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KINETICS OF OXIDATION OF THIOMALIC ACID BY ACIDIC HEXACYANOFERRATE(III)

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ABSTRACT

The reaction between thiomalic acid and acidic hexacyanoferrate(III) at constant ionic strength gave the disulfide. The rate of the reaction was first order in the concentrations of substrate and oxidant, but showed an inverse dependence on the concentration of the acid. The radical intermediate formed in the slow step of the reaction was detected by ESR spectroscopy as a 1:2:1 triplet.

Меркаптоянтарная кислота, взаимодействуя с кислым гексацианоферратом(III) при постоянной ионной силе, даёт дисульфид. Скорость реакции подчиняется закону первого порядка относительно концентраций субстрата и окислителя и обратно-пропорциональна концентрации кислоты. Радикальный промежуточный продукт, образующийся на медленной ступени реакции, был детектирован с помощью ЭПР спектроскопии и имеет спектр триплета с интенсивностями 1:2:1.

INTRODUCTION

Thiols were oxidized to disulfides by peroxidic compounds [1], DMSO [2], halogens [3], diethyl azodicarboxylate [4], nitro and nitroso compounds [5], iodosobenzene [6], transition metal ions [7-12], LTA [13], metal oxides [14-15], flavine derivatives [16], and by photooxidation [17]. In this investigation, we report the kinetic features of the oxidation of

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thiomalic acid (2-mercaptosuccinic acid) by acidic hexacyanoferrate(III), at constant ionic strength, under nitrogen.

EXPERIMENTAL

(a) Materials, methods and stoichiometry

Thiomalic acid was recrystallized before use (m.p. 154 °C, SD's make). KCl (BDH, Analar) was used to maintain a constant ionic strength. All other materials used were E. Merck samples. The methods used for the preparation of solutions, and for the kinetic determinations have been described earlier [18]. The stoichiometry of the reaction was determined [18] to be:

$$2RSH + 2\ Fe(CN)_6^{3-} \rightarrow RSSR + 2Fe(CN)_6^{4-} + 2H^+$$

(b) Product analysis

Using the same experimental conditions as for the kinetic determinations, thiomalic acid and hexacyanoferrate(III), in a mole ratio of 1:1 were allowed to react at 35 °C for 24 h. At the end of the reaction, the solution was extracted with ether, washed with water, the ether evaporated, and the residue refluxed with toluene for 1 h. On concentration of the toluene solution and cooling overnight, crystals of the disulfide were precipitated, which were recrystallized from ether (m.p. 167 °C).

RESULTS AND DISCUSSION

The rate of the reaction was dependent on the first powers of the concentrations of each, substrate and oxidant, but showed an inverse dependence on the concentration of acid (Table 1). A plot of k_{obs} against $1/[H^+]$ was linear. Such an inverse relationship between the rate and $[H^+]$ has been observed in earlier investigations [19,20], and can be explained if the dissociation step of the sulfhydryl group in the thiol molecule is also included. This, however, appears unlikely in the acidic medium under consideration. In fact, it is difficult to state with any certainty the extent of involvement of protons

Table 1

Rate data for oxidation of thiomalic acid at 35.0 °C (μ = 0.05 M)

[Substrate]x10^3 (M)	[$K_3Fe(CN)_6$]x10^3 (M)	[HCl] (M)	k_{obs}x10^4 (s^{-1})
7.5	1.0	0.1	14.1
10.0	1.0	0.1	19.2
25.0	1.0	0.1	46.0
75.0	1.0	0.1	140.0
100.0	1.0	0.1	192.0
10.0	0.75	0.1	19.0
10.0	0.50	0.1	19.2
10.0	0.10	0.1	19.0
10.0	1.0	0.075	20.0
10.0	1.0	0.25	12.8
10.0	1.0	0.50	8.8
10.0	1.0	0.1	12.2*
10.0	1.0	0.1	16.2$^+$
10.0	1.0	0.1	27.2$^{\neq}$

* 25.0 °C; $^+$30.0 °C; $^{\neq}$40.0 °C;

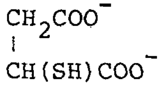
all values of rate constants were the average of two or more experiments, agreement being ±1.5% or better vis-a-vis $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ ions. Ferricyanic acid is a strong acid, but ferrocyanic acid is strong only for the first two protons. According to Jordan and Ewing [21], the protonation of $Fe(CN)_6^{4-}$ would result in species such as $HFe(CN)_6^{3-}$ or $H_2Fe(CN)_6^{2-}$.

Variation in the ionic strength of the medium (0.01 M to 0.10 M), changes in $K_4Fe(CN)_6$ concentration ($1.0x10^{-4}$ M to $1.0x10^{-3}$ M), and the addition of the product ($1.0x10^{-4}$ M to $6.0x10^{-4}$ M), did not have any effect on the rate of the reaction.

The ESR spectrum (E-4, Varian) of the radical generated, in a flow system, during the oxidation of thiomalic acid, showed a 1:2:1 triplet signal, indicating the presence of the thiyl radical.

The rate was enhanced by an increase in temperature (Table 1), and the activation parameters were evaluated: $E = 39.8 \pm 2$ kJ mol^{-1}, $A = 1.2x10^4$ s^{-1}, $\Delta S^{\neq} = -176 \pm 5$ JK^{-1} mol^{-1}. The increase in the reaction rate is due to a favorable activation energy term. If the d orbitals of the sulfur atoms are involved in the bonding to the oxidant in the course of the reaction, then the transition state produced will be quite stable. An increase in the bond strength accounts for the large $\Delta S^{\neq}$ value obtained. Values of $\Delta S^{\neq}$ in this range in radical reactions have been ascribed [22] to the nature of the electron pairing and electron unpairing processes, and to the loss of degrees of freedom formerly available to the reactants on the formation of a rigid transition state. Simple electron transfer reactions leading to the formation of free radicals, and subsequent dimerization of free radicals to give rise to the product, generally exhibit moderately large negative values of $\Delta S^{\neq}$ [23].

The pK_a value for thiomalic acid has been reported [24] to be 10.45. It can be assumed that the thiol exists mostly in the ionized form in aqueous medium. Owing to the acidic medium employed in the present study, this would preclude the ionization of the weak -SH group. Since disulfide was the final product of oxidation, the sulfhydryl group (-SH) provides the site of attack. For convenience, if the species,



$$\begin{array}{l} CH_2COO^- \\ | \\ CH(SH)COO^- \end{array}$$

is designated as HSR^{2-}, then the proposed mechanism can be written as:

$$Fe(CN)_6^{3-} + HSR^{2-} \xrightarrow[slow]{k_{obs}} HFe(CN)_6^{3-} + RS^{2\dot{-}}$$

$$RS^{2\dot{-}} + SR^{2\dot{-}} \xrightarrow{fast} {}^{2-}RSSR^{2-}$$

which gives

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = k_{obs}\,[Fe(CN)_6^{3-}][RSH]$$

where k_{obs} is the pseudo-first order rate constant. The formation of the thiyl radical has been observed by ESR spectroscopy as a 1:2:1 triplet.

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