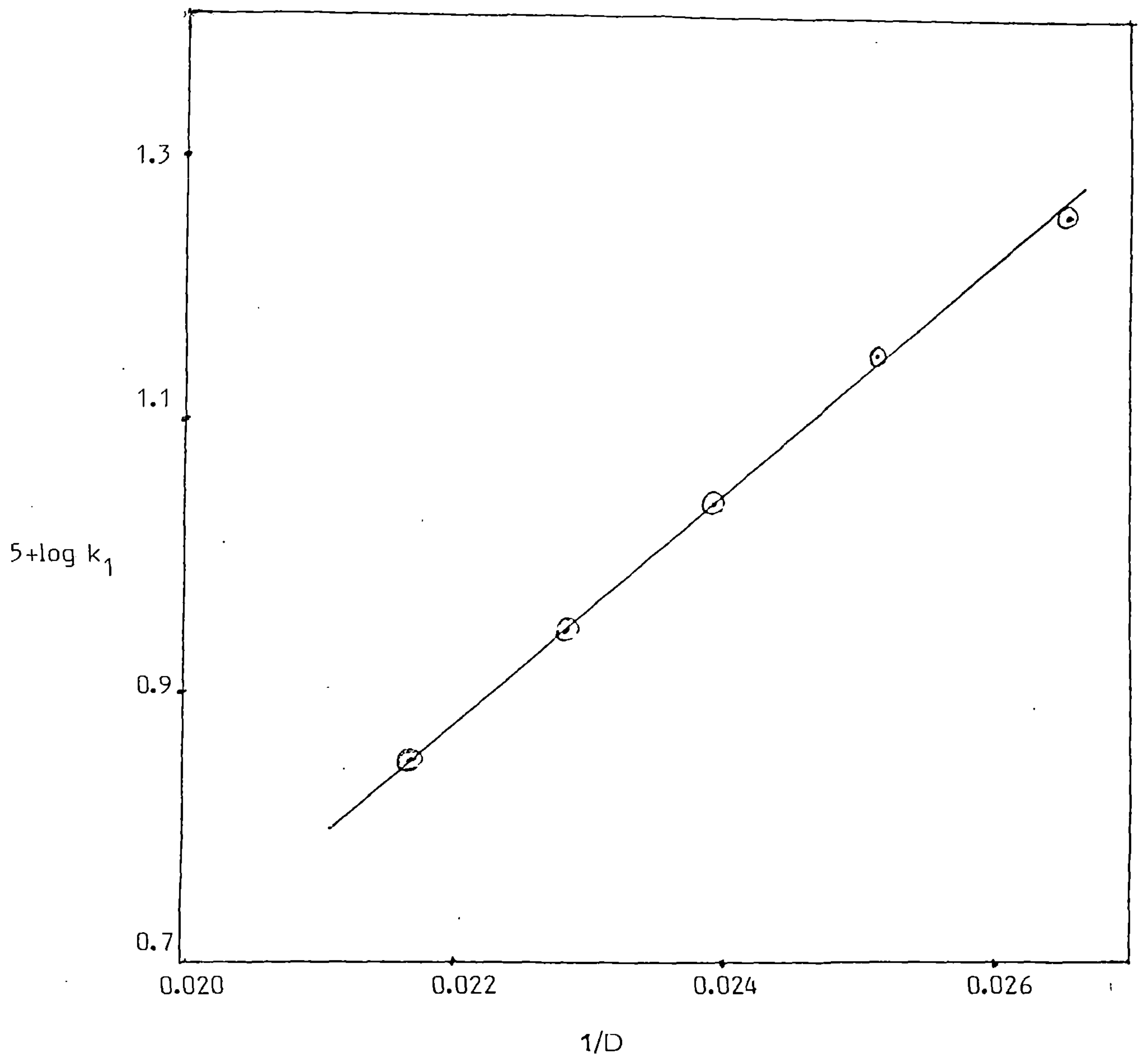


Fig.6: Plot of log k_1 against the reciprocal of dielectric constant (Phenanthrene)

Plots of log k_1 against the reciprocal of temperature were linear (Figs. 7-8), and the slopes of these plots were used to calculate the activation energies. The other activation parameters were evaluated, and have been shown in Table 7.

Table 7. Activation parameters for the oxidation of naphthalene and phenanthrene in DMF.

Parameters	Naphthalene	Phenanthrene
E (kJ mol^{-1})	28±2	35±2
$\Delta H^{\neq}$ (kJ mol^{-1})	25±2	32±2
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	-230±5	-213±3
$\Delta G^{\neq}$ (kJ mol^{-1})	97±2	99±2

Hammett plot

The effect of substituents on the rates of reactions were studied, and it was observed that electron-releasing groups accelerated the rate of the reaction, whereas electron-withdrawing groups caused a decrease in the rate of the reaction (Tables 8-9).

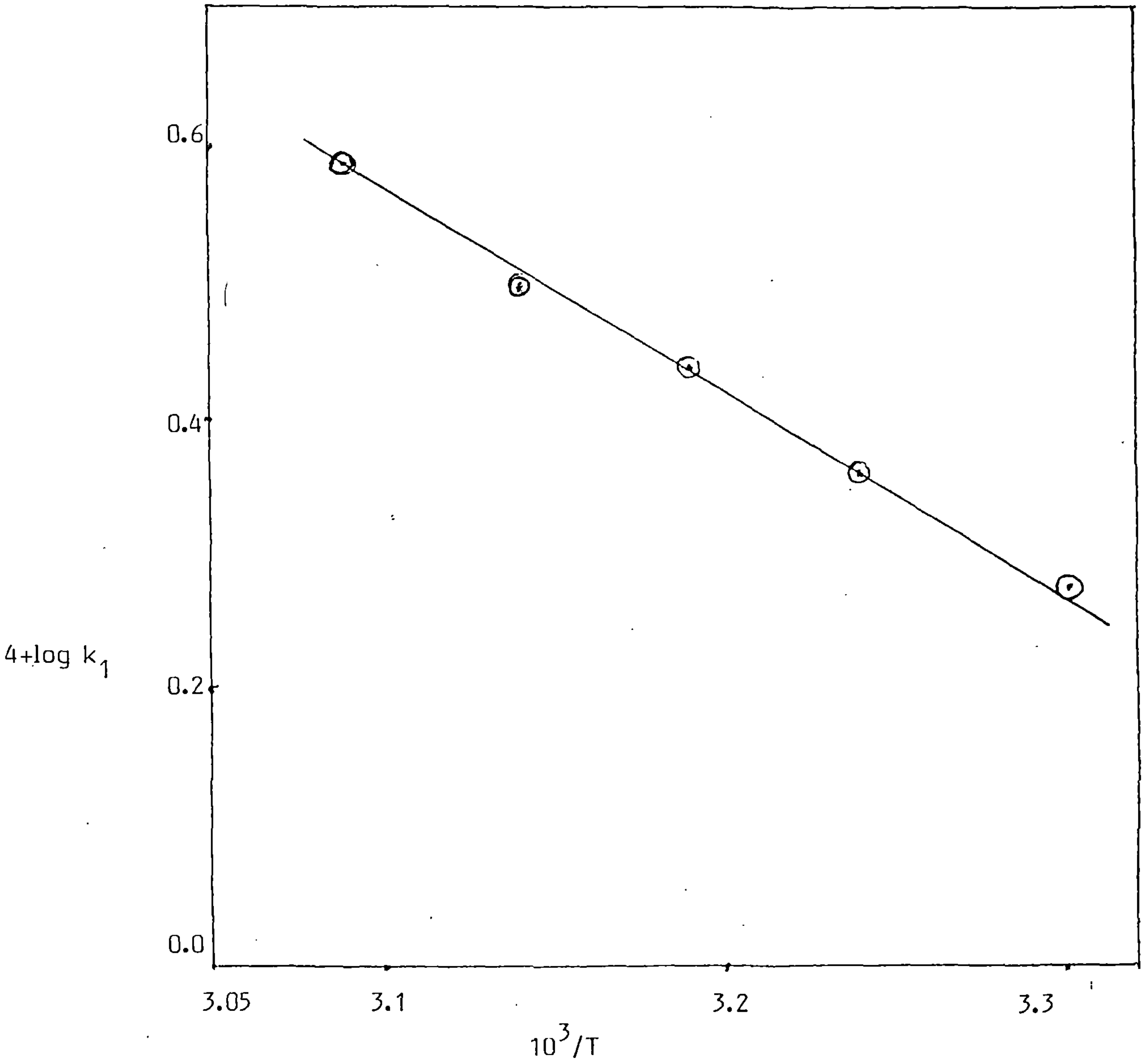


Fig. 7: Plot of log k_1 against the reciprocal of temperature (Naphthalene

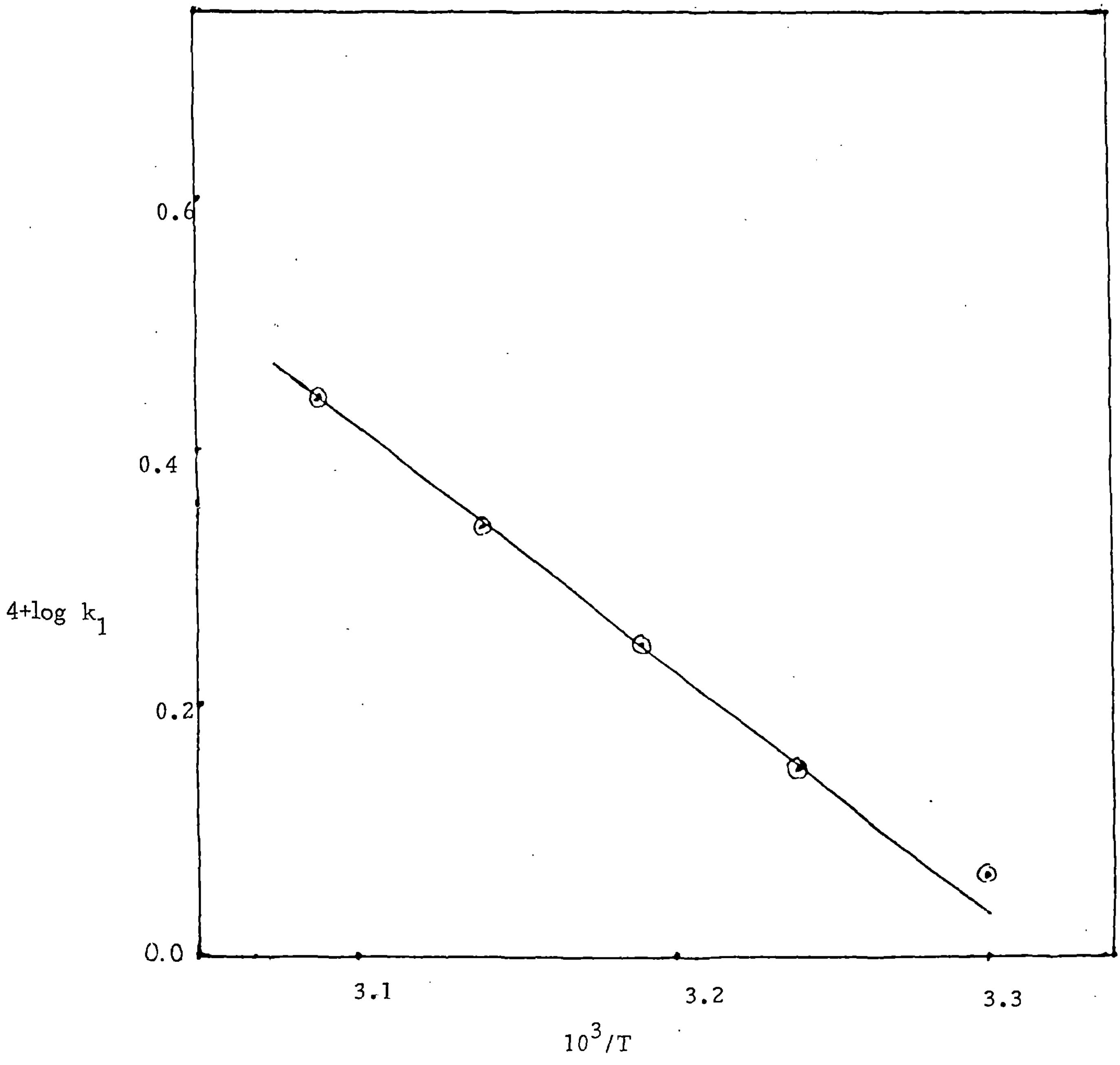


Fig.8: Plot of log k_1 versus inverse of temperature (Phenanthrene)

Table 8. Effect of substituents on the oxidation of naphthalene in DMF.

Substituent	$10^4 \times k_1$ (s^{-1})	$10^2 \times k$ ($M^{-2}\ s^{-1}$)	k_{rel}
1-Methoxy	9.95	39.9	7.13
1-Methyl	6.31	12.6	2.25
Naphthalene	2.80	5.6	1.0
1-Chloro	1.99	3.98	0.71
1-Bromo	1.58	3.16	0.56
1-Nitro	0.32	0.64	0.11

[Substrate]=0.01M, [QDC]=0.001M, $[HClO_4]$=0.5M,
T = 313K; $k = k_1$/[Naphthalenes] $[H^+]$.

Table 9. Effect of substituents on the oxidation of phenanthrene in DMF.

Substituent	$10^4 \times k_1$ (s^{-1})	$10^2 \times k$ ($M^{-2}s^{-1}$)	k_{rel}
9-Methoxy	8.9	17.8	4.94
9-Methyl	2.8	5.6	1.56
Phenanthrene	1.8	3.6	1.0
9-Nitro	.7	1.4	0.39

[Substrate] = 0.01M, [QDC] = 0.001M, $[HClO_4]$ = 0.5M,
T=313K, $k = k_1$/[Phenanthrenes]$[H^+]$.

Structure-reactivity correlations were obtained using the Hammett equation (Figs.9-10). The effect of substituents were correlated with a reaction constant (ρ) of -1.30 (naphthalenes) and -1.79 (phenanthrenes).

Kinetic isotope effect

The kinetic isotope effect was determined so as to derive more information regarding the order of bond making and bond breaking, and about the structure of the intermediate. When the reaction was performed with naphthalene-d_8, the rate of the reaction showed a significant decrease, and the k_H/k_D value obtained was 5.80 (Table 10).

Table 10. Kinetic isotope effect at 313K.

Substrate	$10^5 \times k_1 (s^{-1})$	$10^3 \times k\ (M^{-23}s^{-1})$
Naphthalene	28.0	56.0
Naphthalene-d_8	4.83	9.66
$k_H/k_D = 5.80$		

[Substrate] = 0.01M, [QDC] = 0.001M,
$[H^+] = 0.5M$, k_H and $k_D = k_1/[\text{Substrate}][H^+]$.

Mechanism

For the oxidation of naphthalene and phenanthrene,

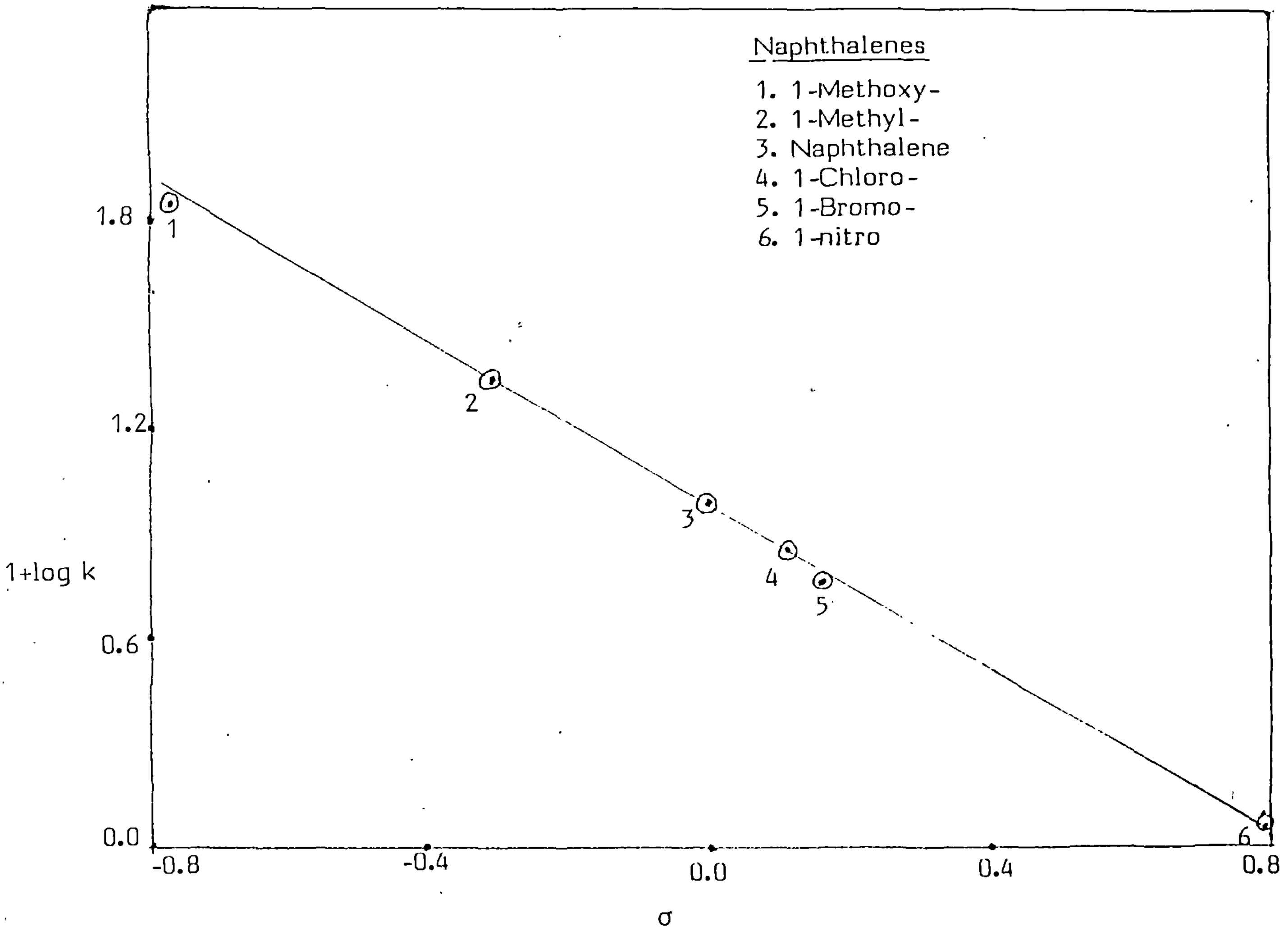


Fig.9: Hammett plot (Naphthalenes)

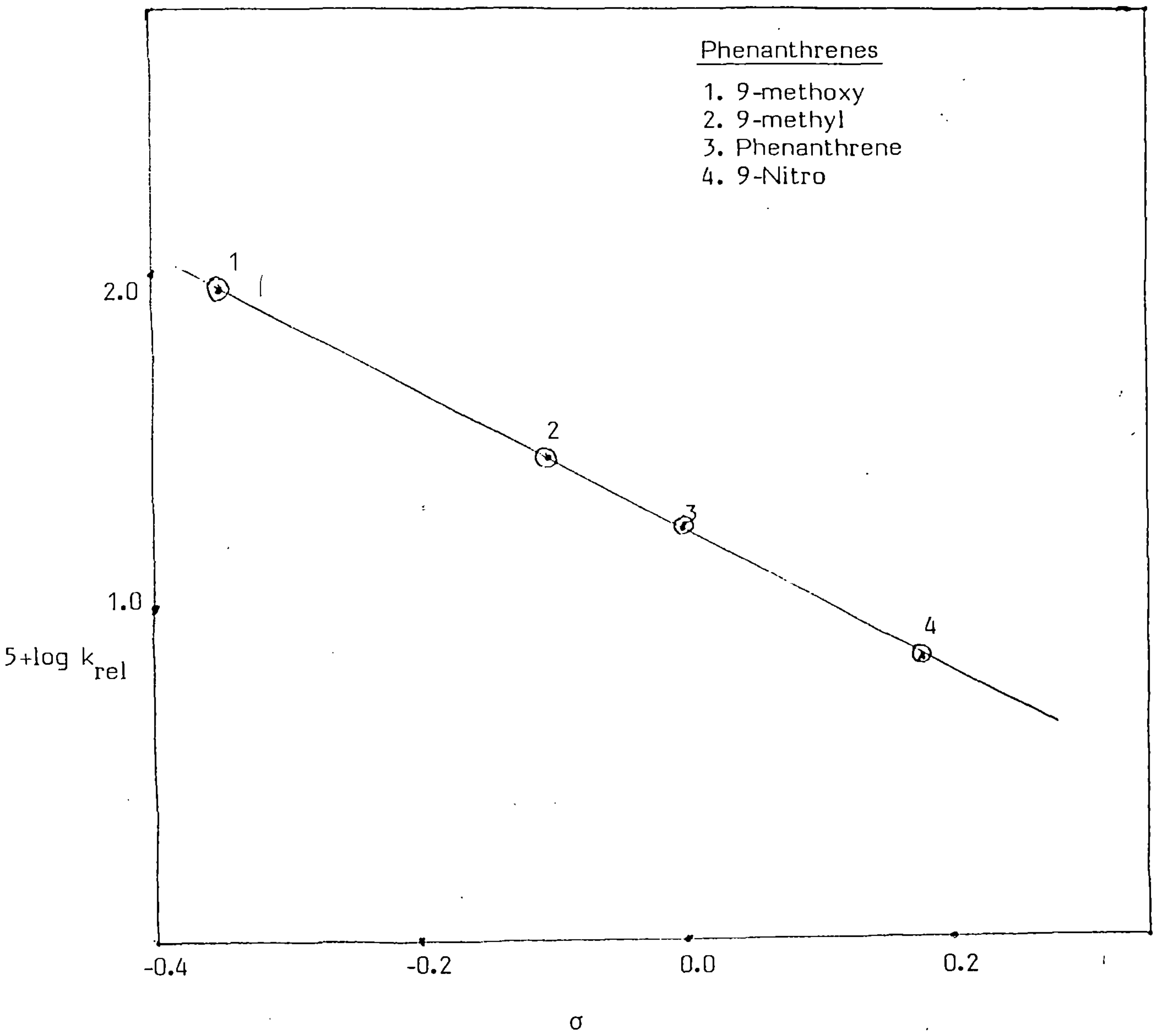


Fig.10: Hammett plot (Phenanthrenes)

the observed kinetic data could be summarized as folllows:

(a) The linear increase in the rate of oxidation with acidity (Tables 3-4) indicated the involvement of a protonated Cr(VI) species in the rate determining step. The initial reaction would be between the substrate and the protonated Cr(VI) species.

(b) The observed increase in the rate of reaction, with a decrease in the polarity of the solvent medium (Table 5), indicated that the transition state was much less polar than the reactants. This would contribute to the facile formation of a radical intermediate, rather than an ionic species, in the rate determining step of the reactions. Linear plots of log k_1 against the inverse of dielectric constant (Figs.5-6) yielded positive slopes. This suggested an interaction between a positive ion and a dipole(29), and was in consonance with the observation that in the presence of an acid, the rate determining step involved a protonated Cr(VI) species.

(c) The kinetic isotope effect, k_H/k_D=5.80, for naphthalene, indicated that the carbon-hydrogen bond was cleaved in the rate determining step of the reaction.

(d) The effect of substituents on the rates of the reactions was correlated using the Hammett equation. The values of reaction constants (ρ) were -1.30 (for naphthalenes) and -1.79 (for phenanthrenes). This was similar to the effect of substituents observed in the oxidation of toluene by chromic acid(33), and suggested the formation of a radical intermediate in the slow step of the reaction.

(e) The presence of radical intermediates was indicated by the initiation of polymerisation of acrylonitrile and the induced reduction of $HgCl_2$.

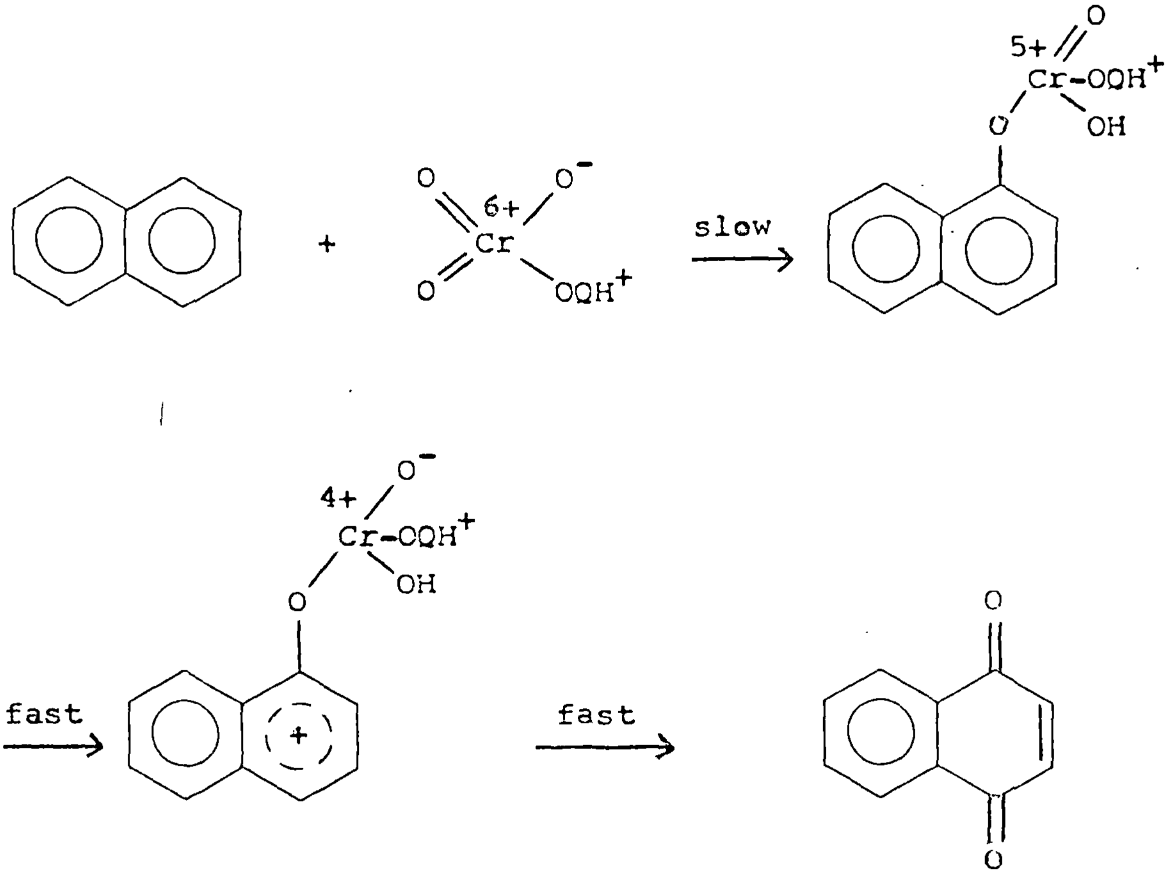
The mechanistic pathway of the oxidation process would thus involve a hydrogen abstraction process, resulting in the formation of a radical intermediate. The initially formed radical would be expected to react instantaneously with the Cr^{5+} species formed in the initial step, similar to the observation in the oxidation of saturated hydrocarbons by Cr(VI) compounds(27b,34). The negative values of the reaction constants observed in these oxidation reactions (ρ =-1.30 for naphthalenes and ρ = -1.79 for phenanthrenes) clearly indicated the possibility of a hydrogen abstraction mechanism.

The cleavage of the carbon-hydrogen bond, in the rate determining step of the reaction, was supported by the observed kinetic isotope effect, $k_H/k_D=5.80$, for naphthalene (Table 10). The radical intermediate formed was rapidly oxidized via the formation of a chromate ester. The similarity in rate laws observed in the present investigation and those observed for chromic acid oxidations(27a) would favour the formation of a chromate ester. The steps leading from the radical to the products (1,4-naphthoquinone from naphthalene, and 9,10-phenanthraquinone from phenanthrene) could not readily be studied since they followed the rate determining step and were very rapid.

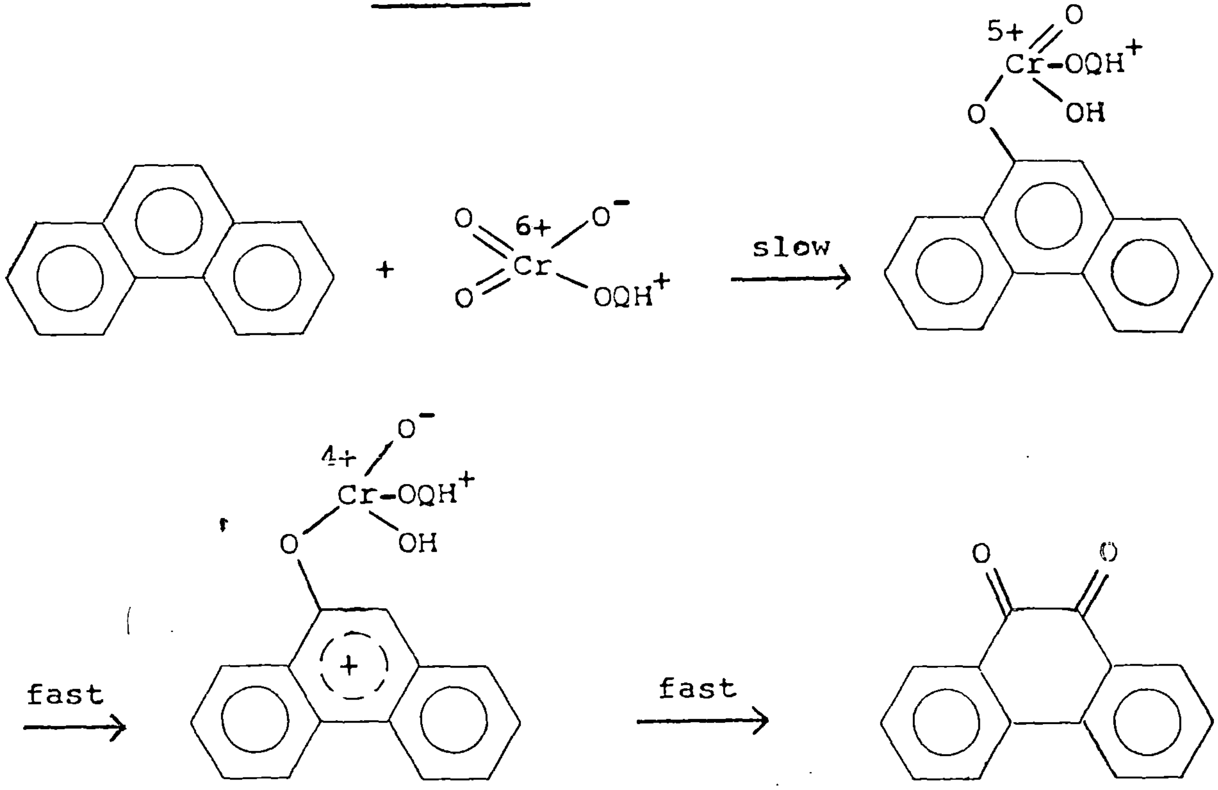
Earlier investigations have shown that polynuclear aromatic hydrocarbons have been converted to quinones. For example, the two-phase oxiation of naphthalene and phenanthrene to the corresponding quinones, 1,4-naphthoquinone and 9,10-phenanthroquinone respectively, was accomplished by using ammonium persulphate in the catalytic presence of ceric ammonium sulphate, silver nitrate and sodium dodecylsulphate(35). Various quinones have been prepared from aromatic hydrocarbons with chromium trioxide by the addition of 18-crown-6-ether(36). The oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone was achieved with aqueous hydrogen peroxide, in acetic acid, in the presence of a palladium catalyst supported on sulphonated polystyrene type resins(37).

In the present investigation, the oxidation of naphthalenes and phenanthrene by QDC, in acid medium, yielded 1,4-naphthoquinone and 9,10-phenanthraquinone, respectively. The sequence of reactions has been shown in Schemes 1-2.

SCHEME 1



SCHEME 2



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KINETICS OF OXIDATION OF SOME AROMATIC HYDROCARBONS BY QUINOLINIUM DICHROMATE

SUMMARY

SUMMARY

Hexavalent chromium compounds have been widely used as oxidizing agents, reacting with diverse kinds of organic substrates. The mechanism of oxidation varies with the nature of the chromium(VI) species and the solvent used. The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be a subject of interest. A number of novel chromium(VI) oxidizing agents have been introduced, especially for complex or highly sensitive substances where great selectivity and effectiveness, coupled with mildness of conditions, are prerequisites for success.

Some of the chromium(VI) reagents which have been used as efficient oxidizing agents are:

Chromium trioxide; chromyl chloride; Jones reagent — a solution of Cr(VI) oxide in concentrated sulfuric acid(1); Collins' reagent — dipyridinium Cr(VI) oxide in dichloromethane(2); Corey's reagent — pyridinium chlorochromate(3); pyridine oxodiperoxy chromium(VI) reagent(4); pyridinium dichromate(5); bis tetrabutylammonium dichromate(6); Chaudhuri's reagent — pyridinium fluorochromate(7); 4-(dimethylamino)-pyridinium chlorochromate(8); Cr(VI) oxide diperoxide(9); Chlorotrimethylsilane-chromium trioxide(10); chromium peroxide complexes(11); imidazolium dichromate(12); pyridinium bromochromate(13); biphosphonium dichromate(14); and 3-carboxy pyridinium dichromate(15).

New procedures have been emerging involving non-aqueous chromium(VI) reagents with the general idea that anhydrous conditions are more conducive to mild oxidation.

The reagent employed in the present investigation, quinolinium dichromate(QDC), $(C_9H_7NH^+)_2Cr_2O_7^{2-}$, has emerged as a very useful and versatile oxidant(16), which is clearly deserving of widespread application.

CHAPTER-I Kinetics of Oxidation of Toluene and Substituted Toluenes

The kinetics of oxidation of toluene and substituted toluenes (xylenes, methoxytoluenes and nitrotoluenes) by quinolinium dichromate(QDC) has been studied in acid medium, using dimethyl formamide as the solvent, under a nitrogen atmosphere. The progress of the reaction was followed spectrophotometrically, by observing the disappearance of chromium(VI) at 440nm. A stoichiometric ratio, Δ[QDC]/ Δ[Substrate], of 1.09 indicated a two-electron transfer. The rate of the reaction was found to be dependent on the first powers of the concentrations of each reactant (substrate, oxidant and acid). The linear increase in the oxidation rate with acidity suggested the involvement of a protonated Cr(VI) species in the rate determining step.

The reaction has been found to be fastest in those solvent mixtures containing the largest proportions of dimethyl formamide. Plots of log k_1 (the pseudo-first-order rate constant) against the reciprocal of the dielectric constant were linear, with positive slopes, indicating an ion-dipole type of reaction. This was also in consonance with the observation that, in the presence of an acid, the rate-determining step involved a protonated Cr(VI) species.

The effect of changes in temperature on the rate of the reaction has been studied, and the activation parameters have been evaluated. The reactions were characterized by negative entropies of activation. This would suggest an ordered transition state, relative to the reactants. The isokinetic temperature was 359K. Although current views do not attach much physical significance to isokinetic temperatures, a linear correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is usually a necessary condition for the validity of the Hammett equation. Further, the values of the free energies of activation were nearly constant, indicating that the same mechanism operated for the oxidation of all the substrates studied.

The kinetic rates of oxidation were in accordance with the theory of electronic substituent effects. It was found that electron-releasing groups caused an acceleration in the rate of the reaction, while electron-withdrawing groups caused a retardation in the rate of the reaction. A plot of log k_{rel} against σ^+ gave a value of $\rho = -0.20$. For most hydrogen abstraction reactions, the reaction constants (ρ) have small magnitudes.

A kinetic isotope effect, k_H/k_D, was observed in the range 5.0-5.3 for substituted toluenes, which indicated that the rate-determining step involved the cleavage of the carbon-hydrogen bond of the methyl group attached to the arene ring.

There was no induced polymerization of acrylonitrile or the reduction of mercuric chloride. No ESR signals could be detected. These results do not rule out free radical intermediates; they simply do not provide evidence that radicals are formed. This may be due to the high rate of oxidation of the free radicals.

Although the reaction did not give any ESR signals and there was no evidence for the induced polymerization of acrylonitrile or the reduction of mercuric chloride, the possibility of a hydrogen abstraction mechanism cannot be completely excluded. The radical formed initially would react rapidly with the Cr^{5+} species formed in the initial step. The transition state could be considered as involving a carbon atom which would exist with both, radical and carbonium ion character. This resonance hybrid would possess lower energy than either the radical or the carbonium ion, which would account for the stability of the intermediate. Efforts to isolate the possible intermediate, benzyl alcohol, were not successful. This indicated that the intermediate, formed in the slow step of the reaction, was converted rapidly to the product. The only isolable product, in each case, was the corresponding aldehyde, which was characterized as the respective 2,4-dinitrophenyl hydrazone derivative, obtained in good yields. Since drastic conditions of concentrations and temperatures were not employed in the present investigation, only one methyl group (in the case of xylenes) underwent oxidation to give the corresponding aldehyde. There was no formation of acid in any of these reactions, implying that the product (the corresponding aldehyde in each case) was stable, and did not undergo further oxidation , under the experimental conditions employed in this investigation.

CHAPTER 2 Kinetics of Oxidation of Diphenylmethane, Triphenylmethane and Fluorene

The kinetics of oxidation of diphenylmethane, triphenylmethane and fluorene by quinolinium dichromate(QDC) has been studied in acid medium, using dimethyl formamide as solvent, under a nitrogen atmosphere. The stoichiometry of the reaction was determined to be 1:2 (substrate: oxidant). The rate of the reaction showed a first order dependence on the concentrations of each reactant — substrate, oxidant and acid. The increase in the rate with acidity suggested the involvement of a protonated Cr(VI) species in the rate-determining step of the reaction.

With an increase in the dielectric constant of the medium, there was a decrease in the rate of the reaction, which was in consonance with the observation that the use of more polar solvents required larger reaction times.

The rate of the reaction was enhanced, with an increase in the temperature of the medium. The activation parameters have been evaluated.

Conjugation influences and resonance factors seem to play an important role in these oxidation reactions. The observed order of reactivity was:

Fluorene >triphenylmethane> diphenylmethane.

Fluorene was oxidized rapidly, owing to the labile nature of the 9-position. The electromeric effect would be higher in fluorene, which would contribute to a much higher rate of oxidation of fluorene over that for triphenylmethane and diphenylmethane. Steric hindrance due to the triarylmethane group would result in triphenylmethane being oxidized at a faster rate, compared to diphenylmethane.

Structure-reactivity correlations were obtained using the Hammett equation. Electron-releasing groups caused an increase in the rate of oxidation, whereas electron-withdrawing groups caused a retardation in the rate of the reaction. Plots of log k_{rel} against σ were linear, and the values of the reaction constants (ρ) were obtained as -1.50 (fluorenes) and -1.25 (diphenylmethanes). The values of the reaction constants (ρ) indicated that the initial reaction was the abstraction of a hydrogen atom, forming a radical intermediate in the rate-determining step of the reaction.

The kinetic isotope effect, k_H/k_D=6.0 for 9,9'-dideuterofluorene, indicated the cleavage of a carbon-hydrogen bond in the rate-determining step of the reaction, yielding a radical intermediate.

The presence of radical intermediates was detected by ESR spectroscopy and by the polymerization tests.

The mechanistic pathway of the reaction involved the formation of a radical intermediate in the slow step of the reaction. The conversion of the radical to the carbocation was rapid, and hence the formation of the carbocation could not be detected. The intermediates, benzhydrol and fluorenol (formed during the oxidations of diphenylmethane and fluorene, respectively) could not be isolated from the respective reaction mixtures. This indicated that the radical intermediate was converted, in rapid steps, to the products.

The major products obtained in these oxidation reactions, in good yields, were benzophenone (from diphenylmethane), triphenylcarbinol (from triphenylmethane), and fluorenone (from fluorene). These products were characterized by analytical and spectral methods.

CHAPTER 3 Kinetics of Oxidation of Polynuclear Aromatic Hydrocarbons

The kinetics of oxidation of polynuclear aromatic hydrocarbons (naphthalene and phenanthrene) by quinolinium dichromate (QDC) has been studied in acid medium, using dimethyl formamide as the solvent, under a nitrogen atmosphere. The stoichiometries of the reactions were determined. The rate of the reaction was dependent on the first powers of the concentrations of each reactant — substrate, oxidant and acid. The first order dependence of the rate on acid concentration indicated that a protonated Cr(VI) species was involved in the rate-determining step of the reaction.

The rate of the reaction was increased, with increasing proportions of dimethyl formamide. Plots of log k_1 against the reciprocal of the dielectric constant were linear, with positive slopes, suggesting an ion-dipole type of reaction.

Increasing the temperature of the reaction medium resulted in an increase in the rate of the reaction. The activation parameters have been evaluated.

Hammett plots of log k_{rel} against the σ values of substituents yielded values of the reaction constants (ρ)

of -1.30 (naphthalenes) and -1.79 (phenanthrenes), indicating the formation of a radical intermediate in the slow step of the reaction.

When the reaction was performed with naphthalene $-d_8$, the rate of the reaction showed a significant decrease, and the k_H/k_D value obtained was 5.80. This indicated a cleavage of the carbon-hydrogen bond in the rate-determining step of the reaction.

The reaction pathway involved a hydrogen abstraction process, resulting in the formation of a radical intermediate, which was detected by the polymerization of acrylonitrile and by the reduction of mercuric chloride.

The products obtained from the oxidation reactions, in good yields, were 1,4-naphthoquinone (from naphthalene), and 9,10-phenanthraquinone (from phenanthrene). These products were characterized by analytical and spectral methods.

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