somewhat low, hence their pressures are probably too high. Fraser[15] has expressed the opinion that the pressures recorded by Harteck are probably too low, because of too large an orifice area in his cell. It is therefore probable that the true vapor pressures lie somewhere between the values of Harteck and of Bauer and Brunner. The results reported here confirm this view. For example, calculation of the vapor pressure of gold at 1200°K. yields the following values; Bauer and Brunner, 4.5×10^{-8}; Hall, 2.1×10^{-9}; Harteck, 1.9×10^{-10}.

Because of the large number of consistent points which were obtained over a wide temperature range and under equilibrium conditions, it is believed that the present study has established reliable values for the vapor pressure and heat of vaporization of gold.

The results obtained for the gold–copper solid solutions are less certain, but the general trend of the activity coefficients is similar to that calculated from the data of Wagner and Englehardt[16] and Weibke and Quadt,[17] who measured the e.m.f.'s of electrolytic cells with electrodes of pure copper and gold–copper alloys of various compositions. Unfortunately, internal inconsistencies in their data and lack of agreement between the respective authors make quantitative comparisons very difficult. Nevertheless, the curve of Fig. 3 agrees roughly with that to be expected from calculations based on their data, which were obtained at lower temperatures.

The activity coefficient curve of Fig. 3 has been drawn so as to conform to Henry's law at the low gold compositions. The experimental points obtained at the two lowest compositions studied lie well below the curve, thus demanding some explanation. It is probable that the evaporation of copper affects the gold vapor at these concentrations, reducing the quantity of the latter which reaches the collector plate. This could conceivably occur if the copper partial pressures were high enough. The existing data for copper are ambiguous, but a recent report by Dushman[18] as well as some exploratory work by the author has indicated that the vapor pressure of copper may be several orders of magnitude higher than that of gold at the temperatures considered. The ratio between the partial pressures at the low gold compositions would be even greater, leading to a qualitative prediction of copper partial pressures which might be high enough to cause interference with the gold vapor.

The results of the present investigation show that the radioactive tracer technique is well adapted to the investigation of the vapor pressures of pure metals over large temperature ranges. In view of the large discrepancies which exist between the data of different investigators for many of the common metals, it is apparent that re-examination of these values is a fruitful field for future study.

Acknowledgments.—The author is greatly indebted to Professors E. R. Parker and Leo Brewer of the Mineral Technology Division and Chemistry Department, respectively, of the University of California, and to Dr. K. K. Kelley of the Pacific Experiment Station, U. S. Bureau of Mines, for their helpful advice and unfailing encouragement.

Summary

1. Measurements using the Knudsen method of equilibrium effusion, with radioactive gold as a tracer, have established the heat of vaporization of gold at the absolute zero as 84.6 ± 0.8 kcal. per mole, corresponding to a vapor pressure of 2.1×10^{-9} atm. at 1200°K.

2. The results of the measurements indicate that the radioactive tracer technique is well suited to the determination of metallic vapor pressures.

3. Gold–copper solid solutions were found to exhibit negative deviations from ideality. The low values obtained for the activity coefficients at the low gold compositions may be a result of interference by the copper vapor.

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(15) Fraser, "Molecular Rays," Cambridge University Press, 1931.

(16) Wagner and Englehardt *Z. physik. Chem.*, **A159**, 241 (1932).

(17) Weibke and Quadt, *Z. Elektrochem.*, **45**, 715 (1939).

(18) Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 98.

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The Kinetics and Mechanism of the Reaction of Diphenyldiazomethane and Benzoic Acid in Ethanol[1]

BY JOHN D. ROBERTS, WARREN WATANABE AND ROBERT E. MCMAHON

The reactions of substituted diazomethanes with carboxylic acids have been studied mainly in nonhydroxylic solvents. In one of the earliest papers published on this subject, Staudinger and Gaule[2] reported that a variety of diazomethane derivatives reacted with substituted acetic acids in cumene at rates which depended on the strengths of the acids. Similar observations were later made by Norris and Strain[3] with di-*p*-tolyldiazomethane and substituted benzoic acids in benzene, toluene and ethyl acetate solutions. The reaction of diazoacetic ester in aprotic solvents with various carboxylic acids has also been investigated and found to be roughly second-order in acid[4,5] in

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

(2) Staudinger and Gaule, *Ber.*, **49**, 1897 (1916).

(3) Norris and Strain, THIS JOURNAL, **57**, 187 (1935).

(4) (a) Brønsted and Bell, *ibid.*, **53**, 2478 (1931); (b) Hartman, Hochanadel and Bobalek, *ibid.*, **68**, 2071 (1946).

(5) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 288–289.

contrast to the reaction of di-*p*-tolyldiazomethane with benzoic acid in toluene, which has been reported[3] to be accurately first-order in acid.[6] In non-hydroxylic solvents, the principal (if not the exclusive) reaction products are the carboxylic esters. Thus, diphenyldiazomethane reacts with benzoic acid in ether to give a 92% yield of benzhydryl benzoate[7] and recently Hardegger, El Heweihi and Robinet[8] found that a large variety of carboxylic acids react similarly in non-hydroxylic solvents to form the corresponding benzhydryl esters in high yields.

The rates of reaction of diphenyldiazomethane with a number of substituted benzoic acids in ethanol have been correlated with acid strength[9] and employed to determine Hammett[5] σ (substituent) constants.[9,10] In the present work, the kinetics and mechanism of the reaction of benzoic acid with diphenyldiazomethane in ethanol have been studied as part of an investigation of hydrogen-isotope effects on organic reactions.

At the outset, the reaction in ethanol was found to be more complex than in non-hydroxylic solvents in that benzhydryl benzoate was formed only to the extent of 60% and the remainder of the diazo compound was converted to benzhydryl ethyl ether. Nonetheless, the over-all reaction was strictly first-order in diphenyldiazomethane at all benzoic acid concentrations and, if benzoic acid was present in large excess so that pseudo first-order kinetics were observed, the slopes of the straight line plots of the logarithm of diphenyldiazomethane concentration *vs.* time were accurately dependent on the initial acid concentration. Since there is no reaction of diphenyldiazomethane with ethanol in the absence of benzoic acid, the over-all reaction velocity may be represented as the sum of two terms—the first representing a reaction which consumes benzoic acid (k_2') and, the second, a reaction which does not consume benzoic acid (k_2'').

$$-\,d[\mathrm{DDM}]/dt = k_2[\mathrm{HOBz}][\mathrm{DDM}] = (k_2' + k_2'')[\mathrm{HOBz}][\mathrm{DDM}] \quad (1)$$

where HOBz = benzoic acid

DDM = diphenyldiazomethane

Eq. (1) may be converted to a different form (2) in terms of the initial benzoic acid concentration, *a*, the initial diphenyldiazomethane concentration, *b*, and the concentration of the products, *x*. At all benzoic acid concentrations

$$\frac{dx}{dt} = k_2\left(a - \frac{k_2'x}{k_2}\right)(b - x) \qquad (2)$$

the reaction rates followed Eq. (2) closely and the values of k_2'/k_2 obtained from the rate data agreed, within the experimental error, with the values calculated from acidimetric determinations of the benzoic acid actually consumed.

Addition of water to the solvent led to increased rate of reaction and plot of k_2 against water concentration showed an almost linear relationship (Fig. 1). The increase in rate is in all likelihood due to two factors: (a) an increase in the dielectric constant ϵ of the medium and (b) an increase in the ionization of benzoic acid with the emergence of an oxonium ion-catalyzed decomposition of diphenyldiazomethane of the type studied previously.[11] Correction for the latter effect was made by calculating the proportion of oxonium ion-catalyzed reaction at each solvent composition with the use of the appropriate rate constants[11] and benzoic acid dissociation constants.[12] Since benzoic acid was in large excess, it was possible to use the following relationship

$$k_2 = (k_2'''[\mathrm{HOBz}] - k_2''''K_A{}^{1/2}[\mathrm{HOBz}]^{1/2})/[\mathrm{HOBz}] \quad (3)$$

where k_2 is the corrected second order rate constant, k_2''' the measured over-all constant, k_2'''' the second order constant for the oxonium ion-catalyzed reaction[11] and K_A the ionization constant of benzoic acid. The corrected k_2's are plotted in Fig. 1 against water concentration and again the relationship is practically linear. Similar relationships between rate and water concentration have been observed previously in solvolyses of organic halides including benzhydryl chloride in ethanol,[13] α-phenylethyl chloride in acetic acid,[14] and propyl and isopropyl bromides and iodides in alcohol.[15] This behavior in halide ethanolysis has been interpreted[13b,14] as arising from direct participation of the solvent molecules in the rate-determining step rather than as a general medium effect since nitrobenzene which like water increases the dielectric constant of ethanol causes a decrease in the reaction rates. The effect of water on the reaction between benzoic acid and diphenyldiazomethane in ethanol may be of a different kind since addition of nitrobenzene to the solvent also increases the reaction rate. It might appear that the dielectric

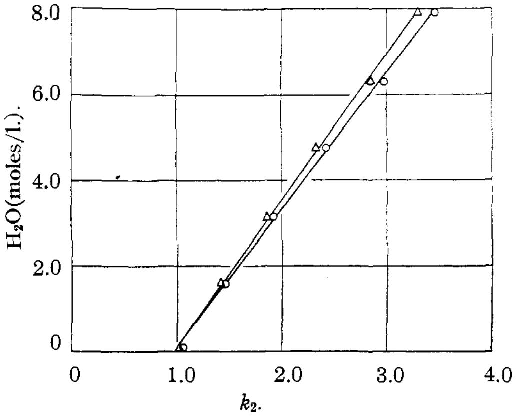

Fig. 1.—Variation of k_2 of diphenyldiazomethane–benzoic acid reaction in ethanol with water concentration: ○, observed points; △, corrected points.

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[6] The rate of reaction of diphenyldiazomethane with benzoic acid in benzene, ethylene dichloride or acetone appears not to be of exactly integral order in benzoic acid (unpublished experiments).

[7] Staudinger, Anthes and Pfenninger, *Ber.*, **49**, 1928 (1916).

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

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

[10] (a) Roberts, Webb and McElhill, *ibid.*, **72**, 408 (1950); (b) Roberts and McElhill, *ibid.*, **72**, 628 (1950).

[11] Roberts and Watanabe, *ibid.*, **72**, 4869 (1950).

[12] Estimated from the data of Halford, *ibid.*, **55**, 2272 (1933).

[13] (a) Norris and Morton, *ibid.*, **50**, 1795 (1928); (b) Farinacci and Hammett, *ibid.*, **59**, 2542 (1937); (c) Ward, *J. Chem. Soc.*, 2285 (1927).

[14] Steigman and Hammett, THIS JOURNAL, **59**, 2536 (1937).

[15] Nicolet and Stevens, *ibid.*, **50**, 135 (1928).

constant of the medium, rather than the direct participation of solvent in the rate-determining step, is the important factor since log k_2 against $(\epsilon - 1)/(2\epsilon + 1)$ for alcohol–water mixtures shows a linear dependence (Fig. 2) characteristic of reactions between dipolar molecules[16] and the rate of the reaction in 28.6% nitrobenzene–71.4% ethanol (by volume) agreed well with the rate in alcohol–water of the same dielectric constant.[17] However, the dielectric constant is clearly not the most important factor, since addition of chloroform and benzene to the solvent also increases the reaction rate (*cf.* Table II).

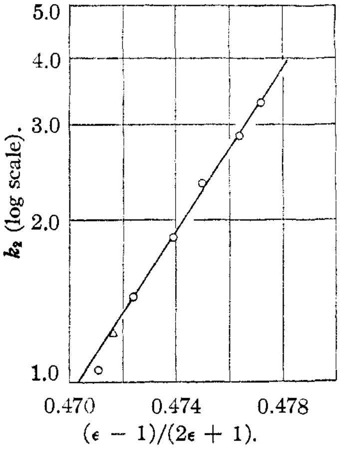

Fig. 2.—Variation of k_2 of diphenyldiazomethane–benzoic acid reaction with dielectric constant of the solvent: O, ethanol–water mixtures; Δ, 28.6% nitrobenzene–71.4% ethanol.

Replacement of 38% of the O–H bonds by O–D bonds in 82.5% ethanol–17.5% water brought about a 38% decrease in the rate of reaction between diphenyldiazomethane and benzoic acid. This result indicates a mechanism in which the rate-determining step involves a proton-transfer.[18]

In absolute ethanol, the salt effect, with either lithium perchlorate or lithium chloride as the inert salt, was small and positive. A plot (Fig. 3) of log k against ionic strength was found to be linear with a slope of 0.7. The salt effect is smaller by a factor of ten than would be expected for a primary salt effect in absolute ethanol. The product composition was affected only about 2–3% by increasing the ionic strength to 0.1. In 82.5% ethanol–17.5% water solutions the salt effect was positive and somewhat larger than in pure ethanol. The greater effect of inert salt in aqueous ethanol was probably due to an increase in the dissociation of the benzoic acid ionization with a resulting increase in oxonium ion-catalysis. This effect of inert salt in increasing the oxonium ion-catalyzed reaction resulted in a decrease of about 10% in the proportion of benzhydryl benzoate formed in the reaction at ionic strength 0.1. Suppression of the ionization of the benzoic acid by addition of 0.1 *M* sodium benzoate resulted in about the same proportion of benzhydryl benzoate as in the absence of inert salt.

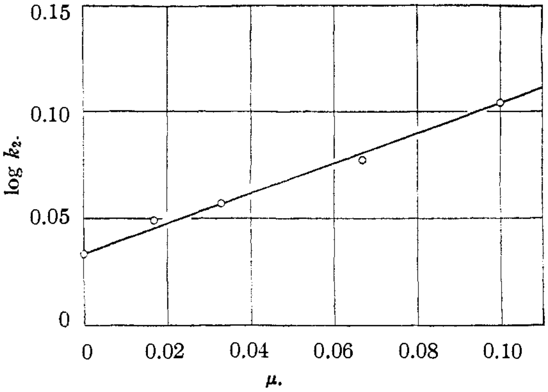

Fig. 3.—Relation between k_2 of diphenyldiazomethane–benzoic acid reaction and ionic strength in absolute ethanol.

Benzoate ion as tetraethylammonium benzoate monohydrate markedly reduced the rate of reaction of benzoic acid with diphenyldiazomethane in absolute ethanol. The product ratio was not materially affected by benzoate ion. The decrease in rate is not due to suppression of the ionization of benzoic acid since, from the ionization constant of benzoic acid[19,20] and the rate constant of the oxonium ion-catalyzed reaction[11] in ethanol, it can be shown that not more than 1% of the total reaction is due to oxonium ion-catalysis. Since the decrease in rate is roughly linear in benzoate ion up to 0.30 *M* tetraethylammonium benzoate, the most likely explanation for the effect is formation of a complex between benzoate ion and benzoic acid which reduces the effective concentration of the acid.

In 82.5% ethanol–17.5% water addition of benzoate ion caused a sharp decrease in the reaction rate followed by a leveling off at moderate concentrations (Fig. 4). Here the results are in accord with a mass-law suppression of the ionization of the benzoic acid with practical elimination of oxonium ion-catalysis.

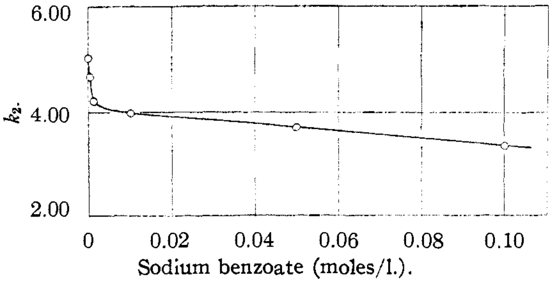

Fig. 4.—Variation of k_2 of diphenyldiazomethane–benzoic acid reaction with sodium benzoate concentration in aqueous ethanol solutions.

In absolute ethanol, iodide ion appeared to decrease the rate slightly but had no important effect on the product ratio. Thiocyanate ion had only

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[16] (a) Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); (b) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 419–423.

[17] The dielectric constant (26.0) of the 28.6% nitrobenzene–71.4% ethanol (by volume) mixture was obtained from the data of Graffunder and Heymann, *Z. Physik*, **72**, 744 (1931).

[18] Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, pp. 143–152.

[19] Goodhue and Hixon, This Journal, **57**, 1688 (1935).

[20] Varsila, *Z. physik. Chem.*, **A181**, 221 (1938).

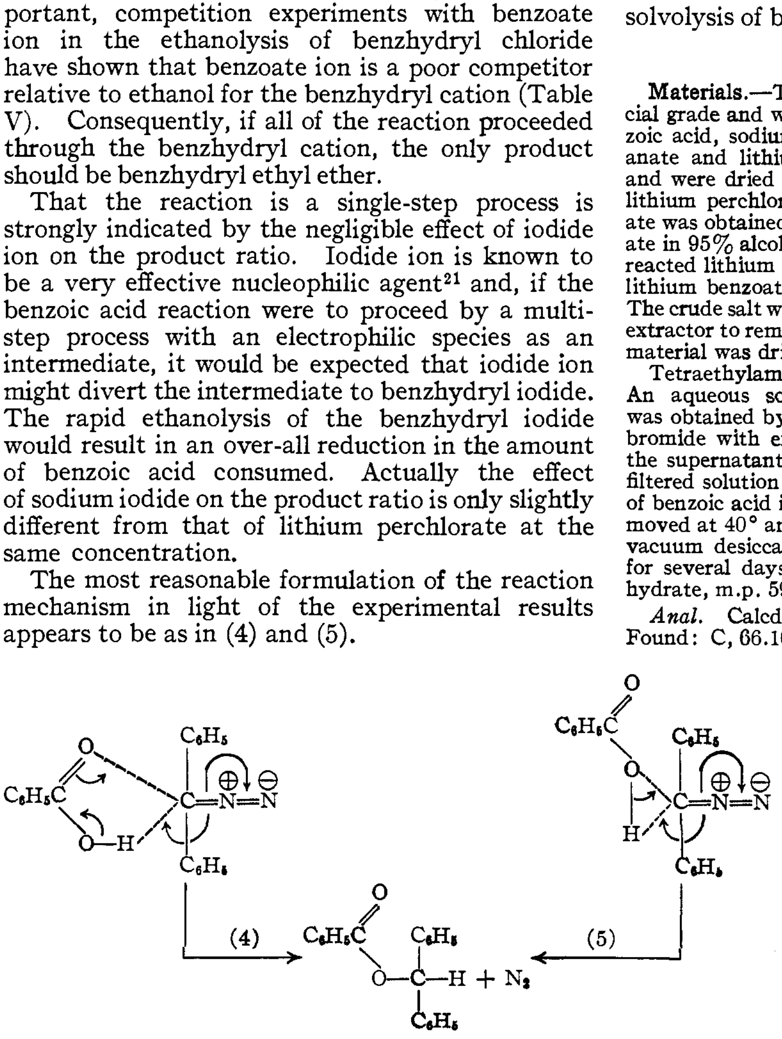
a normal salt effect on the reaction rate but noticeably increased the acid consumption when it was present in relatively high (0.5 *M*) concentrations.

Discussion

The experimental data favor a *single-step* mechanism for the formation of benzhydryl benzoate involving one molecule of benzoic acid and one molecule of diphenyldiazomethane. The alternative would be a rate-determining formation of a carbonium ion or diazonium ion intermediate which would react with benzoic acid or benzoate ion, in free competition with ethanol, to give benzhydryl benzoate. This interpretation is unsatisfactory since it has been shown that increasing the benzoate ion concentrations does not lead to an increase in the proportion of benzhydryl benzoate formed in the reaction (Table III). More important, competition experiments with benzoate ion in the ethanolysis of benzhydryl chloride have shown that benzoate ion is a poor competitor relative to ethanol for the benzhydryl cation (Table V). Consequently, if all of the reaction proceeded through the benzhydryl cation, the only product should be benzhydryl ethyl ether.

That the reaction is a single-step process is strongly indicated by the negligible effect of iodide ion on the product ratio. Iodide ion is known to be a very effective nucleophilic agent[21] and, if the benzoic acid reaction were to proceed by a multistep process with an electrophilic species as an intermediate, it would be expected that iodide ion might divert the intermediate to benzhydryl iodide. The rapid ethanolysis of the benzhydryl iodide would result in an over-all reduction in the amount of benzoic acid consumed. Actually the effect of sodium iodide on the product ratio is only slightly different from that of lithium perchlorate at the same concentration.

The most reasonable formulation of the reaction mechanism in light of the experimental results appears to be as in (4) and (5).



In either case it is postulated that there is an essentially smooth transition between reactants and products. No direct evidence favoring (4) over (5) is available as yet.

The formation of benzhydryl ethyl ether in the reaction in absolute ethanol seems almost certain to proceed by a rate-determining formation of the benzhydryl cation (or possibly the corresponding diazonium ion) through general-acid catalysis of the variety previously demonstrated for picric acid[11] with undissociated benzoic acid as the catalytic agent. The presence of the benzhydryl cation as an intermediate for this part of the reaction is indicated by the effect of thiocyanate ion on the product ratio. Thiocyanate does not participate in the rate-determining step since it has no direct effect on the rate of the reaction at constant ionic strength. Thiocyanate does increase the benzoic acid consumption, apparently by successfully competing with ethanol for an intermediate to give a stable product (presumably benzhydryl thiocyanate) and sodium benzoate. The benzhydryl cation is a reasonable product of the general-acid catalyzed reaction[11] and it has been found that thiocyanate can compete with ethanol for the cation when it is formed as an intermediate in the solvolysis of benzhydryl chloride.

Experimental

Materials.—The absolute ethanol was a good commercial grade and was used without further purification. Benzoic acid, sodium benzoate, sodium iodide, sodium thiocyanate and lithium chloride were reagent grade chemicals and were dried before use. The preparation of anhydrous lithium perchlorate has been described.[11] Lithium benzoate was obtained by treating a suspension of lithium carbonate in 95% alcohol with an excess of benzoic acid. The unreacted lithium carbonate was removed by filtration and the lithium benzoate recovered by evaporation of the solvent. The crude salt was extracted with boiling benzene in a Soxhlet extractor to remove any excess benzoic acid. The remaining material was dried at 125° for 12 hours before use.

Tetraethylammonium benzoate was prepared as follows. An aqueous solution of tetraethylammonium hydroxide was obtained by shaking a solution of tetraethylammonium bromide with excess freshly precipitated silver oxide until the supernatant liquid gave no test for bromide ion. The filtered solution was then exactly neutralized with a solution of benzoic acid in ethanol. The bulk of the solvent was removed at 40° and 3 mm. and the viscous residue placed in a vacuum desiccator at 30 mm. over phosphorus pentoxide for several days. The product was the crystalline monohydrate, m.p. 59–61°.

Anal. Calcd. for $C_{17}H_{27}NO_3$: C, 66.88; H, 10.10. Found: C, 66.10; H, 10.28.

Recrystallization of the monohydrate from ether–acetone gave partially dehydrated material, m.p. 59–84°, which was converted to material of m.p. 59–61° by addition of water and storage at 30 mm. over phosphorus pentoxide. At 3 mm. over phosphorus pentoxide, the salt lost water to give the partially dehydrated substance, m.p. 59–74°. An attempt to remove the water completely at 140° and 0.1 mm. resulted with decomposition to benzoic acid, triethylamine and, presumably, ethylene. The monohydrate was used in the rate experiments and the amount of water so introduced was of minor importance.

Diphenyldiazomethane was prepared by the method described previously.[22] Since the diazo compound decomposed on standing, it was purified before use by recrystallization from absolute methanol; fluffy reddish-purple needles, m.p. 29–30°. The freshly crystallized material used for the determination of the extinction coefficient was analyzed and shown to be practically pure by measuring the volume of nitrogen evolved when a weighed sample dissolved in acetonitrile was treated with *p*-toluenesulfonic acid. The principle non-gaseous product (87%) of the acid-induced decomposition in acetonitrile was tetraphenylethylene, m.p. 225–225.5°. The balance of the material

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[21] Ogston, *Trans. Faraday Soc.*, **44**, 45 (1948).

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

was acetonitrile-soluble and was not identified. The extinction coefficient of the purified diphenyldiazomethane in absolute ethanol at 525 mμ maximum was found to be 94.0 ± 0.5. As reported earlier,[11] solutions of the compound in absolute ethanol accurately follow Beer's law.

Rate Measurements.—The rates of reaction between benzoic acid and diphenyldiazomethane were determined by following the decrease in diphenyldiazomethane concentration by the spectrophotometric procedure described previously.[9,11] All runs were made at 30.0 ± 0.1°. In the majority of the runs the benzoic acid was present in at least ninefold excess over the diazo compound and consequently the reaction followed pseudo-first order kinetics to a high degree of precision. The first-order rate constant, k_1, was obtained graphically from a plot of the logarithm of the optical density against time. The second-order constant, k_2, in (mole/l.)$^{-1}$ min.$^{-1}$ was obtained by dividing k_1 by the initial acid concentration. The rate data are summarized in Tables I and II.

TABLE I

RATES OF REACTION OF DIPHENYLDIAZOMETHANE WITH BENZOIC ACID IN ABSOLUTE ETHANOL AT 30.0°

Benzoic acid, moles/l.	Diphenyl-diazo-methane, moles/l.	Salt, moles/l.	k_2, moles/l.$^{-1}$ min.$^{-1}$
0.0142	0.00319	....	1.06
.0286	.00284	....	1.08
.0358	.00379	....	1.03
.0714	.00266	....	1.07
.0286	.00283	0.0167 $LiClO_4$	1.12
.0286	.00279	.0333 $LiClO_4$	1.14
.0286	.00277	.0667 $LiClO_4$	1.19
.0286	.00282	.100 $LiClO_4$	1.25
.00721	.00851	.100 $LiClO_4$	1.28
.0144	.00797	.100 $LiClO_4$	1.27
.0289	.00271	.100 $LiClO_4$	1.29
.0286	.00271	.100 LiCl	1.29
.0216	.00324	.100 NaSCN	1.29
.0289	.00535	.100 NaI	1.10[a]
.0283	.00278	.0357 LiOBz .0643 $LiClO_4$	1.15
.0283	.00278	.0536 LiOBz .0464 $LiClO_4$	1.09
.0283	.00278	.0714 LiOBz .0286 $LiClO_4$	1.05
.0282	.00270	.0714 LiOBz	.970
.0358	.00371	.100 $(C_2H_5)_4NOBz \cdot H_2O$	.880
.0358	.00372	.200 $(C_2H_5)_4NOBz \cdot H_2O$	.735
.0358	.00377	.300 $(C_2H_5)_4NOBz \cdot H_2O$	.671

[a] At the conclusion of the reaction, the solution was 0.000387 *M* in iodine. On the assumption that iodine formation was first order, the optical density readings were corrected for iodine light absorption. The corrected readings were used to obtain the rate constant.

Product Determinations.—The following experiments are illustrative of the methods used to determine the products and product ratios in the reaction of diphenyldiazomethane with benzoic acid in ethanol solution.

(a) A solution of 2.55 g. of diphenyldiazomethane and 3.0 g. of benzoic acid in 100 ml. of absolute ethanol was allowed to stand in the dark until the color of the diazo compound disappeared. The solvent was removed at room temperature under reduced pressure and the residue was taken up in ether. The ethereal solution was shaken with alkali to remove the excess benzoic acid, then dried and the ether distilled off. The infrared spectrum of the residue indicated that the material was 55% benzhydryl benzoate and 45% benzhydryl ethyl ether. The product (including that used for the infrared spectrum) was distilled through a semi-micro column giving 0.70 g. of liquid, b.p. 96.5–98° (1 mm.), which by means of its infrared spectum was shown to be benzhydryl ethyl ether. The distillation residue gave, after crystallization from aqueous ethanol, 1.96 g. of benzhydryl benzoate, m.p. 87–88°. The mother liquors from the crystallizations were distilled under reduced pressure and afforded an additional 0.25 g. of benzhydryl ethyl ether as well as 0.10 g. of benzhydryl benzoate. The total yield of the ester amounted to 2.06 g. (55%) and that of the ether to 0.95 g. (32%).

TABLE II

RATES OF REACTION OF DIPHENYLDIAZOMETHANE WITH BENZOIC ACID IN 82.5% ETHANOL-17.5% WATER AT 30.0°

Benzoic acid, mole/l.	Diphenyldiazo-methane, mole/l.	Salt, mole/l.	k_2 (mole/l.)$^{-1}$ min.$^{-1}$
0.0142	0.00269	....	3.82
.0142	.00268	0.0667 LiCl	4.34
.0142	.00270	.0667 $LiClO_4$	4.55
.0142	.00273	.100 $LiClO_4$	5.05
.0142	.00274	.0001 NaOBz .100 $LiClO_4$	4.67
.0142	.00274	.001 NaOBz .099 $LiClO_4$	4.22
.0142	.00277	.010 NaOBz .090 $LiClO_4$	3.98
.0142	.00264	.050 NaOBz .050 $LiClO_4$	3.72
.0142	.00270	.100 NaOBz	3.35
.0424	.00274	....	2.35[a]
.0424	.....	....	1.23[b]
.0216[c]	.00222	....	1.26[d]
.0216[c]	.00222	....	2.01[e]

[a] Solvent was 82.5% ethanol–17.5% deuterium oxide. [b] Solvent was 71.4% ethanol–28.6% nitrobenzene (by volume). [c] Experiments by Miss Clare M. McGinnis. [d] Solvent was 71.4% ethanol–28.6% benzene (by volume). [e] Solvent was 71.4% ethanol–28.6% chloroform (by volume).

(b) The effect of benzoic acid, water, inert salt, sodium iodide and sodium thiocyanate on the product ratio was determined by acidimetric measurement of the quantity of benzoic acid consumed. The results of these experiments are summarized in Tables III and IV. The reaction in the presence of sodium iodide took an unexpected turn in that iodine was formed. The iodine was shown to result from dissolved air in the reagents by the following experiment. A weighed sample of benzoic acid was sealed in an evacuated thin-walled bulb and placed in a flask containing a known quantity of diphenyldiazomethane dissolved in a 0.10 *M* solution of sodium iodide in absolute ethanol. The solution was degassed and sealed under reduced pressure. The benzoic acid bulb was then broken by vigorous shaking and

TABLE III

BENZOIC ACID CONSUMPTION IN DIPHENYLDIAZOMETHANE REACTION AT 30.0° IN ABSOLUTE ETHANOL

Benzoic acid, mole/l.	Diphenyl-diazo-methane, mole/l.	Salt, mole/l.	Eq. acid consumed/eq. diphenyldiazo-methane
0.0199	0.0161	....	0.60
.0127	.0124	....	.59
.0202	.00978	....	.60
.0254	.00823	....	.61
.0344	.0101	....	.60
.0307	.00494	....	.64
.0202	.00978	0.100 $LiClO_4$	.57
.0404	.00978	.100 $LiClO_4$	.58
.0300	.0205	.500 $LiClO_4$	.56
.0199	.0161	.100 $(C_2H_5)_4NOBz \cdot H_2O$	.61
.0199	.0161	.200 $(C_2H_5)_4NOBz \cdot H_2O$	.62
.0199	.0161	.500 $(C_2H_5)_4NOBz \cdot H_2O$	.63
.0202	.00975	.100 NaSCN	.61
.0240	.0205	.500 NaSCN	.68
.0258	.0205	.100 NaI	.55[a]

[a] Oxygen excluded.

TABLE IV

BENZOIC ACID CONSUMPTION IN DIPHENYLDIAZOMETHANE REACTION AT 30.0° IN 82.5% ETHANOL–17.5% WATER

Benzoic acid, mole/l.	Diphenyl-diazo-methane, mole/l.	Salt, mole/l.	Eq. acid consumed/eq. diphenyldiazomethan
0.0190	0.0109	....	0.55
.0190	.0109	....	.55
.0190	.0109	0.100 $LiClO_4$	.45
.0190	.0109	.100 LiOBz	.58

the reaction allowed to proceed to completion. Iodine formation was negligible under these conditions.[23]

(c) The benzoic acid consumption in two runs in which the benzoic acid concentration was nearly equal to the diphenyldiazomethane concentration was checked by analysis of the rate data by Eq. (2). For this purpose, x was plotted against t and (dx/dt) determined graphically. Values of $(dx/dt)/(b - x)$ gave linear plots against the corresponding values of x. The slopes and intercepts of the second set of plots are k_2' and k_2a, respectively, as can be seen from the following form of Eq. (2).

$$\frac{dx/dt}{(b - x)} = k_2a - k_2'x \qquad (6)$$

At an ionic strength of 0.1 the two different experiments gave values for k_2'/k_2 of 0.59 and 0.61 which compare favorably with the acidimetric value of 0.58. The calculated figures for k_2, 1.28 and 1.27, checked well with the values (1.25–1.29) obtained at ionic strength 0.1 with higher benzoic acid concentrations.

Competition Experiments with Benzhydryl Chloride in Absolute Ethanol.—The solvolysis of benzhydryl chloride in ethanol produces one equivalent of hydrogen chloride. If the intermediate carbonium ion reacts with an added anion $X^{\ominus}$ to give a stable benzhydryl derivative, $(C_6H_5)_2CHX$, no acid is generated.

The relative efficiencies of various anions as competitors for the benzhydryl cation with respect to ethanol are easily determined by measuring the acid production from a known amount of benzhydryl chloride in the presence of a given salt in ethanol solution. The results of a number of such experiments are given in Table V.

TABLE V

SOLVOLYSIS OF BENZHYDRYL CHLORIDE IN ABSOLUTE ETHANOL AT 30.0°

Benzhydryl chloride, millieq.	Salt, mole/l.	Acid formed, millieq.	Competition factor of 1 M anion relative to ethanol[a]
0.712	....	0.711	..
.710	....	.698	..
.895	0.100 $(C_2H_5)_4NOBz \cdot H_2O$	.880	3.4
.790	.100 NaSCN	.658	34
.721	.100 NaI	.460[b]	..
.599	.100 NaI	.582[c]	..

[a] Competition factor for benzhydryl cation calculated on basis of ethanol concentration of 17 M by the equation [(eq. of benzhydryl chloride/eq. of acid formed) − 1] × 170. [b] No attempt made to exclude oxygen, 0.270 millieq. of iodine formed. [c] Air excluded, 0.010 millieq. of iodine formed.

In an experiment of this type in which sodium iodide was the added salt and air was not excluded, considerable iodine was formed. The sum of the milliequivalents of iodine and acid formed was roughly equivalent to the millimoles of benzhydryl chloride solvolyzed, and the organic product was found to be benzhydryl ethyl ether along with a trace of dibenzhydryl ether. The formation of iodine in the reaction mixture occurred considerably more readily than in a solution of hydrogen chloride and sodium iodide in ethanol. When the solvolysis of benzhydryl chloride was carried out in a solution of sodium iodide in ethanol which was carefully degassed only a trace of iodine was formed.

Summary

The kinetics of the reaction of benzoic acid with diphenyldiazomethane in absolute ethanol have been investigated. The reaction is first order in each of the reactants and yields benzhydryl benzoate and benzhydryl ethyl ether as products.

The effects of inert salt (lithium perchlorate), chloride ion, iodide ion, benzoate ion, thiocyanate ion, nitrobenzene and water on the rate and product composition have been determined.

The replacement of deuterium for hydrogen in the O–H bonds of the solvent markedly slows the rate of the reaction.

The formation of benzhydryl benzoate appears to result from a one-step reaction between the diazo compound and undissociated benzoic acid. Benzhydryl ethyl ether is formed in a multi-step reaction in which undissociated benzoic acid acts as a general-acid catalyst.

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[23] Since neither benzoic acid nor diphenyldiazomethane separately appeared to induce the oxidation of iodide ion by oxygen in absolute ethanol, the formation of iodine must be due to catalysis by one of the reaction intermediates, possibly benzhydryl carbonium ion.