*Kinetic and Spectrophotometric Studies of the Homogeneous Catalytic Activity of Iron(III) Complexes upon the Decomposition of Hydrogen Peroxide in Aqueous Solution**

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The mechanism of the homogeneous catalytic decomposition of hydrogen peroxide by ferric or ferrous ions was first presented by Haber and Weiss,[1] who described how the reaction proceeds through a chain mechanism, with the HO_2 radical or the HO_2^- ion as chain carriers and accompanied by repeated redox cycles, $Fe(III) \rightleftarrows Fe(II)$, at the same time. This idea was examined carefully by Barb and others.[2-4] The existence of the free HO_2 radical as an intermediate was confirmed chemically employing 2, 6-di-*t*-butyl-4-methyl phenol in the reaction system[5] and also physically from the ESR spectrum in the case of the cerric ion catalyst.[6] After all, Wang and Jarnagin[7-9] and Kremer and Stein[10,11] proposed a transient occurrence of complex ions between the catalytic ions and the reaction intermediates. Wang and Jarnagin investigated the influence of ligands which occupy coordination sites other than those occupied by HO_2 in a ferric complex ion and found that triethylenetetramineiron(III) ions are most catalytically active in the decomposition of hydrogen peroxide in an alkaline solution, because this ligand is tetradentate and HO_2 is probably bidentate.[9] The study was ultimately intended for the elucidation of the reaction mechanism of catalase, a large coordination compound of the ferric ion, which exhibits the greatest catalytic ability for the decomposition of hydrogen peroxide.[7,12]

In the present paper, it will be made clear how the varieties and the numbers of the coordinating ligands affect, in connection with the energy of coordinate bonds, the catalytic activity of the ferric ion.

Experimental

Materials.—The pure hydrogen peroxide used was obtained by the vacuum distillation of 30% commercial hydrogen peroxide at 30 mmHg, after removing the contained stabilizers by means of adsorption on stannic acid. The concentration of hydrogen peroxide was determined by titration with potassium permanganate. Iron(III) and iron(II) salts were recrystallized from sulfuric acid solutions of $Fe_2(SO_4)_3 \cdot 9H_2O$ and $FeSO_4 \cdot 7H_2O$ respectively. The ligands employed as complexing reagents were monoethylamine (ea), ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien), tetraethylenepentamine (tetraen), *o*-phenanthroline (phen) and α, α'-dipyridyl (dip), which were used without further purification. Iron(III) complexes were prepared by merely mixing the two solutions of the Fe^{3+} ion and a ligand in an appropriate proportion. The pH of the solution was adjusted by adding perchloric acid and was assayed by a pH-meter. The effect of the ionic strength was negligible in every case, because the concentrations of all ionic components in the solution were extremely low.

Kinetic Measurements.—The reaction was regarded as starting at the moment when a solution of the iron(III) complex ion was quickly poured into a reaction vessel containing a hydrogen peroxide solution in a thermostat. The rate of the reaction was determined by measuring the volume of evolved oxygen with a gas buret.

The Determination of Stability Constants.—The stability constants of several iron(III)-complex ions were measured by the pH method, using a Hitachi-Horiba pH-Meter Model P, with an accuracy of pH ±0.01. Bjerrum's formation function, $\bar{n}$, is thereby defined as follows:

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[1] F. Haber and J. Weiss, *Proc. Roy. Soc. London*, **A147**, 332 (1934).

[2] W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951).

[3] W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, ibid., **47**, 591 (1951).

[4] W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, ibid., **51**, 935 (1955).

[5] G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 2758 (1957).

[6] B. H. J. Bielski and E. Saito, *J. Phys. Chem.*, **66**, 2266 (1962).

[7] J. H. Wang, *J. Am. Chem. Soc.*, **77**, 4715 (1955).

[8] R. C. Jarnagin and J. H. Wang, ibid., **80**, 786 (1958).

[9] R. C. Jarnagin and J. H. Wang, ibid., **80**, 6477 (1958).

[10] M. L. Kremer and G. Stein, *Trans. Faraday Soc.*, **55**, 959 (1959).

[11] M. L. Kremer, ibid., **58**, 702 (1962).

[12] P. George, *Biochem. J.*, **43**, 287 (1948); ibid., **44**, 197 (1949); P. Jones and W. F. K. Wyne-Jones, *Trans. Faraday Soc.*, **58**, 1148 (1962).

$$\bar{n}=\frac{\sum_{i=1}^{m} iK_1K_2\cdots K_i[\mathrm{L}^*]^i}{1+\sum_{i=1}^{m}K_1K_2\cdots K_i[\mathrm{L}^*]^i} \tag{1}$$

$$=\frac{C_L-(C_H-[\mathrm{H}^+])/p^+}{C_M} \tag{2}$$

where K_i is the i-th stepwise stability constant; $[\mathrm{L}^*]$ and $[\mathrm{H}^+]$, the concentrations of the free ligand (coordinating with neither the metal ion nor the hydrogen ion) and of the hydrogen ion respectively; m, the coordination number of the central metal ion; C_M, C_L and C_H, the total concentrations of the Fe^{3+} ion, the ligand and perchloric acid respectively added to the solution, and $\bar{p}$, the ratio between the number of ionizable hydrogen atoms attached to the ligand and the total number of ligand molecules which are not coordinated with the metal ion; namely,

$$\bar{p}=\frac{\sum_{i=1}^{p}\dfrac{i[\mathrm{H}^+]^i}{K_{\mathrm{HL}^+}\cdot K_{\mathrm{H_2L}^{2+}}\cdots K_{\mathrm{H}_i\mathrm{L}^{i+}}}}{1+\sum_{i=1}^{p}\dfrac{[\mathrm{H}^+]^i}{K_{\mathrm{HL}^+}\cdot K_{\mathrm{H_2L}^{2+}}\cdots K_{\mathrm{H}_i\mathrm{L}^{i+}}}}$$

where $K_{\mathrm{H}_i\mathrm{L}^{i+}}$ indicates the acid dissociation constant of $\mathrm{H}_i\mathrm{L}^{i+}$. By putting this relation into Eq. 2, $\bar{n}$ can be calculated, if the $K_{\mathrm{H}_i\mathrm{L}^{i+}}$'s are known. According to the difinition, $[\mathrm{L}^*]$ is also expressed as

$$[\mathrm{L}^*]=\frac{C_H-[\mathrm{H}^+]}{\sum_{i=1}^{p}\dfrac{i[\mathrm{H}^+]^i}{K_{\mathrm{HL}^+}\cdot K_{\mathrm{H_2L}^{2+}}\cdots K_{\mathrm{H}_i\mathrm{L}^{i+}}}}$$

Therefore, by means of titrating a mixed solution of the Fe^{3+} ion and the ligand with perchloric acid and by measuring its pH, one can plot the relation between $\bar{n}$ and $-\log[\mathrm{L}^*]$, from which the stability constants are obtained, as is clear from Eq. 1. K_i's are known at the value $\bar{n}=i-0.5$ according to Bjerrum's approximation.

Spectrophotometry.—The individual absorption spectra of aqueous solutions of the Fe^{3+} ion, the Fe^{2+} ion and their complex ions and hydrogen peroxide were observed separately in advance. Then the variations of the spectra of the solution under reaction with the lapse of time were observed as the catalytically-working state of complex ions. For the observation, a Hitachi recording spectrophotometer type EPS-2 was used at the 220∼900 mμ wevelength range. A tungsten lamp and a hydrogen discharge tube were employed as light sources for the visible and the ultraviolet regions respectively. The cell was one made of quartz and had an optical length of 1 cm.

Results and Discussion

Velocity Curves and Their pH Dependence.—The reaction rates of hydrogen peroxide decomposition catalyzed by the Fe-aq^{3+} ion are generally of the S-type, as Fig. 1 shows. The reaction proceeds nearly linearly, something like a zeroth-order reaction, after the continuance of some induction period, and then it falls off gradually.[*1]

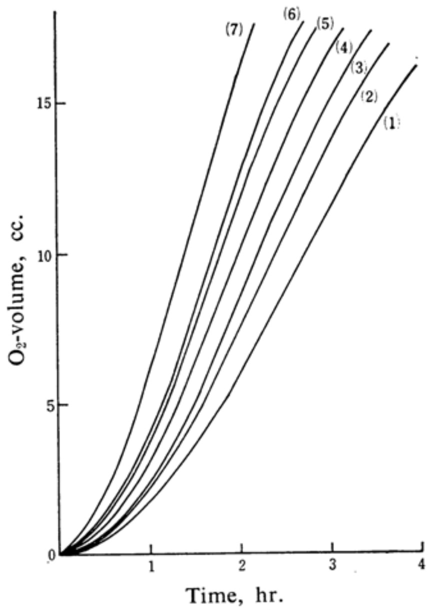

Fig. 1. The pH dependence of the reaction rate at 45°C.
$[\mathrm{Fe\text{-}aq}^{3+}]=1.013\times10^{-4}$ mol./l., $[\mathrm{H_2O_2}]_0=1.010\times10^{-2}$ mol./l. (1) pH 2.65; (2) 2.80; (3) 2.90; (4) 3.01; (5) 3.10; (6) 3.20; (7) 3.40

On the average, it takes as long as a few minutes for an Fe^{3+} ion to decompose only one hydrogen peroxide molecule, judging from the slope of the linear part of the reaction in such cases as in Fig. 1. Considering this fact, together with the stability constant of Fe^{3+}-$\mathrm{HO_2}^-$, $\log K_1=9.31$,[13)] the rate of the reaction may probably be controlled either by an activated collision between the Fe^{3+} ion and $\mathrm{HO_2}^-$ (or $\mathrm{HO_2}$) or by the self-decomposition of the complex. For this reason, the reaction appears as of the zeroth-order. Hereafter, the rate constant, k, will be expressed by the slope of the linear part of the reaction in mol.-$\mathrm{H_2O_2}$/l. hr. The values of k are dependent on the pH of the solution, as is shown in Table I, where the reaction is found to be accelerated as the pH value is raised. However, on account of the restriction arising from the solubility of the iron-complex salts, the pH of the solutions will be generally fixed at

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[*1] As soon as hydrogen peroxide is supplemented up to a concentration equal to that of the initial state when the reaction has almost completely finished, the reaction comes back immediately to the linear part at the same velocity as that of the previous time, without exhibiting the induction phenomenon again.

13) "Stability Constants of Metal-ion Complexes," Part II, Compiled by J. Bjerrum et al., Chem. Soc., London (1958), p. 68; M. G. Evans, P. George and N. Uri, *Trans. Faraday Soc.*, 45, 230 (1949).

3.00 in the following sections, unless otherwise specified.

Variations in the Reaction Rate with Concentration and Temperature.—Table II shows the variations in the reaction rate with the concentrations of the Fe^{3+} ion, hydrogen peroxide and the ligand and with the temperature of the reaction system. The ratios of the concentration of the ligand to that of Fe^{3+} in solutions are expressed by $[L]/[Fe^{3+}]$. The apparent activation energies, E_a, are also obtained from the relation between $\log k$ and $1/T$. It can easily be seen from the table that k diminishes with an increase in $[L]/[Fe^{3+}]$ as long as both $[Fe^{3+}]$ and $[H_2O_2]_0$ are kept constant and that k increases approximately in proportion to $[Fe^{3+}]$ and to the 1.5th power of $[H_2O_2]_0$.

Only when phen is employed as a ligand, is the reaction not of the S-type but appears

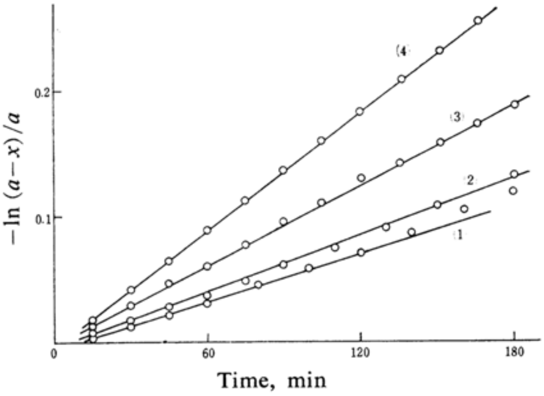

Fig. 2. The reaction rate catalyzed by the Fe(III)-phen complex ion at pH 3.
$[Fe^{3+}]=1.013\times10^{-4}$ mol./l., $[phen]/[Fe^{3+}]=1$, $[H_2O_2]_0=1.010\times10^{-2}$ mol./l. (1) 30°C; (2) 35°C; (3) 40°C; (4) 50°C

TABLE I. THE EFFECT OF pH ON THE REACTION RATE AT 45°C

$[Fe\text{-}aq^{3+}]=1.013\times10^{-4}$ mol./l., $[H_2O_2]_0=1.010\times10^{-2}$ mol./l.

pH	2.65	2.80	2.90	3.01	3.10	3.20	3.40
$k\times10^3$ mol.-H_2O_2/l. hr.	1.31	1.47	1.64	1.79	1.88	2.12	2.51

TABLE II. THE VARIATIONS OF k WITH CONCENTRATIONS AND TEMPERATURES, AND THE APPARENT ACTIVATION ENERGIES, E_a, AT pH 3

Ligand	$[Fe^{3+}]$ $\times10^4$ mol./l.	$[L]/[Fe^{3+}]$	$[H_2O_2]_0$ $\times10^2$ mol./l.	k, $\times10^4$ mol.-H_2O_2/l. hr.					E_a kcal./mol.
				30°C	35°C	40°C	45°C	50°C	
none(aq)	1.013	—	1.008	6.3	9.1	12.8	17.9	25.4	14.7
	3.336	—	1.611	—	28.6	46.4	74.2	117	18.0
ea	1.013	1	1.010	3.7	7.1	9.8	13.0	18.2	16.5
	1.013	2	1.010	3.1	4.5	8.1	11.5	15.8	16.0
	1.013	3	1.010	2.2	4.1	6.1	10.1	14.0	14.9
	1.013	4	1.010	—	3.5	5.5	9.2	11.9	14.7
	1.013	5	1.010	—	3.6	5.4	7.8	11.5	14.3
	1.013	6	1.010	—	3.1	4.6	7.4	10.7	14.6
	1.013	100	1.010	—	0	0	0	0	—
en	1.013a)	1	1.010	6.3	10.3	16.5	25.4	—	18.0
	1.013a)	1	3.391	37.4	59.7	94.0	144	—	17.2
	1.013	2	1.010	6.4	9.9	13.8	22.4	—	16.1
	1.013	3	1.010	5.7	9.3	13.3	19.8	—	15.7
	1.013	3	3.391	33.7	55.4	89.1	168	—	20.8
	1.013	4	1.010	—	9.9	14.7	21.3	31.2	15.1
	1.013	100	1.010	—	2.8	4.3	6.5	9.8	16.6
dien	1.013	1	1.010	—	4.8	8.7	15.4	27.2	22.7
	1.013	2	1.010	—	3.6	6.2	10.9	18.9	21.8
	1.013	100	1.010	—	0	0	0	0	—
trien	1.013b)	1	1.010	2.3	4.1	7.5	13.2	—	22.5
	2.026	2	1.010	—	2.4	4.3	8.3	15.2	24.5
	1.013	100	1.010	—	0	0	0	0	—
tetraen	1.013	1	1.010	—	2.8	4.9	8.2	13.9	20.8
	2.026	2	1.010	—	1.8	2.4	5.0	8.2	19.9
	1.013	100	1.010	—	0	0	0	0	—

a) pH 3.1
b) pH 2.9

as a first-order reaction with respect to the concentration of hydrogen peroxide, since $\ln[(a-x)/a]$ is linear against time, where x and a are the volumes of oxygen evolved at t and the infinite time respectively, as is pictured in Fig. 2. The rate constants at various temperatures and the apparent activation energies are listed in Table III.

Inspection of Tables II and III reveals that the catalytic activities of iron(III) complexes depend upon the sort of ligands, decreasing in the order:

$$\text{en} > \text{dien} \sim (\text{H}_2\text{O}) \sim \text{ea} > \text{trien} > \text{tetraen} \sim \text{dip} \sim \text{phen} \qquad (3)$$

where H_2O indicates the simple iron(III)-aquo ion without any other ligand in the solution.

On the other hand, the apparent activation energies, E_a, of the reaction catalyzed by various complexes generally show peaks near the concentration ratio of $[L]/[Fe^{3+}]=1$, except for the cases of trien and phen, where the former increases and the latter decreases monotonously with the increasing concentration ratio, as is pictured in Fig. 3. Therefore, the order of E_a with respect to ligands is as follows at their low concentration:

$$\text{dien} \sim \text{trien} > \text{tetraen} > \text{en} > \text{ea} > (\text{H}_2\text{O}) > \text{phen} \qquad (4)$$

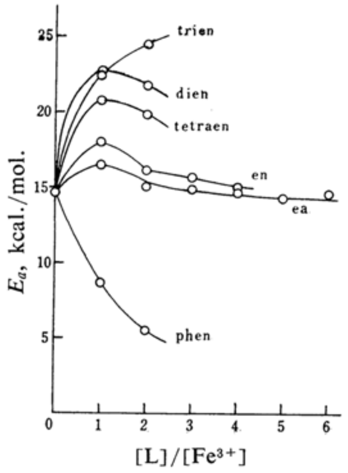

Fig. 3. The variations of the apparent activation energies, E_a, with $[L]/[Fe^{3+}]$ at pH 3. $[Fe^{3+}]=1.013\times10^{-4}$ mol./l., $[H_2O_2]_0=1.010\times10^{-2}$ mol./l.

All the ligands except phen make E_a larger than that for the case of the simple Fe-aq^{3+}, so long as their concentration is low. Wang⁹⁾ said that trien showed the highest catalytic activity in an alkaline solution because of the steric advantage arising from its tetradentate nature. We, however, have found this ligand to be merely a poor catalyst at pH 3, contradictory to Wang's description. In the case of en and dien, since their complexes are more active than Fe-aq^{3+} in spite of the larger E_a, they must make the reaction much easier sterically, overcoming the energetic disadvantage.

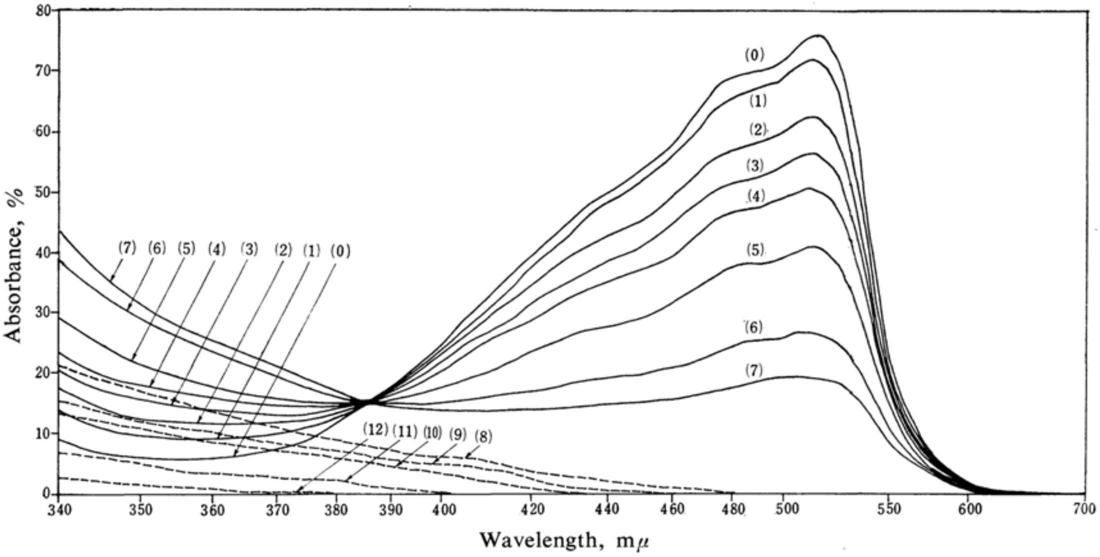

Fig. 4. Time variation of visible absorption spectra of Fe-phen$_3^{2+}$ under a catalytically working state at room temperature.
$[\text{Fe-phen}_3^{2+}]=1.013\times10^{-4}$ mol./l., $[H_2O_2]_0=1.010\times10^{-2}$ mol./l. (0) $t=0$; (1) 5 min.; (2) 15 min.; (3) 30 min.; (4) 50 min.; (5) 80 min.; (6) 140 min.; (7) 200 min.; (8) 300 min.; (9) 400 min.; (10) 1 day; (11) 7 days; (12) 8 days

TABLE III. THE RATE CONSTANT, k (hr^{-1}), AND THE APPARENT ACTIVATION ENERGY, E_a, OF THE REACTION CATALYZED BY THE Fe(III)-phen COMPLEX ION AT pH 3
$[Fe^{3+}]=1.013\times10^{-4}$ mol./l., $[H_2O_2]_0=1.010\times10^{-2}$ mol./l.

$[phen]/[Fe^{3+}]$	30°C	35°C	40°C	45°C	50°C	E_a kcal./mol.
1	0.041	0.048	0.066	—	0.098	8.7
2	—	0.041	0.046	0.054	0.061	5.5

TABLE IV. STABILITY CONSTANTS OF VARIOUS IRON(III) COMPLEXES AT 30° AND 45°C AND PERCENTAGES OF THE COORDINATED IRON AT THE CONCENTRATION
$[Fe^{3+}]=[L]=1.013\times10^{-4}$ mol./l. AT 30°C

Ligand	Temp. °C	Dissociation constant*				Stability constant						α %
		$-\log K_{HL^+}$	$-\log K_{H_2L^{2+}}$	$-\log K_{H_3L^{3+}}$	$-\log K_{H_4L^{4+}}$	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$	
ea	30	10.61				11.36	11.25	11.19	10.94	10.73	10.25	<59.5
	45	9.95				11.07	10.93	10.86	10.52	10.10	9.54	
en	30	9.93	7.26			14.77	14.07	8.90				57.6
	45	9.52	6.79			14.18	13.21	8.12				
dien	30	9.94	9.23	4.78		19.37	17.90					79.1
	45	9.55	8.80	4.40		18.56	16.93					
trien	30	9.99	9.36	7.01	3.89	23.54						92.7
	45	9.64	9.03	6.68	3.70	22.79						

* "Stability Constants of Metal-ion Complexes," Part I, Compiled by J. Bjerrum et al., Chem. Soc., London (1957).

TABLE V. THE TRUE VALUES OF RATE CONSTANTS, ACTIVATION ENERGIES AND ACTIVATION ENTROPIES OF THE REACTION CATALYZED BY FeL^{3+} ION WHEN $[H_2O_2]_0=1.010\times10^{-2}$ mol./l. AND $[FeL^{3+}]=1.013\times10^{-4}$ mol./l.

Ligand	k, $\times10^4$ mol.-H_2O_2/l. hr					E_a kcal./mol.	E kcal./mol.	$\Delta(\Delta S)$ cal./deg. mol.
	30°C	35°C	40°C	45°C	50°C			
aq	6.3	9.1	12.8	17.9	25.4	14.7	14.7	Standard
ea	(2.0)	5.7	7.8	9.6	13.5	16.5	12.2	−9.2
en	6.3	11.1	19.3	31.1	—	18.0	22.3	26.0
dien	—	3.7	7.6	14.8	27.8	22.7	27.2	38.9
trien	1.9	3.7	7.1	12.8	—	22.5	25.9	34.5
tetraen	—	—	—	—	—	20.8	—	—

TABLE VI. THE WAVELENGTHS, λ_{max}, AND THE EXTINCTION COEFFICIENTS, ε, AT PRINCIPAL ABSORPTION MAXIMA OF VARIOUS SUBSTANCES IN AQUEOUS SOLUTIONS IN THE 220∼900 mμ RANGE AT pH 3
( ): shoulder, [ ]; broad or plateau

phen	λ_{max}	324	(310)	(289)	265	229	(225)	
	$\log\varepsilon$	3.12	3.20	3.85	4.29	4.40	4.39	
H_2O_2		Gradual end absorption at $\lambda<300$ mμ						
$Fe\text{-}aq^{3+}$	λ_{max}		298					
	$\log\varepsilon$		3.86					
$Fe\text{-}aq^{2+}$	λ_{max}	[370]			(246)			
	$\log\varepsilon$	0.45			1.17			
$Fe\text{-}phen_3{}^{3+}$	λ_{max}	(350)	326	(289)	266	[230∼225]		
	$\log\varepsilon$	3.41	3.66	4.25	4.75	4.95		
$Fe\text{-}phen_3{}^{2+}$	λ_{max}	515	(480)	(420)	(320)	(289)	267	226
	$\log\varepsilon$	4.11	3.90	3.60	3.32	4.27	4.92	4.82

TABLE VII. THE d-ORBITAL ENERGY LEVELS IN Dq UNIT IN THE LIGAND FIELD

Coordination number	Structure	$d_{x^2-y^2}$	d_{z^2}	d_{xy}	d_{xz}	d_{yz}
5	Trigonal bipyramid	−0.82	7.07	−0.82	−2.72	−2.72
5	Square pyramid	9.14	0.86	−0.86	−4.57	−4.57
6	Octahedron	6.00	6.00	−4.00	−4.00	−4.00
7	Pentagonal bipyramid	2.82	4.93	2.82	−5.28	−5.28

The Stability Constants of Several Complexes.—The stability constants of iron(III) complexes with ea, en, dien and trien at 30 and 45°C are listed in Table IV. Using the data of the stability constants, the percentages of the coordinated iron in the total iron at $[Fe^{3+}]=1.013\times10^{-4}$ mol./l. are calculated as α, shown in the last column of the table.

The various values of k and E_a as shown in Table II are, of course, those which are averaged with respect to the hydrated iron(III) (non-coordinated by ligands, Fe-aq^{3+}) and the coordinated iron (III) (FeL_i^{3+}) in accordance with their percentages of occurrence. The true values, purely due to the catalytic activity of the coordinated complexes calibrated by α, are shown in Table V. Since K_1 does not vary with the temperature in comparison with the experimental errors, α's at 30°C were used withought alteration in the calculation for other temperatures. In the case of $[L]/[Fe^{3+}]=1$, $[FeL_2^{3+}]$ and higher complexes are negligibly rare.

According to Table V, the true activation energies, E, are generally greater than E_a, with the exception of the case of ea. Hence, the activation entropy increments putting the activation entropy of the aquo ion as the standard, $\Delta(\Delta S)$, have been calculated and been found to be positive in the cases of en, dien and trien and negative in the case of ea. The parallelism between E and $\Delta(\Delta S)$ is fairly good (the compensation effect). Judging from the large positiveness of $\Delta(\Delta S)$ in the cases of several iron(III)-*N*-multidentate complexes, the activated states of these complexes are supposed to be looser than the pre-activated states; they may be less coordinated than six. This supposition will be proved later.

The Absorption Spectra of Catalytically-Active Complexes in the Working State.—Table VI shows the positions of the peaks, λ_{max}, and the extinction coefficients, ε, in the absorption spectra of phen, hydrogen peroxide, Fe-aq^{3+}, Fe-aq^{2+}, Fe-phen$_3^{3+}$ and Fe-phen$_3^{2+}$ in aqueous solutions. Hydrogen peroxide, Fe-aq^{3+} and Fe-aq^{2+} exhibit no remarkable characteristic absorptions except their end absorption in the region of very short wavelengths. The observed values of λ_{max} and ε of iron-phen complexes agree with the values in the literature rather well.[14] The reason why the phen-complexes are used here is merely the convenience of the spectrophotometric observation, even though they have a disadvantage that the phen molecules themselves are liable to decompose during the reaction.

The visible spectra of Fe-phen$_3^{2+}$ in the catalytically-working state during the decomposition of hydrogen peroxide are shown in Fig. 4, where the absorption at 515 mμ characteristic of Fe-phen$_3^{2+}$ decreases with time, while that at 350 mμ characteristic of Fe-phen$_3^{3+}$ increases. This means that the iron(II)→iron(III) oxidation is occurring. However, with a longer lapse of time, the absorption at 350 mμ begins to decrease after attaining a maximum, while the absorption band at 515 mμ is never recovered again; the solution becomes almost colorless, and at last the spectrum coincides with that of Fe-aq^{2+}. This is due to the consecutive reduction, iron(III)→iron(II), after the preceding oxidation,[15] as well as to the simultaneous decomposition of phen itself. A similar conclusion can be derived from the observed results in the ultraviolet region.

In the same way, the visible absorption curves of the reaction system containing Fe-phen$_3^{3+}$ and hydrogen peroxide show that, although the height of the comparatively low peak at 350 mμ hardly varies at all, another new peak appears at 515 mμ, changing the color of the solution from yellow to reddish. This indicates the occurrence of the iron(III)→iron(II) reduction. However, after more than three hours, the peak at 515 mμ disappears and the solution again becomes yellow, indicating a recovery of iron(II)→iron(III). After that, the curve gradually approaches the characteristic weak curve of Fe-aq^{3+} on account of the decomposition of phen, just as in the case of Fe-phen$_3^{2+}$.

Figures 5 and 6 show the time variations of the ultraviolet absorption spectra in reaction systems containing Fe-phen$_3^{2+}$ and hydrogen peroxide, and Fe-phen$_3^{3+}$ and hydrogen peroxide respectively. Since Fe-phen$_3^{2+}$, Fe-phen$_3^{3+}$ and phen exhibit their individual peaks at 265~267 mμ with nearly the same extinction coefficients, the fact that the absorption at this wavelength region diminishes monotonously with time indicates that the decomposition of phen has begun even at the initial stage of the reaction. In the 300~320 mμ region, on the other hand, the absorption grows stronger with time in Fig. 5, while it does not vary so much in Fig. 6[*2] because of the difference in ε between Fe-phen$_3^{2+}$ and Fe-phen$_3^{3+}$ in this wavelength region. The electron transfer between iron(II) and iron(III) is, therefore,

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[14] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).

[15] In reactions between cumene hydroperoxide and the ferrous iron, such as aquo-ferrous ion, ferrous versenate and ferrous pyrophosphate, the formation of ferric iron has also been observed. W. L. Reynolds and I. M. Kolthoff, *J. Phys. Chem.*, **60**, 969, 996 (1956).

[*2] The accuracy of Fig. 6 was worse than that of Fig. 5.

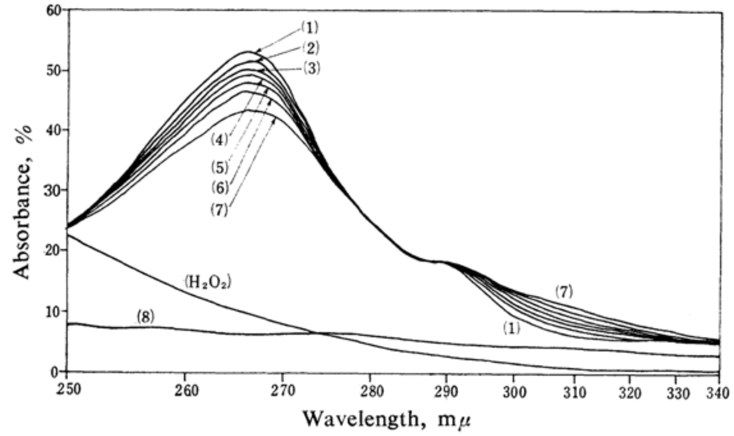

Fig. 5. Time variation of ultraviolet absorption spectra of Fe-phen$_3{}^{2+}$ under a catalytically working state at room temperature.
[Fe-phen$_3{}^{2+}$]$=1.013\times10^{-4}$ mol./l., [H_2O_2]$_0=1.010\times10^{-2}$ mol./l. The original solutions were diluted about 13 times when determined. (1) $t=5$ min.; (2) 20 min.; (3) 55 min.; (4) 100 min.; (5) 180 min.; (6) 290 min.; (7) 430 min.; (8) 24 hr.; (H_2O_2) H_2O_2 only at 9.56×10^{-4} mol./l.

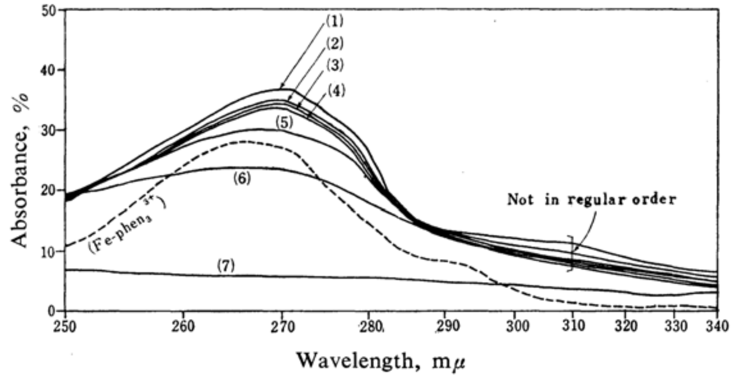

Fig. 6. Time variation of ultraviolet absorption spectra of Fe-phen$_3{}^{3+}$ under a catalytically working state at room temperature.
[Fe-phen$_3{}^{3+}$]$=1.013\times10^{-4}$ mol./l., [H_2O_2]$_0=1.010\times10^{-2}$ mol./l. The original solutions were diluted about 25 times when determined. (1) $t=5$ min.; (2) 15 min.; (3) 30 min.; (4) 60 min.; (5) 120 min.; (6) 210 min.; (7) 20 hr.; (Fe-phen$_3{}^{3+}$) Fe-phen$_3{}^{3+}$ only

proved.*3

Considering that the absorbance of hydrogen peroxide gradually increases towards shorter wavelengths, as Fig. 5 shows, the characteristic peaks of Fe-phen$_3{}^{2+}$ at 267 mμ and Fe-phen$_3{}^{3+}$ at 266 mμ should shift in appearence towards shorter wavelength because of a simple overlapping with hydrogen peroxide, if these complexes do not interact with hydrogen peroxide. In fact, however, according to Figs. 5 and 6, they clearly shift towards rather longer wavelengths as far as 1∼4 mμ. This indicates changes in the strength of chemical bondings in both complexes, probably due to the formation of the coordination of HO_2 to iron. Generally speaking, the absorption bands of any complex are determined by the total influence of all the coordinated ligands, and their wavelengths shift continuously with the exchange of the ligands with others one by one. A red shift means the loosening of the coordinate bondings as the resut of the substitution for one ligand of another. HO_2 may be a ligand that makes the coordinate bonds slightly looser.

The Relation Between the Reaction Mechanisms and the Stabilization Energies of the Ligand Fields.—Concerning the central metal ions with the coordination number of six, the order of the ligand field stabilization energy

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*3 The rate constant of the Fe-phen$_3{}^{2+}\rightarrow$Fe-phen$_3{}^{3+}$ electron transfer was found to be $k>1\times10^5$ mol$^{-1}\cdot$sec^{-1} by the N. M. R. method. M. W. Dietrich and A. C. Wahl, *J. Chem. Phys.*, **38**, 1591 (1963).

TABLE VIII. DIFFERENCES IN LIGAND-FIELD STABILIZATION ENERGIES IN Dq, ΔE, THROUGH S_N1- AND S_N2-MECHANISMS BY Fe(II)- AND Fe(III)-COMPLEXES

			S_N1		S_N1		S_N2	
d^n	Ligand field	Octahedron d^2sp^3	Trigonal bipyramid dsp^3	ΔE	Squre pyramid d^2sp^2	ΔE	Pentagonal bipyramid d^3sp^3	ΔE
Fe(III)-d^5	Strong	20.00	8.98	11.02	19.14	0.86	18.30*	1.70
	Weak	0	0	0	0	0	0	0
Fe(II)-d^6	Strong	24.00	11.72	12.28	20.00	4.00	15.48*	8.52
	Weak	4.00	2.72	1.28	4.57	−0.57	5.28	−1.28

* Among the strong field complexes of ions having d^5 or d^6 electrons, those with the configuration of pentagonal bipyramid are theoretically impossible, because the inner d-orbitals can be completely occupied only by four electrons.

decided from the absorption spectra is known as Fajans-Tsuchida's spectrochemical series:[16]

$$\mathrm{CN^-} > \mathrm{phen} > \mathrm{dip} > \mathrm{trien} \sim \mathrm{dien} \sim \mathrm{en} > \mathrm{NH_3} \sim \mathrm{py} > \mathrm{H_2O} > \mathrm{OH^-} \qquad (5)$$

Although this series is not absolutely applicable for iron(III),[17] one can easily find, by comparing the two series, 4 and 5, that the first ligand of the 4 series, dien, is in the middle of the 5 series and that the succeeding ones in the 4 series are situated before and behind dien in the 5 series, regularly going farther away from the middle.

Since the 5 series generally indicates the order of the strength of the coordinate bonds between the central metal ion and the ligand, the following theory seems reasonable. The stability of iron complexes coordinated by HO_2 is quite decisive on the reaction rate, and their stability depends upon the ligand molecules occupying sites other than that occupied by HO_2. Dien, therefore, is the most suitable ligand for the reaction in this point. Ligands of neither higher nor lower ranking positions than dien in the 5 reries are favorable for the reaction, on account of their too strong or too weak coordinate bondings.

Iron(III) and iron(II) ions have the electron configurations of d^5 and d^6 respectively and ordinarily form complexes with a coordination number of six. According to whether the reaction proceeds through an S_N1 mechanism or through an S_N2 mechanism, there appears an intermediate complex with a coordination number of five or seven respectively. As a complex with the coordination number of five, we must take into account a complex of a trigonal bipyramid with a dsp^3 hybridization orbital and that of a square pyramid with a d^2sp^2 hybridization orbital, and as a complex with the coordination number of seven, that of a pentagonal bipyramid with a d^3sp^3 hybridization orbital. On the basis of the ligand field theory, the energy levels of these d-orbitals can be calculated as shown in Table VII.[18] Accordingly, the ligand field stabilization energies of these complexes and the energy losses, ΔE, of ligand field stabilization on the occasion of the transition from an octahedron to one of other intermediate structures are listed in Table VIII. Since a larger ΔE corresponds to a more difficult transition, the S_N1 mechanism via a square pyramid at the iron(III) state is the most probable in the strong ligand field and the S_N2 mechanism via a pentagonal bipyramid at the iron(II) state in the weak field. Judging from the values of the activation energies and the activation entropies in Table V, the ligands can be divided into two groups: (a) water and ea, which are monodentate ligands with low E and $\Delta(\Delta S)$, and (b) en, dien and trien, which are multidentate ligands with comparatively high E and $\Delta(\Delta S)$. The group a may form weak field complexes with the iron(III) ion (in the case of the $\mathrm{Fe\text{-}aq^{3+}}$ ion, this is already known from the magnetic and optical data) and make the reaction proceed through the S_N2 mechanism after the complex ion has undergone the acceptance of an electron from the surroundings, while the group b may form strong field complexes, driving the reaction through the S_N1 mechanism. These considerations can be justified as quite plausible from miscellaneous aspects of the activation energies, the activation entropies, the spectrochemical series, the molecular shapes and structures of ligands (whether they are monodentate or multidentate), the ligand field theory, and so forth. The paths of the S_N1 and S_N2 mechanisms may be shown schematically as follows:

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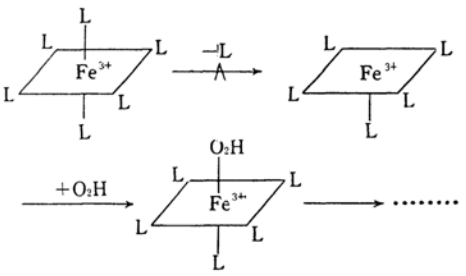
[16] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford (1962), p. 109.

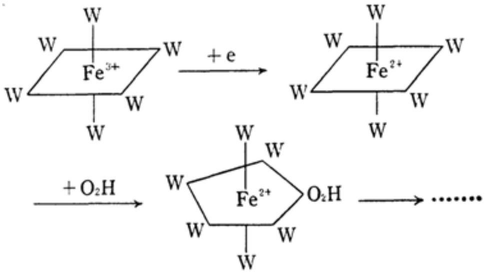
[17] R. J. P. Williams, *J. Chem. Soc.*, **1956**, 8.

[18] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley, New York (1960), p. 55.

S_N1 mechanism (strong field):



S_N2 mechanism (weak field):[*4]



It is especially noteworthy that, since the CN^- ion stands first in the 5 series, the reaction was somewhat suppressed by its stronger coordinate bonding and, therefore, by its greater stabilization in the case of $[Fe^{3+}]:[en]:[CN^-]=1:1:1$,[*5] with the result that the reaction rate was lowered as much as 10% and the apparent activation energy was raised as high as 2 kcal./mol. This fact is also consistent with the above explanation. The well-known retardation by the CN^- ions of the coordination of oxygen to hemoglobin in blood might occur in a similar way.

Summary

Hydrogen peroxide is catalytically decomposed by the Fe^{3+} ion, the activity of which is remarkably affected by the kind and the number of ligands coordinated to it. In this paper, the effects of ligands have been kinetically and spectrophotometrically determined and discussed from the view-point of the ligand field theory.

(1) The reaction generally proceeds linearly with time after a certain induction period, and the rate depends upon the pH of the solution.

(2) The reaction rate varies with the kind of the ligand and with its concentration. When $[L]/[Fe^{3+}]$ is equal to unity, the rate decreases in the order: en>dien~(H_2O)~ea >trien>tetraen~dip~phen.

(3) The apparent activation energy of the reaction exhibits a maximum, except in the cases of trien and phen, at the concentration ratio $[L]/[Fe^{3+}]=1$, and the values of the activation energy at this concentration ratio are in the order: dien~trien>tetraen>en>ea >(H_2O)>phen.

(4) The true activation energy of the reaction catalyzed by the pure iron-complex is calculated from the observation of the stability constants to be in the order: dien>trien>en >(H_2O)>ea, which completely coincides with the order of the activation entropy.

(5) The visible and ultraviolet absorption spectra of Fe-phen$_3^{2+}$ and Fe-phen$_3^{3+}$ as catalysts in the working state were observed, and it was found that there takes place a redox cycle, $Fe^{3+} \rightleftarrows Fe^{2+}$, during the reaction and that phen molecules are gradually decomposed at the same time.

(6) In the course of the reaction, the peaks of the ultraviolet absorption of Fe-phen$_3^{2+}$ and Fe-phen$_3^{3+}$ bring about a slight red shift, which is caused by the coordination of HO_2 to the iron ion.

(7) Judging from a comparison between the activation energy of the reaction and the spectrochemical series of ligands and from the calculation of the stabilization energy due to the ligand field theory, the reaction proceeds through an S_N1 mechanism under the iron(III) oxidation state in the case of strong field complexes and through an S_N2 mechanism under the iron(II) state in the case of weak field complexes.

(8) The reaction is retarded and the activation energy is raised by the addition of the CN^- ion, which strongly coordinates with iron and forms a very strong field complex.

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[*4] W means weak ligands, such as water.

[*5] The stability constant of the complex containing the CN^- ion is not yet known.