Ru(VII) and -(VIII) oxidize water irreversibly in alkaline solution. Furthermore, the disproportionation of Ru(VII) to -(VIII) and -(VI) does not proceed to an appreciable extent; this in accord with spectrophotometric data[3,6] and is in contrast to previous information in the literature.[21]

[21] R. Charonnat, ref. 5, p. 399.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, POLYMER CORPORATION LIMITED]

Reaction between Iron(II) Complexes of Polyethylenepolyamines and *p-t*-Butylcumene Hydroperoxide[1]

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The reaction between *p-t*-butylcumene hydroperoxide and iron(II)-polyethylenepolyamine complexes was investigated. The primary reaction was first order with respect to hydroperoxide for compounds containing secondary amine groups. When primary amines only were used the reaction became more complex. Bimolecular rate constants were measured under various conditions of *p*H and temperature. Apparent values of the Arrhenius constants were calculated from these. When solvated coördination spaces for the hydroperoxide were available on the iron(II) the results could be explained by considering the reaction to follow association of the hydroperoxide and the iron(II) complex. When the coördination shell of the iron(II) tended to be filled with complexing groups other than solvent the mechanism of the electron-transfer was uncertain. Deductions were made on factors affecting the reactivity of the iron(II) complexes and were supported by polarographic evidence of the existence of different complexes. Cathodic and anodic waves have been measured on alkaline solutions of iron(II)-diethylenetriamine and iron(II)-triethylenetetramine complexes. The change in the half-wave potentials with *p*H suggests that the series of hydroxy substitutions involved in the diethylenetriamine complex differs from those in the triethylenetetramine complexes.

Introduction

The quality of butadiene-styrene elastomers increases as the temperature of the polymerization decreases. The basis for these low temperature processes are oxidation-reduction systems which yield free radicals suitable for initiation of the polymerizations. To understand more fully the factors governing these reactions, a study, the earlier results of which have been reported in a series of publications,[2-7] has been continued. Studies were made when iron(II) was complexed with polyethylenepolyamine and the complex reacted with cumene hydroperoxide. The general reaction characteristics were determined, and the effect of the structure of the polyethylenepolyamine was discussed.[7] It was desirable to find the effect of variation in the structure of the substituent on the hydroperoxide on the rate when iron(II) complex with polyethylenepolyamines was the reducer. The hydroperoxide chosen was *p-t*-butyl cumene hydroperoxide and the kinetics of the reaction with the iron(II) complexes of five polyethylenepolyamines of the general formula $H_2N-C_2H_4(NH-C_2H_4)_xNH_2$ for values of x from 0 to 4 was studied.

The structure in alkaline solution of the iron(II) complexes of the polyethylenepolyamines of the general formula $H_2N(C_2H_4)_xC_2H_4NH_2$ was of interest together with some measure of determining the purity of the mixtures of these polyethylenepolyamines. The polarographic behavior of iron(II) and its complexes has been made the subject of a number of investigations.[8-11] The results suggested that similar studies of the iron(II)-polyethylenepolyamine complexes might be of value.

Experimental

The experimental methods used in the study of the reaction of cumene hydroperoxide with iron(II) complexes of polyethylenepolyamines[7] were found to be almost universally applicable with the exception of certain purification details of the reagents. The cumene hydroperoxide was received as a 68% solution. The sodium salt was precipitated and dried. The stock solution of hydroperoxide was made by dissolving this salt in a methanol-water solution. The *p-t*-butylcumene hydroperoxide was received as a slurry of hydroperoxide analyzing about 50% hydroperoxide. Cooling to 0° and separating the solid from the liquid yielded a solid product about 80% hydroperoxide. The purity could be raised above 98% by one fractional reprecipitation from benzene. Analyses were made by an iodimetric procedure.[12]

All polyethylenepolyamines were purified by precipitation as the hydrochlorides. All of the polyamines except the pentaethylenehexamine were found to be free of amine contaminants. The pentaethylenehexamine was contaminated with other complex-forming amines, probably lower polyethylenepolyamines.

Technical grade methyl methacrylate was distilled, discarding initial and final fractions. Once distilled water was redistilled from an alkaline permanganate solution. Iron(II) sulfate, sodium hydroxide, potassium dihydrogen phosphate, α,α'-bipyridine, sodium acetate, acetic acid and methanol were reagent grade. Oxygen was removed from nitrogen gas by passage through three scrubbers containing alkaline pyrogallol solution, over copper filings at 300-400°,

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[1] Presented before the Division of Physical and Inorganic Chemistry, 124th Meeting, American Chemical Society, Chicago, Ill., September 6-11, 1953.

[2] J. W. L. Fordham and H. L. Williams, *Can. J. Res.*, **B27**, 943 (1949).

[3] (a) J. W. L. Fordham and H. L. Williams, THIS JOURNAL, **72**, 4465 (1950); (b) **73**, 1634 (1951).

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[8] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., 1952, p. 475.

[9] J. Prajzler, *Collection Czechoslov. Chem. Communs.*, **3**, 406 (1931).

[10] B. Schrager, *ibid.*, **1**, 275 (1929).

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[12] Hercules Powder Company, private communication.

and through a scrubber containing water at the temperature of the reaction.

The reaction was studied in basic aqueous solutions which were buffered with sodium hydroxide–potassium dihydrogen phosphate buffers. All reagents were added volumetrically to the reaction cell.

Stock solutions of buffer, polyethylenepolyamine, monomer, hydroperoxide and iron(II) sulfate were prepared. The latter two were prepared daily to minimize concentration changes due to oxidation or decomposition. The water used for the latter three solutions was freed of oxygen prior to make-up by bubbling a stream of pure nitrogen through it for 15 minutes. Methanol was added to the hydroperoxide stock solution to solubilize the hydroperoxide so that the stock solution was 37% methanol by volume and the reaction mixture was 3.0% by weight. All reagents except monomer, iron(II) sulfate and hydroperoxide were added to the reaction cell and the oxygen removed by bubbling the purified nitrogen gas through for 15 minutes. It has been shown that this will reduce oxygen content to less than 0.005% in a normal solution.[13] In alkaline solution of iron(II) it may well be that the oxygen is more difficult to remove due to possible complex formation between iron(II) and molecular oxygen. In view of the small experimental effect which could be assigned to oxygen, it was reasonable to conclude that the reaction occurred in oxygen-free conditions. The monomer was added immediately before the beginning of reaction since the alkaline conditions might cause hydrolysis and the iron(II) sulfate could not be added as long as oxygen might be present in the reaction mixture. The hydroperoxide was added last and its addition was considered to start the reaction. Hydroperoxides, which reduce at the dropping mercury electrode, were analyzed in the reaction system with a Sargent–Heyrovsky polarograph Model XII. The cell was an H-type and consisted of a saturated calomel electrode (S.C.E.) immersed in a saturated potassium chloride solution separated from the reaction cell by an agar plug containing 30% potassium chloride on a sintered glass disc. By making up stock solutions from 98% hydroperoxide, the diffusion current at −0.6 v. *vs.* S.C.E. was found proportional to the peroxide concentration.

The iron(II) sulfate was analyzed prior to addition to the reaction cell by a colorimetric procedure.[14]

The polarographic analysis of the iron(II)-polyethylenepolyamine complexes followed removal of oxygen by passing a stream of purified nitrogen through the cell. Current readings were recorded visually rather than automatically. Sodium chloride (10^{-2} M) was used as the supporting electrolyte and the pH adjusted with sodium hydroxide solution. Drop times were approximately 3.5 sec. depending somewhat on the voltage. All measurements were at 20°. Voltages were relative to a saturated calomel electrode (*vs.* S.C.E.). Initial experiments were conducted with the polyethylenepolyamine content 10^{-2} M and the iron(II) sulfate concentration 5×10^{-3} M. It was found that this system was too susceptible to oxidation. On increasing the iron(II) sulfate concentration to 10^{-2} M, the solution was saturated with respect to iron(II). This created a reservoir of iron(II) which replaced any iron(III) which was formed.

Results

The presence of monomer in sufficient concentration reduces to zero the steady state concentration of free radicals capable of attack on the oxidizer or reducer so that reaction of these latter may be attributed to the primary radical-producing reaction. Methyl methacrylate was chosen as the monomer since this is soluble in water and inert toward hydroperoxides at high pH.[7]

That the hydroperoxide was not decomposed by any of the solution constituents other than the iron(II)-polyethylenepolyamine complex was shown by the lack of dependence of the diffusion current of the hydroperoxide on time when all constituents except the iron(II)-polyethylenepolyamine were present.

The semi-logarithmic plot of diffusion current against time for the reactions of polyethylenepolyamines with t-butylcumene hydroperoxide for various initial methyl methacrylate concentrations were linear except initially. This non-linear portion was attributed to non-uniformity of the solution since the only agitation after the addition of the hydroperoxide was by a stream of nitrogen flowing through the reaction solution. The slope of the plot with monomer concentration more than 10^{-2} M was independent of monomer content, indicating suppression of side reactions.

The linearity of the semilogarithmic plot of diffusion current *vs.* time for the reaction mixture of hydroperoxide and triethylenetetramine complexed iron(II) was further checked to confirm the first-order characteristics of the reaction. The hydroperoxide concentration was varied from 2.4×10^{-3} to 1.2×10^{-3} M at 20° and pH 11.5 with no change in the slope of the semi-logarithmic plot of hydroperoxide concentration *versus* time. This was the same as was observed previously with the reaction of polyethylenepolyamine complexes with cumene hydroperoxide.[7] The reaction rate was independent of polyethylenepolyamine concentration if the polyethylenepolyamine were free of heavy metal impurities.

Experiments were done under varying conditions of pH, temperature and initial iron(II) concentration ($[\mathrm{Fe}^{++}]_0$) with an initial concentration of hydroperoxide ($[\mathrm{HP}]_0$) of 2.4×10^{-3} M. The methyl methacrylate concentration was 2×10^{-2} M except in certain instances where it was necessary to increase it to suppress side reactions. All initial polyethylenepolyamine concentrations were 10^{-2} M except where otherwise noted. Results were plotted as log $[\mathrm{HP}]/[\mathrm{HPO}]_0$ *vs.* time. $[\mathrm{HP}]/[\mathrm{HP}]_0$ was equivalent to I_d/I_{d_0} where I_{d_0} was determined polarographically separately for each experiment by extrapolating a plot of log I_d *vs.* time to zero time. All reaction curves were found to be linear. The first-order rate constants could be calculated from the slopes of these plots for the various initial iron(II) concentrations. The bimolecular rate constants could be calculated from these, one for each value of $[\mathrm{Fe}^{++}]_0$, on the assumption that some form of Fe^{++} constituted the reactive species. Under the proper conditions of polyethylenepolyamine concentration these constants were independent of the value of $[\mathrm{Fe}^{++}]_0$. The bimolecular rate constants for reactions of the iron(II) complexes of the polyethylenepolyamines from diethylene to tetraethylene with t-butylcumene hydroperoxide as a function of temperature and pH are in Table I. Data for ethylenediamine differed and are discussed separately. Data for pentaethylenehexamine were only qualitative since this compound was contaminated with other polyethylenepolyamines. Some reaction rates of cumene hydroperoxide with iron(II)-pentaethylenehexamine complex were also measured and the data are in Table I.

TABLE I

RATE CONSTANTS FOR IRON(II)–POLYETHYLENEPOLYAMINE–p-t-BUTYLCUMENE HYDROPEROXIDE REACTION

T, °C.	$k_{\mathrm{av.}}$ (l.m.$^{-1}$ sec.$^{-1}$) at pH		
	9.0–10.1	10.8–11.0	11.5–11.7
	Diethylenetriamine		
20	0.49 ± 0.07	0.46 ± 0.05	0.29 ± 0.06
30	1.15 ± .10	1.05 ± .10	1.39 ± 0.23
40	3.03 ± .21	2.29 ± .21	9.90 ± 1.30
	Triethylenetetramine		
0	7.00 ± 0.04	11.9 ± 0.12	16.9 ± 1.2
14	44.1 ± 1.7	64.7 ± 5.7	61.0 ± 3.3
20	47.0 ± 2.9	73.5 ± 1.7	88.0 ± 2.2
	Tetraethylenepentamine		
	pH 9.1		
0	19.5 ± 0.2	37.3 ± 2.7	90.0 ± 5.1
14	9.2 ± 9	173 ± 6	208
20	112 ± 5	220 ± 18	485 ± 23
	Pentaethylenehexamine		
0	54.0 ± 1.8	80.9 ± 1.8	71.7 ± 2.8
15	105 ± 8	234 ± 20	214 ± 11
20	138 ± 1.3	302 ± 7	332 ± 7
	Cumene hydroperoxide and pentaethylenehexamine		
			pH 10.4
0	32.0 ± 1.3		48.6 ± 4.3
20	208 ± 8		

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It was not possible to determine a rate constant which was independent of either iron(II) or polyethylenepolyamine concentration when ethylenediamine (ED) was used. Apparent bimolecular rate constants together with the conditions under which they were determined are in Table II. A detailed discussion of these data is made later.

TABLE II

APPARENT RATE CONSTANTS FOR REACTION OF ETHYLENEDIAMINE–IRON(II) COMPLEX WITH *t*-BUTYLCUMENE HYDROPEROXIDE

T, °C.	$[Fe]_0$ ($M \times 10^5$)	$[ED]_0$ M $\times 10^2$	$[MMA]_0$ M $\times 10^2$	k_{app} (l.m.$^{-1}$ sec.$^{-1}$) at pH		
				10.0	11.0	11.6
25	0.5–4.0	2	4	..	12	2.2
25	0.5–0.7	4	4	..	31	...
30	2–10	1	2	1.5	2.5	0.3
40	8.3–5.0	2	4	21.4	19.7	1.7

In an effort to verify the existence of the various structures which it later proved necessary to assign to the various iron(II)–polyethylenepolyamine complexes existing in alkaline solution in order to explain the preceding results, the polarographic behavior of these complexes was studied in alkaline solution. A typical polarogram for iron(II)–diethylenetriamine complex showed that the current increase on the cathodic side did not become considerable until −1.4 v., at which time rapid increases in diffusion current took place. At all values of *p*H between 9.0 and 11.6 a well-defined wave with a reproducible maximum occurred with the wave peak at −1.9 v. The current at −1.8 v. *vs.* S.C.E. was measured for the diethylenetriamine complex as a function of *p*H and varied from 13.7 at *p*H 9.0 to 1.4 μa. at *p*H 11.2.

The difficulty in any interpretation of these results was the very acute maximum. Gelatin or methyl orange separately had no suppressive action on this maximum at any *p*H or at any concentration. On mixing the gelatin and methyl orange the results improved for the diethylenetriamine complex. At lower *p*H the maximum vanished. It reappeared on raising the *p*H. At very high *p*H, the maximum decreased in acuity probably due to the disappearance of the species contributing to its formation. The height of the maximum which appeared at higher *p*H with methyl orange and gelatin could be slightly reduced by the addition of 0.002% of the sodium salt of methyl red. This did not entirely remove the maximum but it did give a plateau permitting determination of a diffusion current. Some of the polarograms of the diethylenetriamine complex were extended to a lower voltage range under conditions enabling smaller currents to be observed accurately. Above a *p*H of 10 there are two additional waves indicating at least three species were present.

TABLE III

CATHODIC WAVES OF IRON(II)–POLYETHYLENEPOLYAMINE COMPLEXES

pH	I_d, μa.	$E_{1/2}$
0.29% Methyl orange and 0.05% gelatin: diethylenetriamine		
7.0	18.6	−1.42
8.0	8.5	−1.49
10.2	−1.3	−1.56
0.02% Methyl orange, 0.05% gelatin and 0.002% methyl red: diethylenetriamine		
10.2	1.20	−1.55
	0.067	−0.78
	.132	−0.62
11.6	.70	−1.57
	.065	−0.79
	.22	−0.61
Triethylenetetramine		
8.6	12.4	−1.63
11.4	10.0	−1.62
11.9	8.9	−1.63
12.3	5.8	−1.63

The polarographic data obtained for the diethylenetriamine and triethylenetetramine complexes are presented in Table III. The mixed maximum-suppressors were used as shown. The continual decrease of I_d with *p*H for this wave suggested that it was due to the hydroxy-free polyethylenepolyamine complex of iron(II). Small currents were flowing at voltages lower than −1.2 v. *vs.* S.C.E. in the triethylenetetramine complex with indicated waves similar to those found with the diethylenetriamine complex. These, however, were not investigated.

For the triethylenetetramine at high *p*H a very well-defined anodic wave occurred with at least one (which was less well defined) at more positive voltages. At intermediate *p*H three distinct waves formed, but at lower *p*H one disappeared. With the diethylenetriamine complex, anodic waves were observed at various *p*H in the presence and absence of maxima suppressors. In the absence of suppressors, a small maximum was apparent in the most positive of the waves. This disappeared in the presence of suppressors at low *p*H and reappeared at higher *p*H. There were three distinct anodic waves present indicating a minimum of three species. Table IV is a comparison of the data obtained.

TABLE IV

POLAROGRAPHIC CONSTANTS OF ANODIC WAVES

pH	$\Delta E_{1/2}$	$\Delta E_{1/2}$	I_d, μa.
Triethylenetetramine			
12.1	−0.51	0.60	9.8
	.09		28.5
11.8	− .51	.57	10.0
	.06		22.2
11.6	− .46	.51	10.0
	.05		10.0
10.9	− .38	.22	9.0
	.10	.26	4.5
	− .16		13.3
10.7	− .42	.21	5.8
	− .21	.27	5.8
	.06		8.0
9.0	− .19	.39	10.0
	.20		22.2
Diethylenetriamine			
11.3	−0.32	0.27	1.8^a
	− .05		11.5^a
10.9	− .30	.32	1.3
	.02	.15	19.0
	.17		14.6
10.6	− .33	.35	1.7
	.02	.16	10.6
	.18		14.2
10.2	− .22	.24	7.1^a
	.02	.13	7.1^a
	.15		17.2^a
10.0	− .35	.50	2.2
	.15		20.0
9.8	− .04	.12	5.5^a
	.08	.07	5.1^a
	.15		12.5^a
9.4	− .19	.21	2.4^a
	.02	.12	4.1^a
	.14		11.2^a
9.0	− .39	.19	2.2
	− .20		0.9
8.0	− .22	.37	2.4^a
	.15		10.0^a
7.0	− .22	.37	7.1^a
	.15		7.8^a

[a] Mixed suppressor used.

A sample of pentaethylenehexamine of unknown purity was available and some polarograms were obtained to check the purity of the product. A typical anodic wave showed four separate waves. Very small cathodic waves could be seen at voltages of −0.6 to −1.3 v. *vs.* S.C.E. Only one well-defined hydroxy-free iron(II) complex wave was seen, that at a *p*H of 10.8 with $E_{1/2}$ = 1.56 and I_d = 11 μa.

Discussion

The extent to which the various complexes dissociate into free iron(II) ion, and the relative tendency of formation when more than one structural configuration is possible, was of interest. Data existed[15–17] to calculate this under the conditions used. These are in Table V for an iron(II) content of 10^{-5} *M* and a polyethylenepolyamine content of 10^{-2} *M* except 2×10^{-2} for ethylenediamine (×2).

TABLE V

CALCULATED DISTRIBUTION OF COMPLEX FORMS OF POLYETHYLENEPOLYAMINE–IRON(II) COMPLEXES

Polyethylene- *M*	Diamine	Diamine (×2)	Triamine	Tetramine
$[Fe^{++}]$.	10^{-9}	1.5×10^{-10}	5×10^{-12}	5×10^{-12}
[Fe $amine_1^{++}$].	2×10^{-7}	....	5×10^{-8}	1.0×10^{-5}
[Fe $amine_2^{++}$].	5×10^{-6}	3.3×10^{-6}	1×10^{-5}	....
[Fe $amine_3^{++}$].	5×10^{-6}	6.6×10^{-6}	....	....
[Fe_2 $amine_3^{++}$].	....	....	....	1.5×10^{-7}

Diethylenetriamine complex is mostly in the hexaminated form. Ethylenediamine exists as a mixture of tetra- and hexaminated complexes. The relative proportion of these two latter complexes is dependent on the ethylenediamine concentration.

It was important to know if the primary reduction step could consist completely of free iron(II) reacting with hydroperoxide with a subsequent reduction of the iron(III) by the polyethylenepolyamine. This latter reaction cannot be duplicated on mixing iron(III) salts and polyethylenepolyamines but it was desirable to obtain supporting evidence. Assuming a constant concentration of free iron(II) of 10^{-10} *M* and an initial hydroperoxide content of 2.4×10^{-3} *M*, a rate of hydroperoxide consumption in which the concentration was reduced to 50% of the original in 10 to 20 minutes (a typical reaction velocity for these reagents) would indicate a rate constant of 5 to 10 × 10^6 l.m.$^{-1}$ sec.$^{-1}$. This was excessively large and in conjunction with the previous inability to reduce iron(III) by polyethylenepolyamines would indicate that all the observed decomposition of hydroperoxide was due to reaction with complexed iron(II). The available facts were considered to confirm the conclusion reached previously[7] that the reaction of iron(II) complexes with polyethylenepolyamines with hydroperoxides was a pseudo-unimolecular reaction with respect to hydroperoxide. Either of two alternative mechanisms explain the results. The first is proposed by Horner[18]

$$RNH_2{:}Fe^{++} + ROOH \longrightarrow RO^{\cdot} + H_2O + RNH^{\cdot} + Fe^{++}$$

In a previous publication,[7] this was believed sufficient to explain the data. Since then it has been pointed out[19] that the above reaction was energetically unfavorable, and an alternative mechanism was suggested

$$ROOH + RNH_2Fe^{++} \longrightarrow RO^{\cdot} + HO^{-} + RNH_2Fe^{+++}$$

$$RNH_2Fe^{+++} + ROO^{-} \longrightarrow ROO^{\cdot} + RNH_2{:}Fe^{++}$$

No attempt is made in this paper to distinguish which of these represents the true mechanism. The polyethylenepolyamine in effect must protect the iron(II) from oxidation.

The data obtained for the reaction with ethylenediamine differed from the other in that the apparent rate constant was a function of $[Fe^{++}]_0$ and ethylenediamine concentration. This may indicate not only that the ratio of the tetra- and hexaminated complexes changed appreciably on changing the amine concentration, as was shown in Table V, but there may be a slow oxidation of the iron(II) to iron(III). This would explain the variation in apparent rate constant with $[Fe^{++}]_0$.

The data in Table I were used to calculate the apparent activation energies and frequency factors by plotting the rate constant data in the conventional Arrhenius equation. The contents are summarized in Table VI.

TABLE VI

ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR IRON(II)-POLYETHYLENEPOLYAMINE COMPLEXES REACTING WITH *p-t*-BUTYLCUMENE HYDROPEROXIDE

*p*H	$E_{app.}$, kcal./mole	$A_{app.}$
	Diethylenetriamine	
10.0	16.6	1.2×10^{12}
11.0	15.0	7.1×10^{11}
11.6	31.2	6.7×10^{22}
	Triethylenetetramine	
9.8	16.0	4.8×10^{13}
11.0	14.3	3.6×10^{12}
11.6	12.4	1.4×10^{11}
	Tetraethylenepentamine	
9.1	14.8	1.0×10^{13}
10.9	14.9	2.7×10^{13}
11.7	15.4	1.3×10^{14}
	Pentaethylenehexamine	
10.0	7.15	2.8×10^{7}
11.0	11.3	8.0×10^{10}
11.5	11.3	9.0×10^{10}
10.0[a]	15.0[a]	3.2×10^{13}[a]

[a] Cumene hydroperoxide.

A study of the apparent energy of activation for the reactions with the different polyethylenepolyamines reveals that for reaction with triethylenetetramine and tetraethylenepentamine complexes of iron(II), the apparent activation energies either decrease slowly with or are independent of *p*H. For the diethylenetriamine complex the apparent activation energy increases at higher *p*H.

The apparent energies of activation differ from the true values because of the contribution of the change in the equilibrium constants for the association of the complex with hydroxide ion with tem-

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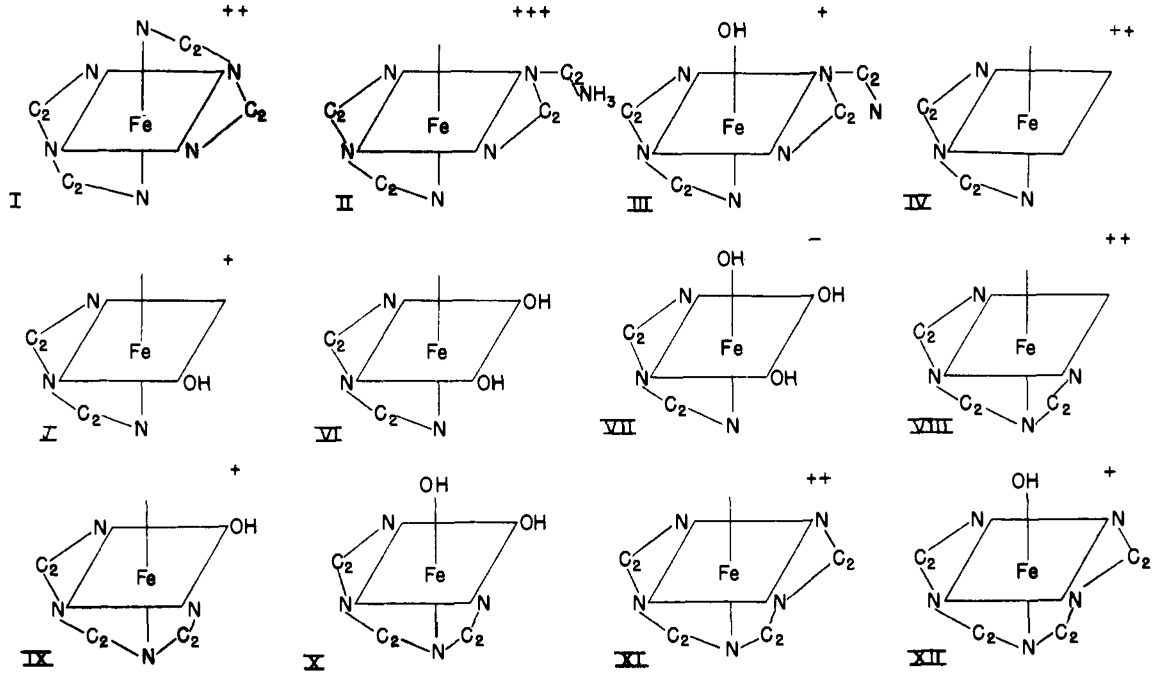

Fig. 1.—Possible structures of iron(II)-polyethylenepolyamine complexes with varying degrees of hydroxyl radical incorporation as influenced by *p*H of the medium.

perature. The apparent activation energy may be low due to the lesser association between complex and hydroxide ion at higher temperatures, since inspection of the reaction rates indicates that a more reactive complex is attained when hydroxide ion associates with the iron(II) complex. With diethylenetriamine at high *p*H there is less association at high temperatures than at low, leading to a diminution in the proportion of the unreactive species present at high *p*H with a substantial increase in the apparent activation energies and frequency factors over the true values.

Comparison of the apparent activation energies of the reaction of iron(II) complexes of triethylenetetramine with *p*-*t*-butylcumene hydroperoxide and cumene hydroperoxide[7] shows that while they were lower at low *p*H for the reaction with *p*-*t*-butylcumene hydroperoxide than with cumene hydroperoxide, at a *p*H of about 10.8 the two curves intersected so that at *p*H higher than this their positions were reversed. Similar behavior is evident for the tetraethylenepentamine iron(II) complex. For the diethylenetriamine iron(II) complex no crossing over occurred within the *p*H range measured. The minimum exhibited by the curve with *p*-*t*-butylcumene hydroperoxide also occurred when cumene hydroperoxide[7] was used. Since the polyethylenepolyamine–iron(II) complexes were the same in each case the differences must be due to the hydroperoxide.

Study of the reaction of uncomplexed iron(II) with hydroperoxides[5,6] revealed that introduction of a *p*-alkyl group on the hydroperoxide resulted in greater rate of reaction due primarily to a decrease of the activation energy. From considerations on the attraction or repulsion of electrons from the O–O bond, it was shown that when the activation energy was decreased by such a structural change, then the donation of the electron from the reducer to the oxidizer occurred through formation of a complex between the hydroperoxide and the iron(II). Conversely, if such a structural change resulted in an increase in activation energy, then the donation of the electron could be considered as taking place in a more direct manner, *i.e.*, that the transfer would be a pure collision process, and the activated complex would be held together only by van der Waals or similar forces.

A brief description of the complexes suggested to exist in solution of iron(II) salts and polyethylenepolyamines is required. Some are shown diagrammatically in Fig. 1. I is a hexaminated complex with two moles of diethylenetriamine, II is the same at low *p*H where a partial ammonium complex may be found where the residual coördination space may be solvated. III is the same at high *p*H where OH^- ion may disrupt the complex. The charges on the complexes are, respectively, 2+, 3+ and +. IV, V, VI and VII are complexes with successive addition of OH^- ions to yield 2+, +, neutral and -ve complex ions with 3, 2, 1 and 0 solvated coördination spaces. VIII, IX and X are similar complexes for triethylenetetramine, charged, respectively, 2+, + and neutral and with 2, 1 and 0 residual solvated coördination spaces. XI and XII are the complexes for tetraethylenepentamine, which are 2+ and + charged and have 1 and 0 solvated coördinated spaces. With both the triethylenetetramine and tetraethylenepentamide, complexes similar to II and III should be possible. Complexes for ethylenediamine and pentaethylenehexamine can be sketched similarly.

At low *p*H the apparent energy of activation for the *p*-*t*-butylcumene hydroperoxide reduction was lower than that of the cumene hydroperoxide reduction for triethylenetetramine and tetraethylenepentamine. While this cannot be interpreted to mean that this is the order of the true activation energies an examination of the probable structures present at these *p*H (Fig. 1, structures VIII, IX and XI) shows no reason why the intermediate complex formation for electron transfer previously observed with "uncomplexed" iron(II)[5] (with all coördination spaces filled with solvent), will not be the type occurring. As the *p*H is raised the solvated coördination spaces on the iron(II) should become filled by hydroxy groups (structures X and XII). Under these conditions it is difficult to visualize the intermediate stable transition complex mechanism as being operative, due to the lack of availability of coördination space for the hydroperoxide. There may be a change in the mechanism of electron transfer under these conditions to a bimolecular collision type, and the differences of the true activation energies would change in sign. A corresponding change in the apparent activation energies would then be expected. An excellent test of this supposition would be if a complexing agent were available which would give a hexaminated complex stable to hydroxide ion. Unfortunately the pentaethylenehexamine was not available in a purified form, and furthermore this complex may show hydroxy forms (structure III) so that the results from the polyethylenepolyamine cannot be used to answer this question. For the diethylenetriamine the preponderant complex at low *p*H will be hexaminated. The lack of available coördination space may explain the greater apparent activation energy when reducing *p*-*t*-butylcumene hydroperoxide. This complex should not be stable to alkali, probably decomposing into structures IV and V, hence the differences in apparent activation energies cannot be considered conclusively indicative of this type of mechanism.

Two factors, *p*H and the molecular weight appear to affect the reactivity of a complex at any temperature. From an inspection of the possible structure it may be seen that the *p*H and the number of nitrogens in the polyethylenepolyamine will affect the charge, the number of solvated coördination spaces and the number of internal degrees of freedom (*i.e.*, the number of bonds) in the complex.

In Table VII are listed some rate constants, together with the structure which probably predominates under the conditions used.

TABLE VII

RATE CONSTANTS AND CHARACTERISTICS OF POSTULATED STRUCTURE OF COMPLEXES

Structures Fig. 1	*p*H	Solvated coördination spaces	Charge	No. of bonds	$k_{\text{app.}}$ (20°)
V	11.0	2	+	23	0.49
VIII	10.0	2	++	31	47.0
IX	11.0	1	+	32	73.5
XI	9.1–10.9	1	++	40	112–220

Comparing VIII and IX, decreasing the number of solvated coördination spaces from 2 to 1 together with a diminution of charge brought about an increase in reactivity. Comparing V and VIII, and IX and XI, an increase in the charge and an increase in the number of bonds brought about an increase in reactivity. This latter behavior may be due to an increase in the frequency factor.[5,20] It seems probable that the difference in reactivity between VIII and IX is entirely due to a diminution in the number of available coördination spaces. This confirms a deduction previously made from the reaction with cumene hydroperoxide.[7] Comparing these data with those obtained with cumene hydroperoxide,[7] it may be seen that *p*-*t*-butylcumene hydroperoxide is almost always more reactive toward these complexes than is cumene hydroperoxide. This was noticed previously with "uncomplexed" iron(II).[5]

For both the triethylenetetramine and diethylenetriamine–Fe(II) complexes, polarographic studies were compatible with the previous deduction that a minimum of three species was present in alkaline solution for each complex. The anodic waves of triethylenetetramine complex showed that additional waves appeared at more positive values of $E_{1/2}$ *vs.* S.C.E. as the *p*H was increased. Increasing the *p*H for this complex shifted the wave structure to more positive voltages continuously. It seems to be indicated that the three species involved differ from each other by one hydroxy group and may correspond to structures VIII, IX and X in Fig. 1. This conclusion was supported by the cathodic waves in which the most negative wave was identified with the hydroxy-free complex (VIII) and less pronounced waves at more positive values of $E_{1/2}$ *vs.* S.C.E. were due to contributions from the hydroxy substituted complex (IX and X).

The waves of the diethylenetriamine–Fe(II) complex, while also indicating a total of three structures in the *p*H range studied, showed certain significant differences from those of the triethylenetetramine–Fe(II) complex. On increasing the *p*H, rather than shifting the emphasis of the anodic wave structure continually to more positive voltages, as was found with triethylenetetramine, it appeared that an additional wave was being formed between the two extreme waves.

It may be that this is the result of a discontinuous series of hydroxide ion additions such as would be the case if structures IV, V and VII were found.

This behavior, however, is only suggested and not proven. In the anodic waves of the diethylenetriamine complex, certain unexplained discrepancies exist between the constants determined in its presence. The $E_{1/2}$ *vs.* S.C.E. values were shifted and the dependence of I_d on *p*H was altered. It may be that one complex was partially destroyed by the maxima suppressors, or it may also be that the maxima suppressors are exerting some catalytic effects on the diffusion currents of the anodic waves.

Facts which would invalidate the conclusions with respect to the number of molecular species present would be the existence of a prewave effect brought about either by the maxima suppressors or by the inclusion of trace amounts of oxygen into the complex. The former cannot be since the number of anodic waves is independent of the presence of suppressor. The latter would indicate

(20) E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, p. 123.

formation of a complex between the iron(II)-polyethylenepolyamine complex and oxygen. Admitting the possibility of its formation such a complex would be the cause of the acute maximum noted in the cathodic wave. Since addition of suppressors would displace the oxygen from the complex, it would have to also eliminate the prewave.

The total of four anodic waves present for the pentaethylenehexamine complex indicate contamination by lower polyethylenepolyamines. These have $E_{1/2}$ values of -0.49, -0.27, $+0.06$ and $+0.24$. Inasmuch as iron(II)-pentaethylenehexamine should be a hexaminated complex, there should be no hydroxy complexes other than those brought about by decomposition of the complex by hydroxide ion. This leads to the conclusion that this sample of polyethylenepolyamine was contaminated by lower polyethylenepolyamines. The three more negative waves ($E_{1/2} = -0.49, -0.27$ and $+0.06$) are similar to those obtained from the triethylenetetramine complex ($E_{1/2} = -0.42, -0.21, +0.06$) at this *p*H. The discrepancies in the two more negative waves may be experimental error but more probably resulted from the contributions of other polyamine complexes present (*e.g.*, iron(II)-tetraethylenepentamine) distorting the waves.

The polarographic evidence presented supports the conclusions reached previously as to the existence and number of these complexes and can probably be considered as confirming those postulates. Due to the irreversibility of the reductions it was not possible to determine the equilibrium constants between complexes having varying numbers of hydroxyl groups.

It is not implied that a structure corresponds with any one wave. It is sufficient that the polarographic behavior may be explained by the postulates as to structure change with *p*H for these complexes that seemed necessary to explain data arising from a completely independent source and to that extent makes these postulates more reliable.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF COLORADO]

Metal–Amine Complexes in Ion Exchange[1]

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We have measured the stability of ammonia and amine complexes of silver and copper in resinous cation exchangers. In sulfonic acid exchangers the ammonia complexes are just as stable as in aqueous solution, but in a carboxylic exchanger they are decidedly less stable. Silver–amine complexes are more or less stable in the resin, depending on the balance between adsorptive and steric effects. An explanation is offered for the special stability of the silver–ethylenediamine complex in the exchanger.

Introduction

Metal–ammonia complex cations enter into ion exchange, as do the hydrated metal cations, and some of these exchanges, such as that of the cupric–ammonia cations, are commercially useful.[3] It has been shown that the metal ion may be coördinated with ammonia in the exchanger, just as it is in water containing ammonia.[3,4] The object of the present investigation was to measure the stability of metal–ammonia and metal–amine complexes in cation exchangers, and to find out whether such complexes were more, or less, stable within the exchanger than they are in aqueous solution.

Most of the work here described was done with the silver ion. A few experiments were made with cupric ions. The behavior of other metal ions is being studied and will be described in a later communication.

Experimental

Materials. Sulfonated Polystyrene Resins.—Two batches of "Permutit Q," both nominally containing 10% divinylbenzene, were used. They showed different swelling characteristics. They were washed thoroughly with 2 *N* hydrochloric acid and air-dried before use. Moisture contents were determined by drying at 110°, and the exchangeable hydrogen ion contents were found by titration with standard base. The swollen volumes (in water) were measured by a microscopic technique, the dry volumes (unswollen) by displacement of hexane. The internal solution volumes in water, found from these data, were: resin A, 0.093 ml./meq.; resin B, 0.150 ml./meq. The exchange capacities per gram of dry H-resin were: resin A, 5.13 meq./g.; resin B, 5.05 meq./g.

Carboxylic Resin.—"Amberlite IRC-50," a cross-linked polyacrylic acid, was washed with 2 *N* sodium hydroxide and hydrochloric acid, then treated with ammonia, washed and air-dried. The resin then contained both ammonium ions and replaceable hydrogen ions. The latter were determined by titration, as was the total exchange capacity. The swollen volume of the resin was found pycnometrically,[5] the dry, unswollen volume of the H-form by displacement of hexane. The internal solution volume was calculated to be 0.268 ml./meq., the exchange capacity, 8.67 meq./gram dry H-resin.

Equilibration Technique.—Weighed quantities of resin, usually 1 gram of H-resin, were placed in 130-ml. polyethylene bottles with measured volumes of solutions containing metal salt, amine salt and free amine. Commonly, 0.300 meq. of nitric acid and 0.200 meq. of metal nitrate were used, together with enough amine to neutralize all the nitric acid and resin acid and in addition to coördinate with the metal ions, and water to make a total volume of 100 ml.

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(2) Taken in part from a thesis presented by Mrs. Ruth H. Stokes in partial fulfillment of requirements for the Master of Science degree.

(3) F. Gerstner, *Z. Elektrochem.*, **57**, 221 (1953).

(4) R. Nelson and H. F. Walton, *J. Phys. Chem.*, **48**, 406 (1944).

(5) H. P. Gregor, K. M. Held and J. Bellin, *Anal. Chem.*, **23**, 620 (1951).