of the rapidity of the reactions and the low temperature coefficients, the reaction solutions were not kept in thermostated baths. The temperature of the room was controlled to within 0.5° by air-conditioning.

The rates of the rapid reactions of diacetyl in solutions of high *p*H were measured with a DK spectrophotometer. A sample of the reaction mixture was placed in the instrument immediately after mixing and the recorder was then turned on. The initial optical densities were calculated from optical density measurements of separate solutions of each of the reaction mixture components. The recorder speed was two inches per minute. The rates were then calculated from the time required for the reaction to proceed a definite fraction toward completion, such as the one-half reaction time to the three-quarter reaction time.

The *p*H of the reaction mixture was adjusted with perchloric acid for low values of *p*H, with sodium acetate and acetic acid for *p*H 3–5, with sodium dihydrogen phosphate and sodium hydroxide for *p*H 6–10 and with potassium hydroxide for *p*H 11 and above. Sodium perchlorate was used to adjust ionic strength for solutions of *p*H 1–10 and potassium sulfate for solutions of *p*H 11 and above.

The concentrations of the various ionized species of periodate were determined spectrophotometrically. The relative amounts of the species with charge −1 and 0 were determined by measuring the optical density of the buffer solution at 222.5 mμ and comparing this with the extinction coefficient of the uncharged periodate as reported by Crouthamel[5,6] and the extinction coefficient of the total singly-charged periodate as determined for a solution containing all singly-charged periodate. The relative amounts of singly and doubly-charged periodate were determined in a similar fashion at 222.5 mμ using a solution of *p*H 10.3 as a standard for the doubly-charged ion. The relative amounts of doubly and triply charged periodate were obtained at 250 mμ using solutions of *p*H 10.3 and 13.6 as standards representing all charge type −2 and −3, respectively.

Ionization constants for the diketones were obtained by spectrophotometric measurements at 264 mμ for benzil, 324 and 460 mμ for camphorquinone and 319 mμ for diisobutyryl. *p*H-measurements were taken with a Leeds and Northrup Model 7664 *p*H meter with calomel and glass electrodes.

Test for Enolization of Camphorquinones.—A 404-mg. sample of camphorquinone was dissolved in 4.035 g. of absolute alcohol to which was added 0.172 g. of sodium hydroxide dissolved in 5.138 g. of 40% deuterium oxide, and the solution was allowed to stand for 20 minutes. The solution was extracted with anhydrous ether and the extracts were dried with potassium carbonate. The ether was then evaporated with an aspirator and the product was recrystallized from a 60–99° fraction of petroleum ether. The camphorquinone was oxidized in a combustion train and the resulting water had a D_2O content of 0.2 mole %.

Preparation of Diisobutyryl Enol Extract.—A 520-mg. sample of diisobutyryl was dissolved in 20 ml. of 95% alcohol. Twenty ml. of water and 40 ml. of an aqueous solution of 1.6 g. of sodium hydroxide were added and, after mixing, 60 ml. of 1.2 *N* HCl was introduced. The solution was then immediately extracted with carbon tetrachloride. The extracts were combined and washed with 0.12 *N* HCl. The extracts was then dried with magnesium perchlorate and partially evaporated with the aspirator. After filtering, the infrared absorption spectrum was recorded on a Perkin-Elmer model 21 infrared spectrophotometer.

Heat of Hydration of Diacetyl.—The extinction coefficient of aqueous diacetyl at 409 mμ is 5.6 at 29° and 7.1 at 42°. If one assumes that (1) the extinction coefficient of 20 for this band observed for diacetyl in non-aqueous solution is characteristic of the diketo form and would obtain for this form in aqueous solutions, (2) that only the diketo form and the mono-hydrated form of diacetyl are present in aqueous solution and (3) that the extinction coefficient of the monohydrated form in aqueous solution at 409 mμ is zero it is possible to calculate approximately the degree of hydration at each of the above temperatures and a heat for the hydration process. The heat of hydration is approximately 5 kcal./mole. Diacetyl is approximately 72 and 65% hydrated at 29 and 42°, respectively.

BLOOMINGTON, INDIANA

[CONTRIBUTION FROM THE POLYMER RESEARCH LABORATORY, MIDLAND DIVISION, THE DOW CHEMICAL COMPANY]

Kinetics of Three-compound Equilibrations. I. The Isomerization of Cymene[1]

BY ROBERT H. ALLEN, TURNER ALFREY, JR., AND LARRY D. YATS

RECEIVED JUNE 2, 1958

This work was carried out in order to study the kinetics of three-compound equilibrations and to aid in elucidating the mechanism of the isomerization of isopropyltoluene. The isomerization was assumed to proceed by the reaction pattern shown below, which yields the integrated rate equations: $O = O^* + Ae^{-\beta\tau} + Be^{-\beta\tau}$ and $P = P^* + Ce^{-\alpha\tau} + De^{-\beta\tau}$, where τ is a function of time, O and P are the *o*- and *p*-cymene concentrations, respectively, O^* and P^* are the *o*- and *p*-cymene equilibrium concentrations, respectively, α and β are constants determined by the set of rate constants and A, B, C, D are constants determined by the initial concentrations. Dilute solutions of five cymene isomer distributions in toluene were isomerized at 0° with small quantities of aluminum chloride. In each case samples were taken periodically, the toluene distilled off and the residue analyzed by infrared. The isomer distributions obtained are in excellent agreement with the following relative rates: $k_{om} = 45.8$, $k_{mo} = 1$, $k_{mp} = 2.4$, $k_{mp} = 5.5$, $k_{po} = 1$, $k_{op} = 19.9$. These relative rates prove that, although the mechanism for the isomerization of xylenes appears to be an intramolecular 1,2-shift, the mechanism for the isomerization of cymenes is not an intramolecular 1,2-shift.

Introduction

According to the literature at present, alkylbenzenes isomerize by intramolecular 1,2-shifts. Two independent studies indicate that the mechanism for xylene isomerization is an intramolecular 1,2-shift.[2,3] A similar mechanism has been proposed by Schlatter for the isomerization of 1,3-dimethyl-2-isopropylbenzene to 1,3-dimethyl-4-isopropylbenzene,[4] and an intramolecular mechanism has been proposed for the isomerization of *n*-propyl-β-C^{14}-benzene to *n*-propyl-α-C^{14}-benzene.[5]

The xylene isomerization kinetics were studied using molar quantities of $HF \cdot BF_3$[2] and using molar quantities of $AlBr_3 \cdot HBr$ in toluene solution.[3] The use of molar quantities of catalyst resulted in homogeneous reaction mixtures, so that absolute rates could be determined; and also resulted in isomerization to 100% *m*-xylene, so that the kinetics would not be complicated by the isomerization of the *m*-xylene formed.

In the present work the isomerization of cymenes was studied as a three-compound equilibration involving six rate constants. The reactions were run

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[1] Presented before the Organic Chemistry Division at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

[2] D. A. McCaulay and A. P. Lien, THIS JOURNAL, **74**, 6246 (1952).

[3] H. C. Brown and J. Jungk, *ibid.*, **77**, 5579 (1955).

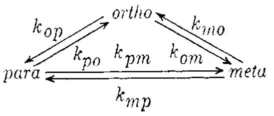
[4] M. J. Schlatter, Synthetic Fuels and Chemicals Symposium, Division of Petroleum Chemistry Preprints, 128th Meeting of The American Chemical Society, Minneapolis, Minn., Sept., 1955.

[5] R. M. Roberts and S. G. Brandenberger, THIS JOURNAL, **79**, 5484 (1957).

using small quantities of catalyst in order to produce convenient rates and to ensure that finite quantities of all three isomers would be present at equilibrium. The use of small quantities of catalyst resulted in heterogeneous reaction mixtures so that only relative constants were determined.

Kinetics of Three-compound Equilibrations

The three-compound equilibration pattern is



Were the above reactions first order or pseudo first-order reactions, the differential rate expressions would be

$$\begin{aligned} \mathrm{d}O/\mathrm{d}t &= -k_{op}O - k_{om}O + k_{po}P + k_{mo}M \\ \mathrm{d}P/\mathrm{d}t &= -k_{po}P - k_{pm}P + k_{mp}M + k_{op}O \qquad (1) \\ \mathrm{d}M/\mathrm{d}t &= -k_{mo}M - k_{mp}M + k_{om}O + k_{pm}P \end{aligned}$$

This set may be integrated[6] to yield the equations

$$\begin{aligned} O(t) &= O^* + Ae^{-\alpha t} + Be^{-\beta t} \\ P(t) &= P^* + Ce^{-\alpha t} + De^{-\beta t} \qquad (2) \\ M(t) &= M^* - (A + C)e^{-\alpha t} - (B + D)e^{-\beta t} \end{aligned}$$

where $O(t)$ is the concentration of *ortho* isomer at time t, O^* is the equilibrium concentration of *ortho* isomer; α and β are the two roots of the determinant

$$\begin{vmatrix} (\alpha - k_{op} - k_{po} - k_{pm}) & (k_{mp} - k_{op}) \\ (k_{pm} - k_{om}) & (\alpha - k_{om} - k_{mo} - k_{mp}) \end{vmatrix} = 0$$

and A, B, C and D may be determined for any particular starting concentrations by setting $t = 0$ in equations 1 and 2.

It will be shown later that the above equations are not strictly applicable to the cymene isomerizations carried out in this work. Under the conditions reported here, the isomerization steps are not first order or psuedo-first order. The cymene isomerization steps are first order in starting aromatic but also involve other time dependent concentrations in the rate expressions. The above equations can be modified to apply to these cymene isomerizations by the following procedure.

If all six reactions involve the same extraneous time-dependent concentrations, such as a catalyst activity that changes during the reaction, the above derivation will be modified in the following manner. Taking (x) and (y) to be time dependent concentrations that appear in each kinetic expression to the mth power and nth power, respectively, then we may define $f(t)$ as

$$f(t) = (x)^m(y)^n$$

the set of differential rate expressions will now be

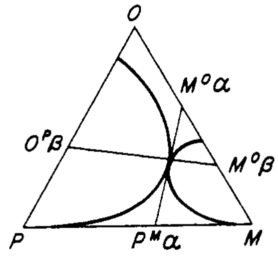
$$\begin{aligned} \mathrm{d}O/f(t)\mathrm{d}t &= -\,k_{op}O - k_{om}O + k_{po}P + k_{mo}M \\ \mathrm{d}P/f(t)\mathrm{d}t &= -\,k_{po}P - k_{pm}P + k_{mp}M + k_{op}O \\ \mathrm{d}M/f(t)\mathrm{d}t &= -\,k_{mo}M - k_{mo}M + k_{om}O + k_{pm}P \end{aligned}$$

Integration of this set of differential rate expressions in the same way as previously, produces the same solution except that t will be replaced by $\int f(t)\mathrm{d}t$. When the analytical expression for $f(t)$ is not known, the so-modified integrated rate equations may be used to determine relative rates by regarding $\int f(t)$ merely as a parameter involving time. This has been done in the present work.

Properties of the Integrated Rate Equations.—When the concentrations obtained between $t = 0$ and $t = \infty$ from the above equations are plotted on a triangular composition diagram, a continuous curve connecting the starting concentrations and the equilibrium concentrations will be obtained. This reaction trajectory will be a straight line for the following percentage compositions.

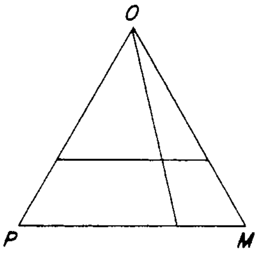
$$\begin{aligned} O^p{}_0 &= (\alpha M^* - 100k_{pm})/(k_{om} - k_{pm}) \\ P^m{}_0 &= (\alpha O^* - 100k_{mo})/(k_{po} - k_{mo}) \\ M^o{}_0 &= (\alpha P^* - 100k_{op})/(k_{mp} - k_{op}) \end{aligned}$$

where O^p is the percentage of *ortho* isomer in a mixture of *ortho* and *para* isomers, etc. These equations will always yield a pair of compositions for α and a pair of compositions for β, each pair lying on a straight line through the equilibrium point. The following figure would be a case in which no two of the rate constants are equal



A

If $k_{po} = k_{mo}$, it can be shown that one of the straight lines will pass through the 100% *ortho* apex, and the other will be parallel to the 0% *ortho* side of the triangular diagram, as



B

This type of degeneracy is evident in the cymene isomerizations reported in the present work.

If $k_{po} = k_{mo}$ and $k_{mp} = k_{op}$, then $k_{om} = k_{pm}$ and $\alpha = \beta = k_{po} + k_{mp} + k_{om}$ and all reaction trajectories will be straight lines.

Isomerization of Cymenes.—The relative rates of decomposition of the cymene isomers were obtained by fitting the data from Table I to the above equations. In Table I are given the experimental isomer compositions obtained by the isomerization of *o*-cymene, *m*-cymene, *p*-cymene, a mixture of *o*-cymene and *p*-cymene, and a mixture of *o*-cymene and *m*-cymene. These compositions are plotted as the points on Fig. 1.

The most striking feature of Fig. 1 is that the decomposition of *o*-cymene gives a straight line trajectory of compositions. It also appears that any mixture containing 1.5% *o*-cymene would yield a straight line trajectory parallel to the 0%

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(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 160.

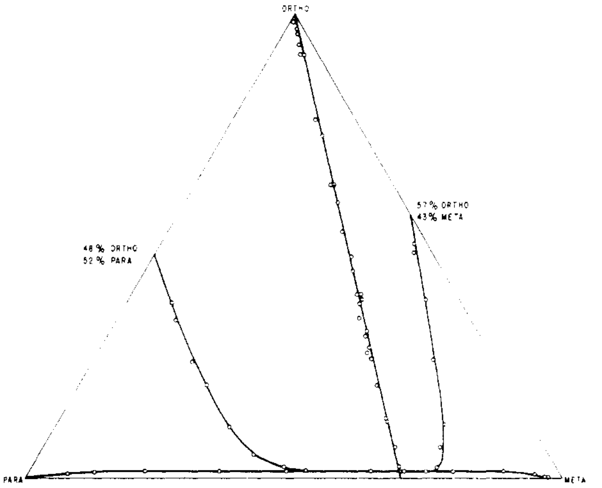


Fig. 1.—Isomer compositions produced by the isomerization of cymenes.

ortho side. As stated above, these characteristics indicate a degenerate set of rate constants; that is, both relative rate constants for the formation of the *ortho* isomer must be nearly equal. Setting the relative rate constants k_{po} and k_{mo} equal to 1.0, then k_{op} and k_{om} may be calculated from equilibrium equations as

$$k_{op}(O^*) = k_{po}(P^*)$$
$$k_{op} = (P^*)/(O^*) = 29.8/1.5 = 19.9$$
$$k_{om} = (M^*)/(O^*) = 68.7/1.5 = 45.8$$

where O^*, P^*, M^* are the experimentally obtained equilibrium percentages. Since $k_{pm}/k_{mp} = (M^*)/(P^*) = 29.8/68.7 = 0.434$, only the value for k_{pm} or k_{mp} is needed in order to establish the complete set of rate constants. The slope of the initial trajectory of compositions for pure *p*-cymene is a function only of the two decomposition rate constants for *p*-cymene, k_{po} and k_{pm}. Therefore, the ratio k_{pm}/k_{po} will be equal to the slope of a line tangent to the *p*-cymene trajectory at 100% *p*-cymene. In a similar manner k_{mp} may be determined. The best set of consistent relative rate constants obtained is

$$k_{op} = 19.9 \qquad k_{po} = 1.0 \qquad k_{mo} = 1.0$$
$$k_{om} = 45.8 \qquad k_{pm} = 5.5 \qquad k_{mp} = 2.5$$

TABLE I

Exp. no.	Time (min.)	Mole %	
		o-	*p*-
1[a]	0	98.5	1.1
	0.33	63.1	11.1
	1	47.4	15.5
	3	39.4	17.8
	6	31.6	20.8
	10	28.1	22.0
	15	20.0	24.6
	25	12.5	26.5
	40	6.8	27.8
	60	2.7	29.1
	120	1.5	29.5
2[b]	0	98.5	1.1
	1	59.3	12.2
	2	53.1	14.4
	6	44.4	17.0
	10	39.4	18.6
	15	37.8	18.9
	25	34.4	20.4
	40	30.4	21.5
	60	25.8	22.6
3[c]	0	98.5	1.1
	270	96.5	1.6
	300	96.0	1.7
	360	95.4	1.9
	1440	73.8	7.8
4[e]	0	98.5	1.1
	120	91.1	3.2
	360	77.1	7.6
	720	62.9	11.8
	1440	43.6	18.1
	2880	27.0	23.0
	5760	13.1	26.4
	11520	1.7	28.8
	15840	1.7	28.9
5[d]	0.02	98.1	1.2
6[d]	.05	93.0	2.5
7[d]	.07	91.0	2.8
8[e]	0	0	100
	0.33	0.8	92.1
	1	1.4	86.3
	5	1.5	76.9
	20	1.5	63.1
	60	1.5	50.6
	180	1.4	36.9
9[e]	0	0	2.5
	0.33	.33	2.6
	1	.38	3.1
	5	.85	4.7
	20	1.53	10.1
	60	1.52	19.6
	180	1.55	25.2
	360	1.60	25.9
	1380	2.42	28.4
10[a]	0.33	37.4	54.2
	1	34.0	55.0
	5	25.1	56.3
	15	20.0	55.8
	45	11.2	56.4
	90	5.2	54.7
	180	2.6	50.8
	360	1.6	47.1
	1440	1.6	35.2
11[a]	0.33	50.3	2.4
	1	48.4	3.4
	5	38.6	6.3
	15	25.5	11.2
	45	11.7	16.1
	90	6.5	19.2
	180	2.7	22.1
	360	1.5	24.8
	1440	1.5	28.8

[a] 1 mole $AlCl_3$, 10 moles cymene, 90 moles toluene. [b] 1 mole $AlBr_3$, 20 moles cymene, 80 moles toluene. [c] 1 mole $AlCl_3$, 10 moles cymene, 90 moles toluene, 1 mole mesitylene. [d] 1 mole $AlCl_3$, 20 moles cymene, 80 moles toluene. [e] 2 moles $AlCl_3$, 10 moles cymene, 90 moles toluene.

This set produces the following integrated equations for the per cent. of *ortho* and *para* isomers in terms of the parameter τ, where

$$\tau = \int_0^t f(t)\mathrm{d}t$$

some unknown function of time.

Starting with 100% *para:*

$$\%\ ortho = 1.5 - 1.5e^{-66.7\tau}$$
$$\%\ para = 29.8 + 69.8e^{-8.9\tau} + 0.44e^{-66.7\tau} \qquad \text{(a)}$$

Starting with 48% *ortho,* 52% *para:*

$$\%\ ortho = 1.5 + 46.5e^{-66.7\tau}$$
$$\%\ para = 29.8 + 36.3e^{-8.9\tau} - 14.1e^{-66.7\tau} \qquad \text{(b)}$$

Starting with 100% *ortho:*

$$\%\ ortho = 1.5 + 98.5e^{-66.7\tau} \qquad \text{(c)}$$
$$\%\ para = 29.8 - 29.8e^{-66.7\tau}$$

Starting with 57% *ortho,* 43% *meta:*

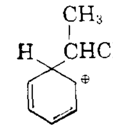
$$\%\ ortho = 1.5 + 55.5e^{-66.7\tau}$$
$$\%\ para = 29.8 - 13.0e^{-8.9\tau} - 16.8e^{-66.7\tau} \qquad \text{(d)}$$

Starting with 97.5% *meta,* 2.5% *para:*

$$\%\ ortho = 1.5 - 1.5e^{-66.7\tau}$$
$$\%\ para = 29.8 - 27.8e^{-8.9\tau} + 0.5e^{-66.7\tau} \qquad \text{(e)}$$

The lines shown on Fig. 1 were obtained from these equations. The agreement between the experimental points and theoretical trajectories is excellent.

Mechanism of Isomerization.—Since k_{op} and k_{po} are not equal to zero, the principal mechanism for the isomerization of cymenes is not an intramolecular 1,2-shift. The postulated mechanism for the isomerization of xylenes is an intramolecular 1,2-shift. This contrast in mechanisms can be explained by the hypothesis that in σ-complexes of the structure



the isopropyl group dissociates as a carbonium ion far more readily than does a methyl group in the same position. The methyl group is therefore constrained to 1,2-shift, while the more labile isopropyl group can change position either by moving around the ring or from one ring to another. Thus the mechanism for the isomerization of cymenes is either an intramolecular delocalized π complex[5] or an intermolecular alkylation-dealkylation[7] or both.

Effect of Catalyst Concentration.—Selective complexing of the *m*-cymene by the catalyst was expected to change the equilibrium of isomers to higher concentrations of *m*-cymene.[8] Since the *o*-cymene trajectory would best show this change, *o*-cymene was isomerized under a variety of catalyst conditions. The mole per cent. of catalyst based on the moles of *o*-cymene was 5 mole % Al_2Cl_6 in exp. 1, 2.5 mole % Al_2Br_6 in exp. 2 and nearly 0% Al_2Cl_6 in exp. 3. In exp. 3 mesitylene was added to complex the catalyst. The results were experimentally indistinguishable, which demonstrates that selective complexing of *m*-cymene by the catalyst was not a significant factor in these isomer distributions. This conclusion is also consistent with the following observations on absolute rates of isomerization.

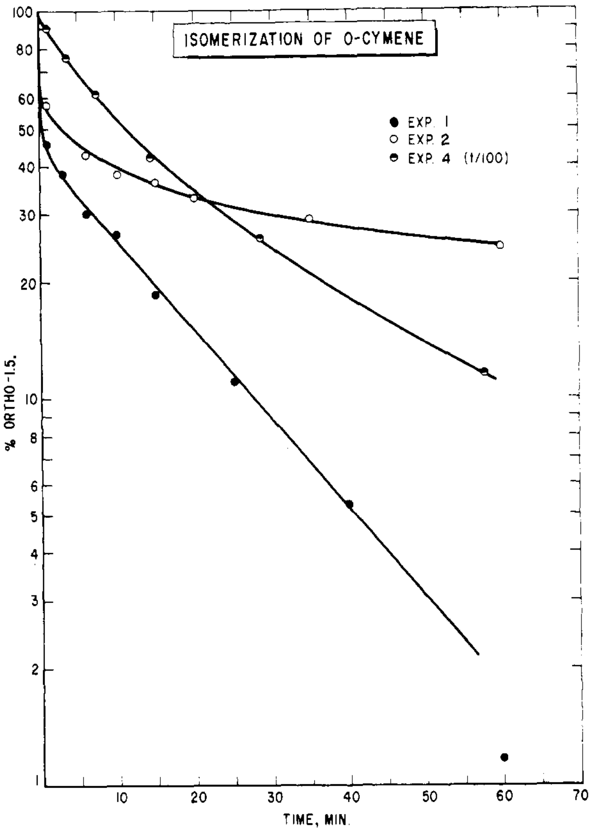


Fig. 2.

In the absence of mesitylene, exp. 7, it required four seconds to reach 91% *ortho* isomer, in the presence of mesitylene, exp. 4, it required 120 minutes, a two-thousand-fold decrease in rate. Since a σ-complex of the cymene is undoubtedly an intermediate in the reaction, the two-thousand-fold decrease in rate indicates a two-thousand-fold decrease in the σ-complex concentration or a one-thousand-fold relative decrease due to the mesitylene, since the cymene was twice as concentrated in exp. 7. If the exp. 7 cymene σ-complex mole fraction was assumed to be 2×10^{-3} (40% of the catalyst present), then the mole fraction in exp. 4 would be 2×10^{-6}, and the basicity of *o*-cymene relative to toluene would be 2.8, about one hundredth that of *o*-xylene.[9]

The accuracy of the above *o*-cymene basicity is questionable, especially since $HF{\cdot}BF_3$ basicity figures were used rather than $AlCl_3{\cdot}HCl$, but the conclusion that the basicity of cymene is low compared to that of the xylenes is consistent with the observation that hexaethylbenzene is less basic than hexamethylbenzene.[10] The low basicity of cymene is also consistent with the lack of evidence for changes in the equilibrium concentrations of the cymenes with changes in the catalyst concentrations.

Absolute Rates.—The data on the isomerization of *o*-cymene shows the difficulty of determining absolute rates in this system. The first-order rate equation for the decomposition of 100% *o*-cymene would be

$$\%\ ortho = 1.5 + 98.5e^{-\beta t}$$

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[7] G. M. Vriens, *Ind. Eng. Chem.*, **46**, 669 (1954).

[8] A. P. Lien and D. A. McCaulay, U. S. Patent 2,741,647 (1956); U. S. Patent 2,770,662 (1957).

[9] D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

[10] D. A. McCaulay and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

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

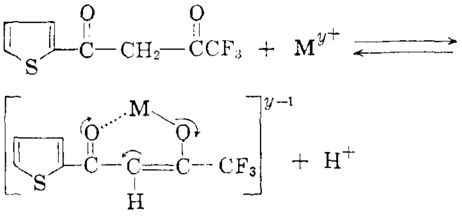
BY ROBERT W. TAFT, JR., AND E. H. COOK[1]

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).