Dq from fundamentals have not as yet been very successful, but we do feel that in the absence of a fundamental theory it is best to use the empirical theory as accurately as possible in terms of the matrices of Tanabe and Sugano with no additional approximations.

The fine structure observed at the ${}^4A_{1g}$, ${}^4E_g$ twin peaks at 24960 and 25275 cm.$^{-1}$ could be due to a variety of causes such as: (1) a resolving of the accidental degeneracy of these levels due to electrostatic interaction with their environments, (2) spin orbit interaction and (3) a crystal field that is not purely octahedral but has some distortion.

The second possibility is unlikely for the following reason. The two main peaks are separated by about 300 cm.$^{-1}$. The fine structures of the ${}^4G$ and ${}^4D$ states of the free gaseous ion are about 10 and 50 cm.$^{-1}$, respectively.[11] The spin orbit interaction responsible for this splitting, therefore, is too small to explain the effect.

The third possibility is unlikely since if it were the case, splittings of comparable order of magnitude would be present in some of the other degenerate levels in the crystal field. The same argument could also be used against the second possibility.

The first possibility then appears to be the most likely even though it is a little difficult to predict an order of magnitude for the effect. The degeneracy predicted for the ${}^4A_{1g}$ and ${}^4E_g$ levels is purely accidental and is due essentially to our approximations. A general interaction of cubic symmetry could remove this degeneracy.

Another point worth mentioning is the occurrence of the very low peak in absorption at about 26500 cm.$^{-1}$. This peak is most likely caused by a transition from the ground state to a state of spin 1/2. This spin change of 2 is doubly forbidden[11] and would give rise to the relatively weak absorption which is observed. There is one such state which cuts across the Orgel diagram and has about the proper values of E at the value of Dq for the other levels in the crystal field. This state is of ${}^2T_{2g}$ symmetry and is designated as the ${}^2F_2(d\epsilon^5)$ state by Tanabe and Sugano; it has the ${}^2I$ state of the free ion as its parent. Unfortunately the value of E for this energy level is the root of a 10 × 10 secular equation, and we have not as yet calculated the values of E for this level as a function of Dq from our best values of B and C.

Transitions between states of different multiplicity are "forbidden,"[11] consequently the probability of transitions from the ground state ${}^6S$ to states of fourfold multiplicity is small so the light absorption coefficients, ϵ, would be expected to be small as observed, namely, 0.02. The doubly forbidden transition ${}^6S$ to the state ${}^2T_{2g}$ derived from ${}^2I$ would be expected to give rise to an even smaller value of ϵ as is observed, namely, 0.002.

CAMBRIDGE, MASS.

[CONTRIBUTION NO. 1506 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Further Studies on the Catalytic Decomposition of Hydrogen Peroxide by Triethylenetetramine–Fe(III) Complex and Related Substances

BY RICHARD C. JARNAGIN[1] AND JUI H. WANG

RECEIVED JUNE 27, 1958

The rate-determining step in the catalytic decomposition of hydrogen peroxide by $(TETA)Fe(OH)_2^+$ was determined by studying the hydrogen isotope-effect on the reaction rate. A similar study was also made on the enzyme catalase. The complex tris-(2-aminoethyl)-amine–Fe(III) was synthesized and studied for its similar catalytic action. The inhibition of $(TETA)Fe(OH)_2^+$-catalysis by cyanide was quantitatively investigated and correlated with some magnetic susceptibility data.

Introduction

The catalytic decomposition of hydrogen peroxide by triethylenetetramine–Fe(III) complex, $(TETA)Fe(OH)_2^+$, was studied previously.[2] The mechanism of this catalysis may be represented by Fig. 1, in which the ferric ion is polarized in the strong ligand-field of the triethylenetetramine and forms octahedral complexes. In these complexes, four of the octahedral orbitals of Fe(III) are used to form coördination bonds with the tetramine, the two remaining adjacent orbitals may be used to combine with hydroxide ions or hydroperoxide ions or both. The hydroperoxide ion, OOH^-, is potentially capable of acting as a bidentate ligand and forming metal chelates such as compound III in Fig. 1. But as depicted in Fig. 1, the O–O bond in compound III is too short to allow the maximum overlap of the bonding orbitals of Fe(III) and those of the bidentate ligand. Consequently the O–O bond in compound III is under strain and rendered more reactive, because the energy consumed in breaking this O–O bond is partially compensated by the energy gained in forming the two stronger Fe–O bonds. Accordingly it was found[2] that $(TETA)Fe(OH)_2^+$ decomposes hydrogen peroxide with great efficiency; the measured activation energy was only 6.6 kcal./mole. The above mechanism is further supported by the observation that tetraethylenepentamine–Fe(III) complex is practically inert for the decomposition of hydrogen peroxide as compared to $(TETA)Fe(OH)_2^+$.

Kinetic measurements showed that the rate of oxygen liberation in the above catalysis is approximately proportional to the concentration of hydrogen peroxide up to $[H_2O_2] = 0.94\ M$. This shows that, at least in the concentration range studied,

---

(1) National Science Foundation Predoctoral Fellow, 1957–1958. This work was taken from the dissertation of R. C. Jarnagin submitted to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1958.

(2) J. H. Wang, THIS JOURNAL, **77**, 4715 (1955).

the transition from compound II to compound III cannot be the rate-determining step in the above catalytic cycle, for in that case a Michaelis–Menten type of saturation curve would have been observed. However, it was not possible to decide from the previous kinetic data whether the rate-determining step is the transition from compound I to compound II or from compound III back to compound I.

Recently, with the help of doubly O^{18}-labeled hydrogen peroxide as tracer, Jarnagin and Wang[3] showed that the two O-atoms in each O_2 molecule liberated in the above catalytic decomposition of hydrogen peroxide originate from the same H_2O_2 molecule. This means that the last step in the above catalytic cycle, whereby III goes back to I with the liberation of O_2, involves hydride ion or hydrogen-atom transfer instead of oxygen-atom transfer. This observation suggests an investigation of the hydrogen isotope effect on the rate of the present catalysis as a means for diagnosing the rate-determining step in the above cyclic mechanism.

Hydrogen Isotope Effect

Since the transition from compound I to compound II involves the displacement of a complete hydroxide ion by a hydroperoxide ion, its rate should not be drastically reduced if deuterium is used to replace ordinary water as the solvent. On the other hand since the transition from III to I was shown to involve hydride ion or hydrogen-atom transfer,[3] its rate may be pronouncedly affected if deuterium oxide is used to replace ordinary water as the solvent.

Preparation of Solutions.—Two TETA–Fe(III) catalyst solutions, one in ordinary water and one in deuterium oxide, and two corresponding TETA-blank solutions were prepared. The preparation and detailed composition of the catalyst solutions are given below. A conservative estimate indicated greater than 95% readily exchangeable deuterium in the deuterium oxide solutions.

	Catalyst soln. in ordinary water		Catalyst soln. in deuterium oxide (95%)
(a)	15 μl. 50% H_2SO_4 in H_2O	(a)	15 μl. 50% H_2SO_4 in 99.5% D_2O
(b)	100 μl. of 4.79 × 10^{-4}F $Fe_2(SO_4)_3$ in H_2O	(b)	100 μl. of 4.79 × 10^{-4}F $Fe_2(SO_4)_3$ in H_2O
(c)	3 ml. H_2O	(c)	3 ml. 99.5% D_2O
(d)	75 mg. TETA (Matheson)	(d)	75 mg. TETA (Matheson)
(e)	The mixture was diluted to 5.0 ml. with H_2O and adjusted to *p*H 10.0 with 50% H_2SO_4 and 50% NaOH in H_2O	(e)	The mixture was diluted to 5.0 ml. with 99.5% D_2O and adjusted to *p*H 10.0 with 50% H_2SO_4 and 50% NaOH in D_2O

The D_2O_2 solutions were prepared by diluting a maximum of 900 μl. of 30% H_2O_2 with 32.0 ml. of D_2O. The *p*H was adjusted to 10.0 with 50% NaOH in D_2O.

Rate Measurements.—The rate measurements were made by the usual manometric procedure but reduced in scale. One ml. of catalyst or blank solution was mixed with 10.0 ml. of peroxide solution in a Warburg-type apparatus of total volume of about 55 ml. The pressure readings were taken at 5 to 10 sec. intervals for a total period of about 2 or 3 minutes.

The data in Table I clearly show that the hydrogen isotope-effect on the rate of the present reaction is quite pronounced, corresponding to a factor of 2.2 in the rate constants. We may therefore conclude that the reaction of compound III in Fig. 1 with a second hydroperoxide ion to form compound I and O_2 is the rate-determining step in the whole catalytic cycle.

TABLE I

RELATIVE RATES OF DECOMPOSITION OF H_2O_2 AND D_2O_2 BY TETA–Fe(III) CHELATE

*p*H 10.0, temp. = 20°, [Fe(III)] = 1.94 × 10^{-6} *M*, [TETA] = 9.1 × 10^{-2} *M*, [H_2O_2] or [D_2O_2] = 0.168 *M*

Rate for $H_2O_2 + H_2O$ (arbitrary units)	Rate for $D_2O_2 + D_2O$ (arbitrary units)	$\frac{\text{Rate for } H_2O_2 + H_2O}{\text{Rate for } D_2O_2 + D_2O}$
10.1	4.40	2.3
10.2	4.73	2.2
10.2	5.38	1.9
10.5	4.56	2.3
	Av.	2.2 ± 0.17

The hydrogen isotope effect on the rate of decomposition of hydrogen peroxide by the ferric enzyme catalase also was studied. The procedure is outlined below, the results are summarized in Table II.

TABLE II

RELATIVE RATES OF DECOMPOSITION OF H_2O_2 AND D_2O_2 BY CATALASE AT 20° AND *p*H 7.0 ± 0.1

[H_2O_2] or [D_2O_2] (mole l.$^{-1}$)	Catalase soln.	Rate for H_2O_2 + H_2O (arbitrary units)	Rate for D_2O_2 + D_2O (arbitrary units)	$\frac{\text{Rate for } H_2O_2 + H_2O}{\text{Rate for } D_2O_2 + D_2O}$
0.185	A(1.4 × 10^{-2} μ*M*)	11.6	6.5	1.8
.184	A(1.4 × 10^{-2} μ*M*)	11.9	8.4	1.4
.18	A(1.4 × 10^{-2} μ*M*)	11.6	4.8	2.4
.092	A(1.4 × 10^{-2} μ*M*)	8.9	4.4	2.0
.091	B(1.1 × 10^{-2} μ*M*)	13.1	5.4	2.4
.089	B(1.1 × 10^{-2} μ*M*)	14.1	4.8	3.0
.045	B(1.1 × 10^{-2} μ*M*)	6.2	2.4	2.6
.045	B(1.1 × 10^{-2} μ*M*)	5.3	2.7	2.0
			50% D_2O and 50% H_2O)	
.089	B(1.1 × 10^{-2} μ*M*)	10.6	8.1	1.3

Experiments with Catalase.—Two catalase solutions were prepared from the crystalline enzyme obtained through Delta Chemical Works. Catalase solution A was prepared by dissolving 0.46 mg. of enzyme per ml. of cold phosphate buffer at *p*H 7.0. After standing in the cold for 36 hr., a filmy ppt. was thrown down. The ppt. was removed by centrifugation. Catalase solution B was prepared in a similar manner with 0.59 mg. of enzyme per ml. of phosphate buffer in 99.5% D_2O. The *p*H as measured with the glass electrode was 7.1 under conditions for which it should have been 7.0 in ordinary water. Both solutions were stored under refrigeration.

The procedure consisted of mixing 100 or 200 μl. of catalase solution with a peroxide solution made by adding 200 to 300 μl. of 30% H_2O_2 to 10.0 ml. of a phosphate buffer prepared in either ordinary water or 99.5% D_2O. The rate of oxygen liberation was followed manometrically as before.

The experimental uncertainty of the data in Table II is considerably larger than that in Table I. Nevertheless, it still seems rather certain that the hydrogen isotope effect on the rate of catalytic decomposition of hydrogen peroxide by catalase is also quite pronounced. The explanation of this observation, as the detailed mechanism of catalase action, is unknown.

Catalysis by Tris-(2-aminoethyl)-amine–Fe(III) Complex.—Tris-(2-aminoethyl)-amine, $(H_2NCH_2CH_2)_3N$, forms a chelate compound with ferric ion. This chelate, which may be abbreviated as (TAEA)-

---

(3) R. C. Jarnagin and J. H. Wang, THIS JOURNAL, **80**, 786 (1958).

$Fe(OH)_2^+$, has two readily exchangeable hydroxide ions attached to the ferric ion through two adjacent octahedral orbitals of the latter. Thus one may also expect $(TAEA)Fe(OH)_2^+$ to catalyze the decomposition of hydrogen peroxide through a cyclic mechanism similar to that depicted in Fig. 1 for $(TETA)Fe(OH)_2^+$. Molecular models indicate that on the average the four coördinating groups in TAEA do not fit the octahedral orbitals of the ferric ion as well as the corresponding groups in TETA do. This could result in a weaker ligand-field and consequently a lower catalytic efficiency for $(TAEA)Ge(OH)_2^+$.

Preparation of Tris-(2-aminoethyl)-amine.—This was prepared by a procedure similar to that of Ristenpart[4] by the ammonolysis of N-(2-bromoethyl)-phthalimide at 155 ± 10°, followed by the acid hydrolysis of the resulting triphthalimido compound. The glistening white needles of $(H_3NCH_2CH_2)NCl_3$ began to decompose at 300° without melting.

The picrate formed from the trihydrochloride melted at 228–300°.

Rate Measurements.—Measurement of the rate of the catalytic decomposition of hydrogen peroxide by TAEA–Fe(III) complex was carried out by two different methods with consistent results. In the first method, 2.0-ml. samples of the decomposing hydrogen peroxide solution were withdrawn at convenient time intervals, blown into 1.5 *F* H_2SO_4 solution in order to quench the reaction and titrated for unreacted hydrogen peroxide with standard ceric sulfate solution, using *o*-phenanthroline–Fe(II) as indicator.

In the second method, the catalytic decomposition of hydrogen peroxide was followed manometrically by means of a Warburg type of apparatus.

The temperature of the reaction mixture was never observed to vary more than 0.2° during the course of the reaction.

In order to correct for traces of Fe(III) present as impurity in the reaction system, a blank measurement with TAEA and hydrogen peroxide but without added Fe(III) was made for each temperature and hydrogen peroxide concentration studied. These blank rates were subtracted from the corresponding measured rates before the latter were used to compute the second-order rate constants.

The results of these measurements are summarized in Table III. The second-order rate constant *k* is defined by the relation $-d[H_2O_2]/dt = k[H_2O_2][\text{TAEA-Fe(III)complex}]$.

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE CATALYTIC DECOMPOSITION OF H_2O_2 BY TAEA–Fe(III) COMPLEX

*p*H 10.0, [TAEA] = 1.5×10^{-3} mole/l.: [Fe(III)] = 8.9×10^{-7} mole/l.

$[H_2O_2]$ (mole $l.^{-1}$)	Temp. (°C.)	$k \times 10^{-3}$ (l. $mole^{-1}$ $sec.^{-1}$)	
0.19	25	0.62	Av. 0.75 ± 0.12
.30	25	.69	
.41	25	.57	
.50	25	.81	
.75	25	.79	
.91	25	.85	
1.00	25	.92	
0.439	0.2	.17	
.446	5.0	.19	
.434	14.7	.38	
.436	25.0	.60	
.438	36.1	1.3	
.438	45.1	2.2	

Thus the catalytic decomposition rate was found to be proportional to the concentration of hydrogen peroxide. This behavior parallels that of $(TETA)Fe(OH)_2^+$ catalysis and shows that for a mechanism similar to that in Fig. 1, the second step cannot be the rate-determining one, at least up to 1.0 *M* H_2O_2, for in that case a saturation phenomenon should have been observed. The measured second-order rate constant at 25° for $(TAEA)Fe(OH)_2^+$ is only slightly less than the value $k = 1.2 \times 10^3$ l. $mole^{-1}$ sec. for $(TETA)Fe(OH)_2^+$. On the other hand, a plot of ln *k vs.* $1/T$ from the data in Table III yields an activation energy of 8.9 kcal. $mole^{-1}$ which is considerably higher than the value 6.6 kcal. $mole^{-1}$ for $(TETA)Fe(OH)_2^+$-catalysis.

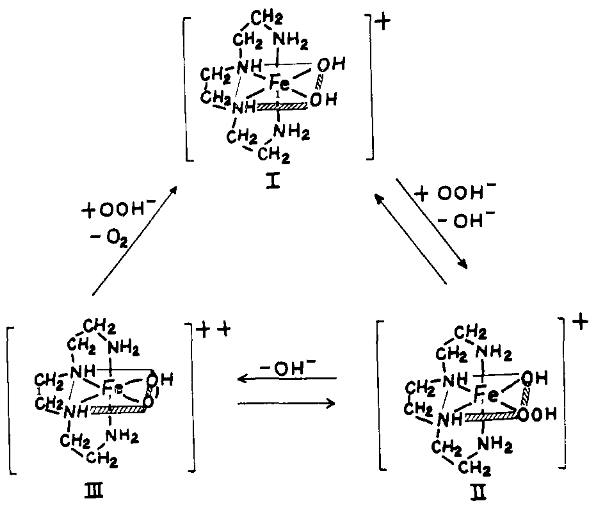

Fig. 1.—The detailed mechanism of the catalytic decomposition of hydrogen peroxide by $(TETA)Fe(OH)_2^+$.

Inhibition Studies

The possible inhibition of $(TETA)Fe(OH)_2^+$-catalysis by fluoride, azide and cyanide, respectively, was studied in this work, since these three ions were reported to inhibit catalase action.[5–7]

In a previous recent study,[2] it was reported that fluoride ion appears to activate $(TETA)Fe(OH)_2^+$ in its catalytic decomposition of hydrogen peroxide. A quantitative study on the effect of added fluoride was made in the present work. In order to get reproducible results, it was found necessary to mix the fluoride and $(TETA)Fe(OH)_2^+$ solutions first and allow a sufficient time (*ca.* 5 minutes) to elapse before adding the hydrogen peroxide.

The results are summarized in Table IV. The quantity "ratio of corrected rates" is defined as

$$\text{Ratio of cor. rates} = \frac{(\text{rate with catalyst} + F^-) - (\text{blank rate} + F^-)}{(\text{rate with catalyst}) - (\text{blank rate})}$$

These data show that there was no activation of $(TETA)Fe(OH)_2^+$-catalysis by fluoride. Indeed the data in Table IV do not rule out the possibility that fluoride may even have a small inhibitory effect. It also was found in these measurements that the blank rates with fluoride frequently were as large or larger than the rate with catalyst in the

---

(4) E. Ristenpart, *Ber.*, **29**, 2526 (1896).

(5) R. Lemberge and J. W. Legge, "Hematin Compounds and Bile Pigments," Interscience Publishers, Inc., New York, N. Y., 1949, p. 409.

(6) J. B. Sumner and K. Myrbäck, "The Enzymes," Vol. II, Part I, Academic Press, Inc., New York, N. Y., 1951, p. 422.

(7) B. Chance, *J. Biol. Chem.*, **179**, 1299 (1949).

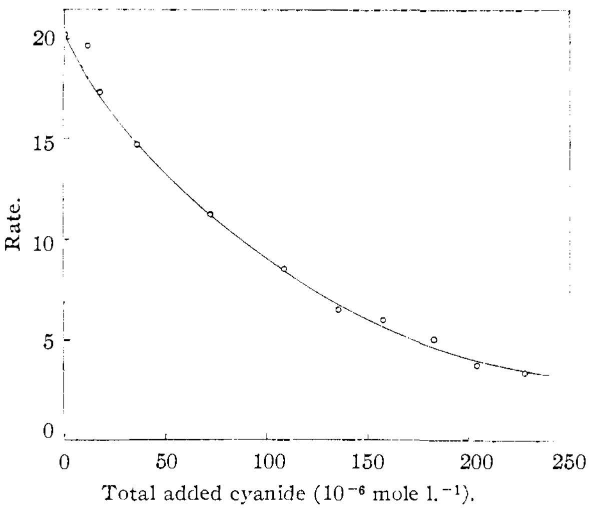

Fig. 2.—Inhibition of (TETA)Fe$(OH)_2^+$ by cyanide.

absence of fluoride. This suggests that the apparent activation observed previously[2] could be due to the failure to correct for the Fe(III) which might be present in the sodium fluoride as an impurity.

Similar studies were made on the effect of azide on (TETA)Fe$(OH)_2^+$-catalysis. It was found that in the range *p*H 8 to 10, the azide ion has no marked effect on the rate of this catalytic reaction.

TABLE IV

THE EFFECT OF FLUORIDE ON (TETA)Fe$(OH)_2^+$

Temp. = 20.0 ± 0.2°, *p*H 10.0 ± 0.2

$[F^-]$ (mole l.$^{-1}$)	[Fe(III)] × 10^7 (mole l.$^{-1}$)	[TETA] × 10^3 (mole l.$^{-1}$)	$[H_2O_2]$ (mole l.$^{-1}$)	Ratio of cor. rates
0.41	7.3	1.8	0.18	0.6
.41	7.3	1.8	.18	.8
.38	13.1	3.4	.33	.6
.40	7.3	2.0	.27	1.0
.25	7.3	2.0	.27	0.9
.082	7.3	2.0	.27	0.9

On the other hand, cyanide ion was shown, as reported previously, to be a very strong inhibitor for (TETA)Fe$(OH)_2^+$. The data of the present cyanide-inhibition studies are summarized in Table V.

TABLE V

INHIBITION OF (TETA)Fe$(OH)_2^+$ BY CYANIDE

Temp. = 25.0 ± 0.2°, *p*H 9.0 ± 0.1, [Fe(III)] = 4.4 × 10^{-6} *M*, [TETA] = 9.1 × 10^{-3} *M*, $[H_2O_2]$ = 0.200 ± 0.005 *M*

Total amt. of KCN added × 10^5 (for. wt./l.)	Reaction rate (in arbitrary units, cor. for blank)	Total amt. of KCN added × 10^5 (for. wt./l.)	Reaction rate (in arbitrary units, cor. for blank)
0	20.3 ± 0.6	13.6	6.52
1.09	19.6	15.8	6.04
1.82	17.3	18.2	5.02
3.63	14.7	20.4	3.84
7.28	11.3	22.7	3.36
10.9	8.54		

The data in Table V may be interpreted in the following way

Let [E] = concn. of all active species in the catalyst
[I] = concn. of free cyanide ion
[EI] = concn. of the monocyanide complex
$[EI_2]$ = concn. of the dicyanide complex.

We may also define the apparent formation constants K'_1 and K_2' as

$$K_1' = \frac{[EI]}{[E][I]} \qquad K_2' = \frac{[EI_2]}{[EI][I]}$$

These are not the true equilibrium constants, since [E] represents the total concentration of all the active species of the catalyst, *e.g.*, (TETA)Fe$(OH)_2^+$, (TETA)Fe(OH)(OOH)$^+$, etc.

If we assume that both EI and EI_2 are catalytically inactive, then the ratio of the inhibited rate R to the uninhibited rate R_0 is given by

$$\frac{R}{R_0} = \frac{1}{1 + K_1'[I] + K_1'K_2'[I]^2}$$

The apparent formation constants, K' and K_2', were evaluated from the experimental values of R/R_0 by computing [I] for each of the inhibition measurements and graphically solving the resulting set of equations. In these computations we used Latimer's value of 4 × 10^{-10} for the ionization constant of hydrocyanic acid.[8] For the present data, K_1' and K_2' were found to be 3.6 × 10^4 and 2.5 × 10^4 l. mole^{-1}, respectively.

The measured rates R in Table V are plotted *vs.* total cyanide concentration in Fig. 2. The curve represents the values computed from the above equation with these experimental values of K_1' and K_2', *i.e.*, $R = R_0/(1 + 3.6 \times 10^4[I] + 9 \times 10^8 [I]^2)$.

The satisfactory representation of the observed rates with the computed curve in Fig. 2 supports our assumption that both EI and EI_2 are inactive. It is known that the hydroxy, aquo and halogen complexes of Fe(III) exchange their ligands rapidly whereas the cyanide complexes do not.[9] It is possible that the substitution of one of the mobile ligands by a single cyanide ion may produce a strong enough ligand-field to slow down the rapid exchange by hydroperoxide ions and hence upset the catalytic cycle.

In as much as a strong ligand-field often leads to low-spin complexes,[10] it seemed advisable to study the effect of added cyanide on the magnetic property of the present catalyst.

Magnetic Measurements

The molar paramagnetic susceptibilities of the TETA-Fe(III) complexes were determined by means of a conventional Gouy apparatus with a compensation tube. The inhomogeneous magnetic field was provided by a Varian 4-inch (V-4004) Electromagnet with 2-inch tapered pole caps. The maximum field strength in the $^5/_8$ inch air gap was between 18 and 20 kilogauss. The vessel temperature was held at 15 ± 1°. The calibration and checking of the apparatus, the magnetic determinations and the computation of experimental data were carried out by standard procedures. The results are summarized in Tables VI and VII. In these tables, ΔW represents the difference in weights of the sample in the presence and absence of the magnetic field, respectively. Because of the insta-

---

(8) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 137.

(9) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

(10) J. S. Griffith and L. E. Orgel, *Quart. Rev.*, **II**, No. 4, 388 (1958).

TABLE VI

DETERMINATION OF THE MAGNETIC MOMENT OF Fe(III) IN $(TETA)Fe(OH)_2^+$

[TETA] = 1.0 *M*, temp. = 15°

[Fe(III)] × 10^3 (mole l.$^{-1}$)	*p*H	ΔW (mg.)	Molar paramagnetic susceptibility × 10^6	Magnetic moment (Bohr magnetons)
1.02	8.6	0.289 ± 0.028	11800	5.3
1.02	9.6	.318 ± .022	12600	5.4
2.04	8.6	.576 ± .021	11900	5.3
2.04	9.6	.712 ± .019	14500	5.8
			Av.	5.4 B.M.

TABLE VII

MAGNETIC TITRATION OF $(TETA)Fe(OH)_2^+$ BY CYANIDE

[TETA] = 1.0 *M*, [Fe(III)] = 2.04 × 10^{-3} *M*, *p*H 9.0 ± 0.1

Total added KCN × 10^3 (for. wt./l.)	ΔW (mg.)	Total added KCN × 10^3 (for. wt./l.)	ΔW (mg.)
None	0.713	5.50	0.328
2.00	.549	6.00	.257
2.52	.513	6.52	.215
3.00	.497	7.02	.150
3.51	.479	7.54	.112
4.00	.328	8.00	.143
4.52	.412	10.0	.120
4.98	.294	11.0	.111
5.02	.288	12.0	.128
5.26	.465		

bility of these rather concentrated catalyst solutions, the accuracy of these magnetic data is much lower than the inherent accuracy of the apparatus.

The data in Table VI show that $(TETA)Fe(OH)_2^+$ is in high-spin state, because the measured moment of 5.4 B.M. compares favorably with the calculated moment of 5.92 B.M. for five unpaired electrons per Fe(III) without orbital contribution.

The data in Table VII show that the molar paramagnetic susceptibility of the catalyst decreases as cyanide is added to the solution. In principle, one could plot the values of *W* in Table VII *vs.* total added KCN and determine formation constants of the mono- and dicyanide complexes from the resulting curve by the same procedure which we used to treat the rate data in Table V. Unfortunately the data in Table VII are not suitable for such treatment because of the large experimental uncertainties. However, since the observed molar susceptibility of the catalyst continued to decrease as more KCN was added to the solution, we may still conclude the compound $(TETA)Fe(CN)_2^+$ to be a low-spin complex.

Acknowledgment.—This work was supported in part by a grant (USPHS-RG-4483) from the Division of Research Grants, U. S. Public Health Service.

NEW HAVEN, CONN.

[CONTRIBUTION FROM CALIFORNIA RESEARCH CORPORATION]

Kinetics of the Oxidation of *m*-Toluic Acid to Isophthalic Acid by Aqueous Sulfur Solutions[1]

BY WILLIAM A. PRYOR

RECEIVED JULY 14, 1958

The kinetics of the oxidation of *m*-toluic acid to isophthalic acid are reported at 230–290° for three aqueous oxidizing systems: sodium polysulfide, ammonium polysulfide and sodium hydroxide plus sulfur. *m*-Toluic acid is always present in limited concentration, and under these conditions the reaction is pseudo-unimolecular with first-order dependence on the concentration of *m*-toluate ion. The reaction is quantitative, and the rate of appearance of product equals the rate of disappearance of *m*-toluate ion. There is no induction period. Rate dependence on the true concentration of any one sulfur species is difficult to measure since most sulfur anions are interconvertible through disproportionation reactions at these temperatures. However, data are consistent with a mechanism in which a polysulfide radical abstracts a benzyl hydrogen atom in the slow step. Possible analogies to vulcanization and to the Willgerodt reaction are discussed.

Introduction

Oxidation of organic materials by sulfur has been known for many years. In vulcanization, a reaction nearly 120 years old, rubber is oxidized by sulfur. Another classical example is the reaction Willgerodt discovered in 1887, in which acetophenone is converted to a mixture of phenylacetamide and ammonium phenylacetate by ammonium polysulfide.[2a] Willgerodt also found sodium polysulfide oxidized acetophenone to sodium phenylacetate, although in very poor yield.[2b] A considerable amount of work has shown a rearrangement is not involved in the Willgerodt reaction.[3]

This reaction, or a modification of it using morpholine as base, has been applied to oxidize compounds containing virtually every possible functional group α to a benzene ring.[2] However, early attempts to extend the reaction to the oxidation of aryl methyl groups failed.[2a]

Recently it has been shown that at higher temperatures, aryl methyl groups can be oxidized and

---

(1) Presented at the Symposium on Recent Developments in Chemicals from Petroleum, 133d Meeting of the American Chemical Society, Division of Petroleum Chemistry, San Francisco, California, April, 1958. Research supported by Oronite Chemical Company.

(2) (a) For review and references to early work see: M. Carmack, M. A. Spielman, R. Adams, Ed., "Organic Reactions," Vol. III, John Wiley and Sons, New York, N. Y., 1946, p. 83; (b) C. Willgerodt and F. H. Merk, *J. prakt. Chem.*, [2] **80**, 192 (1909); (c) M. Carmack and D. F. DeTar, THIS JOURNAL, **68**, 2029 (1946); (d) R. T. Gerry and E. V. Brown, *ibid.*, **75**, 740 (1953); (e) J. A. King and F. H. McMillan, *ibid.*, **68**, 1369 (1946); (f) F. H. McMillan and J. A. King, *ibid.*, **70**, 4143 (1948); (g) W. G. Dauben and J. B. Rogan, *ibid.*, **78**, 4135 (1956); (h) P. A. Barrett, *J. Chem. Soc.*, 2056 (1957).

(3) W. G. Dauben, J. C. Reid, P. E. Yankwich and M. Calvin, THIS JOURNAL, **72**, 121 (1950); E. V. Brown, E. Cerwonka and R. C. Anderson, *ibid.*, **73**, 3735 (1951); J. A. King and F. H. McMillan, *ibid.*, **68**, 633 (1946).