Table VI: Estimate of pk Values of Halogen Acids from Protonation in Sulfuric and Perchloric Acids

Acid solvent	Halogen acid	Acid solvent concn at half-protonation of halogen acid, %	H_- at half-protonation	pk
H_2SO_4	HCl	~75	−6.8	−6.5
H_2SO_4	HBr	>80	<−7.3	<−10.0
H_2SO_4	HI	>70	<−6.2	<−9.0
$HClO_4$	HCl	~57	−5.5	−6.4
$HClO_4$	HBr	>80	<−8.5	<−10.0
$HClO_4$	HI	>80	<−8.5	<−10.0

solvation by the solvent anion as influenced by solute charge and modified by nonelectrolyte interaction.

An estimate of the pk of HCl was previously made[2] from the sulfuric acid concentration where protonation of chloride ion takes place. The observation of this point in perchloric acid in the present work affords us the opportunity of confirming the previous estimate and correcting it for the revised log f_-* for chloride ion. The equation[2]

$$pk = H_- - \log (C_{X^-}/C_{HX}) - \log (f_{X^-}/f_{A^-}) - \log (f_{HA}/f_{HX}) \quad (14)$$

relates the pk of the halogen solute to an H_- indicator scale where X^- and HX refer to the halogen and A^- and HA refer to the indicator family used in the H_- scale.[12,13] By neglecting the last term, approximating the third term by log f_-* for Cl^- and PCP^-, and estimating the acid concentration where the second term is zero ($C_{X^-} = C_{HX}$) an estimate of pk for the halogen acid may be obtained. We previously estimated the half-protonation point for Cl^- to be at ~75% H_2SO_4 and in the present work at ~57% $HClO_4$. The estimated pk values are listed in Table VI. Good agreement between the pk values in the systems H_2SO_4 and $HClO_4$ is obtained.

Bromide and iodide are not observed to protonate at the highest acid concentrations studied and so only an upper limit can be established for their pk values. Bell[14] reports estimates of −7, −9, and −10 for HCl, HBr, and HI, respectively.

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Kinetics of the Reduction of Hexacyanoferrate(III) by Ascorbic Acid

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The reduction of hexacyanoferrate(III) has been studied in an acidic medium using ascorbic acid (AH_2) as the reducing agent. The reaction has been found to have first-order dependence in both AH_2 and $Fe(CN)_6^{3-}$. Acid concentrations retard the rate and the inverse order with respect to H^+ is unity. The effect of addition of neutral salts like potassium chloride and potassium sulfate is positive and an increase in the dielectric constant of the medium also shows an accelerating effect on the reaction rate. The energy and entropy of activation for the reduction process have been calculated as 10.8 kcal and −39.8 cal deg^{-1} mol^{-1}, respectively. A mechanism involving intermediate formation of ascorbate radical (AH·) has been proposed and the derived rate law agreed well with the experimental observations.

Introduction

Ascorbic acid has been well known for its reducing properties in aqueous solutions. As uncatalyzed reductions by ascorbic acid are, in general, fairly fast, it has been used for the titrimetric determination of several inorganic and organic substances.[1] Variamine blue, introduced as a redox indicator by Erdey and Bodor,[2] gives an excellent null point in various ascorbinometric titrations.

Some of the recent publications have described the reductions by ascorbic acid from the kinetic stand-

(1) L. Erdey and G. Svehla, *Chem. Anal.* (Warsaw), **52**, 24 (1962).
(2) L. Erdey and E. Bodor, *Z. Anal. Chem.*, **137**, 410 (1953).

point. Khan and Martell[3] have investigated the kinetics of the uncatalyzed and iron(III) and copper(II) catalyzed oxidation of ascorbic acid by molecular oxygen and have found the monoionic ascorbate ion as the main reacting species. Mattok[4] has reported the reduction of adrenochrome dye in aqueous and nonaqueous media. Kremer[5] has put forward some evidence for a second complex between heamin and hydrogen peroxide during the heamin-catalyzed reduction of hydrogen peroxide by ascorbic acid. In the present communication, the kinetics of the reduction of hexacyanoferrate(III) by ascorbic acid has been investigated in an acidic medium.

Experimental Section

Materials. (i) An aqueous solution of ascorbic acid was prepared fresh daily from a Merck sample of GR grade and its strength was checked by titrating against a standard solution of iodine by use of a starch indicator. (ii) An aqueous solution of potassium hexacyanoferrate(III) was always prepared from an AnalaR, B.D.H. sample and the concentration was checked by iodometry.[6] (iii) All other reagents were of analytical grade. (iv) Bidistilled water was employed for preparing the solutions and diluting where necessary. The reaction vessels were of Jena glass and were coated on the outside with black Japan to exclude photochemical discrepancies.

Procedure. The kinetics of the reduction of hexacyanoferrate(III) by ascorbic acid was followed by estimating the amount of unconsumed $Fe(CN)_6^{3-}$ with time. Ten milliliters of the reaction mixture was drawn at definite time intervals and estimated for $Fe(CN)_6^{3-}$ colorimetrically using a Klett-Summerson photoelectric colorimeter with blue filter (transmission 400–450 mμ). The procedure was similar to one described earlier[7] for the oxidation of thiourea and thioacetamide by $Fe(CN)_6^{3-}$. All the kinetic runs were investigated at 15°. Owing to high initial concentrations of the acid (pH 1.1) it was observed that there is no change in pH during the progress of the reaction.

Table I: Ascorbic Acid Dependence

$[AH_2]$, $M \times 10^3$	$[Fe(CN)_6^{3-}]$, $M \times 10^4$	k_1,[a] min^{-1}	$k' = k_1/[AH_2]$,[b] l. mol^{-1} min^{-1}
5.0	4.0	0.077	15.7
4.0	4.0	0.062	15.8
3.0	4.0	0.048	16.3
2.0	4.0	0.031	15.9
1.0	4.0	0.015	15.8
3.0	5.0	0.049	16.6
3.0	3.0	0.045	15.4
3.0	2.0	0.047	16.0

[a] First-order constants in $Fe(CN)_6^{3-}$ at pH 1.1. [b] Second-order constants (pseudo first order).

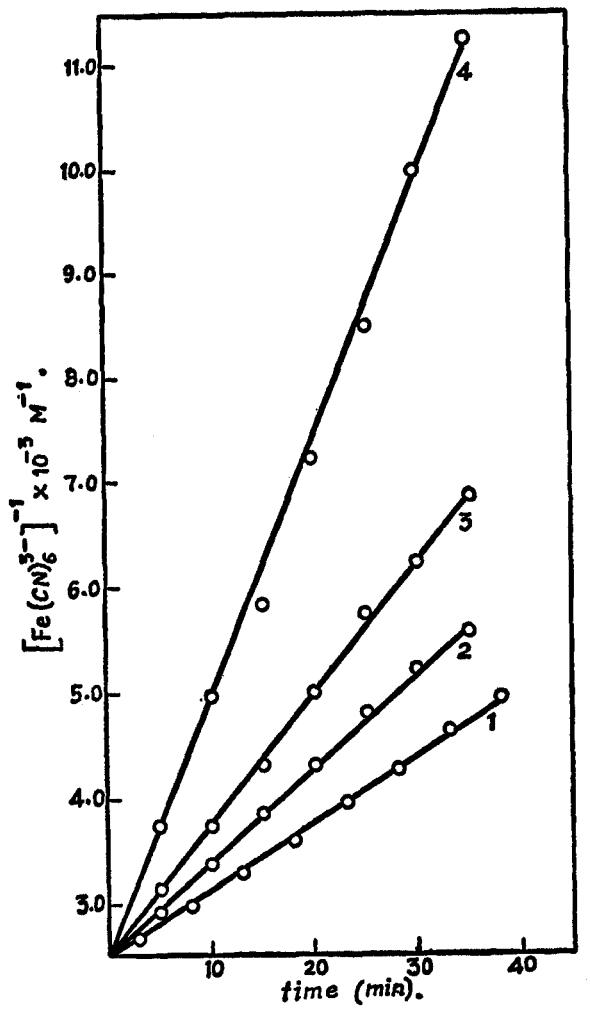

Figure 1. Plots of $[Fe(CN)_6^{3-}]^{-1}$ *vs.* time; $[Fe(CN)_6^{3-}] = 4 \times 10^{-4}$ *M*, $[AH_2] = 2 \times 10^{-4}$ *M*, and $[H^+] = 9.72, 7.32, 4.88,$ and 2.44 *M* in curves 1, 2, 3, and 4, respectively.

pH measurements were made on a Leeds and Northrup pH meter using glass electrodes.

Results

Stoichiometry. The determination of hexacyanoferrate(III) by ascorbic acid, described by Erdey and Svehla,[1] is based on the reaction

$$C_6H_8O_6 + 2Fe(CN)_6^{3-} = C_6H_6O_6 + 2Fe(CN)_6^{4-} + 2H^+ \quad (I)$$

Reaction mixtures containing a known amount of hexacyanoferrate(III) and slight excess of ascorbic acid were kept for 4 hr at 40° in the presence of sulfuric acid (pH 2) until the reaction was complete. The

(3) M. M. T. Khan and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 4176 (1967).
(4) G. L. Mattok, *J. Chem. Soc.*, 4728 (1965).
(5) M. L. Kremer, *Trans. Faraday. Soc.*, **63**, 1208 (1967).
(6) A. Berka, J. Vulterin, and Z. Jyka, "Newer Redox Titrants," Pergamon Press, Inc., New York, N. Y., 1965.
(7) M. C. Agrawal and S. P. Mushran, *J. Phys. Chem.*, **72**, 1497 (1968).

amount of ascorbic acid left, estimated by titrating against standard iodine with a starch indicator, showed that the reaction can be represented by the same stoichiometric equation (eq I).

Ascorbic Acid Dependence. The reduction of hexacyanoferrate(III) by ascorbic acid was investigated at different initial concentrations of the reducing substrate. The reaction followed first-order disappearance in hexacyanoferrate(III) at high concentrations of ascorbic acid and the $\log(a/a - x)$ *vs.* time plots were linear to 80% of the reaction. The average pseudo-first-order rate constant (k') in five experiments was 15.9 l. mol^{-1} min^{-1} (Table I). In experiments with equivalent amounts of the reactants ($[Fe(CN)_6^{3-}] = 4 \times 10^{-4}$ M, $[AH_2] = 2 \times 10^{-4}$ M) $[Fe(CN)_6^{3-}]^{-1}$ was linear with time (Figure 1), showing an overall second-order reaction whose rate may be defined as

$$-(d/dt)[Fe(CN)_6^{3-}] = k'[Fe(CN)_6^{3-}][AH_2] \quad (II)$$

Owing to high concentration of acid (μ = *ca.* 0.24), it is assumed that ionic strength remains constant during these observations.

Acid Dependence. The reduction of hexacyanoferrate(III) has been found to depend on the hydrogen ion concentration (Table II).

A plot of k' against $1/H^+$ showed a straight line (Figure 2) at constant ionic strength and therefore it is concluded that the rate of the reaction is directly proportional to the reciprocal of the hydrogen ion concentration. This gives rise to the rate law equation as

$$-\frac{d}{dt}[Fe(CN)_6^{3-}] = \frac{k[Fe(CN)_6^{3-}][AH_2]}{[H^+]} = k'[Fe(CN)_6^{3-}][AH_2] \quad (III)$$

where k' includes only the dependence on H^+ and

$$\log k' - pH = \log k \quad (IV)$$

and, therefore, the value of k is 1.26 in units of moles per liter and minutes.

Ionic Strength Dependence. The effect of change in ionic strength was investigated in the presence of neutral salts such as potassium chloride and potassium sulfate. The results show (Table III) that the addition of neutral salts accelerates the rate of the reaction and thus establishes a positive salt effect.

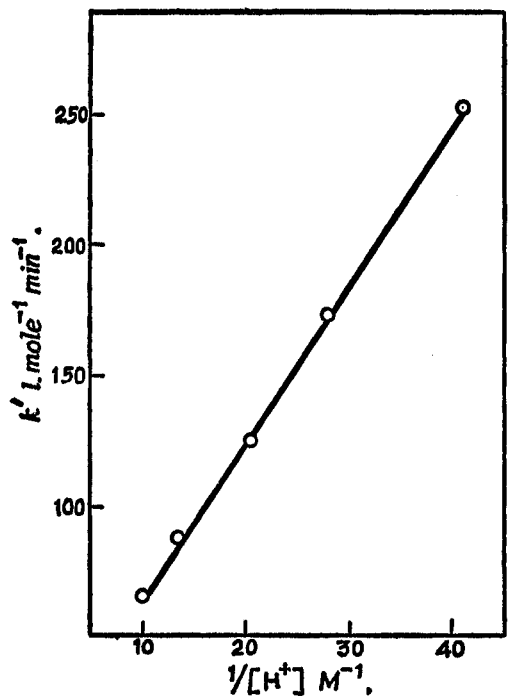

Figure 2. Plot of k' *vs.* $1/[H^+]$.

Dielectric Constant Dependence. Influence of dielectric constant has been investigated by altering the dielectric constant of the reaction medium employing suitable amounts of water–methanol mixtures. The results (Table IV) show that an increase in the methanol concentration has a considerable retarding influence on the rate of reduction of hexacyanoferrate(III) by ascorbic acid.

The influence of some other factors on the rate of reduction of hexacyanoferrate(III) by ascorbic acid was also studied. The addition of hexacyanoferrate(II) has a negligible effect on the rate. The reaction was investigated at 20, 25, and 30°. The same kinetics were followed and the energy and entropy of activation have been calculated at 10.8 kcal mol^{-1} and −39.8 cal deg^{-1} mol^{-1} from the mean slope of the Arrhenius plot.

Discussion

Reduction of hexacyanoferrate(III) usually involves single electron transference and occurs in a

Table II: Acid Dependence[a]

$[H^+]$	$1/[H^+]$, M^{-1}	k',[b] l. mol^{-1} min^{-1}
9.72	10.25	65
7.32	13.66	88
4.88	20.49	125
3.66	27.32	174
2.44	40.98	253

[a] $[AH_2] = 2 \times 10^{-4}$ M; $[Fe(CN)_6]^{-3} = 4 \times 10^{-4}$ M; $[KCl] = 1$ M. [b] From the slope of the plot of $[Fe(CN)_6^{3-}]^{-1}$ *vs.* time.

Table III: Ionic Strength Dependence[a]

$[KCl]$, M	k', l. mol^{-1} min^{-1}	$[K_2SO_4]$, M	k', l. mol^{-1} min^{-1}
0.03	17.1	0.03	21.5
0.06	17.8	0.06	24.5
0.09	18.7	0.09	27.0
0.12	19.7	0.12	29.3
0.15	20.5	0.15	32.7

[a] $[Fe(CN)_6^{3-}] = 4 \times 10^{-4}$ M; $[AH_2] = 3 \times 10^{-3}$ M; pH 1.1.

Table IV: Dielectric Constant Dependence[a]

[Methanol], %	Dielectric constant	k',[b] l. mol^{-1} min^{-1}
5	78.89	17.08
10	77.83	12.06
15	75.71	8.52
20	73.59	5.68

[a] In the presence of 0.15 *M* KCl. [b] Conditions same as in Table III.

number of steps in which no single step is regularly the rate-determining one. In an alkaline medium, Agrawal and Mushran[7] have found that the reduction of hexacyanoferrate(III) by thiourea and thioacetamide shows first-order and zero-order dependence, respectively, in the oxidant and thus involves two different rate-determining steps. However, hexacyanoferrate(III) reductions have, in general, been found to be pH dependent.

For the reduction of hexacyanoferrate(III) by ascorbic acid in an acidic medium, a mechanism has been proposed which involves the formation of an intermediate ascorbate anion (AH^-) from ascorbic acid in a primary reversible process. This intermediate ion is attacked by hexacyanoferrate(III) in a slow and rate-determining step (2) as

$$AH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AH^- + H^+ \quad (1)$$

$$AH^- + Fe(CN)_6^{3-} \xrightarrow{k_2} AH\cdot + Fe(CN)_6^{4-} \quad (2)$$

Step 2 is followed by a fast step (3) in which the ascorbate free radical ($AH\cdot$) is attacked by a fresh hexacyanoferrate(III) ion to give the end product, dehydroascorbic acid.

$$AH\cdot + Fe(CN)_6^{3-} \xrightarrow{k_3} A + Fe(CN)_6^{4-} + H^+ \quad (3)$$

From the above mechanism the rate of disappearance of hexacyanoferrate(III) can be calculated by applying the steady-state treatment to give

$$-\frac{d}{dt}[Fe(CN)_6^{3-}] = \frac{2k_1k_2[AH_2][Fe(CN)_6^{3-}]}{k_{-1}[H^+] + k_2[Fe(CN)_6^{3-}]} \quad (4)$$

since step 2 is slow and rate determining $k_{-1} \gg k_2[Fe(CN)_6^{3-}]$ for moderately low concentrations of $Fe(CN)_6^{3-}$ or

$$-\frac{d}{dt}[Fe(CN)_6^{3-}] = \frac{2k_1k_2[AH_2][Fe(CN)_6^{3-}]}{k_{-1}[H^+]}$$

$$-\frac{d}{dt}[Fe(CN)_6^{3-}] = -\frac{2d}{dt}[AH_2]$$

$$= k'[AH_2][Fe(CN)_6^{3-}] \quad (5)$$

The derived rate law equation (5) exhibits the observed dependence on ferricyanide and ascorbate concentrations, and the data obtained give

$$k = 2k_1k_2/k_{-1} \sim 1.26 \text{ min}^{-1}$$

The value of k_1/k_{-1} is known to be 6.16×10^{-5} and, therefore, $k_2 = 1.0 \times 10^4$/min.

In the proposed mechanism the rate-determining step (2) involves the interaction between a negative univalent ascorbate and a negative trivalent hexacyanoferrate(III) ion. This contention is supported by the fact that the rate of reduction of hexacyanoferrate(III) by ascorbic acid increases with an increase in the ionic strength and the dielectric constant of the media. Furthermore, the activation entropy for the reduction of hexacyanoferrate(III) by ascorbic acid, computed from the overall second-order constants, is also in agreement with the theoretically expected negative value for a reaction involving similarly charged ions.

Thus the proposed mechanism for the reduction of hexacyanoferrate(III) by ascorbic acid in an acidic medium clearly accounts for all the experimental observations. The formation of ascorbate ion (AH^-) and ascorbate free radical ($AH\cdot$) was well established by Grinstead[8] while he studied the reduction of hydrogen peroxide by ascorbic acid catalyzed by an iron(III) salt of EDTA. The inverse order dependence of H^+ has also been supported by Grinstead.[8]

Acknowledgments. The authors are thankful to the Council of Scientific and Industrial Research, New Delhi, India, for providing financial assistance.

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