

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

The Kinetics and Mechanism of the Reaction of Diphenyldiazomethane with 2,4-Dinitrophenol in Ethanol¹

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Diphenyldiazomethane reacts with 2,4-dinitrophenol in ethanol to give a mixture of benzhydryl ethyl ether and benzhydryl 2,4-dinitrophenyl ether. The phenolic ether appears to result from a direct reaction of diphenyldiazomethane with 2,4-dinitrophenol while the benzhydryl ethyl ether is formed in a stepwise reaction initiated by undissociated 2,4-dinitrophenol or ethyloxonium ion acting as general-acid catalysts. The effects of inert salt, water and lithium 2,4-dinitrophenoxide on the reaction rate have been determined and correlated with the proposed reaction mechanisms.

In an earlier paper² the kinetics and mechanism of the picric acid-catalyzed reaction of diphenyldiazomethane with ethanol were described. It was shown that the reaction was subject to general-acid catalysis in that undissociated picric acid, as well as ethyloxonium ions resulting from the ionization of picric acid, was an effective catalyst. The major, if not the exclusive, reaction products were benzhydryl ethyl ether and nitrogen. In the present investigation, a detailed study has been made of the reaction of 2,4-dinitrophenol with diphenyldiazomethane in ethanol since this reaction, unlike that with picric acid, results in considerable formation of the corresponding phenyl ether.³

The reaction between diphenyldiazomethane and 2,4-dinitrophenol in ethanol is strictly first order in diphenyldiazomethane. When 2,4-dinitrophenol was present in large excess, the second-order rate constant k_2 , obtained by dividing the apparent first-order constant k_1 by the dinitrophenol concentration, was constant over a threefold range of dinitrophenol concentration (Table I). The reaction products in the absence of added salt were 61% benzhydryl 2,4-dinitrophenyl ether and 39% benzhydryl ethyl ether. It seems reasonable to consider the possibility that the phenolic ether is formed through a direct reaction between the diazo compound and 2,4-dinitrophenol similar to

that postulated for benzoic acid⁴ while the ethyl ether results from the reaction of an intermediate benzhydryl cation (or possibly benzhydryldiazonium ion) with ethanol.^{2,4} This latter reaction may be catalyzed either by undissociated 2,4-dinitrophenol in the manner demonstrated for picric acid² and benzoic acid,⁴ or by ethyloxonium ion resulting from dissociation of the phenol. In the absence of added salt and at high phenol concentrations it is unlikely that catalysis by ethyloxonium ion is significant since the over-all constant k_2 is independent of the phenol concentration.

At an ionic strength of 0.1, using lithium perchlorate as the inert salt, the reaction rate was 40% greater than in the absence of salt and the extent of formation of benzhydryl ethyl ether was 57 instead of 39%. These salt effects are much greater than those found for the benzoic acid reaction⁴ and probably result from an increase in the ionization of the 2,4-dinitrophenol of sufficient magnitude to make catalysis by ethyloxonium ion of considerable importance. This view is supported by the following observations. First, at ionic strength 0.1 (but not at $\mu = 0$), the over-all rate constant k_2 was found to increase with decreasing phenol concentration. Such a variation of k_2 would be expected if the phenol were partially ionized since the extent of ionization would increase with decreasing phenol concentration and it is known that the catalytic constant of ethyloxonium ion (320 mole⁻¹ liter min.⁻¹ at $\mu = 0.1$)² is much larger than for the undissociated phenol. Second, addition of even 0.001 *M* 2,4-dinitrophenoxide ion resulted in marked decrease of the reaction rate at $\mu = 0.1$. This slowing of the rate is large at low concentrations (*cf.* Fig. 1) as would be anticipated if the dinitrophenoxide ion suppressed the ionization of the phenol and, hence, catalysis by ethyloxonium ions. Third, the extent of benzhydryl ethyl ether formation at $\mu = 0.1$ is very sharply reduced by 2,4-dinitrophenoxide ion and, at 0.1 *M* lithium 2,4-dinitrophenoxide, the products are 34% benzhydryl ethyl ether and 66% benzhydryl 2,4-dinitrophenyl ether as compared with 57% and 43%, respectively, in 0.1 *M* lithium perchlorate solutions. The reduction in formation of benzhydryl ethyl ether by 2,4-dinitrophenoxide ion is particularly significant since the change in product composition (23%) is equal, within experimental error, to the value (24%) calculated from the concomitant reduction in the over-all reaction rate on the assumption that the ethoxonium ion-cat-

TABLE I

RATES OF REACTION OF DIPHENYLDIAZOMETHANE WITH 2,4-DINITROPHENOL IN ABSOLUTE ETHANOL AT 30.0°

2,4-Dinitrophenol, mole/l.	Diphenyldiazomethane, mole/l.	Salt, mole/l.	k_2 , mole ⁻¹ min. ⁻¹
0.0207	0.00449	1.45
.0414	.00438	1.49
.0429	.00343	1.47
.0621	.00440	1.47
.0214	.00526	0.100 LiClO ₄	2.61
.0429	.00519	.100 LiClO ₄	2.31
.0643	.00526	.100 LiClO ₄	2.22
.0429	.00267	.100 LiOR ^a	1.47
.0572 ^b	.00234	.100 LiOR ^a	1.80

^a LiOR = lithium 2,4-dinitrophenoxide. ^b Solvent was 71.4% ethanol-28.6% nitrobenzene (by volume).

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

(2) J. D. Roberts and W. Watanabe, *THIS JOURNAL*, **72**, 4869 (1950).

(3) The formation of other phenyl ethers from the reactions of diphenyldiazomethane with various phenols in ether solution or in the absence of a solvent has been reported by H. Staudinger, E. Anthes and F. Pfenninger, *Ber.*, **49**, 1928 (1916); P. Schorlgin, *ibid.*, **59**, 2502 (1926); and M. Busch and R. Knoll, *ibid.*, **60**, 2243 (1927).

(4) J. D. Roberts, W. Watanabe and R. E. McMahon, *THIS JOURNAL*, **73**, 760 (1951).

alyzed reaction yields only benzhydryl ethyl ether.²

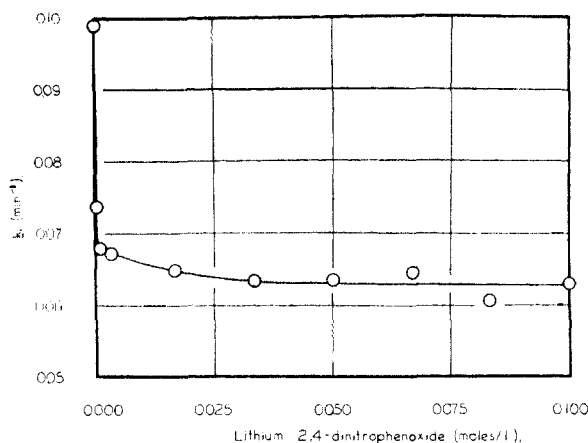


Fig. 1.—Effect of concentration of 2,4-dinitrophenoxide ion on k_1 of reaction between 2,4-dinitrophenol and diphenyldiazomethane in absolute ethanol at 30°.

The effect of chloride ion on the course of the reaction is in accord with the mechanistic scheme so far developed. At 0.1 *M* lithium chloride, the initial rate of the reaction (Fig. 2) is faster than in 0.1 *M* lithium perchlorate due to formation of benzhydryl chloride by reaction of the diazo compound with undissociated hydrogen chloride.²

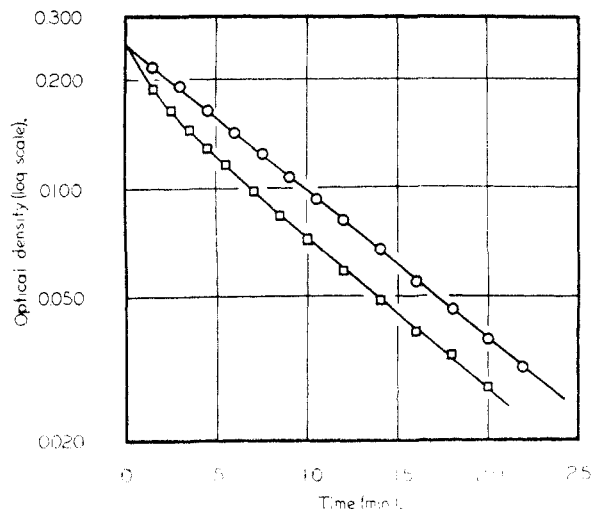


Fig. 2.—Effect of chloride ion on reaction of 0.0429 *M* 2,4-dinitrophenol and diphenyldiazomethane in absolute ethanol at 30°: □, 0.1 *M* lithium chloride; O, 0.1 *M* lithium perchlorate.

The reaction rate soon slackens since the formation of benzhydryl chloride is accompanied by formation of 2,4-dinitrophenoxide ion which affects the rate by reducing the ethyloxonium and undissociated hydrogen chloride concentrations. If the ethyloxonium ion concentration is reduced at the outset by adding lithium 2,4-dinitrophenoxide, then chloride ion shows only a normal inert salt effect (Fig. 3).

The rate constant for undissociated 2,4-dinitrophenol in absolute ethanol is only about one-fifth of that for hydronium ion in aqueous ethanol²

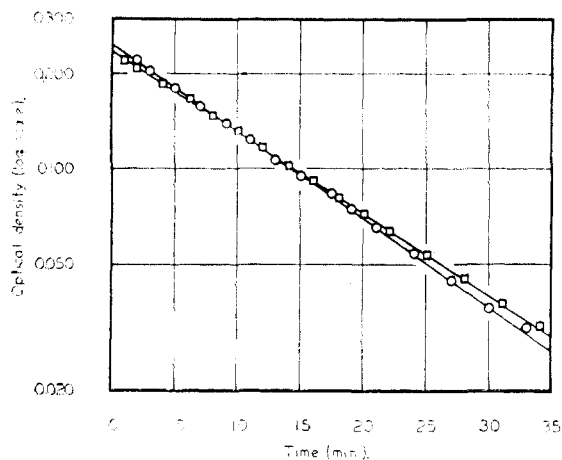


Fig. 3.—Effect of chloride ion on reaction of 0.0429 *M* 2,4-dinitrophenol and diphenyldiazomethane in the presence of 0.050 *M* 2,4-dinitrophenoxide in absolute ethanol at 30°: □, 0.05 *M* lithium chloride; O, 0.050 *M* lithium perchlorate.

and, consequently, it is expected that the addition of water to the solvent would increase the over-all rate of the reaction by increasing the extent of ionization of the phenol. This expectation is realized in the absence of added salt as shown by curve A of Fig. 4. In order to determine whether there is a general medium effect on the reaction with undissociated 2,4-dinitrophenol similar to that observed with benzoic acid,⁴ the influence of water on the reaction rate in the presence of 0.1 *M* lithium 2,4-dinitrophenoxide was studied. Under these conditions, where the ionization of the phenol is largely suppressed, the reaction rate increases substantially linearly up to a water concentration of 4 *M* (*cf.* curve B of Fig. 4). At low water concentrations, $dk_2/d[\text{H}_2\text{O}]$ is about 0.25 and quite comparable to the value of 0.28 for the benzoic acid reaction. Further substantiation of the similarity of the general medium effect for the undissociated 2,4-dinitrophenol and benzoic acid

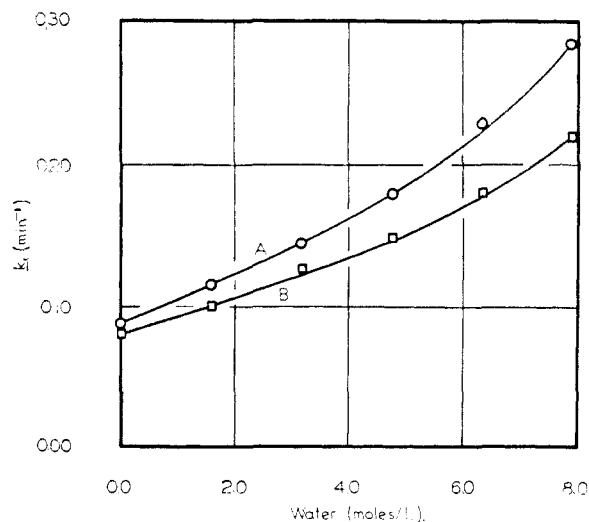
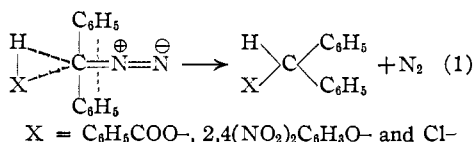


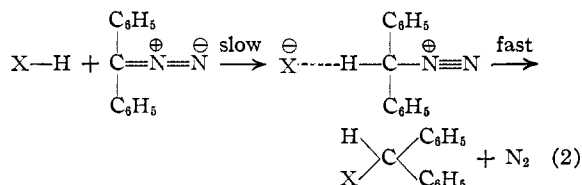
Fig. 4.—Effect of water on k_1 of reaction between 0.0572 *M* 2,4-dinitrophenol and diphenyldiazomethane in ethanol solution at 30°: O, no added salt; □, 0.100 *M* lithium 2,4-dinitrophenoxide.

reactions is provided by the observation that k_2 for each increases about 20% on going to 71.4% ethanol-28.6% nitrobenzene (by volume) solutions.⁵

It is particularly interesting that the reactions of undissociated 2,4-dinitrophenol and benzoic acid with diphenyldiazomethane have parallel characteristics in that each appears to act as a general acid catalyst² as well as undergo a direct reaction with formation of benzhydryl 2,4-dinitrophenyl ether or benzoate. The latter processes seem best formulated as involving essentially smooth transitions between reactants and final products since, so far, no intermediate stages have been detected. The fact that 2,4-dinitrophenol, benzoic acid and apparently undissociated hydrogen chloride² are effective in the direct reaction suggests that a rather novel three-center process of the following type may be occurring.



A reasonable alternative mechanism is an initial slow transfer of a proton from HX to the diazocarbon with the production of an ion-pair in a solvent "cage." The ion-pair would then undergo a rapid-follow reaction to yield the final products as shown in Equation (2).



Since (1) and (2) can be regarded as shading more or less imperceptibly into one another, it is likely that a final experimental distinction may be difficult or impossible.

(5) The effect of nitrobenzene on k_2 of the ethyloxonium ion-catalyzed reaction is much larger and in 71.4% ethanol-28.6% nitrobenzene the rate is 70% greater than in pure ethanol (unpublished experiments by Miss Clare M. McGinnis).

Experimental

Materials.—The absolute ethanol was a good commercial grade and was used without further purification. The preparation and purification of lithium perchlorate and diphenyldiazomethane have been described previously.^{3,4} The 2,4-dinitrophenol was purified by crystallization from ethanol and had m.p. 113-114°. Reagent grade lithium chloride was dried before use. Lithium 2,4-dinitrophenoxide was prepared by treatment of a solution of 25 g. of 2,4-dinitrophenol in absolute ethanol with 5.5 g. of lithium carbonate. The mixture was stirred overnight, filtered, and evaporated to dryness. The residue was extracted twice with boiling benzene to remove unreacted 2,4-dinitrophenol and then crystallized from absolute ethanol. The large yellow crystals (13.5 g.) were dried at 125° at 4 mm. for twenty hours.

Rate Measurements.—The techniques have been described earlier in detail.^{3,4,6} At the wave length used for the spectrophotometric determination of diphenyldiazomethane (525 mμ), both 2,4-dinitrophenol and 2,4-dinitrophenoxide ion show considerable absorption and corrections were made as described earlier for picric acid.³ The data for a number of typical experiments are given in Table I.

Product Determinations.—The formation of benzhydryl 2,4-dinitrophenyl ether in the reaction of diphenyldiazomethane with 2,4-dinitrophenol in absolute ethanol was demonstrated by isolation from the reaction mixture of a white solid having m.p. 149-150° after recrystallization from ethanol-water.

Anal. Calcd. for C₁₉H₁₄O₆N₂: C, 65.14; H, 4.03. Found: C, 64.97; H, 4.05.

The product did not depress the m.p. of an authentic sample, m.p. 147-149°, prepared by heating lithium 2,4-dinitrophenoxide and benzhydryl chloride in benzene-acetone solution.

The extent of formation of the phenyl ether in the reaction was determined by titration of the excess 2,4-dinitrophenol with sodium hydroxide using a glass electrode. The results are summarized in Table II.

TABLE II

2,4-DINITROPHENOL CONSUMPTION IN DIPHENYLDIAZOMETHANE REACTION AT 30.0° IN ABSOLUTE ETHANOL

2,4-Dinitrophenol, mole/l.	Diphenyldiazomethane, mole/l.	Salt, mole/l.	Eq. phenol consumed Eq. diphenyldiazomethane
0.0429	0.0122	0.60, 0.62
.0429	.0122	0.100 LiClO ₄	.42, .44
.0429	.0122	.100 LiOR ^a	.66, .66

^a LiOR = lithium 2,4-dinitrophenoxide.

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(6) J. D. Roberts, E. A. McElhill and R. Armstrong, *THIS JOURNAL*, **71**, 2923 (1949).