authors the trimethylcarbonium ion appears as a highly undiscriminating reactant, doubtless in consequence of its very great instability.

Further work is in progress on the mechanisms of reaction of β-propiolactone with these and other types of reagents.

Acknowledgment.—The authors are grateful to the B. F. Goodrich Company for a grant in support of this work and for the supply of β-propiolactone, and to Drs. T. L. Gresham and J. E. Jansen for interesting discussions.

Summary

The rates of reaction of β-propiolactone with chloride, bromide, iodide, acetate, thiocyanate, thiosulfate and hydroxyl ions have been measured and found to be of the second order. The lactone reacts with first order kinetics at 25° in aqueous solutions of perchloric acid from 0.01 to 0,05 *M*. The reaction with thiosulfate is rapid enough to be adapted to the quantitative determination of β-propiolactone in solution. Acetate ion is the only reagent of this group whose reaction with β-propiolactone in dilute solution always is attended by substantial polymerization. Except for water and hydroxyl ion, the latter of which is believed to attack the lactone by a mechanism of normal ester hydrolysis, the relative reactivities of the reagents are quite parallel to the reported reactivities of the same reagents toward the β-chloroethylethylenesulfonium ion and toward epichlorohydrin.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Kinetics and Mechanism of the Acid-Catalyzed Reaction of Diphenyldiazomethane with Ethyl Alcohol[1,2]

BY JOHN D. ROBERTS AND WARREN WATANABE

Although the acid-catalyzed solvolysis reactions of diazoacetic ester have been thoroughly studied, both from the standpoint of kinetics and of mechanism,[3] comparatively little attention has been paid to the possible analogous reactions of other substituted diazomethanes. While it was early reported that in the acid-induced decomposition of several aliphatic and aryl diazomethanes in inert solvents the rate of evolution of nitrogen gas increases with increasing acid strength,[4] no parallel measurements appear to have been carried out in polar solvents.

We have found that diphenyldiazomethane reacts smoothly and in high yield with ethyl alcohol, in the presence of a strong acid, *p*-toluenesulfonic acid, to give ethyl benzhydryl ether. Minor by-products, comprising less than

$$(C_6H_5)_2CN_2 + C_2H_5OH \xrightarrow{H^{\oplus}} C_2H_5OCH(C_6H_5)_2 + N_2$$

5% of the total yield, are diphenylketazine, $(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$, and tetraphenylethylene. In the absence of acid, diphenylketazine is obtained as the major product, together with some of the ether, through a thermal and a photochemical decomposition.[5] The presence of tetraphenylethylene appears to be due to a simultaneous acid-catalyzed reaction which proceeds in ethyl alcohol solution only to a negligible extent.

With several classes of acids the acid-catalyzed reaction with solvent is accompanied or superseded by a reaction in which the acid anion appears in the product. Thus hydrochloric acid both catalyzes the reaction with solvent and reacts directly with diphenyldiazomethane to form benzhydryl chloride. In ethyl alcohol solution (as well as in inert solvents)[5,6] carboxylic acids yield mostly the benzhydryl esters of the acids, while with strongly acidic phenols, phenol ethers are the major product.

In the present investigation the kinetics of the simple acid-catalyzed reaction as well as the more complex case of the hydrochloric acid reaction have been studied and certain aspects of the mechanisms of these reactions have been considered.

Experimental

Technique of Rate Measurements.—The rates of all reactions were followed by measuring the rate of decrease in concentration of diphenyldiazomethane by the spectrophotometric method described earlier.[7] The solvent was absolute ethyl alcohol. All measurements were made at constant ionic strength, with anhydrous lithium perchlorate as the inert salt. As a rule stock solutions of all reactants were made up and thermostated at least an hour before the start of the reaction. The reaction mixtures were prepared at zero time and rapidly transferred to a Corex cell already in place in the thermostated cell compartment of the Beckman spectrophotometer. The rate of the reaction was followed by measuring the decrease in optical density at 525 mμ with time. By this method

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[1] Supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission.

[2] Presented at the Atlantic City Meeting of the American Chemical Society, September, 1949.

[3] (a) Bredig and Ripley, *Ber.*, **40**, 4015 (1907); (b) Fraenkel. *Z. physik. Chem.*, **60**, 202 (1907); (c) Snethlage, *Z. Elektrochem.*, **18**, 539 (1912); (d) Brønsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

[4] Staudinger and Gaule, *Ber.*, **49**, 1897 (1916).

[5] Staudinger, Anthes and Pfenninger, *ibid.*, **49**, 1928 (1916).

[6] Hardegger, El Heweihi and Robinet, *Helv. Chim. Acta*, **31**, 439 (1948).

[7] Roberts, McElhill and Armstrong, THIS JOURNAL, **71**, 2923 (1949).

rates of reactions having half-lives as short as two minutes could be measured reproducibly. Within any single run the deviations from first order kinetics were usually less than 1% and for duplicate runs the precision was better than 5%. The first order rate constants, k_1, were obtained graphically. Figure 1 shows the data for a typical rate experiment. When rate measurements were made in the presence of picric acid or lithium picrate, corrections were made for the small absorption of these substances (always present in constant concentration) by assuming additivity in optical density of all the absorbing species. The reactions were followed as usual and the solutions left to stand for periods greater than ten half-lives of the diphenyldiazomethane. The residual optical density was then measured and this value subtracted from all the previous measurements; the corrected data always gave very accurate first order plots. The second order constants, k_2, in mole^{-1} liter min.$^{-1}$ were obtained by dividing the first order constants by the starting concentrations of the acid. All measurements were made at 30.0 ± 0.05°.

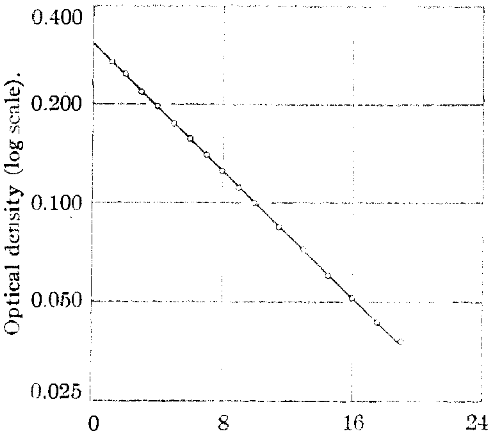

Fig. 1.—Typical rate experiment with *p*-toluenesulfonic acid as catalyst: 0.0020 *M* diphenyldiazomethane, 0.000466 *M* *p*-toluenesulfonic acid in absolute ethyl alcohol at 30.0°.

The rate runs with benzhydryl chloride were made by adding directly weighed amounts of benzhydryl chloride to the reaction mixture. Very dilute solutions of benzhydryl chloride were prepared by dissolving weighed amounts of benzhydryl chloride in measured volumes of alcohol and rapidly pipetting aliquots into the reaction mixture. Uncertainties in zero time resulting from this procedure were on the order of several seconds.

Since absorption cells used for most of the measurements were not glass-stoppered, a check was made to determine whether or not solvent evaporation increased the concentration of diphenyldiazomethane during those runs which were followed over several hours. It was found that a solution of diphenyldiazomethane in ethyl alcohol at the concentration of the rate runs did not change in optical density by more than 0.002 (less than 1% in concentration) in 150 minutes. In order to determine the reliability of the spectrophotometer at low optical densities, and to check Beer's law for low concentrations of diphenyldiazomethane, an acid-catalyzed reaction was followed through 93% of reaction. Throughout the entire range the kinetics were found to be accurately first order. In all runs the rates were followed through at least two half-lives of the diphenyldiazomethane.

Materials.—The absolute ethyl alcohol was the best commercial grade, used without further purification. Diphenyldiazomethane prepared by the method of "Organic Syntheses"[8] was kindly made available by Dr. J. C. Sheehan. While the solid was found to undergo decomposition into diphenylketazine even though kept in a refrigerator, solutions in ethyl alcohol were stable under the same conditions for several weeks. The presence of diphenylketazine in the reaction mixtures had no effect on the rates.

p-Toluenesulfonic acid monohydrate was recrystallized from alcohol–water; m. p. 102–103.5°. The use of the monohydrate at the concentrations of the rate experiments introduced less than 0.06% water. Lithium chloride was Mallinckrodt reagent grade. Picric acid was recrystallized from absolute alcohol; m. p. 121.8–122.2°. Benzhydryl chloride was prepared by passing dry hydrochloric acid into a benzene solution of benzhydrol over anhydrous calcium chloride.[9] The product was kept in a sealed tube and weighed in a small ground-glass dropping bottle.

Lithium perchlorate was prepared by the reaction of lithium carbonate, in water suspension, with perchloric acid.[10,11] The trihydrate which was obtained was recrystallized twice from water and dried over phosphorus pentoxide. This material was transferred to a flask connected through two traps to an oil-pump; the flask was evacuated to 5–10 mm. while being heated to 160° in an oil-bath. The salt did not melt, but water of hydration was removed smoothly and completely during a period of 10 hours. The anhydrous salt, which is very hygroscopic, was pulverized and stored in a vacuum desiccator over phosphorus pentoxide; m. p. 248–249° (lit. 236°).[10] Anhydrous lithium perchlorate is suitable for use as an inert salt in absolute ethyl alcohol as it is highly soluble and completely dissociated.[12]

Lithium picrate was prepared by dissolving picric acid in alcohol and adding lithium carbonate until the evolution of carbon dioxide ceased. The solution was filtered, concentrated by evaporation, and benzene was added to throw down a crystalline precipitate of lithium picrate.[13] This material was reprecipitated and extracted with benzene until the extracting solvent no longer showed the yellow color of picric acid.

Ethyl benzhydryl ether was prepared by refluxing benzhydrol with a catalytic amount of concentrated hydrochloric acid in absolute ethyl alcohol.[14]

Dissociation Constant of Picric Acid.—This was measured by the optical method of Gross and Goldstern.[15] In absolute ethyl alcohol, at 30°, and an ionic strength of 0.100, the "concentration" dissociation constant was found to be 3.5×10^{-3}. The data are given in Table I.

Product Determination.—Diphenyldiazomethane was purified by successive crystallizations from pentane and methyl alcohol; about 5 g. of the purified material was dissolved in 100 cc. of absolute ethyl alcohol and 5 cc. of 0.0233 *M* *p*-toluenesulfonic acid in absolute ethyl alcohol added. The reaction flask was cooled and the temperature of the mixture never exceeded 25°. After the reaction was complete, the excess alcohol was removed at room temperature under reduced pressure, leaving 5.7 g. of a yellow viscous liquid. On fractionation 2.6 g. of material boiling at 95–110° (0.5 mm.) was obtained; the residue, on cooling, deposited a white solid which was recrystallized from benzene–hexane (20 mg., m. p. 223–224°). This material was identified as tetraphenylethylene by comparison with an authentic sample prepared from diphenyldichloromethane[16,17] (mixed m. p. 223.5–225°). After the tetraphenylethylene had been removed the remaining residue was further fractionated, yielding about 0.6 g. more of the liquid and 10 mg. (purified yield) of a white solid, m. p. 163–164°, which was identified as diphenyl-

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[8] *Org. Syntheses*, **24**, 53 (1944).

[9] Farinacci and Hammett, This Journal, **59**, 2542 (1937).

[10] Richards and Cox, *ibid.*, **36**, 819 (1914).

[11] Berglund and Sillen, *Acta Chem. Scand.*, **2**, 116 (1948).

[12] Koch and Frivold, *Kgl. Norske Videnskab. Selskabs, Forh.*, **14**, 153 (1941); *C. A.*, **40**, 6006 (1946).

[13] Walden, Ulich and Busch, *Z. physik. Chem.*, **123**, 429 (1926).

[14] v. Kostanecki and Lampe, *Ber.*, **39**, 4019 (1906).

[15] Gross and Goldstern, *Monatsh.*, **55**, 316 (1930).

[16] "Organic Syntheses," Coll. Vol. II, p. 573.

[17] Schlenk and Bergmann, *Ann.*, **463**, 15 (1928).

TABLE I

DISSOCIATION CONSTANT OF PICRIC ACID IN ABSOLUTE ETHYL ALCOHOL AT 30°

A. Lithium picrate

Concn., moles/l.	d, cm.	D	ϵ
0.0000500	1.003	0.220, 0.220	4387
.0000714[a]	0.999	.3225, .3235	4528
.000100	1.002	.449, .448	4476
.000143[a]	1.003	.637, .637	4441
.000143	0.999	.642, .646	4508
.000200	0.999	.883, .887	4429
.000214[a]	1.002	.954, .952	4444
.000250	1.003	1.11, 1.11	4427
		Average	4455

B. Picric acid

Concn., moles/l.	d, cm.	D	ϵ	α	$K_c \times 10^{-3}$
0.000715	1.003	2.45[b]	(3416)	(0.769)	(1.83)
.000285	1.003	1.178, 1.181	4128	.929	3.47
.000214	1.002	0.895, 0.897	4179	.940	3.16
.000143	1.002	.613, .613	4278	.962	3.48
.0000952	0.999	.417, .417	4385	.986	(6.60)[c]

[a] At an ionic strength of 0.100. [b] Solution too concentrated for accurate measurement. [c] Value poor as acid is essentially completely dissociated.

ketazine. Since it has been found that tetraphenylethylene is produced rapidly and in excellent yield through an acid-catalyzed reaction in acetonitrile,[18] it is reasonable to expect that the presence of this material in the ethyl alcohol reaction is due to a similar acid-catalyzed reaction.

The liquid product was refractionated several times but could not be obtained completely pure. Successive fractions showed rising refractive indices (lowest value found, $n^{25}D$ 1.5537; ethyl benzhydryl ether, $n^{25}D$ 1.5525). The ultraviolet absorption spectrum of this product was compared with that of an authentic sample of ethyl benzhydryl ether. Both substances were found to have maxima at the same wave lengths (253.5, 259 mμ) and the form of both spectra were similar. However, the extinction coefficients of the product were somewhat higher than those of ethyl benzhydryl ether. These discrepancies in refractive index and extinction coefficients may be attributed to traces of tetraphenylethylene or diphenylketazine, both of which absorb very strongly in the ultraviolet and it has been found that a solution of pure ethyl benzhydryl ether to which was added a trace of tetraphenylethylene gave a spectrum which was closely similar in shape and extent of absorption to that of the product.

Experimental Results

The reaction is first order in diphenyldiazomethane at all acid concentrations. The second order rate constant, obtained by dividing the first order constant by the acid concentration, is constant (at constant ionic strength) over a sixfold variation in acid concentration; the reaction is thus also first order in acid (Table II).[19] Below 0.00025 *M* acid concentrations marked irregularities appeared in the second order constants, although accurate first order kinetics were always observed for diphenyldiazomethane; the values were uniformly lower and appeared to follow no regular trend. This behavior may be due to traces of basic impurities in the reagents or solvents.

TABLE II

RATE CONSTANTS WITH *p*-TOLUENESULFONIC ACID, ABSOLUTE ETHYL ALCOHOL, 30°, μ = 0.100

TsOH, moles/l.	DDM, moles/l.	k_2
0.0000503	0.00193	189
.0000754	.00296	228
.000126	.00172	274
.000251	.00193	328
.000251	.00384	329
.000334	.00170	324
.000503	.00186	328
.000754	.00186	330
.00126	.00278	338

Test-tube experiments in which visual comparisons were made against a blank showed no perceptible reaction of diphenyldiazomethane with ethyl alcohol in the presence of sodium ethoxide, diethylamine or *p*-toluidine. There thus appears to be no base catalysis.

The salt effect is positive and much larger than in the aqueous diazoacetic ester hydrolysis, in which a linear increase in rate constant with total salt concentration leads to a rate at 0.1 *M* salt about 15% higher than in infinitely dilute solution.[3d] The results for diphenyldiazomethane in ethyl alcohol, plotted in Fig. 2, show an increase of almost 50% in rate at 0.1 *M* lithium perchlorate. This heightened effect of inert salt is characteristic in the transition from water to a solvent of lower dielectric constant, and allows comparisons of only those data taken at the same ionic strength.

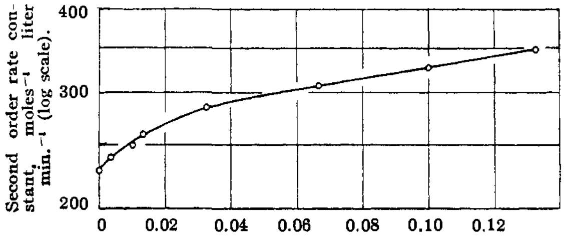

Fig. 2.—Effect of neutral salt on *p*-toluenesulfonic acid-catalyzed reaction: 0.0016 *M* diphenyldiazomethane, 0.000334 *M* *p*-toluenesulfonic acid in absolute ethyl alcohol at 30.0°.

The effect on the rate of adding increasing amounts of water to the absolute ethyl alcohol solvent is shown in Fig. 3. Similar rapid drops in rate constant upon the addition of small amounts of water to ethyl alcohol have been noted before in the alcoholysis of diazoacetic ester,[3b,20] in acid-catalyzed esterification,[21] and in the acid-catalyzed anionotropic rearrangement of propenylethynylcarbinol to hex-3-en-5-yn-2-

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(18) The kinetics of this reaction will be the subject of a later communication.

(19) The following abbreviations are used throughout this paper in tables and reaction schemes: TsOH for *p*-toluenesulfonic acid, DDM for diphenyldiazomethane, DMCl for benzhydryl chloride, DMOEt for ethyl benzhydryl ether, DDMH$^{\oplus}$ for benzhydryldiazonium ion $(C_6H_5)_2CHN_2^{\oplus}$ and DM$^{\oplus}$ for benzhydrylcarbonium ion $(C_6H_5)_2CH^{\oplus}$.

(20) (a) Bredig, *Z. Elektrochem.*, **18**, 535 (1912); (b) Millar, *Z. physik. Chem.*, **85**, 129 (1913); (c) Braune, *ibid.*, **85**, 170 (1913).

(21) Goldschmidt, *Z. Elektrochem.*, **20**, 473 (1914).

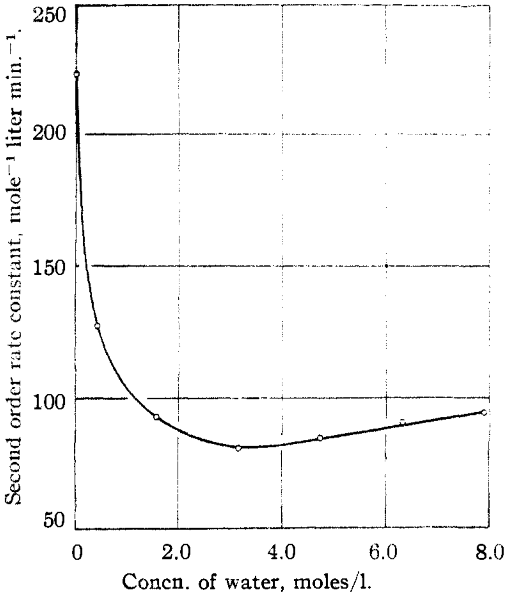

Fig. 3.—Effect of water on *p*-toluenesulfonic acid-catalyzed reaction: 0.00115 *M* diphenyldiazomethane, 0.000668 *M* toluenesulfonic acid in absolute ethyl alcohol at 30.0°; no added salt.

ol.[22] The effect has been attributed to the conversion of ethyloxonium ion to hydronium ion by reaction with water.[23] This view has been recently confirmed by the demonstration that the catalytic efficiency of strong acids in mixed ethyl alcohol–water solvents can be correlated with the proton-donating power of the solvent,[24] as expressed by Hammett's H_0 function.[25] Thus in the anionotropic rearrangement mentioned above, variations in the rate constant k with change in proportion of ethyl alcohol to water were found to run parallel to H_0, the quantity $\log k - H_0$ remaining approximately constant over the entire range. The acid-catalyzed reactions exhibiting this decelerating effect of water have all been found to show only specific hydronium ion catalysis. Consequently, the rate-determining steps have been presumed to be preceded by acid-substrate equilibria, the respective equilibrium constants of which are diminished by conversion of ethyloxonium ion to hydronium ion and the reaction rates thereby lowered. The diphenyldiazomethane reaction, on the other hand, shows general acid catalysis. The rate-determining step is therefore a proton transfer and the water effect may then be simply explained by assuming a lower catalytic efficiency for hydronium ion than for ethyloxonium ion.

$$C_2H_5\overset{\oplus}{O}H_2 + H_2O \rightleftarrows C_2H_5OH + H_3O^{\oplus}$$

General Acid Catalysis.—The reactions of diphenyldiazomethane were indicated to involve general acid catalysis by the effect on the reaction rate of substitution of deuterium for hydrogen in the hydroxyl groups of the solvent. In 82.5% alcohol–17.5% water solution with 38% of the O–H bonds replaced by O–D bonds, the rate of the toluenesulfonic acid-catalyzed reaction was 69% of the rate in the non-deuterium containing solvent. By way of contrast, the rate of reaction of diazoacetic ester in acidic aqueous solution is markedly increased by addition of deuterium oxide to the solvent.[26] Since it seems fairly generally true that the hydrogen isotope effect on specific hydronium ion-catalyzed reactions such as the diazoacetic ester decomposition is opposite in direction from that on general acid-catalyzed processes,[27] the marked rate decrease with diphenyldiazomethane is evidence of general acid catalysis. Further study of isotope effects on these reactions is currently in progress.

Some difficulty was encountered in finding a moderately weak acid suitable for the direct demonstration of general acid catalysis, as most types of acids ordinarily used for this purpose react directly with diphenyldiazomethane to give esters or ethers. Picric acid, however, showed no perceptible direct reaction to form an ether, but the reaction rate with this acid was so large that it was necessary to use concentrations comparable in magnitude to its dissociation constant. This made unreliable the classical procedure of measuring rates in buffered solutions of constant hydrogen ion concentration. An alternative, though less satisfactory, procedure was therefore adopted of measuring a series of rates with increasing concentrations of picrate ion at a constant concentration of picric acid and constant ionic strength. The results are given in Table III. The concentrations of ethyloxonium ion and undissociated picric acid were calculated from the separately measured dissociation constant of picric acid. In the transition from 85% dissociation to 4% dissociation of picric acid there was no marked decrease in the rate constant, as would be expected if ethyloxonium ion were the

TABLE III

GENERAL ACID CATALYSIS WITH PICRIC ACID, ETHYL ALCOHOL, 30°

Picric Acid = 0.000715 mole/l., μ = 0.100

Lithium picrate, mole/l.	$H^{\oplus}$, mole/l.	Calcd. concn. undissoc. acid, mole/l.	Dissoc., %	k_1, min.$^{-1}$
0.0000	0.000608	0.000107	85.0	0.224
.0333	.000065	.000650	10.0	.212
.0667	.000035	.000680	5.2	.212
.1000	.000025	.000690	3.6	.211

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(22) Braude, *J. Chem. Soc.*, 443 (1944); *cf.* also Ritchie and McBurney, This Journal, **71**, 3736 (1949).

(23) Deyrup, *ibid.*, **56**, 60 (1934).

(24) Braude and Stern, *J. Chem. Soc.*, 1982 (1948).

(25) Hammett, *Chem. Revs.*, **16**, 67 (1935).

(26) Gross, Steiner and Krauss, *Trans. Faraday Soc.*, **32**, 877 (1936).

(27) Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, pp. 143-152.

only effective catalyst. Moreover, the rate curves showed no deviations from first order kinetics through three half-lives of diphenyldiazomethane, even though in all these runs the concentration of picric acid was about half that of the diphenyldiazomethane. This shows that very little, if any, picric acid could have reacted directly with diphenyldiazomethane, for any decrease in concentration of the acid through accumulation of the picryl ether would have been reflected in a drop in the first order rate during the reaction.

The small decrease in the first order rate constant on adding 0.0333 *M* lithium picrate and the constancy of rate at higher picrate concentration can only be explained by a catalytic constant for ethyloxonium ion just slightly greater than that for undissociated picric acid. The expression which best satisfies these results is

$$k_1 = k_{H^\oplus}c_{H^\oplus} + k_{HOPic}c_{HOPic}$$

where $k_{H^\oplus}$ is the previously obtained value from *p*-toluenesulfonic acid, 330 (moles/l.)$^{-1}$ min.$^{-1}$, and k_{HOPic} is about 300 (moles/l.)$^{-1}$ min.$^{-1}$.

Further confirmation of catalysis by undissociated acid was obtained from studies on the effect of water on the rate of the picric acid reaction. Two series of runs were made—the first with 0.1 *M* lithium perchlorate and the second with 0.1 *M* lithium picrate, both at the same picric acid concentration. The rates so obtained are plotted in Fig. 4 against the water concentration. These curves may be interpreted qualitatively if it is assumed (a) that while the ratio of formation of benzhydrol to benzhydryl ethyl ether may increase as the concentration of water increases, this ratio is the same for each curve at any given water concentration, and (b) that the substitution of lithium picrate for lithium perchlorate, both completely dissociated salts in ethyl alcohol, introduces no considerable variation in ionic strength effects. First, it may be noted that when picric acid is almost completely dissociated and the catalytically active species is mainly ethyloxonium ion (Curve A, Fig. 4), the variation in rate is exactly like that observed in the *p*-toluenesulfonic acid reaction and admits of the same explanation.

Second, since the rate of reaction of diphenyldiazomethane with undissociated benzoic acid or undissociated 2,4-dinitrophenol increases with increasing water concentration[28] the initial increase in rate in Curve B (Fig. 4) may be attributed to this same effect with undissociated picric acid operating as the active agent. The subsequent drop in rate as the water concentration increases follows from the drop in concentration of undissociated picric acid (water being a stronger base than picrate ion) and results in a larger proportion of reaction through hydronium ion catalysis.

Finally, since the catalytic constant of undissociated picric acid is comparable in magnitude to that of ethyloxonium ion, and since the most logical explanation of Curve A (and Fig. 3) requires that the catalytic constant of hydronium ion be less than that of ethyloxonium ion, it follows that the catalytic constant of hydronium ion may be less than that of undissociated picric acid. That this is actually the case is borne out by the fact that (except in pure ethyl alcohol) the total rate of reaction under the conditions shown by Curve B is greater than that of Curve A. Thus repression of the ionization of picric acid increases the contribution of a faster reaction and decreases the contribution of a slower reaction. The slow reaction must be that of hydronium ion, the faster reaction that of undissociated picric acid.

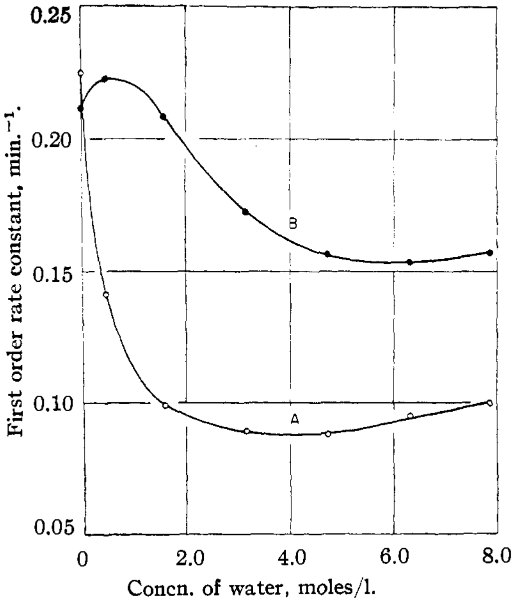

Fig. 4.—Effect of water on picric acid reaction: 0.000715 *M* picric acid, 0.0015 *M* diphenyldiazomethane: Curve A, with 0.100 *M* lithium perchlorate; Curve B, with 0.100 *M* lithium picrate.

Effect of Chloride Ion.—When chloride ion is present in the *p*-toluenesulfonic acid-catalyzed reaction, or if hydrochloric acid is used as the catalyzing acid, benzhydryl chloride is formed through a side reaction. This reaction occurs with gaseous hydrogen chloride and in ether solutions at temperatures as low as −80°.[5] There is no reaction of chloride ion alone with diphenyldiazomethane. The kinetics of the hydrochloric acid reaction are complicated by the fact that the formation of benzhydryl chloride is kinetically of higher order than the first order acid-catalyzed reaction. Furthermore, when the concentration of benzhydryl chloride becomes moderately large, its alcoholysis to regenerate hydrochloric acid occurs at a rate comparable to the over-all rate of decrease of diphenyldiazomethane. Typical rate curves showing these effects are given in Fig. 5. In Curve A (Fig. 5)

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[28] These reaction rates will be described in detail in a later paper.

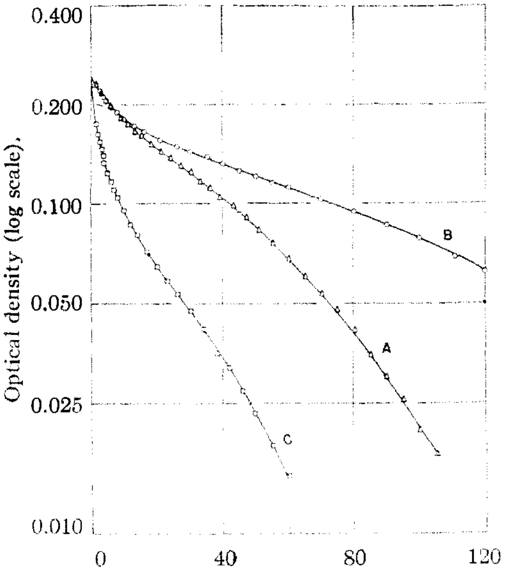
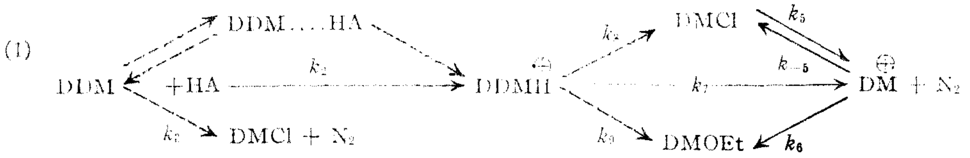
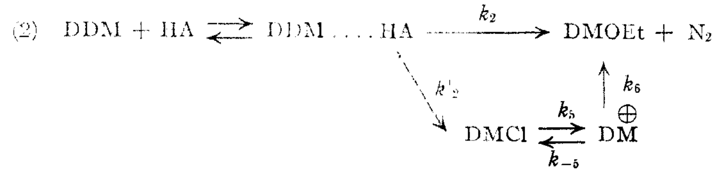


Fig. 5.—Rate measurements with HCl in absolute ethyl alcohol with 0.0016 *M* diphenyldiazomethane at 30.0°: □, 0.000699 *M* HCl; ○, 0.000233 *M* HCl; △, 0.000233 *M* HCl, 0.00043 *M* benzhydryl chloride.

the reaction mixture contained both benzhydryl chloride and hydrochloric acid and the initial rate was similar to that for Curve B in which there was an equal starting concentration of hydrochloric acid alone. This shows that there is no direct reaction between diphenyldiazomethane and benzhydryl chloride as such, but that the effect of benzhydryl chloride on diphenyldiazomethane is a secondary one, through its alcoholysis to ether and hydrochloric acid. The sum of hydrochloric acid and benzhydryl chloride for Curve A is about equal to that of hydrochloric acid in Curve C, and the similarity in the later stages of the two rate curves is good evidence that benzhydryl chloride is indeed a product of the hydrochloric acid reaction.





Discussion

The immediate consequence of general acid catalysis is to limit the number of possible mechanisms to two small groups. It is generally accepted that in a reaction showing general acid catalysis there is either a rate-determining proton transfer from the general acid to the substrate or a reversible hydrogen bonding between the acidic hydrogen of the acid and the substrate, followed by a rate-determining reaction of the complex.[29] In the latter case there are two further possibilities. First, the complex may react with a molecule of the solvent (possibly in a concerted process)[30] to lead essentially directly to the final product or, second, it may break down in a slow step into the anion of the acid (or a molecule of the solvent, if the general acid is solvated proton) and a protonated substrate, which subsequently reacts to yield the product. If the complex breaks down only in this latter fashion, then the total process is in practice indistinguishable from a direct proton transfer.

Thus for diphenyldiazomethane we consider (1) a direct (or indirect) proton transfer, leading to ionic intermediates, and (2) a reversible hydrogen bonding, leading to a complex which, without proceeding through ionic intermediates, reacts with solvent to form the product. The general acid HA may be either ethyloxonium ion or picric acid. In each of the mechanisms k_2 is the rate-determining step in the absence of chloride ion. The dashed arrows show possible alternative reaction routes. It is highly probable that, in analogy to the mechanism of diazotization of amines, the first ionic intermediate in mechanism (1) is the diazonium ion, $(C_6H_5)_2CHN_2^{\oplus}$, which may react directly with solvent (or chloride ion) or may lose nitrogen to form the relatively stable benzhydryl carbonium ion.[31] Since diazotization reactions of primary amines lead to the formation of rearrangement products, which must have come by loss of nitrogen from the diazonium ion to give the carbonium ion,[32] it is not at all unlikely that in the present reaction the benzhydryl carbonium ion is also an intermediate. Either the diazonium ion or the carbonium ion may be the immediate precursor of the ether; in the special case when benzhydryl chloride is formed, and solvolyzes, the benzhydryl carbonium ion is definitely an intermediate.[33]

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(29) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 241.

(30) Swain, THIS JOURNAL, **72**, 4578 (1950).

(31) It is also possible that the proton may be attached to one of the nitrogen atoms, as $(C_6H_5)_2C{=}N{-}NH^+$, but this would require a rearrangement of the proton to the carbon atom when nitrogen is split off, or else a further addition of a proton to the carbon atom and the loss of the proton on the nitrogen.

(32) *E. g.*, from *n*-propylamine there are obtained besides *n*-propyl alcohol, isopropyl alcohol and propylene [Siersch, *Ann.*, **144**, 140 (1867)].

(33) Bateman, Church, Hughes, Ingold and Taher, *J. Chem. Soc.*, 966, 979 (1940).

As an aid in determining which of these mechanisms represents the actual path through which the acid-catalyzed reaction proceeds, it was of importance to determine through which of several possible routes benzhydryl chloride is formed as a co-product with ethyl benzhydryl ether in the chloride ion reaction. The formation of benzhydryl chloride may have occurred in the rate-determining step, or through reaction of chloride ion in a subsequent rapid step with benzhydryl diazonium ion, or through a similar reaction with benzhydryl carbonium ion, or finally through a combination of several or all of these paths. Each of these possible routes is shown in Eqns. (1) and (2) and evidence which bears on each is discussed below.

If benzhydryl chloride is formed in a rate-determining step, then chloride ion must accelerate the initial rate of the over-all reaction. Figures 6 and 7 show that this is true in the presence of *p*-toluenesulfonic acid or with picric acid under conditions in which picric acid is almost completely dissociated. This behavior admits of two possible explanations. It may be due to a direct reaction of diphenyldiazomethane with undissociated hydrochloric acid,[34] or alternatively chloride ion may compete with ethyl alcohol in the rate-determining reaction of the hydrogen-bonded complex (k'_2 in mechanism 2) or participate in a termolecular process with solvated proton and diphenyldiazomethane (k_3 in mechanism 1).

While no final choice may be made from the present data, there are certain indications favoring reaction through undissociated hydrochloric acid. Thus, in Fig. 6 the accelerating influence of chloride ion is shown to be entirely absent at a concentration of chloride ion low enough so that there can be no appreciable molecular hydrochloric acid. Moreover, in 82.4% alcohol, in which solvent hydrochloric acid is completely dissociated even at high concentrations of chloride ion, chloride ion does not accelerate either the reaction catalyzed by *p*-toluenesulfonic acid or by dissociated picric acid (Figs. 8 and 9). The initial rate of reaction with either of these acids in the presence of excess chloride ion is approximately the same as the rate of an identical reaction, at the same ionic strength, run in the absence of chloride ion.

It would, furthermore, be reasonable to expect that if chloride ion could enter into k'_2 or k_3 for the case when the general acid is ethyloxonium ion, it should be able to participate in similar reactions when the acid catalyst is undissociated picric acid.[30] Figure 10 shows, however, that if there is a large excess of picrate ion present to repress almost completely the ionization of picric acid, there is no accelerating effect of chloride ion. Thus, in the absence of ethyloxonium ion, chloride ion does not affect the rate-determining step; this is again an indication that the fast reactions of Figs. 6 and 7 are due to molecular hydrochloric acid.

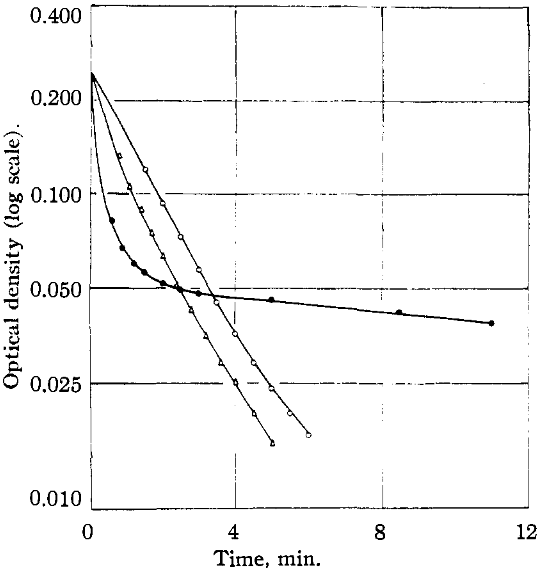

Fig. 6.—Acid-catalyzed reactions in presence of chloride ion with 0.0016 M diphenyldiazomethane and 0.00166 M *p*-toluenesulfonic acid at an ionic strength of 0.100 in absolute ethyl alcohol at 30.0°: ○, 0.00166 M lithium chloride; △, 0.010 M lithium chloride; ●, 0.100 M lithium chloride.

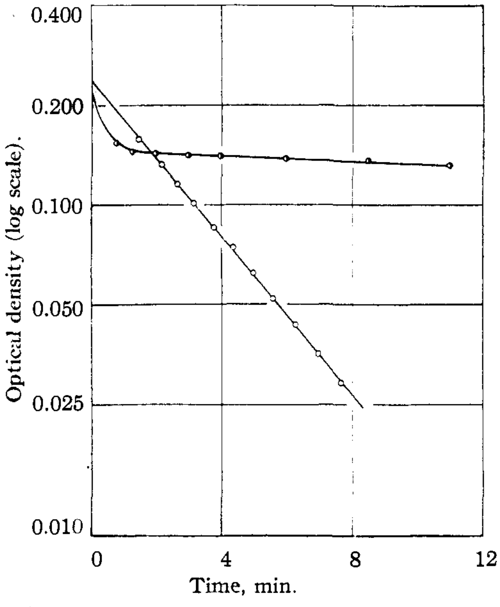

Fig. 7.—Effect of chloride ion on picric acid reaction: 0.0016 M diphenyldiazomethane, 0.000715 M picric acid, ionic strength = 0.1667 in absolute ethyl alcohol at 30.0°: ○, no chloride ion present; ◑, 0.0667 M lithium chloride.

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(34) This possibility is not as remote as it may on first sight appear. Calculations from the thermodynamic dissociation constant (0.011) of hydrochloric acid in absolute ethyl alcohol at 25°, Bezman and Verhoek, THIS JOURNAL, **67**, 1330 (1945), and the mean activity coefficient, Butler and Robertson, *Proc. Roy. Soc.* (*London*), **125A**, 694 (1929), give 0.20 for the "concentration dissociation constant" and a value of 73% dissociation for 0.1 M hydrochloric acid in absolute ethyl alcohol. At a chloride ion concentration of 0.1 M, hydrochloric acid at 0.001 M is only about 66% dissociated.

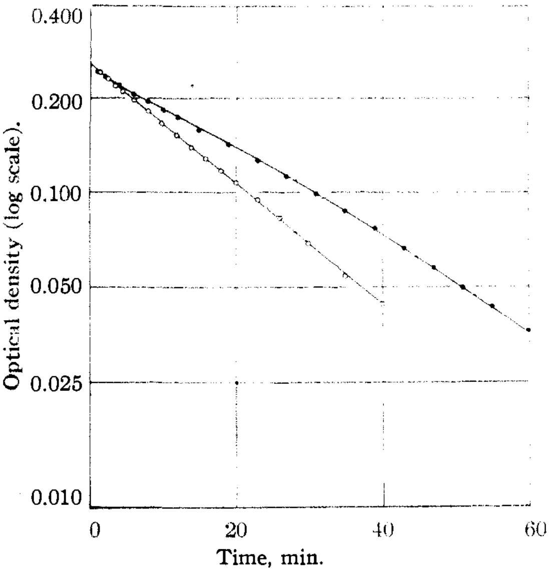


Fig. 8.—Acid-catalyzed reactions in presence of chloride ion in 82.4% ethyl alcohol–17.6% water at 30.0°: 0.0016 *M* diphenyldiazomethane, 0.000344 *M* *p*-toluenesulfonic acid, ionic strength = 0.100: O, no chloride ion; ●, 0.100 *M* lithium chloride.

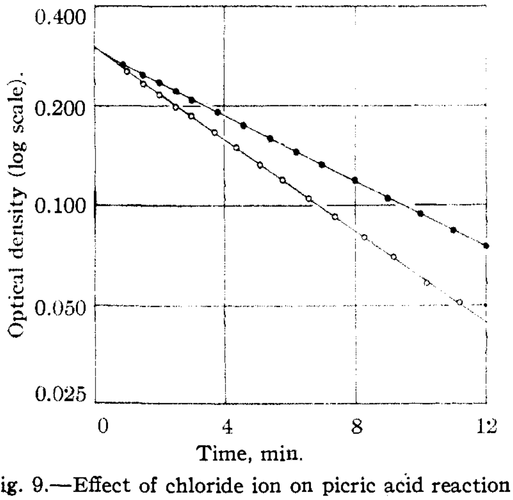


Fig. 9.—Effect of chloride ion on picric acid reaction in 82.4% ethyl alcohol–17.6% water at 30.0°: 0.0019 *M* diphenyldiazomethane, 0.000715 *M* picric acid, ionic strength = 0.1667: O, no chloride ion present; ●, 0.0667 *M* lithium chloride.

But while chloride ion as such may not, in the several cases mentioned above, enter into the rate-determining step, it must be able to participate in some fashion in a later rapid step. That this is true may be seen in Figs. 8, 9 and 10, which show that the initial rate of the chloride ion reaction, which is identical with the rate of the chloride ion-free reaction, is followed by a decrease in rate which can only occur if the catalyzing acid is effectively removed by being bound up in a fairly stable by-product. Such a reaction cannot occur through any step of

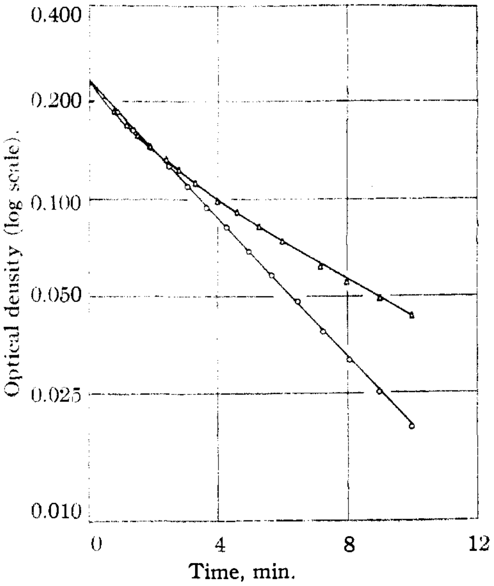


Fig. 10.—Effect of chloride ion on picric acid reaction in presence of picrate ion in absolute ethyl alcohol at 30.0°: 0.0016 *M* diphenyldiazomethane, 0.000715 *M* picric acid, ionic strength = 0.1667 *M*: O, 0.100 *M* lithium picrate, no chloride ion; Δ, 0.100 *M* lithium picrate, 0.0677 *M* lithium chloride.

Eqn. (2), but can take place through the diazonium ion or carbonium ion of Eqn. (1). Thus (1) is much to be favored over (2). Moreover in (1) it is doubtful that benzhydryl chloride is formed by a termolecular reaction among diphenyldiazomethane, ethyloxonium ion and chloride ion (as part of k_3), especially since, as mentioned above, such a reaction does not occur with picric acid. There is a further possibility that if molecular hydrochloric acid is the species responsible for the rate-accelerating effects of Figs. 6 and 7, it may act also as a general acid catalyst, with a catalytic constant much greater than that of either ethyloxonium ion or picric acid.

Reactions with Benzhydryl Chloride. Calculations of Rate Constants.—In mechanism (1) the alcoholysis of benzhydryl chloride is formulated in the generally accepted manner.[33]

$$(C_6H_5)_2CHCl \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} (C_6H_5)_2\overset{\oplus}{C}H + Cl^{\ominus} \qquad (4)$$

$$(C_6H_5)_2\overset{\oplus}{C}H + C_2H_5OH \xrightarrow{k_6} (C_6H_5)_2CHOC_2H_5 \quad H^{\oplus} \qquad (5)$$

While the rate of this reaction in ethyl alcohol has been previously measured,[35] it is also possible to obtain an independent value for k_5 by measuring the rate of decrease of diphenyldiazomethane when benzhydryl chloride is allowed to react (through its alcoholysis to ether and hydrochloric acid) with diphenyldiazomethane. Kinetics different

(35) Ward, *J. Chem. Soc.*, 2285 (1927).

from those of simple acid-catalyzed reactions are expected to be observed in this case, for the initial rate-determining step is now the formation of benzhydryl carbonium ion (4) instead of the reactions of ethyloxonium ion and hydrochloric acid with diphenyldiazomethane. If the alcoholysis of benzhydryl chloride is very slow compared with the rate of its replenishment through the reactions of ethyloxonium ion and chloride ion with diphenyldiazomethane, then the concentration of benzhydryl chloride should remain constant throughout the reaction and a zero order decrease in diphenyldiazomethane should be observed. However, the reaction is not zero order (Fig. 11) in the absence of added chloride ion, but this is understandable since the chloride ion concentration is low and it is unlikely that much replenishment of benzhydryl chloride would occur. Indeed, if we assume (a) that there is no significant replenishment of benzhydryl chloride by reaction of diphenyldiazomethane with hydrochloric acid or with ethyloxonium ion and chloride ion in a termolecular process and (b) that k_{-5} may be neglected at low chloride concentrations, we can calculate the rate of disappearance of diphenyldiazomethane to within experimental error. Letting

y = concn. of diphenyldiazomethane
x = concn. of $H^{\oplus}$
a = initial concn. of benzhydryl chloride
k_2 = rate of acid-catalyzed reaction

then

$$-\,dy/dt = k_2xy \qquad (6)$$

$$dx/dt = k_5(a - x) \qquad (7)$$

$$\ln a/(a - x) = k_5t$$

$$x = a(1 - e^{-k_5t})$$

$$dy/dt = -k_2a(1 - e^{-k_5t})y \qquad (8)$$

$$\ln\left(\frac{(dy/dt)}{yk_2a} + 1\right) = -k_5t \qquad (9)$$

In Fig. 11 are plotted data for a number of runs made with benzhydryl chloride at an ionic strength of 0.100. Values for k_5 may be calculated from Eqn. (9); the results are summarized in Table IV. In each case the slope was taken from the middle straight position of the curves. There is reasonable agreement between the value found from these calculations, 0.0090 min.$^{-1}$ at an ionic strength of 0.100, 30.0°, and those found from the direct measurement of the rate of alcoholysis (0.00345 min.$^{-1}$ at 25.0°, 0.0102 min.$^{-1}$ at 35.0°, zero ionic strength).[35]

TABLE IV

CALCULATION OF k_5 FROM DATA OF FIG. 11 AND EQ. (9)

y = 0.000960 m./l., k_2 = 330 (moles/l.)$^{-1}$ min.$^{-1}$

a, m./l.	t, min.	$dy/dt \times 10^4$	k_5
0.000443	32.00	−0.312	0.0080
.00116	18.00	−0.527	.0088
.00230	13.00	−0.788	.0090
.00500	8.45	−1.17	.0093
.00730	6.90	−1.42	.0094
.0107	5.80	−1.70	.0090
.0116	5.35	−1.76	.0093
.0214	4.00	−2.32	.0089
.0347	3.00	−2.88	.0090
.0479	2.50	−3.50	.0096

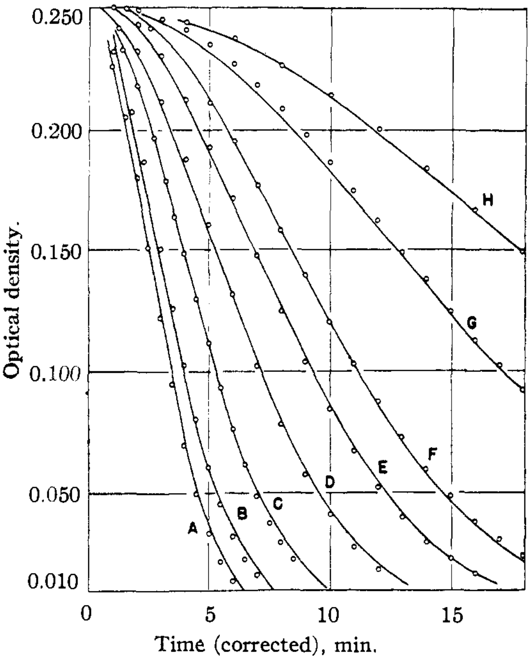


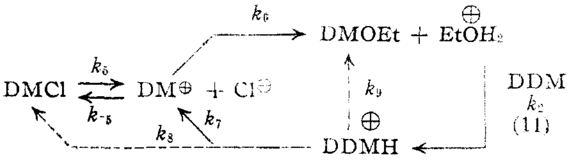
Fig. 11.—Reactions with benzhydryl chloride in absolute ethyl alcohol at 30.0° using 0.0016 M diphenyldiazomethane with ionic strength = 0.100. Benzhydryl chloride concentrations: A, 0.0479 M; B, 0.0347 M; C, 0.0214 M; D, 0.0116 M; E, 0.0073 M; F, 0.00500 M; G, 0.00230 M; H, 0.00116 M. Circles represent experimental points; solid lines, calculated curves.

The expression obtained on integrating Eqn. (8) is

$$\ln\frac{y}{b} = -k_2a\left[t - \frac{1}{k_5}(e^{-k_5t} - 1)\right] \qquad (10)$$

where b is the initial concentration of diphenyldiazomethane. Using the value of k_5 obtained above, theoretical curves for the rate of change of diphenyldiazomethane with time can be calculated from Eqn. (10). Such curves are shown in Fig. 11. The calculated curves did not match the experimental points exactly, but did give the agreement as shown when corrections on the time axis only, not exceeding ±25 seconds, were applied. The excellent fit justifies the assumptions made in deriving Eqn. (9).

At constant high chloride ion concentration the rate of disappearance of diphenyldiazomethane becomes almost exactly zero order (Fig. 12). This is in itself conclusive proof that benzhydryl chloride is indeed the product of the chloride ion reaction, for zero order kinetics would not be observed unless there is rapid and complete replenishment of benzhydryl chloride. The cycle of reactions is



(11)

with the probable supplementary route

$$\text{DDM} + \text{HCl (or } \text{EtOH}_2^{\oplus} + \text{Cl}^{\ominus}) \xrightarrow{k_3} \text{DMCl} + \text{N}_2 \quad (12)$$

Benzhydryl chloride may thus be replenished by way of the cycle (11) or by direct reaction (12) of hydrochloric acid and diphenyldiazomethane (or a termolecular reaction), by-passing the benzhydryl carbonium ion. If benzhydryl diazonium ion also leads (by k_8) to benzhydryl chloride, then again another route is afforded. We consider first replenishment through the cycle and outside the cycle neglecting the reactions of the diazonium ion except k_7. The consequences of ignoring k_8 are negligible as will be shown later. We do not believe that k_9 can be important if the reaction is to be zero order in diphenyldiazomethane since k_9 does not result with regeneration of benzhydryl chloride.

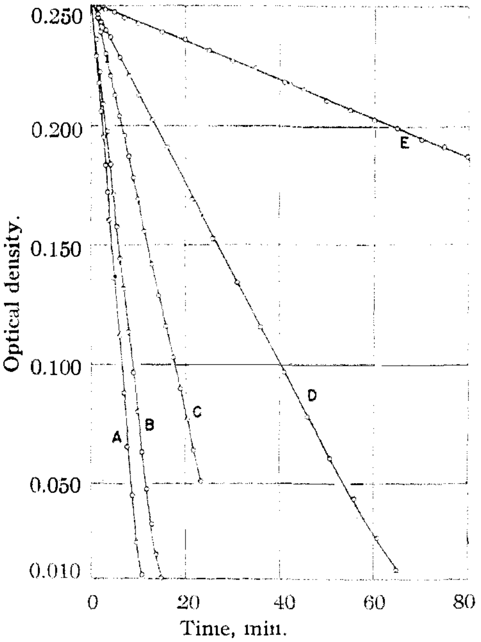


Fig. 12.—Rate measurements with benzhydryl chloride in the presence of 0.100 M chloride ion in absolute ethyl alcohol at 30.0° with 0.0016 M diphenyldiazomethane. Benzhydryl chloride concentrations: A, 0.0304 M; B, 0.0214 M; C, 0.0106 M; D, 0.00443 M; E, 0.000814 M.

The zero order kinetics require that the rate-determining step of the cycle be the hydrolysis of benzhydryl chloride and thus the production of ethyloxonium ion. Since k_9 is neglected, ethyloxonium ion can only be produced through the benzhydryl carbonium ion. Then

$$-\mathrm{d}y/\mathrm{d}t = k_6[\mathrm{DM}^{\oplus}]$$

$$\frac{\mathrm{d}[\mathrm{DMCl}]}{\mathrm{d}t} = k_{-5}[\mathrm{DM}^{\oplus}][\mathrm{Cl}^{\ominus}] - k_5[\mathrm{DMCl}] + \frac{k_3[\mathrm{Cl}^{\ominus}]}{k_3[\mathrm{Cl}^{\ominus}] + k_2}\left(-\frac{\mathrm{d}y}{\mathrm{d}t}\right) = 0$$

$$[\mathrm{DM}^{\oplus}] = \frac{k_5[\mathrm{DMCl}]}{k_{-5}\,[\mathrm{Cl}^{\ominus}] + \dfrac{k_3[\mathrm{Cl}^{\ominus}]k_6}{k_5[\mathrm{Cl}^{\ominus}] + k_2}}$$

$$-\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{k_5[\mathrm{DMCl}]}{\dfrac{k_{-5}}{k_6}\,[\mathrm{Cl}^{\ominus}] + \dfrac{k_3[\mathrm{Cl}^{\ominus}]}{k_3[\mathrm{Cl}^{\ominus}] + k_2}}$$

The term

$$\frac{k_{-5}}{k_6}\,[\mathrm{Cl}^{\ominus}] + \frac{k_3[\mathrm{Cl}^{\ominus}]}{k_3[\mathrm{Cl}^{\ominus}] + k_2}$$

may be obtained readily as the reciprocal of the slope of a plot of $\mathrm{d}y/\mathrm{d}t$ against k_5[DMCl] at constant chloride ion concentration (Fig. 13), 0.0090 being used for k_5. With 0.1 M chloride ion, the value of the term was 1.75 which if $k_2 >> k_3[\mathrm{Cl}^{\ominus}]$ (replenishment through the cycle) corresponds to k_{-5}/k_6 equal to 17.5. If on the other hand, $k_3[\mathrm{Cl}^{\ominus}] >> k_2$ (replenishment outside the cycle) then k_{-5}/k_6 assumes a minimum value of 7.5. More definite information as to the magnitudes of k_{-5}/k_6 and k_3 were obtained from a run at 0.01 M chloride ion with a equal to 0.000848 M. For this run, the calculated value of

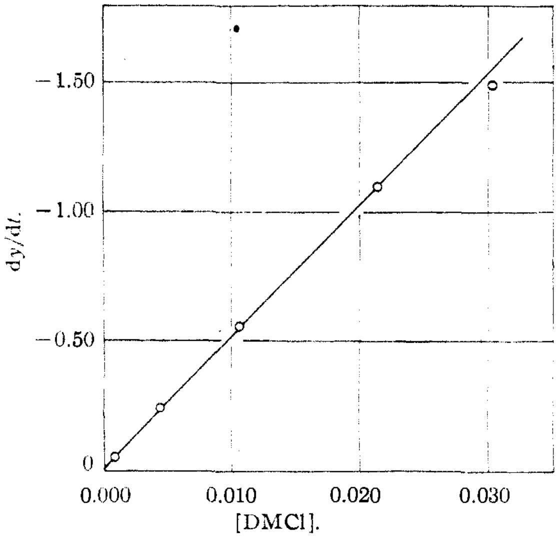


Fig. 13.—Variation of rate with benzhydryl chloride concentration at 0.100 M lithium chloride.

$$\left[\frac{k_{-5}}{k_6}\,[\mathrm{Cl}^{\ominus}] + \frac{k_3[\mathrm{Cl}^{\ominus}]}{k_3[\mathrm{Cl}^{\ominus}] + k_2}\right]$$

was 0.72. The equations for the slopes of the runs with 0.1 and 0.01 M chloride ion concentrations were solved and values of 57,300 and 8.0 were obtained for k_3 and k_{-5}/k_6, respectively.

The formation of benzhydryl chloride by k_8 in the reaction scheme (11) has essentially no effect on the calculated values of k_3 and k_{-5}/k_6. Indeed, even if $k_8 >> k_7$, the values of k_3 and k_{-5}/k_6 are not changed by as much as 1%. It is interesting to note that a twofold increase in the zero order rate results on decreasing the chloride ion concentration from 0.1 to 0.01 *M* at a constant concentration of benzhydryl chloride. Since the rate-controlling step in the zero order reaction is the rate of solvolysis of benzhydryl chloride, chloride ion can influence the rate only by participating in the equilibrium of Eqn. (4). The increase in rate is therefore a spectacular instance of the mass law effect on Eqn. (4) (with k_{-5}/k_6 equal to 8.0) which has been noted previously in other cases and interpreted as compelling evidence for the S_N1 mechanism for alkyl halide hydrolysis.[33] Analysis of the effect in the present case is of course complicated by the presence of a double sequence of reactions: the simple solvolysis of benzhydryl chloride and the accompanying cycle of reactions in which diphenyldiazomethane participates. However, if Eqn. (4) were not an equilibrium step the zero order rate should show no dependence on chloride ion concentration; that the rate is actually affected can only be the result of the S_N1 mechanism.

Summary

1. In ethyl alcohol solution diphenyldiazomethane reacts with ethyl alcohol in the presence of an acid catalyst to form ethyl benzhydryl ether. Kinetic studies by a spectrophotometric method have established that this reaction is subject to general acid catalysis. The effects on the rate of inert salt and of increasing concentrations of water in the ethyl alcohol solvent, both when the catalyst is solvated hydrogen ion and undissociated picric acid, have been determined.

2. In the presence of chloride ion, benzhydryl chloride is produced in a side reaction. With ethyloxonium ion in absolute alcohol the rate of disappearance of diphenyldiazomethane is accelerated by chloride ion; this effect vanishes in aqueous alcohol or if undissociated picric acid is the catalyst. The acceleration in rate is attributed to either a third order reaction involving diphenyldiazomethane, ethyloxonium ion, and chloride ion, or more probably a reaction between undissociated hydrochloric acid and diphenyldiazomethane.

Cambridge 39, Mass. Received April 10, 1950

[Contribution from the Department of Chemistry, Duke University]

The Action of Elementary Fluorine upon Organic Compounds. XV. Fluorine and Cobaltic Fluoride as Fluorinating Agents for Ketones[1]

By Fred F. Holub[2] and Lucius A. Bigelow

This paper reports the results of a qualitative comparison of cobaltic fluoride with elementary fluorine as fluorinating agents for aliphatic ketones. Earlier work[3] here has shown that the direct fluorination of acetone over copper screen at about 100° and a molar reaction ratio of 6:1:18 yielded CF_3COCF_3 and CH_2FCOCH_3, together with CF_4, COF_2, CF_3COF and $(COF)_2$, about half the product being cleaved and a fifth of it self-condensed. This indicated that a good yield of the perfluoroketone should be obtained by using the milder cobaltic fluoride as the fluorinating agent.

Accordingly, acetone was fluorinated over cobaltic fluoride in a Fowler reactor (Fig. 2) at 60°, 0.2 mole per hour, and dilution (N_2) 1:10. Under such mild conditions only a trace of CF_4 was formed, but nevertheless the ketone was completely cleaved into COF_2, CHF_3, CH_3F, CH_2F_2, CH_3COF and CH_2FCOF. The appearance of CH_3F and CH_3COF in nearly equal amounts showed that part of the ketone had been cleaved before any hydrogen was substituted, and since no more highly fluorinated acyl fluorides than CH_2FCOF were formed, the molecule must have been split completely before half the hydrogen had been replaced, but no perfluoroketone was formed.

This quite unexpected result was shown to be general by fluorinating methyl ethyl ketone and diethyl ketone at 80 and 105°, respectively, under the same general conditions. Both were completely cleaved, the former yielding COF_2, CHF_3, impure CH_2F_2, $CH_3CHF_2 + CHF_2CHF_2$, CHF_2CH_2F, and CH_2FCOF; and the latter COF_2, $CF_3CHF_2 + (?)CH_3CF_3$, $CH_3CHF_2 + CHF_2CHF_2$, and CHF_2CH_2F, as could be predicted, but essentially nothing else. The unsymmetrical ketone was split mostly on the side of the carbonyl group next to the ethyl group and yielded much CHF_2CH_2F, while the symmetrical one as expected gave neither CH_2F_2 nor CH_2FCOF.

The general nature of the direct fluorination of acetone referred to above[3] was established by fluorinating methyl ethyl ketone over a copper shot packing in an improved reactor (Fig. 1)

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[1] This paper has been constructed from the Doctorate Thesis presented by Fred F. Holub to Duke University in March, 1949.

[2] Allied Chemical and Dye Corporation Fellow, 1946–1947. Present address: du Pont Experimental Station, Wilmington, Delaware. This project was also sponsored in part by the Naval Research Laboratory and aided by the Duke University Research Council. Grateful acknowledgment is hereby made for this material assistance.

[3] Fukuhara and Bigelow, This Journal, 63, 788 (1941).