and constructive interest taken in the work by Professors W. D. Walters, J. P. Fugassi and D. S. McKinney is also acknowledged with thanks.

PITTSBURGH 13, PENNSYLVANIA RECEIVED JULY 13, 1950

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Formation of Benzophenone and its Diethylketal in the Ethanolysis of Diphenyldichloromethane[1]

BY L. J. ANDREWS AND W. W. KAEDING

A study of the ethanolysis of diphenyldichloromethane shows that benzophenone diethylketal is the reaction product only if the initial dichloride solution is very dilute or sodium ethoxide is present in the reaction medium. In solutions in which the dichloride concentration is 0.02 *M*, benzophenone is formed in quantitative yield.

A study of the kinetics of ethanolysis of the dichloride indicates that the reaction rate is first order with respect to dichloride concentration and independent of sodium ethoxide concentration. Kinetics studies of the hydrogen chloride catalyzed conversion of benzophenone diethylketal to the ketone in absolute ethanol support the assumption that the ketone formed on ethanolysis of the dichloride is produced by an acid catalyzed decomposition of the initially formed ketal.

Rate constants for the conversion of the ketal to ketone have been determined for various ethanol–water solvent mixtures. The constants reach a minimum value in a solvent which contains 15 mole per cent. water. The changes in the rate constants with changing solvent composition are explained in terms of the acidity functions of ethanol–water solutions of hydrogen chloride.

In connection with a study of solvolysis reactions of methylene chloride derivatives under way in this Laboratory an investigation of the ethanolysis of diphenyldichloromethane has been made. By spectrophotometric studies of the reaction products and by investigation of the reaction kinetics those conditions which favor the production of benzophenone as opposed to its diethylketal have been established.

The Ethanolysis Products.—Diphenyldichloromethane is converted in good yield in ethanol solution in the presence of excess sodium ethoxide to benzophenone diethylketal.[2] The dichloride readily undergoes hydrolysis to form benzophenone.[3] It has been shown now that at room temperature in 99.7% absolute ethanol containing no sodium ethoxide, diphenyldichloromethane reacts to form the ketal in stable condition only if the dichloride concentration of the solution is extremely small. In ethanol solutions in which the initial dichloride concentration is appreciable, benzophenone is formed.

By means of ultraviolet absorption spectrum measurements it was shown that benzophenone was formed in quantitative yield when a 0.02062 *M* solution of the dichloride in absolute ethanol stood at room temperature for 90 minutes after preparation. A sample of the resulting solution was diluted with ethanol to yield a solution (3.30×10^{-5} *M* with respect to concentration of the original dichloride), the spectrum of which showed the pronounced absorption maximum at 252 mμ ($d = 0.588$) characteristic of the benzophenone spectrum and lacking in that of its diethyl ketal. Figure 1 gives the absorption spectra of known samples of the ketone and ketal in ethanol.

The benzophenone concentration of the diluted dichloride solution was calculated from the expression $d = \epsilon lc$ using the measured optical density (d) at 252 mμ and the molecular extinction coefficient ($\epsilon = 1.74 \times 10^4$) of benzophenone at this wave length (l, the light path length, was 1 cm. in all experiments described in this report). The resultant value, 3.38×10^{-5} *M*, compared favorably with the concentration assigned to the solution on the basis of the original dichloride concentration of the parent solution.

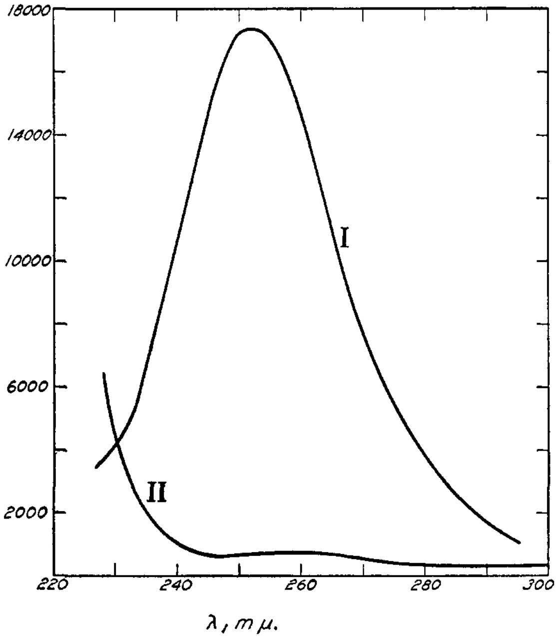

Fig. 1.—The absorption spectra of benzophenone (I) and its diethyl ketal (II) in absolute ethanol.

A very dilute solution (*ca.* 4×10^{-5} *M*) of diphenyldichloromethane was prepared by adding 1 drop (approximately 1 mg.) of the halide to 100 ml. of absolute ethanol. The optical density at 252 mμ for this solution was initially small (0.090) and diminished as the solution stood at room temperature. The optical density readings at 230 mμ decreased rapidly with time to reach a constant value (0.196) at about 80 minutes after preparation of the solution. The absorption curve after cessation of reaction was of the same shape

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[1] Presented before the Organic Division of the American Chemical Society, Chicago, Illinois, September, 1950.

[2] Mackenzie, *J. Chem. Soc.*, **69**, 985 (1896).

[3] Kekulé and Franchimont, *Ber.*, **5**, 908 (1872).

as that of benzophenone diethylketal. Assuming that the final $d_{230\ \mathrm{m}\mu}$ reading represented exclusively ketal absorption, a ketal concentration of 4.26×10^{-5} *M* was assigned to the solution ($\epsilon_{230\ \mathrm{m}\mu}$ for the ketal in ethanol is 4.60×10^3). One drop of concentrated hydrochloric acid was then added to the remaining 80 ml. of this ketal solution. This treatment initiated reaction to form benzophenone as evidenced by the rapid appearance of an absorption peak at 252 mμ. The $d_{252\ \mathrm{m}\mu}$ reading increased to a final value of 0.750, corresponding to a ketone concentration of 4.31×10^{-5} *M*.

These experiments suggest strongly that in the more concentrated dichloride solutions hydrogen chloride is produced in sufficient quantity to catalyze the formation of ketone from the ketal produced as an initial reaction product.[4] Further information concerning the mechanisms of these reactions has been obtained by kinetic studies of the dichloride ethanolysis and of the conversion of the ketal to ketone in ethanol.

Kinetics of Ethanolysis of the Dichloride.—In a series of runs using 0.02–0.05 *M* absolute ethanol solutions of diphenyldichloromethane, which in some cases contained sodium ethoxide, the rate of production of chloride ion was followed by analyzing samples of the solutions for hydrogen chloride or unreacted sodium ethoxide. The resultant data were interpreted satisfactorily on the assumption that chloride-free organic product was produced at a rate first order with respect to organic dichloride concentration and independent of ethoxide ion concentration of the medium. The first order rate constants listed in Table I were calculated from equation (1).

$$k = \frac{2.303}{t} \log \frac{(\varphi_2\mathrm{CCl_2})_{t=0}}{(\varphi_2\mathrm{CCl_2})_{t=0} - (\mathrm{Cl^-})_t/2} \qquad (1)$$

A typical run is summarized in Table II. All runs were followed to over 80% of completion of the reaction.

TABLE I

RATE CONSTANTS FOR THE ETHANOLYSIS OF DIPHENYLDICHLOROMETHANE AT 25°

$(\varphi_2\mathrm{CCl_2})_{t=0}$, mole/liter	$(\mathrm{NaOEt})_{t=0}$, mole/liter	*k*, min.$^{-1}$
0.0479	....	0.049
.0260	....	.048
.0167	....	.048
.0353	....	.045
.0211	0.0590	.047
.0204	.1220	.051
.0318	.3295	.049

TABLE II

A TYPICAL RATE RUN FOR THE ETHANOLYSIS OF DIPHENYLCHLOROMETHANE AT 25°, $(\varphi_2\mathrm{CCl_2})_{t=0} = 0.0318$

Time, min.	$(\mathrm{NaOEt})_{t=0}$ mole/liter	*k*, min.$^{-1}$
..	0.3295	...
3.4	.3193	0.051
9.9	.3043	.051
17.6	.2924	.050
24.5	.2851	.049
31.8	.2799	.048
41.0	.2754	.046
	Av.	0.049

Since these *k* values were the same for runs both with and without sodium ethoxide, conditions which should lead, respectively, to the formation of ketal and ketone, it seems demonstrated conclusively that any α-chlorodiphenylmethyl ethyl ether formed as an intermediate in these reactions must be extremely unstable with respect to reaction to form ketal or ketone.

A check on the ethanolysis constant was obtained by measuring the rate of formation of ketal in a 4.26×10^{-5} *M* ethanol solution of the dichloride by noting the change in $d_{230\ \mathrm{m}\mu}$ readings for the solutions as a function of time. Equations (2) and (3)

$$(d_{230\ \mathrm{m}\mu})_{t=\infty} = \epsilon_K[(K)_t + (D)_t] \qquad (2)$$

$$(d_{230\ \mathrm{m}\mu})_t = \epsilon_K(K)_t + \epsilon_D(D)_t \qquad (3)$$

where $(D)_t$ and $(K)_t$ represent the dichloride and ketal concentrations at time t and ϵ_D and ϵ_K are the extinction coefficients of the two compounds at 230 mμ, were used to obtain equation (4)

$$(D)_t = \frac{(d_{230\ \mathrm{m}\mu})_t - (d_{230\ \mathrm{m}\mu})_{t=\infty}}{\epsilon_D - \epsilon_K} \qquad (4)$$

On the assumption that the rate of ketal formation was dependent only on the dichloride concentration and by use of equation (4) to evaluate $(D)_t$, equation (5)

$$k = \frac{2.303}{t_2 - t_1} \log \frac{(d_{230\ \mathrm{m}\mu})_{t_1} - (d_{230\ \mathrm{m}\mu})_{t=\infty}}{(d_{230\ \mathrm{m}\mu})_{t_2} - (d_{230\ \mathrm{m}\mu})_{t=\infty}} \qquad (5)$$

was derived for use in evaluating the rate constants reported in Table III. While the rate constants thus obtained drift upward slightly with time, probably as a result of cooling during introduction of samples into the absorption cells, the average constant agrees favorably with those obtained in the runs based on measurements of the rate of chloride ion formation.

TABLE III

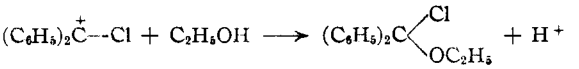
THE RATE OF CONVERSION OF THE DICHLORIDE TO THE DIETHYLKETAL AT 25°

Time,[a] min.	$d_{230\ \mathrm{m}\mu}$	*k*[b]
4.5	0.450	...
6.5	.429	0.043
11.5	.377	.048
17.5	.325	.053
23.5	.284	.056
34.5	.239	.057
41.5	.226	.057
∞	.196[c]	...
	Av.[d]	0.054

[a] Time elapsed after preparation of solution. [b] Based on $t_1 = 4.5$ min. in equation (5). [c] Final $d_{230\ \mathrm{m}\mu}$ value represents absorption of the ketal and indicates $(\varphi_2\mathrm{CCl_2})_{t=0} = 4.26 \times 10^{-5}$ *M*. [d] Based on nine readings.

A reasonable mechanism for the production of the ketal from the dichloride based on an $\mathrm{S_N1}$ process as indicated by these kinetic measurements is

$$(\mathrm{C_6H_5})_2\mathrm{CCl_2} \xrightarrow[\text{slow}]{k} (\mathrm{C_6H_5})_2\overset{+}{\mathrm{C}}\text{—Cl} + \mathrm{Cl^-}$$



$$(\mathrm{C_6H_5})_2\overset{+}{\mathrm{C}}\text{—Cl} + \mathrm{C_2H_5OH} \longrightarrow (\mathrm{C_6H_5})_2\mathrm{C}\begin{smallmatrix}\diagup\mathrm{Cl}\\ \diagdown\mathrm{OC_2H_5}\end{smallmatrix} + \mathrm{H^+}$$

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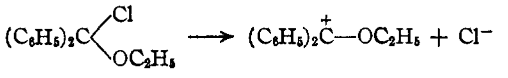
[4] The behavior of cinnamal chloride on ethanolysis has been explained in a similar manner; Andrews, THIS JOURNAL, **69**, 3062 (1947).



$$(C_6H_5)_2C(Cl)(OC_2H_5) \longrightarrow (C_6H_5)_2\overset{+}{C}{-}OC_2H_5 + Cl^-$$

$$C_6H_5)_2\overset{+}{C}{-}OC_2H_5 + C_2H_5OH \longrightarrow (C_6H_5)_2C(OC_2H_5)_2 + H^+ \tag{6}$$

This mechanism pictures all reactions subsequent to the first one as being rapid.

The pronounced reactivity of diphenyldichloromethane toward ethanol is in accord with the reactivities of similarly constituted S_N1 reacting organic halides. The ethanolysis rate constant at 25° for this compound is over ten times that for benzhydryl chloride.[5] This is consistent with the observations of Hughes[6] concerning the effect of the accumulation of halogens on the same carbon atom on solvolysis rates. Studies of the solvolysis of benzal chloride in aqueous ethanol[7] or acetone[8] and in absolute ethanol[9] indicate a much lower reactivity than that observed for diphenyldichloromethane. The enhanced reactivity of the latter can be ascribed to the high degree of resonance stabilization provided by the two phenyl groups in the carbonium ion produced in the rate-determining step.

Kinetics of the Conversion of Ketal to Ketone.—A series of kinetic measurements of the hydrogen chloride catalyzed conversion of ketal to ketone in ethanol solution were made by following the increase in optical density of the solutions at 252 mμ (ketone peak) as a function of time. In connection with these experiments a series of measurements using various ethanol–water mixtures as the solvent were made in an attempt to clarify certain features of the reaction mechanism.

On the assumption that the rate law given by equation (7) governed these reactions

$$\frac{-d[\varphi_2C(OC_2H_5)_2]}{dt} = \frac{d(\varphi_2C{=}O)}{dt} = k'[\varphi_2C(OC_2H_5)_2] \tag{7}$$

k' values were calculated from equation (8), in which the numerator and denominator of the

$$k' = \frac{2.303}{t}\log\frac{(d_{252\ m\mu})_{t=\infty}}{(d_{252\ m\mu})_{t=\infty} - (d_{252\ m\mu})_t} \tag{8}$$

logarithmic term are directly proportional to the ketal concentrations at zero time and time t, respectively.

Since the $d_{252\ m\mu}$ readings at time t included a small contribution from the low absorption of the unreacted ketal itself, the k' values originally obtained using equation (8) were corrected. The uncorrected k' values were used to estimate the ketal concentration at time t. Using the known extinction coefficient of the ketal at this wave length ($\epsilon = 500$) the $d_{252\ m\mu}$ readings were altered to represent only the ketone absorption, and k' values were recalculated. The k' values listed for a typical run (Table IV) and in the summary of runs (Table V) are thus corrected.

TABLE IV

THE CONVERSION OF KETAL TO KETONE IN ALCOHOLIC HYDROGEN CHLORIDE AT 25°

$[\varphi_2C(OC_2H_5)_2]_{t=0} = 4.96 \times 10^{-5}\ M$; (HCl) $= 0.0101\ M$ mole%$H_2O = 15.4$

Time, min.	d_{252} mμ	k', min.$^{-1}$
5	0.120	0.023
10	.182	.020
17	.273	.020
33	.449	.020
57	.605	.021
97	.718	.018
∞	.860	....
		Av. 0.020[a]

[a] Average based on fifteen readings; data of run VI.

TABLE V

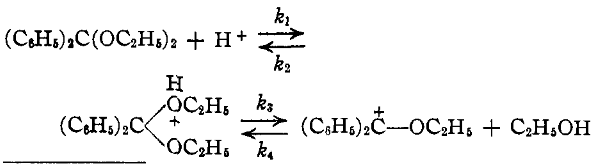
THE RATE OF CONVERSION OF KETAL TO KETONE (25°) IN AQUEOUS ETHANOL

Run	$[\varphi_2C(OEt)_2]_{t=0}$, mole/l. × 10^5	(HCl), mole/l.	Solvent, mole % H_2O	k', min.$^{-1}$
I	4.96	0.0050	0.76[a]	0.016
II	4.47	.0101	.76	.029
III	4.96	.0202	.76	.059
IV	2.98	.0202	.76	.062
V	4.86	.0202	6.5	.050
VI	4.96	.0101	15.4	.020
VII	4.96	.0202	14.8	.040
VIII	4.98	.0202	14.8	.041
IX	4.98	.0202	14.8	.044
X	4.96	.0202	24.8	.049
XI	4.98	.0202	33.0	.054
XII	4.98	.0202	46.1	.067
XIII	4.86	.0050	49.6	.021
XIV	4.86	.0101	49.6	.043
XV	4.86	.0202	49.6	.075
XVI	4.86	.0202	65.6	.194
XVII	4.96	.0202	70.8	.320

[a] This represents the water content of 99.7% ethanol.

Runs I–IV, VI–IX and XIII–XV indicate a direct dependence of the reaction rate on the hydrogen chloride concentration in any of the several alcohol–water solvent mixtures. The data for absolute ethanol solutions confirm the assumption that these reactions are sufficiently rapid to explain the formation of benzophenone through acid-catalyzed decomposition of the ketal as observed in the ethanolysis of 0.02062 *M* dichloride. Unfortunately, for dichloride solutions of this concentration the simultaneous rates of formation of ketal and ketone cannot readily be determined by spectrophotometric procedures. Therefore the possibility must not be overlooked that some of the ketone formed in dichloride ethanolysis may be derived directly by an acid-catalyzed decomposition of the proposed intermediate, α-chlorodiphenylmethyl ethyl ether.

A reasonable process for the formation of the ketone from the ketal which parallels the revision of the Hammett mechanism[10] as applied to orthoesters[11] is



$$(C_6H_5)_2C(OC_2H_5)_2 + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (C_6H_5)_2C(\overset{+}{O}HC_2H_5)(OC_2H_5) \underset{k_4}{\overset{k_3}{\rightleftharpoons}} (C_6H_5)_2\overset{+}{C}{-}OC_2H_5 + C_2H_5OH$$

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(5) Farinacci and Hammett, THIS JOURNAL, **59**, 2542 (1937).

(6) Hughes, *Trans. Faraday Soc.*, **37**, 625 (1941).

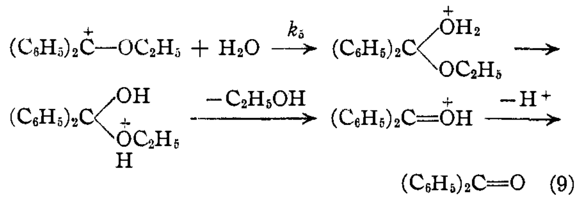
(7) Asinger and Lock, *Monatsh.*, **62**, 323 (1933).

(8) Olivier and Weber, *Rec. trav. chim.*, **53**, 869 (1934).

(9) Andrews and Linden, THIS JOURNAL, **69**, 209 (1947).

(10) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 303.

(11) Winstein and Buckles, THIS JOURNAL, **65**, 613 (1943).



$$(C_6H_5)_2\overset{+}{C}—OC_2H_5 + H_2O \xrightarrow{k_5} (C_6H_5)_2C\begin{smallmatrix}\overset{+}{O}H_2\\ OC_2H_5\end{smallmatrix} \longrightarrow (C_6H_5)_2C\begin{smallmatrix}OH\\ \overset{+}{O}C_2H_5\\ H\end{smallmatrix} \xrightarrow{-C_2H_5OH} (C_6H_5)_2C{=}\overset{+}{O}H \xrightarrow{-H^+} (C_6H_5)_2C{=}O \quad (9)$$

While this mechanism requires the presence of water for the production of ketone, it should be noted that even the small quantities of water in the absolute ethanol could be responsible for the formation of benzophenone in the quantity encountered in this series of experiments. In view of the instability of hemiacetal type compounds it is reasonable to assume that the reactions by which the ketone is formed from $(C_6H_5)_2C\begin{smallmatrix}\overset{+}{O}H_2\\ OC_2H_5\end{smallmatrix}$ are rapid and irreversible in arriving at a rate law for the over-all reaction. On the further assumptions that the equilibrium between the ketal and its oxonium salt is established rapidly ($K = k_1/k_2$), that a steady state is established with respect to the concentration of $(C_6H_5)_2C^+—OC_2H_5$ and that

$$\frac{d(\varphi_2C{=}O)}{dt} = k_5(\varphi_2\overset{+}{C}—OC_2H_5)(H_2O) \qquad (10)$$

the following rate law for ketone formation can be derived

$$\frac{d(\varphi_2C{=}O)}{dt} = \frac{Kk_3k_5(H_2O)(H^+)[\varphi_2C(OC_2H_5)_2]}{k_4(C_2H_5OH) + k_5(H_2O)} \qquad (11)$$

The observation that k' values for the formation of ketone from ketal in any chosen solvent were directly dependent on the hydrogen chloride concentration of the medium is in conformity with equation (11).

Equation (11) predicts a uniform trend in k' values with increasing water concentration of the medium provided the effective concentration of the acid catalyst is not altered as the solvent is changed.[12] Figure 2, in which k' values for 0.0202 *M* hydrogen chloride solutions are plotted against solvent composition shows that the reaction actually proceeds at a minimum rate in a solution containing 15 mole per cent. water (approximately 90 volume per cent. ethanol). The appearance of a minimum in the curve of Fig. 2 can be interpreted as a further illustration of the marked influence of changes in solvent composition on the acidic properties of hydrogen chloride in ethanol–water systems. This influence has been demonstrated by conductivity measurements[13] and is apparent in the results of rate studies of the hydrogen chloride catalyzed reactions leading to the inversion of sucrose[14] and to the formation of diethylacetal.[15]

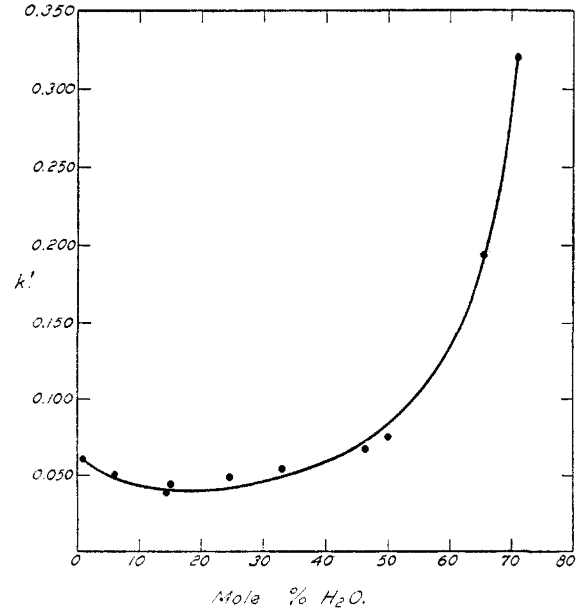


Fig. 2.—Rate constants for the conversion of ketal to ketone in 0.0202 *M* solutions of hydrogen chloride in aqueous ethanol.

A strikingly similar parallel to the results of the present study is to be found in the work of Braude and Stern[16] concerning the rates of the hydrogen chloride catalyzed rearrangement of phenylpropenylcarbinol and ethynylpropenylcarbinol in various ethanol–water mixtures. The rate constants observed for these reactions were found to vary with the acidity function[17] of the medium, which for 0.1 and 1 *M* hydrogen chloride solutions reaches a minimum value in 90 volume per cent. ethanol.

The same trends observed by Braude and Stern in the acidity function for these solutions with changes in solvent composition very likely apply to 0.02 *M* hydrogen chloride solutions. Thus the changes in k' values for the reaction of benzophenone diethylketal as influenced by changes in the solvent must parallel to a degree the proton transfer ability of the solvent. That is, the magnitude of the equilibrium constant *K*, appearing in equation (11), for the formation of the oxonium salt of the ketal is dependent on the acidity function of the solvent. The large increases in k' values as the water concentration of the solvent becomes appreciable may indicate in part the function of water itself in the reaction mechanism (equation 9).

Experimental

The Preparation of Diphenyldichloromethane.—A modification of the procedure of Cone and Robinson[18] was used. Twenty-five grams (0.14 mole) of benzophenone and 31 g. of phosphorus pentachloride (0.15 mole) were added to a dried mixture of 250 ml. of benzene and 50 ml. of carbon disulfide. After refluxing the mixture for 2 hours, the solvent was removed by slow distillation. The remaining material was distilled at reduced pressure to yield 23 g. (70% yield) of crude diphenyldichloromethane. This was fractionated

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[12] A similar prediction would apply to an alternative mechanism in which water and ethanol compete for an ethyl group in a reaction of the type

$$(C_6H_5)_2C^+—OC_2H_5 + C_2H_5OH \text{ (or } H_2O) \longrightarrow (C_6H_5)_2C{=}O + (C_2H_5)_2\overset{+}{O}H \text{ (or } C_2H_5\overset{+}{O}H_2).$$

[13] (a) Goldschmidt, *Z. physik. Chem.*, **89**, 131 (1914); (b) Bezman and Verhoek, THIS JOURNAL, **67**, 1330 (1945).

[14] Amis and Holmes, *ibid.*, **63**, 2231 (1941).

[15] (a) Adkins and Broderick, *ibid.*, **50**, 178 (1928); (b) Deyrup, *ibid.*, **56**, 60 (1934).

[16] Braude and Stern, *J. Chem. Soc.*, 1976, 1982 (1948), and previous papers in this series.

[17] Hammett, ref. 10, p. 267.

[18] Cone and Robinson, *Ber.*, 40, 2161 (1907).

through a centered rod column to yield a sample of b.p. 193° (32 mm.), $n^{22}\mathrm{D}$ 1.6015. For analysis a weighed sample of this product (about one gram) was dissolved in warm 95% ethanol and titrated with 0.5 *N* aqueous sodium hydroxide to the phenolphthalein end-point. Hydrolysis to yield two moles of hydrogen chloride per mole of organic dichloride is very rapid under these conditions. Eq. wt. based on Cl, calcd., 118.5; found, 120.0. As a check the resultant solution was made neutral and titrated with standard silver nitrate solution. Eq. wt. based on Cl, found, 120.0.

Diphenyldiethoxymethane.—The ketal of benzophenone was prepared from diphenyldichloromethane and sodium ethoxide by the method of Mackenzie[2]; m.p. 51–51.5°.

Absorption Spectra.—These were measured using a Beckman model DU spectrophotometer equipped with a water-jacketed cell housing for maintenance of constant temperature. In all cases the material in the blank cell was of the same composition as the solvent used for the substance the absorption of which was being measured. The spectra of the ketone and ketal showed no marked deviations with changes in the alcohol–water content or variations in hydrogen chloride concentration of the solvents in which they were investigated.

Absolute Ethanol.—Commercial Solvents absolute ethanol which analyzed as 99.7% ethanol by the paraffin oil test[19] was used in most of these studies. For use in the rate runs on dichloride ethanolysis in the presence of sodium ethoxide it was further dried by the sodium–ethyl formate procedure.[20] The ethanolysis rate constant for the dichloride in the "dried" ethanol without sodium ethoxide was not appreciably different from that obtained using the Commercial Solvents ethanol directly.

For the spectrophotometric rate studies the Commercial Solvents ethanol was used without drying since the experimental procedures were of such a nature that rigidly anhydrous conditions could not be maintained during the course of the runs.

Kinetics of Ethanolysis of Diphenyldichloromethane (A) Volumetric Method.—Samples of the dichloride were weighed into volumetric flasks, and ethanol or standard ethanol solutions of sodium ethoxide at the desired temperature were added to the mark. The flasks were placed in the constant temperature bath (25 ± 0.050°), and aliquots were withdrawn from time to time and added to ice-cold absolute ethanol. The samples were titrated rapidly with alcoholic sodium hydroxide or hydrogen chloride using methyl red indicator.

(B) Spectrophotometric Method.—A solution of approximately 1 mg. of dichloride per 100 ml. of ethanol (previously adjusted to 25°) was prepared using a capillary tip eye dropper, calibrated in terms of the weight of a drop of dichloride, to deliver the dichloride to the solvent. A sample of this solution was placed in an absorption cell in the spectrophotometer cell housing which was maintained at 25°. The sample was allowed to equilibrate to the cell housing temperature for a few minutes before optical density measurements were begun. The exact initial concentration of the solution was calculated from the $d_{230\ \mathrm{m}\mu}$ reading at the completion of reaction and the extinction coefficient of the ketal at this wave length. Absolute ethanol was used as a solvent blank in making optical density readings.

Kinetics of Conversion of Ketal to Ketone.—A stock stolution of diphenyldiethoxymethane in absolute alcohol was prepared. Known volumes of this solution were mixed with measured volumes of solutions of hydrogen chloride in absolute or aqueous ethanol. All solutions were adjusted to 25° before mixing. Samples of the solutions were transferred to absorption cells for measurement of $d_{252\ \mathrm{m}\mu}$ values at 25°. The solvent blank cells contained alcohol and water in the same ratio as was used in the solution investigated. The ketal solutions in aqueous or absolute ethanol were stable in the absence of hydrogen chloride as evidenced by the fact that their spectra did not alter with time.

DAVIS, CALIFORNIA RECEIVED AUGUST 11, 1950

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[19] Robertson, "Laboratory Practice of Organic Chemistry," The Macmillan Company, New York, N. Y., 1937, p. 178.

[20] Reference 19, p. 296.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Reactivities of 4- and 5-Substituted 2-Methylbenzoic Acids

BY JOHN D. ROBERTS AND JOEL A. YANCEY

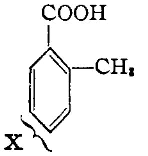
The Hammett equation has been shown to be applicable to the reactivities of a series of 4- and 5-substituted 2-methylbenzoic acids. The results may be interpreted as indicating that the steric effect of an ortho-group on the reactivity of the carboxyl group of benzoic acid can be independent of other substituent groups which might be present.

Hammett[1] has shown that the equilibrium and rate constants *k* of a large number of side-chain reactions of benzene derivatives carrying meta- or para-substituents are related to the corresponding constants k^0 for the unsubstituted compounds by the equation

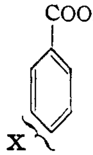
$$\log k - \log k^0 = \sigma\rho$$

The constant σ is, by definition, dependent only on the nature and position of the substituent while ρ is a reaction constant determined by the experimental conditions and the type of side-chain reaction. The equation is not generally valid for ortho-substituents which suggests the operation of a steric hindrance or proximity effect for such groups.[1]

In the present investigation, the reactivities of some 4- and 5-substituted 2-methylbenzoic acids (I) were measured and compared with those of the corresponding benzoic acids (II) to determine whether the steric influence of a methyl ortho to the reactive carboxyl group is constant when 4- or 5-substituents are introduced. The reactions employed were the ionizations of the acids in 50% water–50% ethanol (by volume) at 25.0° and the relative reactivities toward diphenyldiazomethane in absolute ethanol at 30.0°. The procedures have been described earlier in detail.[2] The experimental data are given in Table I along with the physical constants for the compounds used. The values of the logarithms of the apparent ionization constants (pK_A) of the 4- and 5-substituted 2-methylbenzoic acids are plotted against the Hammett σ-constants in Fig. 1. Here, the σ-values



I



II

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[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, Chap. VII.

[2] J. D. Roberts, R. Armstrong and E. A. McElhill, THIS JOURNAL, 71, 2923 (1949).