which may be transformed to

$$\log(\%\ ortho - 1.5) = -\frac{\beta}{2.303}t + \log 98.5$$

A plot of log (% *ortho* − 1.5) against *t* should therefore yield a straight line. The fact that in Fig. 2 it does not, demonstrates the presence of a time dependent concentration or activity other than that of the cymenes in the absolute rate expressions.

The fact that there is no extremely rapid initial rate in exp. 4 is most likely due to the mesitylene present, since mesitylene was absent in the other two experiments. This hypothesis suggests that the dramatic deviation from linearity in expt. 1 and 2 was due to the formation of some strongly basic side-product.

Experimental

The experimental procedures may be illustrated by the procedure for exp. 4.

To a 2-l., 3-necked creased flask, equipped with a gas inlet tube, thermometer, stirrer and a water trap connected to the flask through a $CaCl_2$ drying tube, was added 869.4 g. (9.45 moles) of toluene, 12.6 g. (0.105 mole) of mesitylene and 14 g. (0.105 mole) of $AlCl_3$. Through the stirred reactants HCl was passed for five minutes while they were being cooled to 0°. To this solution at 0° was added 140.7 g. (1.05 moles) of *o*-cymene. At specific times, 50-ml. portions of the reaction mixture were withdrawn, quenched, washed and dried. The toluene was distilled off of each sample in a Piros-Glover spinning band micro still. The residue then was analyzed by infrared spectroscopy. The results given in Table I are normalized for the cymenes.

Experiments 5, 6 and 7 were carried out on a one-tenth scale in a 200-ml. beaker. To quench the reaction, water was added directly to the stirred reaction mixture.

The aluminum chloride was Baker and Adams powdered anhydrous reagent grade.

Acknowledgments.—The authors are indebted to D. S. Erley and H. J. Sloane of the Dow Spectroscopy Department for the infrared data.

MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Rate and Equilibrium in First Complex Formation between Thenoyltrifluoroacetone (TTA) and Aqueous Metal Ions

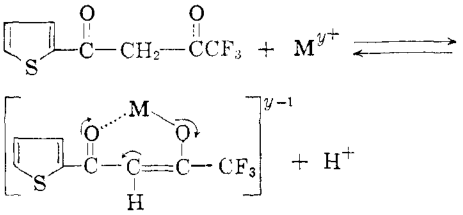
BY ROBERT W. TAFT, JR., AND E. H. COOK[1]

RECEIVED AUGUST 1, 1958

A kinetic study has been made of the reaction of a series of aqueous metal ions with TTA. Under the reaction conditions the rate-determining step for the formation of the first (one-one) complex with Sc^{III}, Cu^{II}, Zn^{II} and Mg^{II} is the rate of enolization of TTA. With Fe^{III} the kinetics are consistent with the rate-determining reaction of the metal ion with the enolate ion. The rate constants for the reaction of Cu^{+2} and Sc^{+3} ions with the enolate ion exceed 10^6 l. mole^{-1}-min.$^{-1}$, while those Fe^{+3}, Be^{+2}, Al^{+3} and Cr^{+3} are less than this figure. These results indicate qualitatively that the free energy of activation in first complex formation increases with increasing Born charging energy of the central ion. However, the equilibrium constants for the first complex formation show, in addition, a dependence on the availability of open *d* orbitals. The results are taken as an indication that the interaction between the central ion and its immediate shell of water molecules parallels that expected of ion-dipole interaction.

Although equilibrium studies of the formation of coördination complexes of metal ions with organic ligands (*i.e.*, displacements in the aquo complexes of metal ions) have been systematically investigated,[2] few kinetic studies of these systems have been made. The latter are of interest from the standpoint of the mechanism of chelate formation. Further, the comparison of rate and equilibrium of this reaction offers insight into the nature of the interaction between water molecules and polyvalent ions in aqueous solution.

In this paper are reported results of studies by spectrophotometric means of the kinetics of first (one-one) complex formation for a series of aqueous metal ions with a common β-diketone, thenoyltrifluoroacetone (TTA), in dilute nitric acid solution. TTA was selected as the common ligand in this work because of its importance in solvent extractions of metal ions[3] and the convenient absorption maximum (approx. 350 mμ) exhibited by the first complexes. The aquo complexes of Sc^{III}, Fe^{III}, Al^{III}, Cr^{III}, Cu^{II}, Zn^{II}, Mg^{II} and Be^{II} have been investigated. The results provide evidence that studies of this kind may be used to determine the rates of the very fast reactions ($k \cong 10^7$ l. mole^{-1} min.$^{-1}$) between enolate and aqueous metal ions. The method is the same in principle as that used by Bell and students[3e] to determine the rate constants for the reaction of enolate ions with halogens.



Procedure and Results

(1) **Ionization of Aqueous TTA.**—This β-diketone exists in acidified aqueous solution largely as the hydrate[4]

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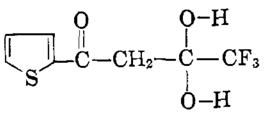
[1] Taken from the Ph.D. Thesis of E. H. Cook, Pennsylvania State University, June, 1953.

[2] (a) *Cf.* A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1952, Chap. 3; (b) L. G. Van Uitert and C. G. Haas, THIS JOURNAL, **75**, 451 (1953); (c) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 457, 2736 (1953); (d) L. G. Van Uitert and W. C. Fernelius, *ibid.*, **75**, 3862 (1953); **76**, 375 (1954).

[3] (a) E. H. Huffman and L. J. Beaufait, *ibid.*, **71**, 3179 (1949); (b) R. A. Bolomey and L. Wish, *ibid.*, **72**, 4483 (1950); (c) E. M. Larsen and G. Terry, *ibid.*, **75**, 1560 (1953); (d) R. A. James and W. P. Byran, *ibid.*, **76**, 1982 (1954); (e) R. P. Bell and P. Engel, *J. Chem. Soc.*, 247 (1957), and earlier references cited there.

[4] (a) E. Zebroski, A. E. C. Report BC-63 (1947); Ph.D. Thesis, University of California; (b) E. L. King and W. H. Reas, THIS JOURNAL, **73**, 1806 (1951); (c) E. H. Cook and R. W. Taft, Jr., *ibid.*, **74**, 6103 (1952).



The apparent pK_a cannot be determined by titration with strong base because of interfering cleavage of the hydrate to acetylthiophene and trifluoroacetate ion.[4a,c] An unambiguous apparent pK_a has been obtained by the titration of TTA enolate ion solution with a strong acid. The value obtained is 6.4 at 25°.[4c]

The rate of ionization of aqueous TTA has been studied by Reid and Calvin[5] using a bromine titration method. Their method gives results pertaining to a solution very dilute in ethanol. Reid and Calvin obtained first-order rates which are independent of the acid concentration in the approximate region *p*H 1 to 4. The need for the ionization rate in completely aqueous solution for purposes of the present work prompted us to redetermine the rate under these conditions. A spectrophotometric procedure was employed to analyze for the rate of consumption of bromine.

To determine the rate of ionization $k_{-\mathrm{H}}$ by a decrease in optical density of the bromine solution, the following expression was developed

a = initial concn. of ketone
K = concn. of diketone at time t
b = initial concn. of bromine
x = amount of Br_2 and diketone reacted at time t
D = optical density at time t due to absorption by bromine at 400 mμ
ϵ_{Br} = molar extinction coefficient at 400 mμ

$$x = a - (K) \tag{1}$$

$$(b - x) = (\mathrm{Br}_2) \tag{2}$$

$$(\mathrm{Br}_2) = (b - a + (K)) = \frac{D}{\epsilon_{\mathrm{Br}}} \tag{3}$$

$$(K) = \frac{D}{\epsilon_{\mathrm{Br}}} + a - b \tag{4}$$

Since the rate equation[5] is

$$\frac{-\mathrm{d}(K)}{\mathrm{d}t} = k_{-\mathrm{H}}\,(K) \tag{5}$$

then

$$\ln\,(K) = k_{-\mathrm{H}}\ t + c \tag{6}$$

or

$$\ln\left(\frac{D}{\epsilon_{\mathrm{Br}}} + a - b\right) = K_{-\mathrm{H}}\ t + c \tag{7}$$

Plots of log $(D/\epsilon_{\mathrm{Br}} + a - b)$ *vs.* time give linear results (Fig. 1 is a typical example). It was also determined that one equivalent of TTA absorbs one equivalent of bromine. An average value of $k_{-\mathrm{H}}$ = 0.59 min.$^{-1}$ was obtained from the rate of bromination at 25.0°.

Extrapolation to zero time of the plot of log $(D/\epsilon_{\mathrm{Br}} + a - b)$ *versus* time, indicates that approximately 2% of the TTA brominated instantly, thus giving a measure of the enol content of aqueous TTA. The present results are in close agreement with those of Reid and Calvin who obtained $k_{-\mathrm{H}}$ = 0.61 min.$^{-1}$ and 1.5% for the enol content.[5]

(2) **First Complex Formation.**—Complex formation takes place in a series of reversible steps,[6] *e.g.*

$$M^{\nu+} + HA \rightleftharpoons MA^{(\nu-1)+} + H^+$$

$$M^{(\nu-1)+} + HA \rightleftharpoons MA_2^{(\nu-2)+} + H^+, \text{ etc.}$$

so that higher complexes are favored by high *p*H. Previous work has indicated that the formation constants for the first complex (the product of the first step) of β-diketones generally exceed those for the second complex (the product of the second step) by factors of about ten.[7] It is thus possible to regulate the point of equilibrium so as to stop the reaction at the first step, at least to a reasonable approximation.

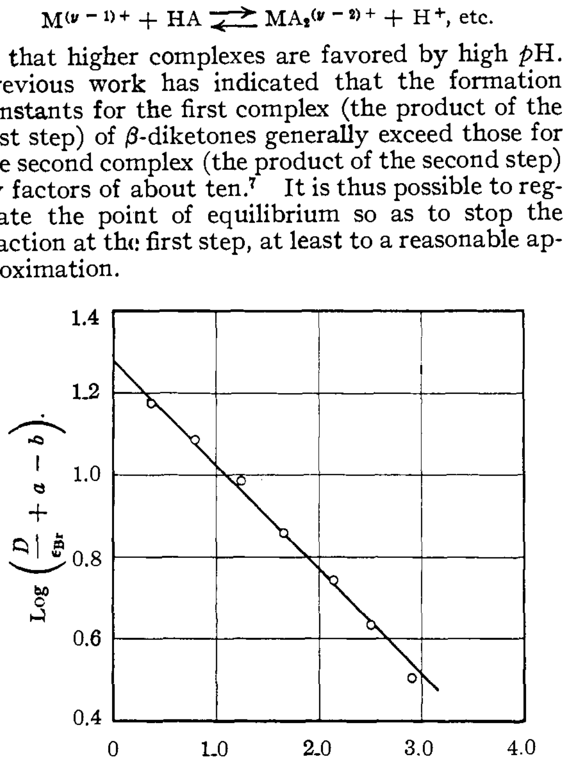


Fig. 1.—Bromination of TTA in aqueous solution at 25°. Typical plot of log $\left[\frac{D}{\epsilon_{\mathrm{Br}}} + a - b\right]$ *vs.* time. Initial TTA concentration 2.00 × 10^{-3} *M* and initial bromine concentration 5.34 × 10^{-3} *M*.

In the present work, the *p*H was kept low and other concentrations were adjusted so that usually only 5 to 30% of the TTA or the metal ion, whichever was present in the smaller amount, was converted to first complex. The rate of formation of first complexes has been found to be appreciably faster than that for the higher complexes, a further factor permitting the study of only the first step.

Sc^{III}, Cu^{II}, Mg^{II}, Zn^{II}.—With these metal ions the first complex with TTA has an absorption maximum in the region around 350 mμ. Experiments were carried out in the 1-cm. absorption cells. The aqueous TTA solutions were rapidly injected into the metal ion solutions using a hypodermic syringe. In each experiment the acid and metal ions were in sufficient excess so that their concentrations remained constant. The ratio of the metal ion to acid concentration was varied by factors of five to one hundred in separate experiments. In each experiment plots of log $(D_e - D)$ were linear with respect to time (D = optical density at time, t; D_e = equilibrium optical density) over the range of reaction studied (generally 70% of the total change in optical density). Increasing the acid concentration in a given experiment increases the slope of the plot, whereas increasing the metal ion concentration decreases the slope. The intercepts of the log (D_e

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[5] J. C. Reid and M. Calvin, THIS JOURNAL, **72**, 2948 (1950).

[6] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[7] W. C. Fernelius, B. E. Bryant and L. G. Van Uitert, unpublished compilation of formation constants.

$-\ D)$ *vs.* time plots fall below the intercepts expected on the basis of no reaction at zero time. Several typical plots are shown in Fig. 2.

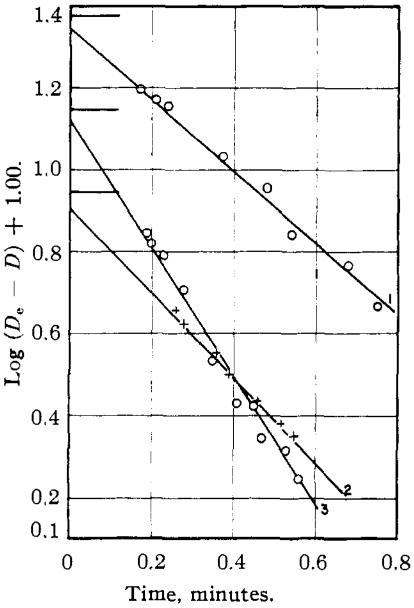

Fig. 2.—Rate of first complex formation for scandium(III) and copper(II) with TTA. Typical plots of log ($D_e - D$) *vs.* time at 25°: (1) 2.00 × 10^{-2} *M* Cu^{II}, 1.00 × 10^{-2} *M* HNO_3, initial TTA, 5.0 × 10^{-4} *M;* (2) 2.80 × 10^{-3} *M* Sc^{III}, 1.00 × 10^{-2} *M* HNO_3, initial TTA, 5.0 × 10^{-4} *M;* (3) 2.26 × 10^{-3} *M* Sc^{III}, 1.00 × 10^{-2} *M* HNO_3, initial TTA, 5.0 × 10^{-4} *M.*

Fe^{III}.—In the work with Fe^{III}, the TTA and acid concentrations were held constant in a given experiment. Rates were observed by the increase in optical density at 520 mμ accompanying complex formation. Contrary to the previous cases, the slope of the linear plots of log $(D_e - D)/D_e$ *vs.* time are virtually independent of the hydrogen ion concentration. The results are summarized in Table I.

TABLE I

SUMMARY OF RESULTS FOR KINETICS OF FIRST COMPLEX FORMATION OF Fe^{III} WITH TTA

Initial $(Fe^{3+}) \times 10^4$	(HNO_3)	$10^3 \times$ (TTA) range	Slope, min.$^{-1}$
	Results at 24.86°		
4.09	0.100	3.0 to 7.0	0.153 ± 0.007
4.09	.200	7.0 to 13.0	.158 ± .006
	Results at 15.70°		
4.09	0.100	6.0	0.054
	Results at 34.51°		
4.09	0.100	6.0	0.390

Al^{III}.—Experiments were carried out so that the metal ion and acid concentrations remained constant. The Al^{III} chelate has a maximum absorption near 350 mμ. A typical half-life of the first complex formation under the conditions employed was 100 min. This is appreciably slower than that for the other chelations. Increasing both the acid and the metal ion concentrations increases the slope of the linear plots of log ($D_e - D$) *vs.* time. Figure 3 illustrates some typical plots.

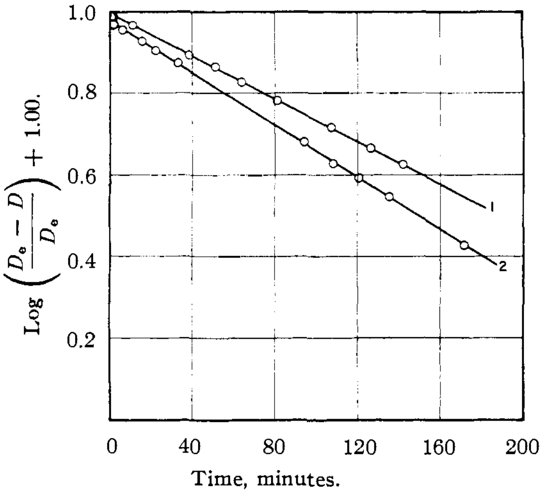

Fig. 3.—Rates of first complex formation for aluminum(III) with TTA at 25°: typical plots of log $\left[\frac{(D_e - D)}{D_e}\right]$ *vs.* time: (1) 1.35 × 10^{-2} *M* Al^{III}, 0.100 *M* HNO_3, initial TTA, 5.0 × 10^{-4} *M;* (2) 4.00 × 10^{-2} *M* Al^{III}, 0.100 *M* HNO_3, initial TTA, 5.0 × 10^{-4} *M.*

Cr^{III} and Be^{II}.—Only qualitative observations were made with these ions. Cr^{III} ion reacted so slowly with TTA that a satisfactory equilibrium value for optical density could not be obtained. Under equivalent conditions the rate of first complex formation with Cr^{III} ion must be at least an order of magnitude slower than with Al^{III}. The qualitative results with Be^{II} indicate that the rate-determining step also involves the metal ion.

Interpretation of Kinetics

Sc^{III}, Cu^{II}, Mg^{II} and Zn^{II}.—The lower-than-theoretical intercepts obtained in the first-order plots indicate that the Sc^{III}, Cu^{II}, Mg^{II} and Zn^{II} aquo complexes react instantaneously with the enol form of TTA. The following two-step sequence is thus suggested for the formation of the first complex of these metal ions, with step (a) rate determining.

(a) Ionization of the β-diketone:

$$HA \underset{k_{+H}}{\overset{k_{-H}}{\rightleftharpoons}} H^+ + A^- \tag{8}$$

(b) Complexing of the enolate ion:

$$M^{y+} + A^- \underset{k_{-M}}{\overset{k_{+M}}{\rightleftharpoons}} MA^{(y-1)+} \tag{9}$$

In terms of this sequence, the over-all equilibrium is given by

$$K_{eq} = \frac{(MA^{(y-1)+})(H^+)}{(M^{y+})\ (HA)} = K_aK_f = \frac{k_{-H}\ k_{+M}}{k_{+H}\ k_{-M}} \tag{10}$$

From the earlier work (*cf.* section on bromination of TTA) we have $K_a = 4.2 \times 10^{-7}$; $k_{-H} = 0.59$ min.$^{-1}$; $k_{+H} = 1.43 \times 10^6$ l. mole^{-1} min.$^{-1}$. Applying the steady state approximation to the enolate ion, the following equations may be derived for the conditions that $k_{+M}(M^{y+}) > k_{+H}(H^+)$

$$\frac{d(A^-)}{dt} = 0 = k_{-H}\ (a - x) - k_{+H}\ (H^+)(A^-) - k_{+M}\ (A^-)(M^{y+}) + k_{-M}(x) \tag{11}$$

where a = initial TTA concentration and x = 1st-complex concentration at time, t

$$\therefore (\mathrm{A}^-)[k_{+\mathrm{M}}\ (\mathrm{M}^{y+}) + k_{+\mathrm{H}}\ (\mathrm{H}^+)] = k_{-\mathrm{H}}\ (a - x) + k_{-\mathrm{M}}(x) \qquad (12)$$

but

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{+\mathrm{M}}\ (\mathrm{A}^-)\ (\mathrm{M}^{y+}) - k_{-\mathrm{M}}\ (x) \qquad (13)$$

Substituting (12) in (13) and collecting terms

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_{+\mathrm{M}}\ (\mathrm{M}^{y+})k_{-\mathrm{H}}\ (a - x) - k_{+\mathrm{H}}\ k_{-\mathrm{M}}\ (x)(\mathrm{H}^+)}{k_{+\mathrm{M}}\ (\mathrm{M}^{y+}) + k_{+\mathrm{H}}\ (\mathrm{H}^+)} \qquad (14)$$

but if $k_{+\mathrm{M}}(M^y) > k_{+\mathrm{H}}\ (\mathrm{H}^+)$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{-\mathrm{H}}\ (a - x_e) - \frac{k_{+\mathrm{H}}\,k_{-\mathrm{M}}\ (\mathrm{H}^+)\ (x_e)}{k_{+\mathrm{M}}\ (\mathrm{M}^{y+})} \qquad (15)$$

therefore at equilibrium

$$\frac{\mathrm{d}x}{\mathrm{d}t} = 0 = k_{-\mathrm{H}}\ (a - x_e) - \frac{k_{+\mathrm{H}}\,k_{-\mathrm{M}}\ (\mathrm{H}^+)\ x_e}{k_{+\mathrm{M}}\ (\mathrm{M}^{y+})}$$

and

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{-\mathrm{H}}\ (x_e - x) + \frac{k_{+\mathrm{H}}\,k_{-\mathrm{M}}\ (\mathrm{H}^+)(x_e - x)}{k_{+\mathrm{M}}\ (\mathrm{M}^{y+})} \qquad (16)$$

therefore

$$\mathrm{d}\ \ln\left(\frac{x_e}{x_e - x}\right)/\mathrm{d}t = \text{slope} = k_{-\mathrm{H}} + \frac{k_{+\mathrm{H}}\,k_{-\mathrm{M}}\ (\mathrm{H}^+)}{k_{+\mathrm{M}}\ (\mathrm{M}^{y+})} \qquad (17)$$

substituting (10) in (17)

$$\text{slope} = k_{-\mathrm{H}}\left[1 + \frac{(\mathrm{HA})_e}{(\mathrm{MA}^{(y-1)})_e}\right] \qquad (18)$$

i.e., $k_{-\mathrm{H}}$ = slope × fraction of HA converted to first complex or

$$k_{-\mathrm{H}} = \text{slope}\left(\frac{D_e}{\epsilon a}\right) \qquad (19)$$

$$1/\text{slope} = \frac{D_e}{(a)\ (k_{-\mathrm{H}})(\epsilon)}$$

For first complex formation with $\mathrm{Sc^{III}}$ ion, eq. 18 and 19 have been confirmed in the following manner. In a series of experiments with a given initial TTA concentration, the ratio of metal-ion to hydrogen-ion concentration was increased from about 0.1 to 10. The equilibrium optical density increased regularly with this ratio and approached a limiting value for ratios of about 10. The latter result indicates that nearly complete conversion to first complex has been achieved. Under these conditions the average value of the slope of the log $(D_e - D)$ *vs.* time plots is 0.56 ± 0.02 min.$^{-1}$, which, in accord with eq. 18 for complete conversion to first complex, is the rate of ionization of TTA (see first section). No attempt has been made here or later to consider the effect of varying ionic strength on rates because the values obtained are not highly precise. There is, indeed, no indication that the effect of the ionic strength for the range used exceeds the experimental error of the rate measurement.

Further confirmation of the indicated kinetics is obtained using the limiting value of equilibrium optical density to obtain the molar extinction coefficient for the first complex (average value ϵ = 16,200). With this value it is found that the rate data for experiments with incomplete conversion follow equation 19—see Table II. From the difference in the theoretical and experimental intercepts of plots (see Fig. 2) and the extinction coefficient obtained above, the equilibrium per cent. of enol in aqueous TTA has been calculated. The results (illustrated in Table IV) are in very reasonable accord with those obtained in bromination experiments.

TABLE II

IONIZATION RATE $k_{-\mathrm{H}}$ FROM RATE OF FORMATION OF FIRST $\mathrm{Sc^{III}}$ COMPLEX, 25.0°

$(\mathrm{Sc^{III}})$ 10^3	$(\mathrm{HNO_3})$ 10^4	Initial (TTA) 10^4	D_e	Slope, min.$^{-1}$	$(x_e)10^5$	$k_{-\mathrm{H}}$, (calcd.) eq. 19, min.$^{-1}$
2.26	100	5.0	1.40	3.82	8.91	0.66
2.26	200	5.0	0.710	7.79	4.52	.68
2.80	200	5.0	0.890	5.50	5.66	.60
2.80	100	5.0	1.76	2.42	12.2	.52
1.81	5.0	1.0	1.52	0.60	9.3	.56
1.81	5.0	1.0	1.52	.61	9.3	.57
1.81	5.0	1.0	1.51	.63	9.3	.59
3.50	5.0	1.0	1.60	.57	9.8	.56
4.96	5.0	1.0	1.63	.56	10.0	.56
4.96	5.0	1.0	1.65	.55	10.0	.55

The low formation constants of $\mathrm{Cu^{II}}$, $\mathrm{Mg^{II}}$ and $\mathrm{Zn^{II}}$ prevent complete conversion to first complex at desirable ratios of hydrogen-ion to metal-ion concentration. Equation 19 was tested for these metal ions by solving for the molar extinction coefficient ϵ using the observed rate data (slopes) and the rate of ionization $k_{-\mathrm{H}}$ of TTA. The rate equation is confirmed by the fact that the values of ϵ calculated are constant within the precision of the measurements, *cf.* Table III. The extinction coefficients also lead to values for enol content (see Table IV) concordant with the bromination results.

TABLE III

MOLAR EXTINCTION COEFFICIENTS FROM RATES OF FIRST COMPLEX FORMATION BY EQ. 19

Copper initial TTA × 10^4	D_e	Slope, min.$^{-1}$		Molar (calcd.) eq. 19
5.0	0.860	4.65		13,300
5.0	1.50	2.97		14,800
5.0	1.55	3.52		18,200
5.0	2.45	1.85		15,100
5.0	1.50	3.14		15,700
5.0	2.36	2.12		16,700
5.0	1.36	4.11		18,500
5.0	0.740	5.94		14,600
5.0	2.36	2.06		16,200
5.0	1.25	3.44		14,400
5.0	3.16	1.38		14,500
5.0	3.70	1.20		14,800
			Av.	14,800 ± 1100
Magnesium$^{\mathrm{II}}$				
5.0	0.790	5.96		15,700
5.0	.380	12.89		16,200
5.0	.530	7.54		13,300
5.0	.900	4.45		13,400
			Av.	14,600 ± 1300
Zinc$^{\mathrm{II}}$				
5.0	2.36	3.36		26,400
5.0	1.40	5.09		23,800
5.0	1.13	5.59		21,000
			Av.	23,700 ± 1800

Minimum values for $k_{+\mathrm{M}}$ may be estimated from the present data. In order that the observed kinetics be followed, it is necessary that the term $(k_{+\mathrm{M}})$

TABLE IV

ENOL CONTENT FROM INTERCEPT DIFFERENCES

Metal ion	ΔD_i	Initial (TTA)10^4	Enol, %
Sc^{III}	0.17	5.0	2.1
	.14	5.0	1.8
	.16	5.0	2.0
Mg^{II}	.15	5.0	2.0
	.11	5.0	1.5
Cu^{II}	.18	5.0	2.4
	.06	5.0	0.8
		Av.	1.8

$(M^{y+})/(k_{+H})(H^+)$ be greater than unity. The minimum value of the $(M^{y+})/(H^+)$ ratio employed, and the experimental value of k_{+H}, thus lead to the following minimum values of k_{+M}.

Ion	Min. k_{+M} l. mole^{-1} min.$^{-1}$
Sc^{III}	$>1.0 \times 10^7$
Cu^{II}	$>3.0 \times 10^6$

In the case of Mg^{II} and Zn^{II} the minimum $(M^{y+})/(H^+)$ ratio necessitated by the instability of the complexes is too large to lead to minimum k_{+M} values of utility ($>10^4$ l. mole^{-1} min.$^{-1}$). It is probable (although not required by the data) that k_{+M} exceeds 10^6 l. mole^{-1} min.$^{-1}$ for these metal ions.

Fe^{III}.—The kinetic data are consistent with the reaction sequence of eq. 8 and 9 but with step b rate determining. Zebroski previously made this interpretation.[4a] The equations derived to interpret the kinetic results are due to Zebroski.

With conditions such that the TTA and acid concentrations are essentially unchanged throughout the reaction, the following equations apply: A = (metal)$_0$, B = (enolate ion)$_0$, x = amount of complex formed at time t. The subscript 0 refers to initial concentrations.

$$\frac{dx}{dt} = k_{+M}\ (a - x)\ (B) - k_{-M}\ (x) \tag{20}$$

at equilibrium

$$\frac{dx}{dt} = 0 = k_{+M}\ (a - x_e)(B) - k_{-M}\ (x_e) \tag{21}$$

$$\frac{dx}{dt} = k_{+M}\ (B)(x_e - x) + k_{-M}\ (x_e - x) \tag{22}$$

$$\frac{dx}{x_e - x} = k_{+M}\ (B) + k_{-M}\ dt \tag{23}$$

$$d \ln \frac{x_e}{x_e - x}\ /dt = \text{slope} = k_{+M}\ (B) + k_{-M} \tag{24}$$

at equilibrium

$$k_{+M}\ (A - x_e)(B) = k_{-M}\ (x_e) \tag{25}$$

$$x_e = \frac{(A)(B)k_{+M}}{k_{+M}\ (B) + k_{-M}}$$

or

$$x_e = \frac{(A)(B)k_{+M}}{\text{slope}} \tag{26}$$

where $B = (b)\ (Ka)/(H^+)$ and $b = (TTA)_0$

$$\therefore\ k_{+M}\ K_a = \frac{x_e\ (\text{slope})(H^+)}{(A)(B)} \tag{27}$$

In accord with eq. 26 the data indicate (*cf.* Table I) that the slope is not charged with increasing acid since both B and x_e show essentially the same dependence on acid concentration.

The reaction of iron(III) with TTA could take place in the following reaction sequence which is kinetically indistinguishable from the enolate ion mechanism.

$$M^{\nu+} + HA \cdot H_2O \underset{}{\overset{\text{fast}}{\rightleftarrows}} MA \cdot H_2O^{(\nu - 1)+} + H^+$$

$$MA \cdot H_2O^{(\nu - 1)+} \overset{\text{r.d.}}{\rightleftarrows} MA^{(\nu - 1)+} + H_2O$$

However, we favor the enolate ion mechanism, largely on the basis of the kinetics shown in the reaction with SC^{III}, Mg^{II}, Cu^{II} and Zn^{II}, as well as some general observations (see Discussion) on the rate of dehydration of TTA hydrate.

The molar extinction coefficient of the first complex of iron(III) with TTA also was obtained by the method used by Zebroski.[4a] The symbols used below are the same as those previously in eq. 20–27 with $x = D/\epsilon$.

$$K_{eq} = \frac{(D_e/\epsilon)(H^+)}{(A - D_e/\epsilon)(b - D_e/\epsilon)} \tag{28}$$

or

$$AbK_{eq} - b(D_e/\epsilon)K_{eq} - A(D_e/\epsilon)K_{eq} = (D_e/\epsilon)(H^+)$$

the term $(D/\epsilon)^2$ being negligible. Rearranging gives

$$\frac{Ab}{D_e} = (A + b)(1/\epsilon) + \frac{(H^+)}{K_{eq}\ \epsilon} \tag{29}$$

According to equation 29 plots of Ab/D_e *versus* $(A + b)$ give a slope of $1/\epsilon$ and intercept of $H^+/(\epsilon K_{eq})$. The results are listed (Table V) and shown graphically in Fig. 4. The average slope gives a value of 1950 for the molar extinction coefficient of the first complex Fe^{III} at 520 mμ. The rate constants derived from eq. 27 and the equilibrium constants from eq. 29 are summarized below. Values of K_{eq} at 15.70° and 34.51° were calculated by eq. 29 from equilibrium optical densities of several experiments carried out at these temperatures.

TABLE V

EVALUATION OF THE MOLAR EXTINCTION COEFFICIENT FOR THE FIRST COMPLEXES OF Fe^{III} AND THE EQUILIBRIUM CONSTANT, K_{eq}

	$(Ab/D_e)\ 10^{-5}$ (av. values)	$10^4\ (A + b)$
0.10 M HNO_3	2.20	3.40
	2.26	5.40
	2.38	6.40
	2.41	6.40
	Intercept =	2.00×10^{-5}
0.20 M HNO_3	4.34	7.40
	4.49	10.40
	4.53	12.40
	4.62	13.40
	Intercept =	4.03×10^{-5}
	Av. slope =	0.0567×10^{-2}

Acid	Temp., °C.	$k_{+M}K_a$	$10^{-5}k_{+M}$, mole^{-1} min.$^{-1}$	K_{eq}
0.1 M HNO_3	15.70	0.073	1.74	1.49
.1 M HNO_3	24.86	.33 (0.288)[8]	7.9 (6.9)[8]	2.56 (2.04)[8]
.1 M HNO_3	34.51	.94	22.4	2.83
.2 M HNO_3	24.86	.34	8.1	2.54

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(8) The values which are given in parentheses were obtained in a second determination (using a second stock solution of TTA) at the time the temperature coefficients of rate and equilibrium were investigated. The discrepancy in the two sets of values is serious, certainly

The temperature coefficients of rate and equilibrium (which follow the Arrhenius and Van't Hoff equation to reasonable precision) lead to the following thermodynamic quantities

For the reaction

$$\mathrm{Fe^{3+} + HA \rightleftharpoons FeA^{2+} + H^-} \quad \Delta H^0 = +6 \text{ kcal.} \quad \Delta S^0 = +22 \text{ e.u.} \quad \Delta F^0_{298} = -0.55 \text{ kcal.}$$

For the over-all rate process

$$\mathrm{Fe^{3+} + HA \longrightarrow (FeA)^{2\ddagger} + H^+} \quad \Delta H^\ddagger = 23 \text{ kcal.} \quad \Delta S^\ddagger = +4 \text{ e.u.}$$

Further, by virtue of the relationship

$$\frac{k_{+\mathrm{M}}\, K_{\mathrm{a}}}{k_{-\mathrm{M}}} = K_{\mathrm{eq}}$$

and the corresponding thermodynamic equalities, these quantities also have been obtained for the rate process

$$\mathrm{(FeA)^{2+} \longrightarrow (FeA^\ddagger)^{2+}} \quad k_{-\mathrm{M}} \text{ (at } 25^\circ) = 0.130 \text{ min.}^{-1} \quad \Delta H^\ddagger = 17 \text{ kcal.} \quad \Delta S^\ddagger = -17 \text{ e.u.}$$

Uncertainties of 1 or 2 kcal. or 4 to 8 e.u. are estimated for these thermodynamic quantities.

The entropy of activation of −17 e.u. for the latter process is reasonable since it involves the dissociation of a bivalent ion to a tervalent and univalent ion. More solvent molecules are tied down by the latter than the former[9] and a part of the accompanying entropy decrease may be expected in the reaction transition state.

The temperature coefficient for the ionization of TTA has not been determined quantitatively, but it probably is quite small. Assuming the standard enthalpy of ionization of aqueous TTA to be +1 to +3 kcal. gives these values for the thermodynamic rate quantities for the process

$$\mathrm{Fe^{3+} + A^- \longrightarrow (FeA^\ddagger)^{2+}} \quad \Delta H^\ddagger = +20 \text{ to } 22 \text{ kcal.} \quad \Delta S^\ddagger = +24 \text{ to } +31 \text{ e.u.}$$

The estimated entropy of activation of +24 to +31 e.u. for the ion-combination process agrees well with the value predicted by equation (30) derived from electrostatic considerations and the transition state rate theory[10]

$$(\text{for H}_2\text{O, } 25^\circ)\ \Delta S^\ddagger = -10 Z_{\mathrm{a}} Z_{\mathrm{b}} = -10(3)(-1) = +30 \text{ e.u.} \qquad (30)$$

Al^{III}.—A satisfactory kinetic law which describes the results with Al^{III} ion has not been found. The rate-determining step must, however, involve the Al^{III} ion.

Experiments at the higher acid concentration (0.5 and 1.0 M HNO$_3$) gave results similar to those for Fe^{III}, *i.e.*, with slope nearly independent of hydrogen-ion concentration. The data are summarized below

(Al^{III}), M	(HNO$_3$), M	(KNO$_3$), M	Initial (TTA) 10^4, M	De	Slope min.$^{-1}$ 25.0°
2.70 × 10^{-2}	0.100	0.00	5.0	0.310	0.00705
4.00 × 10^{-2}	.100	.00	5.0	.485	.00742
4.00 × 10^{-2}	.200	.00	5.0	.214	.0128
1.35 × 10^{-2}	.100	.00	5.0	.156	.00594
2.00 × 10^{-2}	.200	.00	5.0	.109	.0115
4.00 × 10^{-2}	.100	.10	5.0	.440	.00799
4.00 × 10^{-2}	.100	.10	5.0	.440	.00852
2.00 × 10^{-2}	5.00 × 10^{-2}	.00	5.0	.520	.00440
2.00 × 10^{-2}	0.200	1.00	5.0	.086	.0163
3.00 × 10^{-2}	0.100	1.00	5.0	.255	.00965
0.10	1.00	0.00	5.0	.480	.0235
0.100	0.500	0.50	5.0	.845	.0204

Discussion

Ionization of TTA.—Schwarzenbach and Felder have determined the enol content of aqueous acetylacetone to be 15% at 20°.[11] The value of only 2% enol content for aqueous TTA is therefore abnormally low. A reasonable explanation of this result may be made on the basis that hydrate formation shifts these equilibria toward the right

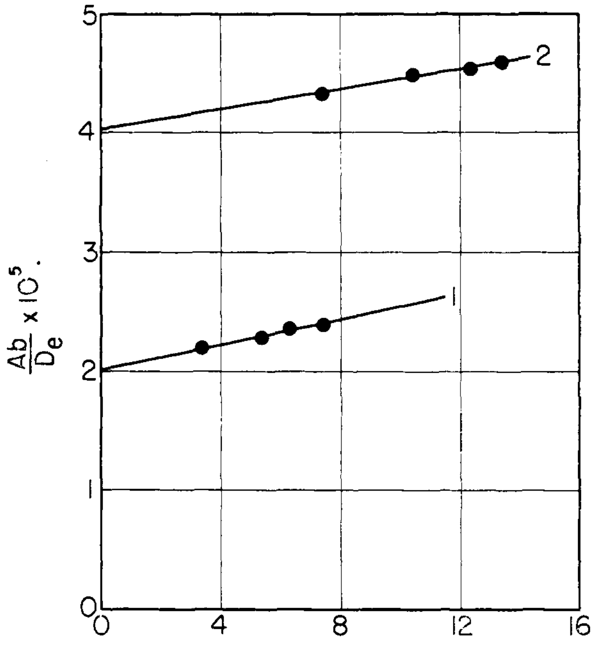
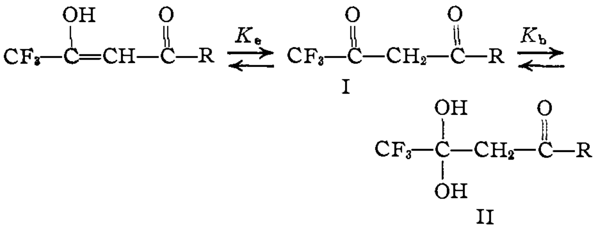


Fig. 4.—Plots for determining the molar extinction coefficient for the first complex of Fe^{III} and TTA, and the equilibrium constant K_{eq}. Plots of $Ab/D_e \times 10^5$ *vs.* $(A + b) \times 10^3$ at 25°: (1) 0.100 M HNO$_3$; (2) 0.200 M HNO$_3$.



$$\mathrm{CF_3{-}C(OH){=}CH{-}C({=}O){-}R} \underset{}{\overset{K_e}{\rightleftharpoons}} \underset{\mathrm{I}}{\mathrm{CF_3{-}C({=}O){-}CH_2{-}C({=}O){-}R}} \overset{K_b}{\rightleftharpoons} \underset{\mathrm{II}}{\mathrm{CF_3{-}C(OH)_2{-}CH_2{-}C({=}O){-}R}}$$

---

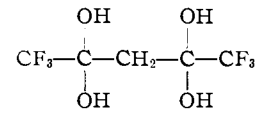
sufficiently so that the temperature coefficients would be virtually valueless if the data at each of the three temperatures contain random uncertainties of the magnitude of the difference in these values. However, since the same stock solutions were used in obtaining the results at the three temperatures the relative values (which determine the enthalpy changes) may be considerably more reliable than the absolute value at any single temperature. The precision with which the results follow the Van't Hoff and Arrhenius equations supports this conclusion.

(9) *Cf.*, for example, E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(10) (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 133; (b) W. F. R. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 492 (1935).

(11) G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1044 (1944).

if one assumes that the equilibrium constant K_e has a value on the order of that for acetylacetone, the relative enol contents may be taken to indicate (in accord with other evidence)[4] that most of the TTA is present as the keto hydrate (II). Nevertheless, the keto form I is probably a necessary intermediate in both the bromination and the first complex formation, *i.e.*, enolate ion is formed directly from I instead of II, with the forward and reverse rates of the equilibrium K_h being relatively fast. This interpretation is consistent with the following facts: (1) the rate of bromination and the rate of first complex formation with Sc^{III} (and others) are the same, indicating the presence of only an unsaturated (and conjugated) enolate ion; (2) the rate of ionization of the keto hydrate II is probably slow since it more closely resembles a mono- than a β-diketone. This conclusion is supported by the fact that hexafluoroacetylacetone which exists in solution as the dihydrate



$$CF_3-\overset{OH}{\underset{OH}{C}}-CH_2-\overset{OH}{\underset{OH}{C}}-CF_3$$

although a relatively strong acid (pK_a = 4.35), ionizes at a relatively very slow rate. Thus, in a titration of 2×10^{-3} mole of this substance with 1 *M* NaOH, Van Uitert reported that over 3 hr. are required for neutralization[12]; (3) the equilibrium between acetaldehyde and its hydrate (not too distant analogs of I and II) in aqueous acid solutions is fast and reversible[13]; (4) the rate of ionization of TTA is slower than predicted on the basis of its pK_a and the rate *vs.* equilibrium correlation of Pearson and Dillon[14] but is more reasonably in line if one corrects the observed rate by an estimate for the equilibrium constant, K_h, *i.e.*, rate ionization (I) = (observed rate, k_{-H},)(K_h).

Ion Structure and Rate of Complex Formation.—A comparison of rate constants, k_{+M}, [for the rate process: $M^{\nu+} + A^- \rightarrow (MA^{(\nu-1)+}]$ with the metal ion structure is both interesting and instructive. The present work permits these constants to be separated into two groups. The first group has a minimum value of 10^6 l. mole^{-1} min.$^{-1}$. The second group has a maximum of a value of 10^6 l. mole^{-1} min.$^{-1}$ and a minimum value less than 10^3 l. mole^{-1} min.$^{-1}$.

Ion	k_{+M} l. mole^{-1} min.$^{-1}$, water, 25°
Cu^{2+}, Sc^{3+}, (Zn^{2+}, Mg^{2+})	10^6 or greater
Fe^{3+}, Be^{2+}, Al^{3+}, Cr^{3+}	less than 10^6

The order of rate constants neither correlates with charge type nor the availability of stable d orbitals in the metal ions involved. Examples of both these types are to be found among the more or the least reactive aquo complexes. There is, however, a clear parallel between the rate constants of first complex formation and the Born charging energy of the central ion, as measured by $(Ze)^2/r$, (where r is the radius of the bare ion). The latter have been estimated using ionic radii in crystals[15] and are summarized below

Ion	Radius, Å.	$(Ze)^2/r$, electronic units^2/Å.	k_{+M}, l. mole^{-1} min.$^{-1}$, 25°
Zn^{+2}, Cu^{+2}	0.74	5.4	
Mg^{+2}	.70	5.7	$>10^6$
Sc^{+3}	.82	11.0	
Be^{+2}	.32	12.5	
Cr^{+3}	.64	14.1	$<10^6$
Fe^{+3}	.60	15.0	
Al^{+3}	.50	18.0	

Ion Structure and Chelate Formation Constants.—The concentration equilibrium constants K_{eq} obtained in this work are listed in Table VI. The values given apply at the ionic strengths listed in the adjacent column. The thermodynamic constants listed for Fe^{III}, Sc^{III}, Cu^{II} and Al^{III} have been estimated by extrapolation of plots of log K_{eq} *vs.* μ, using the limiting slope expected from the Debye–Hückel theory (see Fig. 5).

TABLE VI

EQUILIBRIUM CONSTANTS FOR FIRST COMPLEX FORMATION

Ion	u, *M*	K_{eq}	K_{thermo}	log K_f(TTA)	log K_f[7] (acetylacetone)
Fe^{III}	0.100	2.54[a]	6.30	7.2 (thermo)	10.0
Sc^{III}	.020	1.00	1.84	6.6 (thermo)	8.0
Cu^{II}	.020	0.245	0.340	5.9 (thermo)	8.2
Al^{III}	.100	.20	0.49	6.1 (thermo)	8.6
Zn^{II}	2.25	.00053	..	3.1	5.0
Mg^{II}	2.25	.000098	..	2.4	3.6

[a] Zebroski[4a] gives 5.2, *cf.* ref. 2a, p. 555.

The formation constants show a dependence upon both $(Ze)^2/r$ and the availability of stable d orbitals. For similar $(Ze)^2/r$ values, the formation constants of metal ions which have available stable d orbitals are *less labile* than others by generally one order of magnitude or more (compare Fe^{III} and Sc^{III} with Al^{III}, and Cu^{II} with Zn^{II} and Mg^{II}). This type of dependence of the stability constants on metal-ion structure has been noted earlier by Calvin and Melchior[16], and by Maley and Mellor.[17] By magnetic criterion,[18] this d orbital stabilization does not involve "direct participation" in covalent bond formation. Fe^{III} (also Mn^{III}, Co^{II} and Ni^{II}) acetylacetonate[19] is an "ionic"[18] or "outer orbital complex."[20] The same situation is implied to hold for the less stable TTA complexes.

The parallel between the Lewis acid strengths of metal ions with a series of similar ligands (dissociation constants of complexes, $1/K_f$) and corresponding proton acid strengths (apparent ionization constants, K_a) was first noted by Calvin and Wilson[21] and has received more extensive confirmation by the recent work of Fernelius and co-workers.[22] Listed in Table VI are the loga-

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[12] L. G. Van Uitert, M.S. Thesis, The Pennsylvania State College, 1951.

[13] R. P. Bell and B. B. Darwent, *Trans. Faraday Soc.*, **46**, 34 (1950).

[14] (a) R. G. Pearson and R. L. Dillon, THIS JOURNAL, **75**, 2439 (1953); (b) **72**, 1692 (1950).

[15] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 346.

[16] M. Calvin and N. C. Melchior, THIS JOURNAL, **70**, 3270 (1948).

[17] L. E. Maley and D. P. Mellor, *Australian J. Sci.*, **2A**, 92 (1949).

[18] L. Pauling, ref. 15, Chap. 3-16.

[19] L. Cambi and L. Szego, *Ber.*, **64**, 2591 (1931).

[20] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

[21] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[22] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 457 (1953).

rithms of formation constants $K_f = k_{+M}/k_{-M}$ for both TTA and acetylacetone. Comparison of the two sets of values is not strictly valid in every case because the ionic strengths are not equivalent (the latter are all thermodynamic constants). However, on an order of magnitude basis, it is apparent that two to three log units generally separate the corresponding pairs of constants. The difference in pK_a's of TTA and acetylacetone ($\Delta pK_a = 2.5$) is of the same order.

Rate vs. Equilibrium.—Since the rates of formation of the first complexes do not show the qualitative dependence upon the availability of the stable d orbitals shown by the formation constants, it is readily apparent that there is no simple relationship between rate and equilibrium in these chelation reactions. This situation may be given the following interpretation. The free energy of activation in first complex formation increases qualitatively with increasing ion–dipole interaction (increasing $(Ze)^2/r$) between the central ion and the immediate shell of water molecules. The transition state involves little or no *specific* interactions (d orbital dependent) between the central metal ion and either water molecules or the enolate ion (of the metal ions investigated, Cr^{III} is a possible exception). Covalent interactions in the reactant aquo complexes (*i.e.*, between the bare metal ions and surrounding water molecules), if any, have strengths which qualitatively parallel ion–dipole interactions. On the other hand, the formation constants reflect specific d orbital dependent covalent interactions which exist between the metal ions and enolate ion in the coördination complex.

The anti-parallel that exists in some cases between the rate and equilibrium of first complex formation may have useful consequences. Thus, for example, a solution containing initially equivalent amounts of TTA, Sc^{III} and Fe^{III} at an appropriate hydrogen ion concentration will yield principally the Sc^{III} first complex after the first minute but after several hours will yield an equilibrium mixture containing about four times as much of the Fe^{III} as the Sc^{III} complex.

Experimental

Bromination of TTA.—Kinetic measurements were made using the Beckman Model D. U. Spectrophotometer. The decrease with time in optical density of the bromine solutions was followed at 400 mμ. Bromine water solutions were standardized by addition of acidic KI and titration of the liberated I_2 with standard $Na_2S_2O_3$ solution. The optical density of the bromine water solutions (before and after standardization) were measured over the concentration range 6.4 to 2.8 × 10^{-3} *M*. A value for the molar extinction coefficient of aqueous bromine of 167 ± 3 was found applicable under these conditions. The optical density of a bromine–water solution held constant for about one day. Initial concentrations of bromine for rate runs were obtained from optical densities taken prior to each experiment.

Bromination reactions were carried out in the 1-cm. (length) absorption cells. The aqueous TTA solutions were injected rapidly and forcibly into the bromine water solutions (and *vice versa*) using a hypodermic syringe. The reproducibility of the rate experiments indicates that reactants are mixed essentially instantaneously. Because of the small reaction half-life (1 min.) only two or three optical-density readings could be obtained during the first half-life, and a total of six to eight observations were made during the course of the reaction followed. The procedure used to obtain a point was to balance the spectrophotometer, observe and record the time of balancing, and then record from the instrument the value of the optical density which has been obtained. In obtaining slopes of plots of log $(D/\epsilon_{Br} + a - b)$ *vs.* time, several experiments were performed under identical conditions, and all observations were recorded on a single plot, thus giving an adequate number of points over the entire time range. Slopes were determined by methods of least squares and probably are accurate to about 8%. A 2.00 × 10^{-3} *M* solution of TTA was used and experiments were made in which the initial bromine concentration was varied from 5.34 to 3.23 × 10^{-3} *M*. It was observed that nearly an equivalent of bromine was absorbed by the TTA, followed shortly by precipitation of the brominated material from solution (turbidity and apparent increase in optical density were observed).

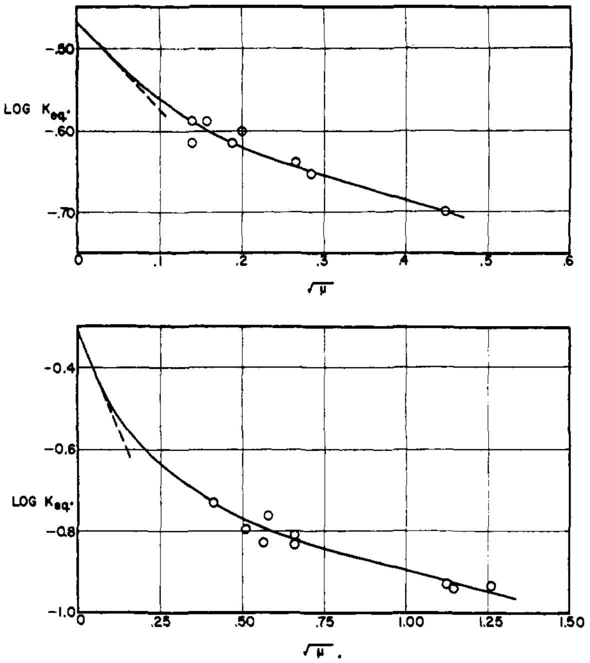

Fig. 5.—Extrapolation of log K_{eq} *vs.* (ionic strength)$^{1/2}$ to obtain thermodynamic constants for first complex formation: upper, Cu^{II} and TTA; lower, Al^{III} and TTA.

First Complex Formation.—The procedure employed was essentially the same as that used in the bromination work. The reaction was carried out in the absorption cell. Equal volumes of the two reactants (acidified metal ion and β-diketone solutions) were mixed by adding one to the other by means of a hypodermic syringe. Each of the complexes studied gives in aqueous solution a discrete absorption maximum (about 350 mμ for all but Fe^{III} for which the peak at 520 mμ was used) so the formation of the complex can be conveniently followed with the D.U. spectrophotometer. Readings were taken at near maximum sensitivity and minimum slit width so as to give an effective spectral bond width of one mμ. The increase in optical density accompanying complex formation (in the fast reactions) was determined and the data treated as described in the section on bromination. Based upon reproducibility, the slopes of plots of log $(D_e - D)$ or log $[(D_e - D)]/D_e$ *vs.* time for Fe^{III} and Al^{III} are accurate to about 5% and those for the faster reactions to about 10%.

For most reactions, cells of 1-cm. light path were used. For relatively high equilibrium optical densities, however, 0.5-cm. cells were used and the values reported have been computed for the 1-cm. length. Temperature was controlled by circulating water from a thermostated bath through the mountings on both sides of the cell compartment and through the lamp housing of the commercial temperature-control unit. This was found adequate to maintain temperatures within ±0.1°. Solutions were brought to temperature in the thermostat before mixing.

The appropriate concentration of nitric acid was added to the blank for all determinations made at 350 mμ to correct for the small absorption of this substance. The change in absorption due to change in concentration of TTA during reaction was so small that it was neglected. Equilibrium optical densities correspond to a steady state of at least twenty minutes duration in the case of complex formation with Sc^{III}, Cu^{II}, Mg^{II} and Zn^{II} and were generally obtained within six minutes. According to expectations for equilibrium in first-complex formation, the steady-state period was obtained after 8 to 10 half-lives of the initial rate. With Fe^{III}, reaction was followed for about 20 minutes and a steady state was reached after 40 minutes. With Al^{III} the reaction was followed for 200 to 300 min. and a steady optical density was reached in about 1000 min. To prevent evaporation of solution during this long period of standing, shellac was used to seal the caps of the absorption cells.

Materials.—The TTA used (m.p. 44–45°) was obtained from the Dow Chemical Company. Solutions of TTA were obtained by dissolving a weighed amount of the solid in a known volume of water and preparing the desired concentrations by dilution of this standard solution. All stock solutions of metal salts were prepared in nitric acid solution to prevent hydrolysis. Iron(III) and scandium(III) nitrate solutions were standardized by precipitation of iron and scandium with NH_4OH and ignition of the precipitates to Fe_2O_3 and Sc_2O_3, respectively.[23,24] Stock solutions of the other metal ions were prepared from weighed amounts of high purity nitrate salts.

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[23] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1947, Chap. 8.

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[CONTRIBUTION FROM THE B. F. GOODRICH COMPANY RESEARCH CENTER]

The Radiation Induced *cis–trans* Isomerization of Polybutadiene. II[1]

BY MORTON A. GOLUB

RECEIVED JULY 18, 1958

The kinetics of the γ-ray induced *cis–trans* isomerization of polybutadiene in benzene were studied over the temperature range 20 to 60°, using diphenyl disulfide as a sensitizer. The isomerization is first order with respect to the *cis* content in the polymer, the rate varying with $[C_6H_5SSC_6H_5]^n$ where n ranges from somewhat greater than 1 at small concentrations of the sensitizer to less than $^1/_2$ at high concentrations. The number of double bonds changed from *cis* to *trans* configuration per 100 e.v. of energy absorbed by the combined polymer–solvent–sensitizer system can exceed 1000. Chain lengths of the order of 10^4 were observed. The mechanism is believed to involve geometric interconversion of the transitory isomeric radical adducts formed from the polymer double bonds and the thiyl radicals generated in the radiolysis of the sensitizer. The over-all activation energy for the radiation induced isomerization, sensitized by diphenyl disulfide, was found to be 2.3 ± 0.3 kcal./mole.

Introduction

The photochemical *cis–trans* isomerization of polybutadiene in solution sensitized by bromine atoms or thiyl radicals was described earlier[2] and considered to occur through a mechanism comparable to that depicted for the isomerization of simple olefins involving the same type of sensitizers.[3] Thus, it was assumed that addition of the bromine atom or thiyl radical to the double bond in the polymer molecule forms a transitory radical structure in which free rotation is possible about the carbon–carbon bond originally present as a double bond. When the attached atom or radical is subsequently released with re-establishment of the double bond, the configuration formed predominantly is the thermodynamically more stable one which, for polybutadiene, is evidently the *trans* form.

Recently, the analogous radiation induced isomerization of this polymer sensitized by bromine atoms was investigated[4] and found to be quite similar to the corresponding photochemical reaction.[2] The present work was undertaken to pursue further the analogy between the photochemical and radiation chemical processes and is concerned with reporting kinetic data for the thiyl radical sensitized γ-ray induced *cis–trans* isomerization of polybutadiene in benzene.

Although the aliphatic disulfides and mercaptans generally are rather weak sensitizers for the radiation chemical isomerization, compared to the organic bromides studied previously,[4] many of the aromatic disulfides, however, are very strong sensitizers. Diphenyl disulfide was selected for use in the present work because it is a very potent source of thiyl radicals and is readily available. It is so efficient in this respect that chain lengths of the order of 10^4 easily were obtained for the isomerization.

Experimental

The polybutadiene samples used in this work were prepared by stereospecific polymerization of 1,3-butadiene to a predominantly *cis* configuration. The viscosity average molecular weights ranged from about 100,000 to 350,000. The polymer structure, as determined by infrared analysis, consisted of approximately 95% *cis*-1,4- and 2% *trans*-1,4 units, with the remaining unsaturation made up of vinyl side groups resulting from 1,2-addition polymerization. Since the last-mentioned type of double bonds was not involved in the isomerization, only the per cent. *cis* double bonds, or *cis/trans* ratio, in the polymer before and after irradiation was important in this study. From an initial *cis/trans* ratio of 98/2, the polymer could be isomerized with diphenyl disulfide at room temperature to an equilibrium *cis/trans* ratio of about 8/92.

Stock solutions of the very high *cis* polybutadiene in benzene, with and without antioxidant, were prepared for γ-irradiation to a polymer concentration of about 10 g./l.

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[1] Presented at the Eighth Canadian High Polymer Forum at MacDonald College, Ste. Anne de Bellevue, Quebec, May, 1958. Work was accomplished under Air Force contract, the sponsoring agency being the Materials Laboratory of Wright Air Development Center.

[2] M. A. Golub, *J. Polymer Sci.*, **25**, 373 (1957).

[3] For the bromine case, see H. Steinmetz and R. M. Noyes, THIS JOURNAL, **74**, 4141 (1952); for the thiyl case, see R. Townshend, R. Pallen and C. Sivertz, Abstract, 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957.

[4] M. A. Golub, THIS JOURNAL, **80**, 1794 (1958).