KINETICS OF OXIDATION OF SOME AROMATIC HYDROCARBONS BY QUINOLINIUM DICHROMATE

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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