tures. Chamie[16] extended these considerations to include the necessity of a polar solvent for the formation of radiocolloids in a liquid medium. The results obtained here with mixed solvent systems bear out this proposal. As can be seen from Fig. 3, non-aqueous solvents decrease the activity which can be removed from the solution. In fact, the amount removed is almost a linear function of the composition. The lower the dipole moment of the solvent the greater is the repressing effect. Small fractions of dioxane produce large decreases whereas there is practically no effect even in high concentrations of ethanol. Bouissieres found that ethanol and acetone cut down the formation of radiocolloids of polonium.[17]

The studies on reformation indicate that once the initially formed radiocolloidal aggregates are removed from the solution further grouping is not too pronounced. This is shown particularly by the centrifugation results. The apparent reformation in the filtered samples is probably due to relations in sizes of the aggregates and the pores of the paper. The small particles not retained by the first filtration are likely to grow and be caught in a second filtration even though no new groups are formed. At first glance this seems to contradict Harrington's theory since new aggregates should be formed as a result of the disintegration of silver atoms in the filtrate but it may be that sufficient time was not allowed for this process to become appreciable.

Exposure of a sample of silver solution containing added bromide ion to strong sunlight produces no change in the amount of activity removable compared to a sample kept in the dark. This seems to indicate that either the silver in the solution is already in the metallic state or that photo-reduction of silver does not occur at such a low concentration in solution.

Bubbling hydrogen sulfide through the silver solution greatly increases the amount of activity which can be removed. This agrees with both the results from added electrolytes whose anions form insoluble silver salts and the results on other nuclides.[18,19]

As shown by the above experiments, addition of sugar to a basic solution of the carrier-free silver indicates that the silver mirror test is valid even when there is not enough silver present to form a visible mirror.

Acknowledgment.—The authors wish to thank the United States Atomic Energy Commission for the research grant which made this work possible.

(17) G. Bouissieres, R. Chastel and L. Vigneron, *Compt. rend.*, **224**, 43 (1947).

(18) M. Guillot, *ibid.*, **190**, 1553 (1930).

(19) M. Guillot, *J. chim. phys.*, **28**, 14 (1931).

KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Influence of Acidity Function and Water Concentration on the Rate of Hydrolysis of *p*-Nitrobenzophenone Diethylketal in Aqueous Ethanol

BY WARREN W. KAEDING AND LAWRENCE J. ANDREWS

RECEIVED JUNE 23, 1952

The kinetics of hydrolysis of *p*-nitrobenzophenone diethylketal in solutions of hydrochloric acid in aqueous ethanol have been investigated. The rate of ketone formation is dependent on the water concentration of the solvent and on the acidity function of the medium. These observations are consistent with a proposed reaction mechanism in which the ketal oxonium salt reacts with a water molecule in the rate-determining step. An alternate mechanism in which the oxonium salt dissociates to yield a carbonium ion which then reacts with a water molecule cannot, however, be rejected on the basis of the present evidence.

The rate of hydrolysis of benzophenone diethyl ketal in 0.02 M solutions of hydrochloric acid in aqueous ethanol does not, as one might expect, increase uniformly with increasing water concentration of the medium.[1] The reaction proceeds at a minimum rate when the solvent contains approximately 15 mole per cent. water. It has been assumed tentatively, therefore, that this reaction, like other acid-catalyzed reactions in aqueous ethanol,[2,3] is dependent in rate on the acidity function of the medium.

Since acidity function values for 0.1 M hydrochloric acid solutions are known,[4] a further investigation of the kinetics of ketal hydrolysis at this higher acid concentration has been undertaken to demonstrate quantitatively the dependence of the reaction rate on both the acidity function and water concentration of the medium. Both the *p*-chloro and *p*-nitro derivatives of benzophenone diethylketal were considered as potentially less reactive substitutes for the parent ketal for use in kinetic studies at the higher acid concentration.

p-Chloro- and *p*-nitrobenzophenone dichlorides were prepared, and a series of measurements of the kinetics of ethanolysis of the dichlorides were undertaken to assist in establishing procedures for their conversion to ketals. On the basis of these measurements, which are described in detail in the Experimental section, it was decided that only the *p*-nitro substitution deactivated the benzophenone nucleus to the degree required for a convenient rate study of ketal hydrolysis in 0.1 M acid solutions. Kinetic measurements of the ketal hydrolysis were therefore restricted to *p*-nitrobenzophenone diethylketal, which was conveniently prepared by ethanolysis of the corresponding dichloride in the presence of sodium carbonate.

(1) L. J. Andrews and W. W. Kaeding, THIS JOURNAL, **73**, 1007 (1951).

(2) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1982 (1948).

(3) J. D. Roberts and W. Watanabe, THIS JOURNAL, **72**, 4689 (1950).

(4) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1976 (1948).

Kinetics of Formation of *p*-Nitrobenzophenone from its Diethylketal.—Studies of the rate of the hydrogen chloride-catalyzed conversion of ketal to ketone in aqueous ethanol solutions were made spectrophotometrically by following the increase in optical density at 265 mμ (ketone peak) of very dilute ketal solutions as a function of time. The spectra of the ketal and ketone are discussed in the experimental section.

If the hydrolysis proceeds by the rate law

$$\frac{-\mathrm{d}[\varphi_1\varphi_2\mathrm{C(OC_2H_5)_2}]}{\mathrm{d}t} = \frac{\mathrm{d}(\varphi_1\varphi_2\mathrm{C{=}O})}{\mathrm{d}t} = k'[\varphi_1\varphi_2\mathrm{C(OC_2H_5)_2}] \qquad (1)$$

where $\varphi_1 = C_6H_5-$ and $\varphi_2 = p\text{-}NO_2-C_6H_4^-$ it can be shown[1] that k' may be evaluated from the spectrophotometric data using equation (2)

$$k' = \frac{2.303}{t_2 - t_1} \log \frac{(d_{265}\ \mathrm{m}\mu)_{t=\infty} - (d_{265}\ \mathrm{m}\mu)_{t_1}}{(d_{265})_{t=\infty} - (d_{265}\ \mathrm{m}\mu)_{t_2}} \qquad (2)$$

Data for a typical run and the corresponding k' values calculated by use of equation (2) are given in Table I, and a summary of all runs is given in Table II. Those runs of Table II (the first three) in which 99.0 mole per cent. ethanol was used as the solvent, show a direct dependence in rate on hydrogen chloride concentration. The second run and the fourth through tenth runs demonstrate the variation in rate constant with changing water concentration of the solvent at fixed hydrogen chloride concentration (0.1 M). As was noted with benzophenone diethylketal[1] the k' values for solutions of fixed hydrogen chloride concentration pass through a minimum value as the water concentration of the solvent is increased. In the present case k' reaches its lowest value in solutions approximately 80 mole per cent. in ethanol.

TABLE I

THE HYDROLYSIS OF *p*-NITROBENZOPHENONE DIETHYLKETAL IN AQUEOUS ETHANOL AT 25°

$(\mathrm{Ketal})_{t=0} = 3.146 \times 10^{-5}\ M$, (HCl) = 0.1031 M, mole per cent. H_2O = 1.0

Time, min.	d_{265} mμ	k' min.$^{-1}$ × 10^3
0	0.285	
72	.320	1.47
135	.346	1.43
213	.376	1.42
272	.395	1.40
322	.410	1.39
407	.433	1.37
506	.457	1.35
∞	.632	. .
		Av. 1.40

TABLE II

SUMMARY OF RUNS ON HYDROLYSIS OF THE KETAL AT 25°

$(\mathrm{Ketal})_{t=0} = 3.146 \times 10^{-5}\ M$

HCl, mole/liter	Solvent, mole per cent. H_2O	k', min.$^{-1}$ × 10^3
0.0516	1.0	0.802
.1031	1.0	1.45
.1547	1.0	2.41
.1031	5.6	1.42
.1031	14.1	1.25
.1031	20.6	1.20
.1031	28.7	1.36
.1031	35.5	1.61
.1031	41.6	1.94
.1031	46.3	2.28

If the reaction rate in 0.1 M hydrogen chloride solutions is controlled by the acidity function of the medium, values of $k'/(H_2O)$ should remain constant with changing water concentration of the solvent only over that range in which the acidity function remains constant. Table III lists the $k'/(H_2O)$ values for the reactions in 0.1 M hydrogen chloride solutions with the corresponding values of the acidity function,[5] H, for these solutions.

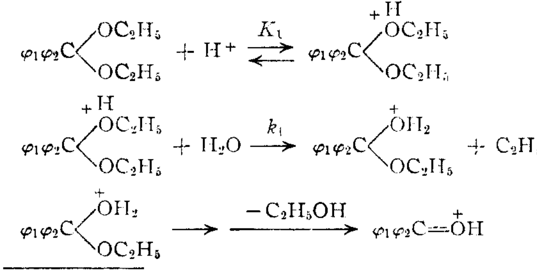
TABLE III

THE INFLUENCE OF ACIDITY FUNCTION AND WATER CONCENTRATION ON THE KETAL HYDROLYSIS RATE

Solvent, moles H_2O/liter	$k'/(H_2O)$, l. min.$^{-1}$ mole^{-1} × 10^4	H	$\log \frac{k'}{(H_2O)} - H$	$\log \frac{k'}{a_{H_2O}} - H$
11.9	1.92	−2.20	−1.52	−1.70
10.2	1.90	−2.25	−1.47	−1.67
8.20	1.97	−2.24	−1.47	−1.70
6.20	2.18	−2.23	−1.43	−1.69
4.15	2.90	−2.13	−1.41	−1.71
2.68	4.65	−2.00	−1.33	−1.67
1.01	14.0	−1.51	−1.34	−1.70
0.26	56.0	−0.81	−1.44	−1.82

For those runs in which the water concentration varies from 6–12 M while the acidity function remains constant, $k'/(H_2O)$ values are closely similar. As the water concentration of the solvent is reduced below 6 M, with corresponding increases in H values, the $k'/(H_2O)$ values also increase. A more direct indication that the reaction rate is controlled by acidity function is the fact that values of $\log k'/(H_2O) - H$, as recorded in Table III, remain constant over the entire range of solvent composition employed in these experiments.[6]

Possible Reaction Mechanisms.—It is interesting to consider the significance of these observations concerning the dependence of the ketal hydrolysis rate on both the water concentration and acidity function of the medium in terms of possible mechanisms for the reaction. Presumably the rate-determining step in the reaction to form ketone is preceded by the establishment of an equilibrium between the ketal and its oxonium salt. In the mechanism outlined in the following sequence of equations the reaction of this oxonium salt with a water molecule is chosen as the rate-determining step



(3)

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[5] Taken from the data of Braude and Stern.[4] The term H as used by Braude and Stern is equivalent to $-H_0$ as used by L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 267.

[6] *Cf.* L. P. Hammett and A. L. Deyrup, THIS JOURNAL, **54**, 2738 (1932).

All reactions subsequent to this step are considered as rapid and irreversible. The Brønsted rate equation for the rate-determining step is

$$\nu = k_1\left(\varphi_1\varphi_2\text{C}\begin{matrix}\overset{\text{H}}{\text{OC}_2\text{H}_5}\\ +\\ \text{OC}_2\text{H}_5\end{matrix}\right)(\text{H}_2\text{O})\frac{f_{\text{Ke}^+}f_{\text{H}_2\text{O}}}{f_{\text{Y}^+}} \tag{4}$$

where f_{Ke^+}, f_{Y^+} and $f_{\text{H}_2\text{O}}$ represent, respectively, the activity coefficients of the ketal oxonium salt, of the activated complex and of water. It then follows that

$$\nu = k_1K_1[\varphi_1\varphi_2\text{C}(\text{OC}_2\text{H}_5)_2](\text{H}_2\text{O})a_{\text{H}^+}\frac{f_{\text{Ke}}f_{\text{H}_2\text{O}}}{f_{\text{Y}^+}} \tag{5}$$

where f_{Ke} represents the activity coefficient of the ketal.

The acidity function is defined by Hammett[5] as

$$H_0 = -H = -\log a_{\text{H}^+}\frac{f_{\text{B}}}{f_{\text{BH}^+}} \tag{6}$$

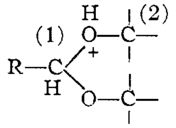
where a_{H^+} is the activity of hydrogen ion and f_{B} and f_{BH^+} are the activity coefficients, respectively, of a neutral indicator and its conjugate acid. If one assumes that $f_{\text{Ke}}f_{\text{BH}^+}/f_{\text{Y}^+}f_{\text{B}}$ remains constant with changes in medium, it follows from equations (1), (5) and (6) that

$$\log\frac{k'}{a_{\text{H}_2\text{O}}} - H = \text{constant} \tag{7}$$

It has been pointed out[7] that the assumption regarding constancy of ratios of the type $f_{\text{Ke}}f_{\text{BH}^+}/f_{\text{Y}^+}f_{\text{B}}$ is most plausible when Ke and Y^+ differ only by a proton. In the present case, in which Ke and Y^+ differ by both a proton and a water molecule this assumption may be less valid.

As indicated in Table III the experimental data conform reasonably well to equation (7) if one substitutes the molar concentration of water for $a_{\text{H}_2\text{O}}$. A more rigorous test of equation (7) was made by subtracting values[8] of $\log f_{\text{H}_2\text{O}}$ for ethanol–water solutions from the calculated values of $\log k'/(\text{H}_2\text{O}) - H$. The resultant values of $\log k'/a_{\text{H}_2\text{O}} - H$ (see last column of Table III) are closely comparable throughout the range of water concentrations.

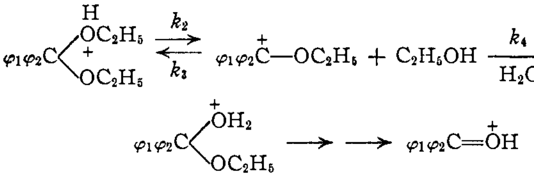
It has been demonstrated conclusively that in the acid-catalyzed hydrolysis of certain acetals the critical rupture in the oxonium salt intermediate



occurs at the C(1)-oxygen bond rather than at the C(2)-oxygen bond.[9] Similar observations have been made concerning the hydrolysis of ketals.[10,11] It is assumed that the hydrolysis of *p*-nitrobenzophenone diethylketal proceeds in this fashion. The manner in which such C–O bond ruptures occur has not, however, been clearly established.

If the mechanism presented for the ketal hydrolysis is correct, it seems likely that the displacement of ethanol from the oxonium salt by a water molecule occurs by a Walden inversion process. In support of this mechanism it should be noted that Bartlett and Brown[12] on the basis of rather convincing evidence have postulated a bimolecular displacement reaction involving a water molecule and an oxonium salt to explain certain observations concerning the *trans–cis* rearrangement of 7,8-diphenylacenaphthenediol-7,8 in acetic acid solution.

It is possible, however, that the hydrolysis proceeds through dissociation of the ketal oxonium salt to produce a carbonium ion as outlined in the sequence of equations



$$\varphi_1\varphi_2\text{C}\begin{matrix}\overset{\text{H}}{\text{OC}_2\text{H}_5}\\ +\\ \text{OC}_2\text{H}_5\end{matrix} \underset{k_3}{\overset{k_2}{\rightleftarrows}} \varphi_1\varphi_2\overset{+}{\text{C}}\text{—OC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{H}_2\text{O}]{k_4} \varphi_1\varphi_2\text{C}\begin{matrix}\overset{+}{\text{O}}\text{H}_2\\ \\ \text{OC}_2\text{H}_5\end{matrix} \longrightarrow \longrightarrow \varphi_1\varphi_2\text{C}{=}\overset{+}{\text{O}}\text{H} \tag{8}$$

As shown previously[1] a rate law consistent with this mechanism is most readily formulated by assuming the existence of a steady state with respect to the carbonium ion concentration. In this case the Brønsted rate equation based on the reaction of the carbonium ion with water is

$$\nu = k_4(\varphi_1\varphi_2\overset{+}{\text{C}}\text{—OC}_2\text{H}_5)a_{\text{H}_2\text{O}}f_{\text{c}^+}/f_{\text{w}^+} \tag{9}$$

and the steady state concentration of carbonium ion is given by the expression

$$\varphi_1\varphi_2(\overset{+}{\text{C}}\text{—OC}_2\text{H}_5) = \frac{k_2\left(\varphi_1\varphi_2\text{C}\begin{matrix}\overset{\text{H}}{\text{OC}_2\text{H}_5}\\ +\\ \text{OC}_2\text{H}_5\end{matrix}\right)f_{\text{Ke}^+}/f_{\text{z}^+}}{k_4(a_{\text{H}_5\text{O}}f_{\text{c}^+}/f_{\text{w}^+}) + k_3(a_{\text{C}_2\text{H}_5\text{OH}}f_{\text{c}^+}/f_{\text{z}^+})} \tag{10}$$

where f_{c^+}, f_{w^+} and f_{z^+} represent, respectively, the activity coefficients of carbonium ion and of the transition state intermediates in the reaction of the carbonium ion with water and of the dissociation of the ketal oxonium salt. If one assumes that f_{z^+} and f_{w^+} are equal, it may be shown using equations (6), (9) and (10) that if this mechanism is correct

$$\log\frac{k'}{a_{\text{H}_2\text{O}}} - H = \text{constant} - \log[1 + k_3a_{\text{EtOH}}/k_4a_{\text{H}_2\text{O}}] \tag{11}$$

Essentially the same expression is obtained if one assumes that the rate of carbonium ion formation is the slow step in the reaction sequence and that the rate of ketone formation is a function of the rate of carbonium ion formation and of the activities of water and ethanol in the solvent. Since the experimental results indicate that the left-hand member of equation (11) is constant, it follows that the logarithmic term of this equation must either be constant or very small over the entire range of solvent composition employed experimentally. The ratio $a_{\text{EtOH}}/a_{\text{H}_2\text{O}}$ varied appreciably and was much greater than unity in these experiments. Therefore it may be concluded that if the ketal hydrolysis

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(7) (a) F. A. Long and M. Purchase, THIS JOURNAL, **72**, 3272 (1950); (b) F. A. Long, F. B. Dunkle and W. F. McDevit, *J. Phys. Colloid Chem.*, **55**, 832 (1951).

(8) Estimated from the data of J. A. V. Butler, D. W. Thomson and W. H. Maclennan, *J. Chem. Soc.*, 678 (1931).

(9) (a) J. M. O'Gorman and H. J. Lucas, THIS JOURNAL, **72**, 5489 (1950); (b) H. K. Garner and H. J. Lucas, *ibid.*, **72**, 5497 (1950).

(10) J. Boeseken and H. G. Derx, *Rec. trav. chim.*, **40**, 519 (1921).

(11) P. H. Hermans, *Ber.*, **57B**, 824 (1924).

(12) P. D. Bartlett and R. F. Brown, THIS JOURNAL, **62**, 2927 (1940).

occurs by the carbonium ion mechanism, the ratio k_3/k_4 must be small.

Since it can be demonstrated that both mechanisms are consistent with the observation that the rate of ketal hydrolysis is controlled by the acidity function of the medium, one cannot choose with assurance between the two possible reaction paths. However, the authors are inclined to doubt, that, as required for the carbonium ion mechanism, the ratio of k_3/k_4 should be small. It should be noted that there is experimental evidence which suggests that in water solutions acetals may undergo hydrolysis by a carbonium ion path.[9,13]

Experimental

***p*-Chlorobenzophenone Dichloride.**—Sixty grams (0.28 mole) of Eastman Kodak Co. *p*-chlorobenzophenone and 62 g. (0.30 mole) of phosphorus pentachloride were refluxed for two hours in a dried mixture of 250 ml. of benzene and 75 ml. of carbon disulfide. The solvent was removed by slow distillation over a one-hour period, and the residue was distilled from a modified Claisen flask to yield 48 g. (64%) of *p*-chlorobenzophenone dichloride, b.p. 170–172° (3 mm.). A chlorine analysis indicated that this material was only about 98% pure. Further purification was accomplished by heating 37 g. of the crude dichloride with 10 g. of phosphorus pentachloride for one hour at 125–150°. Excess phosphorus pentachloride and volatile reaction products were removed by distillation up to a temperature of 150° (4 mm.). The residual liquid was distilled twice from a modified Claisen flask (recovering only middle cuts) to yield 12 g. of colorless liquid of b.p. 187° (8 mm.), $n^{24}\text{D}$ 1.6095.

Anal. Calcd. for $C_{13}H_9Cl_3$: C, 57.49; H, 3.34; equiv. wt. (based on hydrogen chloride produced on hydrolysis), 135.9. Found: C, 57.69; H, 3.41; equiv. wt., 135.5.

***p*-Nitrobenzophenone.**—A solution of 57 g. (0.31 mole) of Eastman Kodak Co. *p*-nitrobenzoyl chloride in a mixture of 250 ml. of thiophene-free benzene and 75 ml. of carbon disulfide was cooled in an ice-bath and treated slowly under constant stirring with 80 g. (1.0 mole) of anhydrous aluminum chloride. The mixture was allowed to stand at a temperature not exceeding 25° for six hours. The resultant complex was decomposed by the addition of crushed ice, and dilute hydrochloric acid. The organic matter was extracted with benzene, and the benzene solution was washed with dilute sodium hydroxide. The benzene solution was concentrated under reduced pressure to a volume of 350 ml. and decolorized. From the cooled solution (10°) 39 g. of *p*-nitrobenzophenone (55% yield) precipitated. This material was recrystallized from absolute ethanol to yield colorless needles of m.p. 138°.[14]

***p*-Nitrobenzophenone Dichloride.**—Twenty-four grams (0.11 mole) of *p*-nitrobenzophenone and 55 g. (0.26 mole) of phosphorus pentachloride were heated for two hours in a mixture of 200 ml. of benzene and 75 ml. of carbon disulfide. The solvent, phosphorus pentachloride and volatile products were removed by distillation at reduced pressure. The residual crude dichloride (27.5 g., 89% yield) crystallized on cooling. After two recrystallizations from Skellysolve B, the pure dichloride was obtained as pale yellow plates, m.p. 56.0–56.5°.

Anal. Calcd. for $C_{13}H_9NO_2Cl_2$: C, 55.34; H, 3.22; equiv. wt. (based on hydrogen chloride produced on hydrolysis), 141.1. Found: C, 55.48; H, 3.35; equiv. wt., 140.5.

Kinetics of Ethanolysis of the Dichlorides.—Solutions of the dichlorides in ethanol or alcoholic sodium ethoxide maintained at 25° were sampled from time to time. The samples were added to ice-cold absolute ethanol and were then titrated to the methyl red end-point with alcoholic solutions of sodium hydroxide or hydrogen chloride. The runs in the absence of sodium ethoxide were made using a sample of 99.2% ethanol. For the runs with sodium ethoxide, the ethanol was further dried before use by the sodium–ethyl formate procedure. As in the analogous studies with benzophenone dichloride,[1] the rate of reaction of *p*-chlorobenzophenone dichloride was found to be zero order with respect to ethoxide ion concentration. Rate constants calculated from the expression

$$k = \frac{2.303}{t} \log \frac{(\varphi_1\varphi_2\text{CCl}_2)_{t=0}}{(\varphi_1\varphi_2\text{CCl}_2)_{t=0} - (\text{Cl}^-)_t/2} \qquad (12)$$

showed no noticeable drifts during the course of individual runs. In all cases reactions were carried to at least 75% completion. In solutions of high ethoxide ion concentration a negative salt effect similar to that found with other methylene chloride derivatives[15,16] was observed.

The reaction of the *p*-nitro dichloride in ethanol also followed rate law (12). However in the presence of added sodium ethoxide a much more rapid reaction occurred. The rate constants calculated from equation (12) drifted upward markedly with time, and the solutions became deep yellow as the reaction proceeded. Attempts to isolate a ketal from the reaction product yielded only a dark brown solid of high indefinite melting point. It should be noted that both *p*-nitrobenzal chloride[15] and *p*-nitrotoluene[17] undergo unusual coupling reactions in basic media.

Rate constants for the ethanolysis reactions are summarized in Table IV. The corresponding rate constant for the ethanolysis of benzophenone dichloride at 25° is approximately 5×10^{-2} min.$^{-1}$.

TABLE IV

ETHANOLYSIS CONSTANTS AT 25° FOR THE DICHLORIDES

p-Chloro dichloride			*p*-Nitro dichloride	
(RCl_2) mole/liter	(NaOEt) mole/liter	*k*, min.$^{-1}$ × 10^2	(RCl) mole/liter	*k*, min.$^{-1}$ × 10^2
0.0110		3.2	0.0285	0.0151
.0205		3.0	.0158	.0154
.0439		2.8	.0093	.0149
.0242	0.1057	2.9		
.0236	.2114	2.4		
.0236	.4228	1.3		

***p*-Nitrobenzophenone Diethylketal.**—Spectrophotometric studies similar to those used with benzophenone dichloride were used to determine a suitable procedure for the conversion of the *p*-nitro dichloride to the ketal. Pure ketal could be produced by ethanolysis of the dichloride in solvents containing as much as 0.5% water only if the dichloride concentration was low (3×10^{-5} *M*). At higher dichloride concentration (0.02 *M*) significant quantities of ketone were formed unless the ethanol was scrupulously dried. Undoubtedly, as with benzophenone dichloride, even relatively small amounts of hydrogen chloride produced in ketal formation are sufficient to catalyze ketal hydrolysis in moist ethanol.

The following procedure was finally adopted for preparation of the ketal:

To a *well agitated* suspension of 35 g. of powdered sodium carbonate in 200 ml. of absolute ethanol (dried by the sodium–ethyl formate method) was added 4.7 g. of *p*-nitrobenzophenone dichloride. The mixture was refluxed and stirred vigorously for three hours. After filtration of the solids and removal of the alcohol by reduced pressure distillation, 5 g. of viscous oily residue remained. The oil was distilled, b.p. 155° (5 mm.), and allowed to stand at room temperature for four weeks by which time partial crystallization had occurred. The ketal was recrystallized from aqueous ethanol to yield colorless plates, m.p. 50°.

Anal. Calcd. for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36. Found: C, 67.92; H, 6.32.

Kinetics of Hydrolysis of the Ketal.—The rate studies were conducted at 25° by following the increase in d_{265} readings (measured against the appropriate solvent blank) of solutions of *p*-nitrobenzophenone diethylketal in aqueous alcoholic hydrogen chloride solutions. The details of the method and of estimating the water content of the solvent have been outlined previously in connection with studies on benzophenone diethylketal.

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(13) A. Skrabal and M. Zlaterwa, *Z. physik. Chem.*, **119**, 305 (1926).

(14) *Cf.* P. Carré, *Compt. rend.*, **144**, 34 (1907).

(15) S. C. J. Olivier and A. P. Weber, *Rec. trav. chim.*, **53**, 869 (1934).

(16) L. J. Andrews, THIS JOURNAL, **69**, 3062 (1947).

(17) O. Fischer and E. Hepp, *Ber.*, **26**, 2231 (1893).

The Absorption Spectra of the Ketal and Ketone.—In absolute ethanol solution p-nitrobenzophenone and its diethylketal showed ultraviolet absorption maxima at 265 and 282 mμ, respectively. The molecular extinction coefficients at these wave lengths (based on the expression $d = \epsilon lc$ in which c represents the molar concentration of the absorbing substance, l the light path length (1 cm.) and d the measured optical densities of the solutions) were 20,100 and 10,200, respectively. At 265 mμ the extinction coefficient of ketal solutions was 9030. The absorption of these solutions followed Beer's law.

DAVIS, CALIFORNIA

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

The Ternary System: Isopropyl Ether–HCl–H_2O[1]

BY D. E. CAMBPELL, A. H. LAURENE AND H. M. CLARK

RECEIVED APRIL 11, 1952

The ternary system isopropyl ether–HCl–H_2O has been studied at 20°. A complete ternary diagram is presented along with plots of (1) the distribution coefficient of HCl as a function of the equilibrium concentration in the aqueous phase, (2) the variation in the equilibrium concentration of HCl in the aqueous phase as a function of the initial hydrochloric acid concentration for equal volume extraction and (3) density data used for analysis of the aqueous phase in the equilibrium study. The system is of interest in connection with the extraction from hydrochloric acid solution by isopropyl ether of inorganic substances such as ferric chloride. In the light of the results obtained, it is possible to interpret the known fact that optimum conditions for extraction of inorganic chlorides exist over a narrow range of hydrochloric acid concentration.

Introduction

The ether extraction of certain metallic chlorides from aqueous hydrochloric acid solutions has been known for some time. In particular, studies have been made of the ether extraction of $AuCl_3$,[2] $GaCl_3$,[3,4] $TlCl_3$,[5] $SbCl_5$[6] and $FeCl_3$[7–9] from strong hydrochloric acid solutions.

In the course of studying the extraction of ferric chloride by isopropyl ether in this Laboratory, it appeared advisable to undertake this investigation of the ternary system, isopropyl ether, hydrogen chloride and water in order to determine the effect of hydrogen chloride on the mutual solubility of isopropyl ether and water.

Experimental

Materials.—The hydrochloric acid used was du Pont, C.P. The isopropyl ether, Eimer and Amend, C.P., alcohol free, was purified by treatment with saturated ferrous sulfate solution followed by sodium hydroxide solution. It was dried over silica gel and distilled twice over calcium hydride. The middle fraction (b.p. 67.4–67.9° uncor.) was collected for use. Its purity was checked by examination of the ultraviolet spectrum. The average of the densities of seven different lots of the purified isopropyl ether was 0.7234 with a mean deviation of a single value from the average of ±0.0001. Standard sodium hydroxide solutions were made from Eimer and Amend, reagent grade material, and were standardized with certified analytical reagent grade sulfamic acid obtained from the G. Frederick Smith Co.

Methods of Analysis.—Isopropyl ether and hydrochloric acid in the aqueous phase were determined by direct analysis. In the ethereal phase, hydrochloric acid and water were determined directly. The third component in each phase was found by difference.

All acid analyses were carried out by titration with standard sodium hydroxide using methyl orange–indigo carmine indicator (pH at transition, 4.2).

The ethereal phase was analyzed for water by the Karl Fischer titration method.[10,11]

The analysis for ether in the aqueous phase proved to be the principal problem associated with the determination of the ternary diagram. Two chemical methods of analysis are available for the quantitative determination of ether—the combustion analysis, and the Zeisel alkoxy method.[12] Since neither of these methods is feasible for solutions containing preponderant amounts of water and hydrochloric acid, recourse was made to physical methods for the determination of the ether content.

The surface tension, refractive index, density and viscosity were measured for several solutions for which the ether and hydrochloric acid concentrations were known. Measurements of the surface tension were made by the capillary rise method and were not satisfactorily reproducible because of the poor wetting characteristics of these solutions on glass. The index of refraction shows large changes with respect to hydrochloric acid concentrations, but very small changes with respect to the ether content. This property, therefore, was not used. The viscosity was found to be extremely sensitive to the quantity of ether present in the acid. The precision of the viscosity measurements, however, was not adequate for analytical purposes. Reasonable changes in density result when isopropyl ether is added to aqueous hydrochloric acid. Furthermore, density measurements can be made precisely. Thus, of the four properties examined, the density proved to be the most readily applicable to the analysis of the aqueous phase for ether.

Procedure.—Five stock solutions were prepared in all-glass dispensing bottles and kept refrigerated to maintain constant composition. For each stock solution, three liters of aqueous hydrochloric acid (approximately 11 molar) was placed in the dispensing bottle and the density and the precise concentration were determined. (All density determinations were made with calibrated 250-ml. LeChatelier specific gravity flasks at 20.00 ± 0.01°.) A predetermined quantity of freshly purified ether of known density was then added to the hydrochloric acid. After thorough mixing, samples of this solution were withdrawn for the determinations of density and the concentration of HCl. The molar ratio Et/HCl for the stock solution was calculated from equations (1) and (2), combined in equation (3).

$$1000d_a + Xd_{Et} = (1000 + X + Y)d_s \tag{1}$$

$$1000M_a = (1000 + X + Y)M_s \tag{2}$$

$$R = \frac{1000(M_a d_s - M_s d_a)}{102.17 M_s M_a} \tag{3}$$

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[1] Abstracted from portions of the Ph.D. Theses of D. E. Campbell and A. H. Laurene.

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