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Keto–Enol Transformation of 1,2-Cyclohexanedione. II. Acid Catalysis in Strongly Acidic Media[1-3]

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The rate of the acid-catalyzed transformation of ketone and enol forms of 1,2-cyclohexanedione to the equilibrium mixture has been studied in aqueous solutions as a function of catalyst concentration. For a given catalyst the rate is the same starting from either tautomer. Combination of the kinetic data with previously obtained data on the equilibrium constant permits determination of the separate first-order rate coefficients of the ketonization and enolization reactions. For the three catalyst acids, perchloric, sulfuric and hydrochloric, studied in the range of from 1 to 7 M, plots of log k_f vs. $-H_0$ are straight lines with slopes ranging from 0.5 to 0.7. For the reverse, enolization reaction the analogous plots are also linear, the slopes varying from 0.8 to 1.0. From temperature coefficient studies it is found that for the ketonization reaction E_A is 17.6 kcal. per mole and ΔS^* is -26 ± 2 e.u. where the latter is for k_e in liter mole^{-1} sec.$^{-1}$ units. For the enolization reaction the values are $E_A = 24.4$ kcal. and $\Delta S^* = -4$ e.u. These entropy of activation values suggest that the rate-determining step involves the monohydrated species, i.e., that the transition state is a monohydrate, but that otherwise the mechanism is the usual one for a keto–enol interconversion. Deuterium solvent isotope effects are consistent with this conclusion. The fact that the rates of reaction of the ketone follow H_0 rather than C_{H^+}, even though the exponent is sometimes less than unity, is at variance with the Zucker–Hammett hypothesis. The reaction of the enol, which involves a slow proton transfer, shows slopes of log k_{H^+} vs. $-H_0$ which are considerably less than unity, but detailed analysis of the rate-determining step is difficult because of the preliminary mono-hydration equilibration which presumably occurs. The data for both reactions have also been analyzed by the recently proposed procedures of Bunnett and it is concluded that these procedures do not contribute significantly to the interpretation of the data.

The keto–enol interconversion has played a major role in the development of correlations between rates and mechanisms of reactions in solutions.[4,5] It is one of the best studied examples of general acid catalysis.[4,6] It has also played a significant role in the development of the Zucker–Hammett hypothesis of utilization of the H_0 acidity function in correlating rates and mechanisms.[7,8] In their original work, Zucker and Hammett investigated the acid-catalyzed iodination of acetophenone in aqueous solutions of from 0.2 to 3.6 M pe chloric acid. Over this acidity range the rate of the reaction was much more nearly proportional to concentration of hydrogen ion than to the h_0 acidity function. This fact, in conjunction with the known mechanism of the reaction, led to their proposal that rates of acid-catalyzed reactions which placed a water molecule in the transition state would follow concentration of hydrogen ion rather than the h_0 acidity function.

Although it is well known by now that there are enough exceptions to the Zucker–Hammett proposal as to limit seriously its utility in mechanism considerations, it is still of some interest to study in more detail the acidity dependence for the keto–enol reaction. Since the reaction in favorable cases reached a measurable equilibrium, it is often possible to get information on both the forward and reverse processes. As may be seen below, the accepted mechanism for reaction of the ketone involves a pre-equilibrium protonation. In contrast, for reaction of the enol, there is a rate-determining slow proton transfer. One-step slow proton transfers have been postulated for various other reactions and it is of some importance to see what acidity function their rates will follow. Hence the acidity dependence for reaction of the enol is of particular interest.
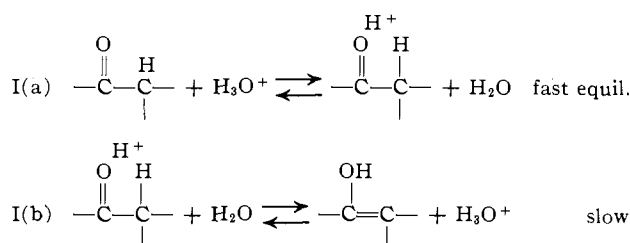
The conversion of the enol of 1,2-cyclohexanedione to its ketone is a particularly favorable case for study. The preliminary studies by Schwarzenbach and Wittwer[9] showed that the rate of the reaction was very slow, sufficiently so that the rate was still easily measurable by conventional procedures up to acidities of ca. 6 or 7 M mineral acid. Furthermore, the reaction appeared to reach a measurable equilibrium in aqueous solution. As noted in paper I of this series, this equilibrium is complicated by the fact that the ketone is almost entirely present in aqueous solutions as its monohydrate.[10] However, this does not change the fundamentals of the reaction and it is still possible to study the rate of approach to equilibrium as a function of acidity and from these data and from information on the equilibrium to determine the rate of reaction of both the enol and the ketone.[11]

A quite different reason for wishing to study this particular reaction concerns the problem of general acid catalysis in strongly acidic media. When a reaction which is known to be subject to general catalysis is studied in concentrated solutions of mineral acids, one might anticipate specific behavior for the different mineral acids depending on the particular characteristics of the strong acid species which are present. Gold in particular has suggested that concentrated solutions of sulfuric acid might show pronounced general acid

(1) Work supported by a grant from the Atomic Energy Commission.

(2) Presented in part at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., April, 1961.

(3) Original data in thesis of Ronald Bakule, Cornell University, 1962; available from University Microfilms, Ann Arbor, Mich.

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VIII.

(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter X.

(6) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter 9.

(7) L. Zucker and L. P. Hammett, J. Am. Chem. Soc., 61, 2791 (1939).

(8) F. A. Long and M. A. Paul, Chem. Rev., 57, 935 (1957), give a general survey of the Zucker–Hammett hypothesis and of applications.

(9) G. Schwarzenbach and C. Wittwer, Helv. Chim. Acta, 30, 663 (1947).

(10) Ronald Bakule and F. A. Long, J. Am. Chem. Soc., 85, 2309 (1963), subsequently referred to as part I.

(11) Shortly after this present work was started, a brief communication appeared by Kresge and Satchell[12] which considered the preliminary data of Schwarzenbach and Wittwer for this reaction and concluded that the rate of the reaction of enol to ketone could be predicted to follow concentration of hydrogen ion rather than h_0. This prediction was based on an incorrect assumption about the acidity dependence of the reaction of the ketone. However, the essential idea of utilizing information on the equilibrium is the same as is employed in the current discussion.

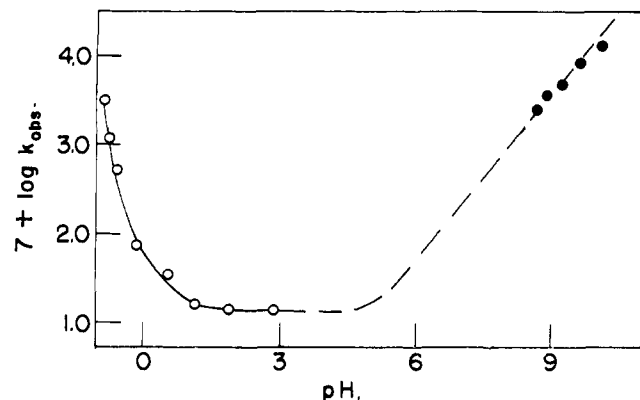(12) A. J. Kresge and D. P. N. Satchell, Chem. Ind. (London), 1328 (1958).

Fig. 1.—Log k_{obs} vs. pH for reaction at 25° of mono-enol of 1,2-cyclohexanedione to give keto–enol equilibrium. Acidic catalyst is perchloric acid, basic is ethanolamine–ethanol–ammonium ion buffer.

catalysis.[13]   However, Gold's latest communication on the subject proposes a rationalization of the fact that this specific behavior has not yet been observed.[14]

Experimental

The enol of 1,2-cyclohexanedione absorbs very strongly (ϵ = 7000 at 262 mμ) in a spectral region where the ketone exhibits negligible absorption so that it is simple and convenient to follow the keto–enol reaction spectroscopically, observing the change of the absorption due to the enol. Since only the enolic species is normally available, the most straightforward measurement is of the rate of disappearance of the enol to form the equilibrium mixture. However, as noted in part I of this series, the ketone can be prepared in virtually pure form through its bisulfite complex and as a consequence it is possible to study the rate of approach to equilibrium starting with the ketone.

Preparation of materials was the same as for the previous study.[10] Kinetic measurements were made either in a Beckman DU or a Cary spectrophotometer utilizing 1-cm. path length cells which were maintained at a constant temperature to within ±0.05°. The rate of approach to equilibrium was accurately first order.

The temperature coefficient of the reaction was studied between the temperature limits of 25 and 60°. The equilibrium constant for the reaction was measured at the same temperatures. In all cases, solutions of ketone or enol in water and solutions of mineral acids were brought to constant temperature and then mixed just before starting the experiment.

Both the ketonization and the enolization reactions were studied in deuterium oxide as solvent. The procedures in both cases were straightforward and varied in no significant detail from the analogous studies with ordinary water as solvent. However, it should be noted that experiments which employ the ordinary enol in deuterium oxide as solvent lead to a sort of pseudo-equilibrium whose characteristics must be considered in obtaining values of the separate rate coefficients.

Results and Discussion

The pH dependence of k_{obs}, the first-order rate coefficient for reaction of the enol to form the equilibrium mixture, is shown in Fig. 1. This is typical behavior for a keto–enol interconversion and shows regions of acid catalysis, base catalysis and a pH independent or "water" reaction. All the rates are, however, substantially slower than for most open-chain ketones, quite possibly due to an additional steric barrier for the cyclic system.[15] In the region where acid catalysis enters one can write the observed rate coefficient as

(13) V. Gold, R. W. Lambert and D. P. N. Satchell, J. Chem. Soc., 2461 (1960).

(14) V. Gold, Proc. Chem. Soc., 453 (1961).

(15) The preliminary studies of Littler[15] which have been confirmed in this Laboratory, show that the rate of acid-catalyzed enolization of cyclohexanone is relatively fast, approximately an order of magnitude faster than that of acetone which is, itself, faster than the present reaction. One reason for the faster rate of cyclohexanone is because it is a somewhat better base.[17] Even so, the relative rates do suggest that there is no great role for steric effects in the case of cyclohexanone. However, 1,2-cyclohexanedione is a considerably more "crowded" molecule.

(16) J. S. Littler, J. Chem. Soc., 827 (1962).

(17) H. J. Campbell and J. T. Edward, Can. J. Chem., 38, 2109 (1960).

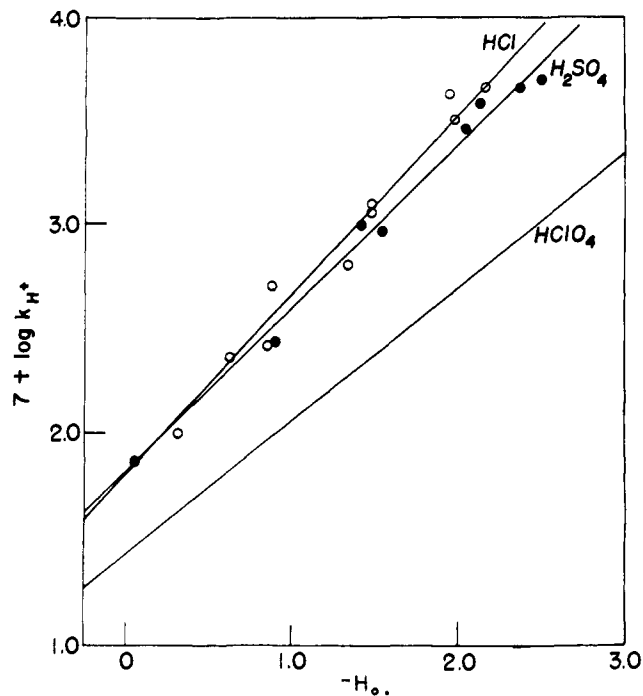Fig. 2.—Log k_{H^+} vs. $-H_0$ for acid-catalyzed rate of approach to equilibrium, 25°. Catalysts are hydrochloric acid and sulfuric acid. The line for perchloric acid is included for comparison but is displaced 0.4 log unit downward.

$$k_{obs} = k_{H^+} + k_{obs}^w$$

Hence k_{H^-}, the first-order coefficient for the acid-catalyzed approach to equilibrium, is to be obtained by subtracting the water contribution from the over-all rate coefficient. From experiments at higher pH, $k_{obs}^w = 1.40 \times 10^{-6}$ sec.$^{-1}$ at 25°. All the values of K_H which are reported involve subtracting this value from k_{obs}.[18] The values of k_{H^+} are of course dependent on acidity. Table I gives a partial listing of the values obtained for aqueous solutions of perchloric acid at 25°. The complete set of 70 measurements for this system shows a linear dependence of log k_{H^+} on H_0, the best straight line calculated by a least squares method having the equation

$$\log k_{H^+} = -0.64 H_0 - 5.14 \qquad (1)$$

As Table I shows, the value of k_{H^-}, which is for rate of approach to equilibrium, is the same whether the starting material is enol or ketone. Very similar results have been obtained for the catalyst acids hydrochloric and sulfuric. The data for these two are plotted in Fig. 2 which includes the line of eq. 1 for comparison.

For a more detailed analysis, we can write

$$k_{H^-} = k_f + k_r$$

where k_f and k_r are first-order rate coefficients for the acid-catalyzed conversion of enol to ketone and of

(18) Consideration was given to the desirability of correcting k_{obs}^w to take account of salt effects, but it was finally concluded that even for a 6 M electrolyte the value would be little changed from the dilute solution value. The argument was as follows. One can write

$$k_{obs}^w = (k_f^w + k_r^w) = k_f^w (1 + 1/K_s) =$$
$$k_{f0}^w \frac{a_{H_2O} f_E}{f_*} \left(1 + \frac{1}{K_e}\right)$$

where k_f^w is the rate coefficient for the "water" reaction of enol to ketone and K_e is the keto–enol equilibrium constant [K]/[E]. From part I, the salt effect on K_e is known, as is that on the activity coefficient, f_E. For a 6 M salt solution, we can insert experimental values for f_E, K_e and a_{H_2O} and assume that f_*, the activity coefficient for the transition state, has a value intermediate between f_K and f_E. The resulting calculated value of k_{obs}^w is only about 50% smaller than the value for dilute aqueous solutions. On the basis of this rough calculation, and recalling that the relative importance of the water reaction is very small for the more acidic solutions, we conclude that it is justifiable to utilize the dilute solution value of k_{obs}^w for the calculation of k_{H^+} at all acidities.
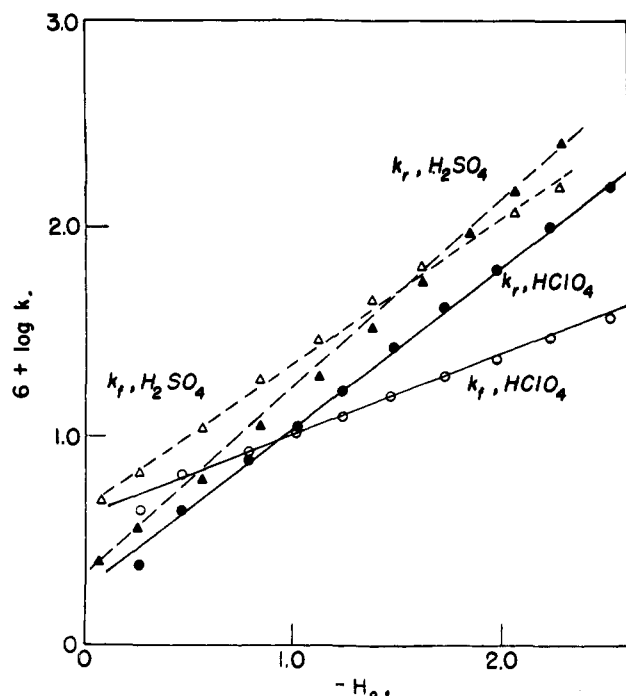
Fig. 3.—Log k_f and log k_r vs. $-H_0$ for catalysts perchloric and sulfuric acid, 25°.

ketone to enol, respectively. Since $K_e = k_f/k_r$, we can combine the equilibrium data of part I with the present kinetic data to determine the separate values of k_f and k_r. For each of these coefficients we can formally write down explicit equations for the dependence of each on acidity and medium changes. Thus the rate coefficient for reaction of the enol can be written

$$k_f = k_e\, C_{H_3O^+} \tag{2a}$$
$$= k_e{}^0\, C_{H_3O^+}(f_{H_3O^+}f_E/f_{*+}) \tag{2b}$$
$$= k_e{}^0\, h_0 a_{H_2O}(f_{BH^+}f_E/f_B\, f_{+*}) \tag{2c}$$

Here k_e is the second-order rate coefficient for reaction of enol and hydronium ion and $k_e{}^0$ is its limiting value for a dilute aqueous solution. The terms $f_{H_3O^+}$, f_E and f_{*+} are activity coefficients for hydronium ion, enol and transition state (positively charged in this case), respectively. The acidity function h_0 is defined as $a_{H^+}f_B/f_{BH^+}$ where f_B and f_{BH^+} are activity coefficients for a Hammett indicator base and and its conjugate acid, respectively. Analogously, the equations for the first-order rate coefficient for reaction of the ketone are

$$k_r = k_k\, C_{H_3O^+} \tag{3a}$$
$$= k_k{}^0\, C_{H_3O^+}\, (f_{H_3O^+}k_K/f_{*+}) \tag{3b}$$
$$= k_k{}^0\, h_0 a_{H_2O}\, (f_{BH^+}f_K/f_B f_{*+}) \tag{3c}$$

where again k_k and $k_k{}^0$ are general and limiting second-order rate coefficients and where k_K is the activity coefficient of ketone.[19]

The implication of eq. 2 and 3 is that for either the forward or reverse reaction one might obtain approximately linear plots of log k_{H^+} vs. either log C_{H^+} or $-H_0$ depending on the detailed medium effects, i.e., depending on whether terms of the type $f_{H_3O^+}f_E/f_{*+}$

(19) As noted in part I, the main reaction for this system actually involves reaction of an unhydrated enol with a water molecule to give a monohydrated ketone. One might therefore plausibly include an additonal a_{H_2O} term on the right-hand side of eq. 2b and 2c. This aspect of the reaction will be discussed in detail later, but we can remark here that for the electrolyte ranges involved the term a_{H_2O} makes only a small contribution. For example, in going from pure water to 6 M sulfuric acid, a_{H_2O} changes only from 1 to 0.56.[20] Note also that the term a_{H_2O} in eq. 2c and 3c enters because these are general acid-catalyzed reactions so that the conjugate base is involved.

(20) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publishing Corp., New York, N. Y., 1950, p. 436.
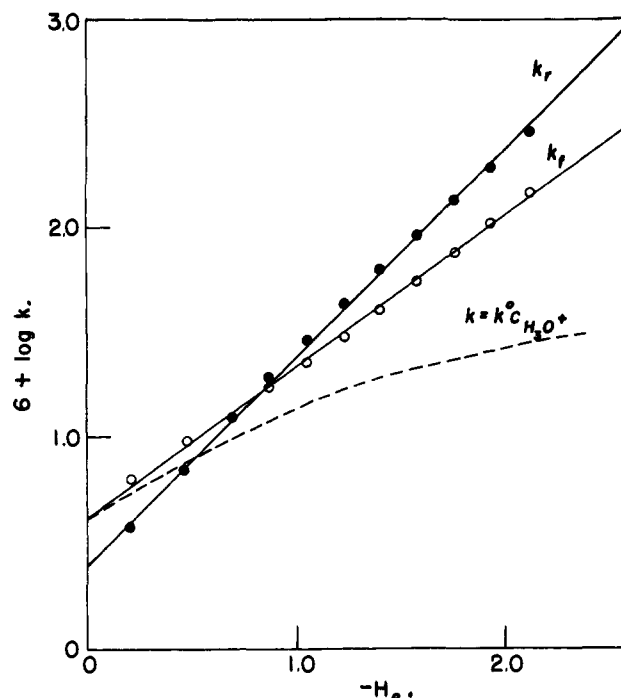

Fig. 4.—Log k_f and log k_r vs. $-H_0$ for aqueous hydrochloric acid, 25°, dotted line gives predicted curve for $k_f = k°C_{H_3O^+}$.

or $a_{H_2O}f_E f_{BH^+}/f_B f_{*+}$ are the more nearly independent of medium. The data of Table I and Fig. 2 show that experimentally the rates increase substantially faster

TABLE I

FIRST-ORDER RATE COEFFICIENTS FOR ACID-CATALYZED RATE OF APPROACH TO EQUILIBRIUM, 25°

Solvent is aqueous perchloric acid. Starred rate coefficients are for reaction of diketone; others are for reaction of mono-enol

C_{HClO_4}	$-H_0$	$7 + \log k_{H^+}$	C_{HClO_4}	$-H_0$	$7 + \log k_{H^+}$
0.26	−0.49	1.23	3.60	1.52	2.72
.43	− .25	1.41*	3.64	1.54	2.71*
.67	− .03	1.67*	4.31	1.87	2.78
.93	.17	1.78	4.59	2.05	2.90
1.16	.32	2.05	4.59	2.05	2.91
1.36	.45	2.09	4.80	2.12	3.00*
1.48	.52	2.16*	4.79	2.11	3.14
1.76	.67	2.14	5.89	2.76	3.43*
1.89	.73	2.16*	5.93	2.79	3.63
2.34	.94	2.28	5.94	2.80	3.47*
2.41	.97	2.27*	6.59	3.29	3.93
2.48	1.00	2.33	7.00	3.61	3.98

than if proportional to C_{H^+} and are much more nearly proportional to h_0.[21] This is illustrated more explicitly in Fig. 3 and 4 which gives plots of k_f and k_r against the Hammett acidity function for each of the catalyst acids. We include for comparison a plot of log k vs. C_{H^+} for one of the systems and this makes it evident that the reaction rates increase much faster than linearly with concentration of hydrogen ion.

Similar studies have been made at five temperatures in the range of from 25 to 60° for a virtually constant medium of 1.75 M aqueous perchloric acid. For each

(21) For one of the six processes under consideration, the reaction of enol with perchloric acid as catalyst, the data are almost as well fitted by log k_f vs. log C_{H^+}. Specifically the k_f values for this reaction increase linearly with concentration of acid (slope of 1.0) up to a value of about 4.8 M acid. Beyond this concentration k_f increases much more rapidly than linearly with C_{M^+}. As noted later, the best fitting slope for a log k_f vs. $-H_0$ plot for these same data is 0.45. The scatter in the k_f data is such that, at least for the concentration range of from 1 to 4.8 M acid, no obvious choice can be made between the alternative ways of plotting. For the other five reactions, however, log k vs. $-H_0$ plots are more satisfactorily linear than those with log C_{H^+}.

temperature the data were resolved into the separate k_f and k_r values and from these the second-order rate coefficients k_e and k_k were calculated by dividing k_f or k_r by the hydrogen ion concentration. Plots of log k_e and log k_k vs. $1/T$ were satisfactorily linear and led to the Arrhenius parameters which are listed in Table II.

Rate coefficient	E_A, kcal./mole	ΔS^*, e.u.
k_e (ketonization)	17.6 ± 1	−26 ± 2
k_k (enolization)	24.4 ± 1	− 4 ± 2

These activation parameters permit a more detailed analysis of the mechanism of the reaction. Recognizing that only the ketone is significantly hydrated, we can schematically indicate a spectrum of transition states
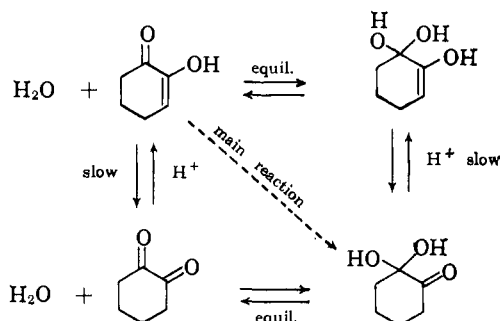
The main reaction is from unhydrated enol to hydrated ketone, i.e., the upper hydration equilibrium lies to the left and the lower one to the right. The transition state might involve any degree of carbonyl hydration. The two extremes, one appropriate to reaction via the left side of this diagram and the other appropriate to reaction via the right side are

unhydrated   hydrated
transition state   transition state
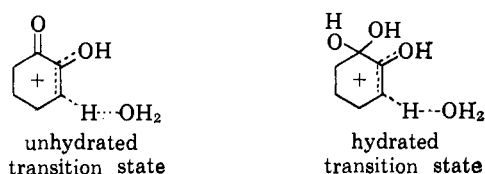
For reaction of ordinary unhydrated ketones the entropies of activation appear to be close to the value of about −10 e.u. which is the expected value for a second-order reaction when rate coefficients are expressed in liter mole^{-1} sec.$^{-1}$. As one example, the value of ΔS^* calculated for the acid-catalyzed iodination of acetone from the data of Rice and Kilpatrick[22] is −12 e.u. Since, as noted in part I, the over-all change in entropy for a normal keto–enol reaction is close to zero, the ΔS^* value for the reverse ketonization reaction should also be normal. From this standpoint the ΔS^* value for reaction of 1,2-cyclohexanedione is decidedly unusual. For the process, enol to ketone, ΔS^* is from 15 to 20 e.u. more negative than normal; for the reverse process, ΔS^* is slightly more positive than normal. The most obvious explanation for these values is that the transition state contains one comparatively firmly bound water of hydration, i.e., that the transition state is close to the right-hand one above. This is a somewhat unexpected conclusion and suggests that further examination of entropies of activation for reactions of carbonyl compounds might be profitable.

Measurements of the *relative initial rate* of reaction of enol in the solvent D_2O led to the results: For 2.5 M perchloric acid, $k_f^D/k_f^H = 0.64 \pm 0.05$; for 2.5 M hydrochloric acid, $k_f^D/j_f^H = 0.42 \pm 0.03$. The fact

(22) Rice and Kilpatrick, *J. Am. Chem. So c.*, **45**, 1401 (1923).

that reaction of the enol is faster in the solvent H_2O is consistent with the expected slow proton transfer mechanism for the enol.[23] Detailed analysis is difficult, partly because of the high concentration of the catalyst, partly because as noted earlier it is probable that the reaction involves a pre-equilibrium hydration of the enol. However, judging from Pocker's studies on acetaldehyde hydrate in H_2O and D_2O,[24] it is likely that the extent of hydrate formation will be virtually the same in the two solvents. If so, one cannot expect these relative rates to aid in distinguishing between the hydrated and unhydrated transition states mentioned earlier.

Experiments on the rate of approach to equilibrium of enol in D_2O were also made for several catalysts and the results compared with rates in H_2O. These data are even harder to analyze quantitatively than those for initial rates, the reason being that the reaction effectively stops at a pseudo-equilibrium which is difficult to characterize precisely, but the approximate results are that k_f^D/k_f^H is about 0.5 with indications of some variation with both acidity and catalyst. An approximate value of k_r^D/k_r^H for reaction of the all hydrogen form of the ketone is also derivable from these data and the average value obtained is about 1.3. Both of these values are consistent with the proposed mechanism.

We now turn to a more detailed consideration of the implication of the observed dependence of the rates on acidity. The over-all situation can best be described by saying that both the ketonization and the enolization reactions show a correlation of rate and H_0, with, however, slopes of plots of log k vs. $-H_0$ which tend to be somewhat less than unity. The average slope is approximately 0.7, but the values depend on the choice of catalyst acid and on whether the forward or reverse reaction is being considered. Table III gives a summary of the slopes.

TABLE III

Catalyst acid	d (log k)/dH_0	
	For ketoniz., k_f	For enoliz., k_r
HClO$_4$	0.5	0.8
H$_2$SO$_4$	.7	0.9
HCl	.7	1.0

Considering first the reaction of the ketone, the present data appear to differ considerably from those for the reaction of acetophenone whose reaction in perchloric acid has been reported by Zucker and Hammett very nearly to follow the concentration of hydrogen ion.[7] However, there is a real difference in the range of acidities which were employed. The Zucker–Hammett studies went only to a perchloric acid concentration of 3.6 M and even for the acidity deviation from parallelism with hydrogen ion concentration was noticeable (see Fig. 2 of ref. 7). It is a quite reasonable guess that had the acetophenone reaction been studied to substantially higher acidities it too would have shown a correlation of rate with h_0 but probably with a slope substantially below unity. The present system does differ in that the reaction actually involves a hydrated ketone, but since the evidence is that the hydration persists with little change into the transition state one can think of the reaction as the enolization of a substituted cyclohexanone. The conclusion then is that for this substituted ketone the rate of reaction in concentrated mineral acids follows h_0 although with a smaller then unity slope. This proposal is of course at variance with the Zucker–Hammett hypothesis. Since a substantial number of similar situations have

(23) F. A. Long and J. Bigeleisen, *Trans. Faraday Soc.*, **55**, 2077 (1959).
(24) Y. Pocker, *Chem. Ind.* (London), 599 (1959).

been found with other acid-catalyzed reactions the conclusion is not at all a surprising one.

One contribution to the somewhat greater influence of acid on the reaction of the cyclohexanedione is an unusually large salt effect for the ketone itself. Recognizing that the ketone is extensively hydrated and that the transition state is also, eq. 3c is directly applicable to the acidity dependence of k_r with only the stipulation that f_K and f_{*r} are actively coefficients for monohydrated species. The experiments of part I show directly that f_K increases by a factor of 13 in going from water to 6 M electrolyte. This is an abnormally large increase[25,26] and explains at least a part of the observed rate dependence.

Turning to the reaction of the enol, the discussion of mechanisms suggests that this should be thought of as a slow proton transfer reaction with, however, a preliminary hydration equilibrium. Schematically the first two steps of the mechanism are

enol + H₂O = enol·H₂O   fast equil.

enol·H₂O + H₃O⁺ = ketone·H₃O⁺ + H₂O   slow
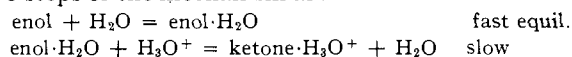
As Table IV shows, this reaction also follows h_0 with, however, a slope which again depends on catalysts and is on the average distinctly less than unity. In recent years several other reactions which are presumed to involve slow proton transfers have been found to exhibit rates which correlate fairly well with h_0; hence the present correlation is not unexpected.[27-29]

We can assume that equilibrium is established for the first step above. Using $K_{assn} = a_{E·H_2O}/a_E a_{H_2O}$ and assuming that the slow step is first order in each of the reactants we have

$$\frac{\text{rate}}{C_{Enol}} = k_f C_{H_3O^+}$$

$$= k_2^0 K_{assn} a_{H_2O}(f_{enol} f_{H_3O^+}/f_{*+})C_{H_3O^+}$$

$$= k_2^0 K_{assn} a_{H_2O}^2(f_{BH}·f_{enol}/f_B f_{*+})h_0$$

Here k_2^0 is the limiting value of the second-order rate coefficient for reaction between hydrated enol and hydronium ion, and f_{enol} is specifically the activity coefficient for the unhydrated species, i.e., the activity coefficient whose value for 6 M sodium bromide was reported in part I as 1.8. These are two reasons why the activity dependence for this reaction might be less than that for the ketone. One is the smaller, more normal increase of f_{enol} with electrolyte concentration. The other is that the activity of water enters into an additional power for this reaction because of the pre-equilibrium hydration.

From this discussion, one can conclude that rates of slow proton transfers to normal unhydrated enols will also at least approximately correlate with h_0, probably with slightly higher slopes of log k vs. $-H_0$ than in the present case. This is a particularly interesting conclusion since on the basis of studies at lower acidities, it is firmly established that the enol reaction normally exhibits general acid catalysis. It thus appears that this is a good example of a reaction which shows general catalysis at low acidities but which follows h_0 at higher acidities.

As mentioned earlier, Gold and co-workers believed at one time that decidedly specific behavior was to be expected for a general acid-catalyzed reaction studies in concentrated mineral acids. Their argument was that the new species which are encountered in strongly acidic solutions, e.g., H_2SO_4, $H_3SO_4^+$, etc., should individually be catalysts and that one might therefore expect specific correlation of rates with con-

centrations of these species. Very recently, Gold has readdressed himself to this question and has considered it in terms of expected rates of proton transfers in the solvent system, the argument being that for solutions of the mineral acids in water the proton transfers occur so rapidly (normally within about the time of one molecular vibration) that it is not particularly useful to think of the protons as being attached to a particular species but rather to think of them being involved with the entire solvent medium. On the basis of this sort of consideration Gold has concluded that one need not expect specific correlation of rates of general acid-catalyzed reactions with concentrations of a specific species in this strong acid region. The present experimental data are in accord with these ideas with, however, two reservations: (1) the media concerned here may not be sufficiently concentrated for there to be significant concentrations of "general acids" and (2) the use of a definite acidity function (as h_0) to describe the medium effects involved may be inaccurate enough to obscure any contribution of general acid catalysis to the rate.

The problem of the reaction of ketones in strongly acidic solutions has also been considered recently by Swain and Rosenberg[30] who measured the rates of racemization of D-α-phenylisocaprophenone in solutions of from 85 to 95% sulfuric acid. At these acidities the ketone is present predominantly as the conjugate acid and the slow step is the reaction of this species with a base, i.e., step I(b) of the mechanism given in the Introduction. The specific proposal was that two distinct bases are involved, H_2O and HSO_4^-, a proposal which is somewhat at variance with the above-mentioned analysis of Gold. Actually the evidence for these separate contributions is far from strong. The Swain and Rosenberg treatment is entirely in terms of concentrations, the neglect of medium effects being justified by the assumption that aqueous sulfuric acid in the range 85 to 95% is an "ideal solvent." What little evidence there is for this ideality refers only to the species water. For larger organic molecules there is direct evidence from solubility measurements of very substantial medium effects for the solvent H_2SO_4, and only fortuitous cancellations of some large changes in activity coefficients would justify the Swain and Rosenberg assumption.[31] Since in the actual Swain and Rosenberg analysis the proposed contribution from bisulfate ion as a base is never very large, it is quite doubtful whether its specific inclusion is justified. Even the proposal that the reaction involves the specific base water, although entirely plausible and intuitively satisfying, is difficult to justify in a quantitative fashion. In spite of these reservations, the major aspects of the Swain and Rosenberg discussion of the reactions of ketones in concentrated acidic solutions seem both reasonable and consistent with the data for the cyclohexanedione system. In particular, these authors' emphasis on the need for determining the medium dependence of the activity coefficients of all reactants is well justified by the markedly different activity coefficients found in the present case for the ketone and enolic species.

A different approach to acid catalysis has recently been advanced by Bunnett[35] which in essence is based

(25) F. A. Long and W. F. McDevitt, Chem. Rev., 51, 119 (1952).

(26) N. Deno and C. Perizzolo, J. Am. Chem. Soc., 79, 1345 (1957).

(27) F. A. Long and J. Schulze, ibid., 83, 3340 (1961).

(28) A. J. Kresge and Y. Chiang, ibid., 81, 5509 (1959).

(29) H. Kuivila and K. V. Nahabedian, ibid., 83, 2159, 2164, 2167 (1961).

(30) C. G. Swain and A. S. Rosenberg, ibid., 83, 2154 (1961).

(31) As one illustration of the magnitude of the medium effects which are found for concentrated sulfuric acid solutions, Brand[32] reports that 2,4-dinitrochlorobenzene, a compound known not to ionize in these solutions, is one-thirteenth as soluble in 90% sulfuric acid as in 100% acid. Similarly large effects have been reported for benzoic acid and nitrobenzene[33] and for other nitrated species.[34]

(32) C. D. Brand, personal communication.

(33) L. P. Hammett and R. Chapman, J. Am. Chem. Soc., 56, 1282 (1934).

(34) R. J. Gillespie and J. A. Leister, Quart. Rev. (London), 8, 40 (1954).

(35) J. F. Bunnett, J. Am. Chem. Soc., 83, 4956, 4968, 4973, 4978 (1961).

on the idea that the problem of activity coefficients for the reactants can continue to be avoided even while recognizing that the rates of many acid-catalyzed reactions fit neither h_0 nor C_{H^+}. The proposal is to introduce the activity of water as a rather fundamental variable and to diagnose a reaction by consideration of one or the other of two empirical parameters w and w^*. These are, respectively, the slopes of plots of log (k_{H^+}/h_0) vs. log (a_{H_2O}) and of log (k_{H^+}/C_{H^+}) vs. log (a_{H_2O}), the idea being that for any given reaction one or the other of these log–log plots will be reasonably linear. (In the event that neither plot is sensibly linear one can of course still look for acidity ranges where one or the other of the slopes is approximately constant.) In an approximate sense, ignoring the problem of non-linear plots, w is close to zero when the slope of log k_{H^+} vs. $-H_0$ is about unity, is negative when the slope is greater than unity and is positive when the slope is less than unity. Similarly, w^* is close to zero when the slope of log k_{H^+} vs. log C_{H^+} is about unity.[36] These additional parameters clearly permit a more detailed classification of acid-catalyzed reactions than do the functions h_0 and C_{H^-} alone. Classification by itself is, however, not a very exciting occupation and the much more interesting question is, does a consideration of w and w^* values give significant new insight into the problem of mechanism? Bunnett considers this question in detail and reaches the somewhat qualified conclusion that w and w^* values are frequently useful for mechanism considerations but that they occasionally lead to inconsistencies.

The data for the cyclohexanedione system cover a wide enough acidity range to permit analysis in terms of w and w^*. The characteristics of the relevant plots are listed in Table IV. Two of the most obvious features of the results are: (a) there is a significant variation of slope with catalyst; (b) for a given catalyst when one of the plots, say for w is straight, that for the other is likely to be curved. Both of these features are frequently indicated by Bunnett in his extensive tabulation of data.

We now turn to the mechanistic implications of these results. The first question is, what is the expected behavior for ketones and enols? Bunnett's Table I-1 lists data for several reactions of ketones to form enols.

(36) Bunnett actually introduces a third, related parameter, w_a, but for the present brief recapitulation we shall avoid consideration of this.

TABLE IV
SLOPES OF BUNNETT-TYPE PLOTS

Catalyst	Type (w plot)	w	Type (w* plot)	w*
For reaction of ketone, k_f				
HCl	Straight	0.0	Curve	~ -5
HClO$_4$	Straight	1.8	Curve	~ -3
H$_2$SO$_4$	Sl. curve	~ 0		
For reaction of enol, k_f				
HCl	Curved	~ 5	Str.	-3.7
HClO$_4$	Curved	~ 8	Str.	-1.1
H$_2$SO$_4$	Curved	~ 3		

The w plots are apparently usually linear with slope ranging from roughly 2 to 7; the w^* plots are only occasionally linear with slopes in the order of -1.5. Bunnett does not list slopes for ketonization of enols, but if one were to assume approximate independence of keto–enol equilibrium with electrolyte concentration then the same slopes as above might be expected for the enol reaction. The results for ketones play a large role in the development of Bunnett's Chart I which lists his conclusions on correlation of w and w^* values with mechanisms. The relevant conclusions are that a larger w than 3.3 and a larger w^* than -2 indicate that water is acting as a proton transfer agent in the slow step.

Since from other considerations it has been concluded that the keto–enol transformation of cyclohexanedione involves a monohydrated ketone and probably also a monohydrated transition state, there is no strong reason to expect this reaction to behave exactly like those of other ketones. In fact, the results are rather different from that expected from Bunnett's Chart I. For the ketone reaction the w plots are straight but w is low and is in the expected range for "water acting as a nucleophile." Furthermore the slopes for the forward and reverse reactions are so different as formally to lead one to say that water was a nucleophile for one of the directions but a "proton transfer agent" for the reverse. This is, of course, an unreasonable conclusion. We do not wish to generalize from these results at the present time and will only indicate our belief that, relative to a consideration of the mechanistic implications of the hydration equilibrium and the Arrhenius parameters, a consideration of w and w^* values does not appear to add significantly to our understanding.

The Structures of Some Aluminum Alkoxides

By V. J. Shiner, Jr., D. Whittaker and V. P. Fernandez

Molecular weight and nuclear magnetic resonance spectral measurements indicate that aluminum t-butoxide exists in solution in a number of organic solvents over a temperature range from -14 to 74° as a cyclic dimer. There was obtained no evidence for dissociation of the dimer at higher temperature or by such basic solvents as dioxane or t-butyl alcohol. Similar evidence indicates that solid aluminum isopropoxide, dissolved in organic solvents, has the tetrameric structure proposed by Bradley.[6] It has also been shown that at higher temperatures, either on melting or in solution, this material is converted into a cyclic trimer which only slowly reverts to the tetramer at lower temperatures in the supercooled melt or in solution. The nuclear magnetic resonance spectra also allow some interesting conclusions concerning the mechanism of intramolecular alkoxide exchange.

Introduction

The structures of aluminum alkoxides have been investigated by measurement of their molecular weights[1–5] and other physical properties such as dipole moment.[1] The available data have recently been summarized by Bradley.[6,7] Ulich and Nespital[1] suggested structure I for tetrameric aluminum alkoxides, such as the isopropoxide, by comparison with the structure of tetrameric thallium alkoxides suggested by Sidgwick and Sutton.[8] Mehrotra[4] suggested structure II (R =

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(5) G. Rudakoff, Kolloid-Z., 170, 62 (1960).

(6) D. C. Bradley, "Metal Alkoxides," Advances in Chem. Series, Vol. 23, American Chemical Society, Washington, D. C., 1959, p. 10.

(7) D. C. Bradley, "Progress in Inorganic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p. 303.

(8) N. V. Sidgwick and L. E. Sutton, J. Chem. Soc., 1461 (1930).