

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Mechanism of the Benzilic Acid Rearrangement

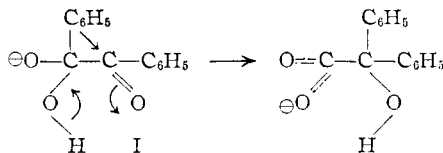
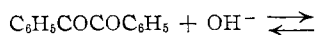
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The rearrangement of benzil to sodium benzilate occurs about 85% faster in 66 $\frac{2}{3}$ % dioxane–33 $\frac{1}{3}$ % D₂O at 50° than in 66 $\frac{2}{3}$ % dioxane–33 $\frac{1}{3}$ % H₂O at the same temperature. The difference in rates is due to the greater basicity of deuterio-oxide ions in "heavy" water compared to hydroxide ions in "light" water and may be used to rule out mechanisms for the rearrangement of benzilic acid that include a proton transfer in their rate-controlling steps.

Introduction

What appears to be the essence of a proposal by Michael¹ concerning the mechanism of the benzilic acid rearrangement has been stated more recently in modern terms.^{2–4} According to this hypothesis the migration of the phenyl group is *accompanied*, rather than followed, by the migration of the oxygen-bound hydrogen atom.



Ott and Smith have suggested an even more concerted mechanism in which the hydroxide ion attacks benzil to form the benzilate anion directly in one step so that I is not an intermediate⁵ (in spite of Roberts and Urey's report of the base-catalyzed O¹⁸ exchange of benzil⁶). The report that the reaction of benzil with ethoxide ions does not follow an analogous path to yield ethyl benzilate (benzaldehyde and ethyl benzoate are produced instead⁷) has been quoted as evidence for the proton transfer as a part of the rate-controlling step of the reaction.⁸ Recently, however, Doering and Urban have reported that the reactions of benzil with sodium methoxide and with potassium *t*-butoxide do yield the corresponding benzilic acid esters and that the reaction with sodium ethoxide is quite seriously complicated by oxidation–reduction *via* hydride-ion transfer.⁴ This observation certainly removes the best experimental evidence for the concerted mechanism but it does not entirely disprove it. It merely shows that even without the possible added driving force of simultaneous proton transfer the migration of the phenyl group occurs more rapidly than any of the competing reactions. In order to learn whether the concerted proton transfer actually occurs in the reaction with hydroxide ions, where it is possible, we have investigated the deuterium kinetic isotope effect.⁸

(1) A. Michael, *THIS JOURNAL*, **42**, 787 (1920).

(2) M. T. Clark, E. C. Hendley and O. K. Neville, *ibid.*, **77**, 3280 (1955).

(3) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 315.

(4) W. von E. Doering and R. S. Urban, *THIS JOURNAL*, **78**, 5938 (1956).

(5) D. G. Ott and G. G. Smith, *ibid.*, **77**, 2325 (1955).

(6) I. Roberts and H. C. Urey, *ibid.*, **60**, 880 (1938).

(7) A. Lachman, *ibid.*, **45**, 1509 (1923).

(8) For a discussion of deuterium kinetic isotope effects see K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

Results and Discussion

The reaction of benzil with sodium hydroxide in 66 $\frac{2}{3}$ % aqueous dioxane was found to follow the second-order rate equation satisfactorily. Some of the rate constants (and average deviations) obtained are listed in Table I. From these data it is seen that the reaction proceeds about 85% faster with NaOD–D₂O than with NaOH–H₂O. This difference in rate cannot be attributed to a solvent effect caused by a small amount of differential evaporation or by the small difference between the molal volume of deuterium and protium oxide. The last entry in Table I shows that the solvent effect is not a large one in this reaction, the rate constant in 60% dioxane being within 3% of that in 66 $\frac{2}{3}$ % dioxane.

TABLE I

REACTION OF BENZIL^a WITH ALKALI^b IN 66 $\frac{2}{3}$ % DIOXANE–33 $\frac{1}{3}$ % WATER^c

Temp., °C.	Water used	10 ⁴ k, l. mole ⁻¹ sec. ⁻¹
50.0	H ₂ O	10.04 ± 0.35
50.0	H ₂ O	9.98 ± .32
50.6	D ₂ O	18.78 ± .52
49.5 ^d	H ₂ O	8.11 ± .10
49.5 ^d	D ₂ O	14.91 ± .08
49.8 ^d	H ₂ O	8.67 ± .02
49.8 ^d	D ₂ O	16.22 ± .03
50.0	H ₂ O ^e	9.72 ± .24

^a Initial concentrations 0.04911–0.06639 *M*. ^b Initial concentrations 0.03247–0.04278 *M*. ^c By volume. ^d These paired runs were carried out in the same thermostated bath at the same time using the same reagents, except for the water. ^e The solvent here was 60% dioxane–40% water.

In the light of our results, the concerted rearrangement of species I and likewise the more concerted mechanism of Ott and Smith⁹ seem quite improbable. The greater reactivity in deuterium oxide solution is no doubt due to the greater basicity of deuterio-oxide ions in deuterium oxide solution compared to hydroxide ions in water. From the ion-product constant of deuterium oxide^{10a} and the acidity constants of several phenols, ammonium ions, and carboxylic and other acids,^{10b} it may be shown that deuterio-oxide ion is from 1.6 to 5 times¹¹ as strong a base as hydroxide ion toward the acids studied. However, since these acids existed in the deuterated form in D₂O and the protonated form in

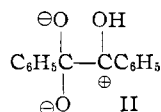
(9) The migratory preferences of substituted benzils mentioned by Ott and Smith in support of their mechanism have been rationalized to our satisfaction on the basis of the stepwise mechanism by G. S. Hammond, *THIS JOURNAL*, **77**, 334 (1955).

(10) (a) R. W. Kingerley and V. K. La Mer, *ibid.*, **63**, 3256 (1941); (b) C. K. Rule and V. K. La Mer, *ibid.*, **60**, 1974 (1938); D. C. Martin and J. A. V. Butler, *J. Chem. Soc.*, 1366 (1939).

(11) The number increases fairly smoothly with the strength of the acid.

H₂O, the comparison with benzil, which exists in the same form in either solvent, is complicated. The comparison of certain reaction rates does not suffer from this complication. Maron and La Mer found that deuteroxide ions remove protons from nitroethane and 2-nitropropane about 40% faster than do hydroxide ions.¹² If the kinetic isotope effect for chloroform is about the same as for dichlorofluoromethane¹³ and bromochlorofluoromethane,¹⁴ then deuteroxide ions remove protons from chloroform about 30% faster than do hydroxide ions.¹⁵ To quote an example of the coordination of a hydroxide ion with a carbonyl group, ethyl acetate has been reported to undergo alkaline hydrolysis 33% faster in "heavy" than in "light" water.¹⁶ Since in each of these reactions the hydroxide ion has only formed a partial bond to the substrate in the transition state we should not expect as large an effect as in the benzilic acid rearrangement, in which the transition state contains a fully bonded hydroxide. Hence the observed effect is quite reasonable for the rearrangement mechanism suggested by Ingold,¹⁷ in which a phenyl group of I shifts to give an intermediate that is transformed to the benzilate anion by subsequent proton transfers.

An alternate mechanism whose rate-controlling step is the rearrangement of the species II (a tautomer of I), which is in mobile equilibrium with



the reactants, perhaps cannot be entirely ruled out, it is shown to be rather improbable by the findings of Doering and Urban as well as by other arguments.

Experimental

Reagents.—When several recrystallizations from ethanol failed to free the benzil that we had at hand (m.p. 96–96.5°)

(12) S. H. Maron and V. K. La Mer, *THIS JOURNAL*, **60**, 2588 (1938).

(13) J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956).

(14) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957).

(15) J. Hine, R. C. Peek, Jr., and B. D. Oakes, *ibid.*, **76**, 827 (1954).

(16) W. F. K. Wynne-Jones, *Chem. Revs.*, **17**, 117 (1935).

(17) C. K. Ingold, *Ann. Rept. Chem. Soc.*, **25**, 124 (1928); **30**, 177 (1933).

from a considerable amount of material that reacted very rapidly with alkali, it was dissolved in benzene, washed with base and again crystallized to give material (m.p. 96–96.4°) whose purity did not appear to be affected by a repetition of the procedure. Dioxane was purified by Fieser's method.¹⁸ Ordinary carbonate-free sodium hydroxide solution was used in the first runs made, but for the runs with deuterium oxide the alkali had to be made by reaction with metallic sodium to prevent contamination by protium oxide. To avoid any effects due to the difference in source of alkali, the alkali was made from sodium and water in those protium oxide runs that were made simultaneously with deuterium oxide runs (and also in some other runs). The source of the alkali had no perceptible effect on the rate constants obtained. The deuterium oxide (99.5+%) used was obtained from D. A. Stuart Oxygen Co.

Kinetic Runs.—After the attack of alkali on glass proved to be a significant complicating factor, the kinetic runs were carried out in polyethylene bottles. In a typical run 1.5442 g. of benzil was weighed into the 125-ml. nitrogen-filled reaction vessel and 80 ml. of dioxane added. After the vessel had equilibrated in the constant temperature bath, 40 ml. of aqueous sodium hydroxide solution at the same temperature was added, the reaction mixture was shaken, and two 10-ml. samples withdrawn into 10 ml. of cold acetone to stop the reaction in the samples and to preserve homogeneity during the titration to the phenolphthalein end-point. The base concentration determined by these titrations was defined as the "initial base concentration" and the time at which the samples were withdrawn was taken as the zero time. This "initial base concentration" was somewhat smaller than that determined by analogous operations with the omission of benzil. From the difference and the assumption that the partial molal volume of benzil was ideal, we corrected the initial benzil concentration (never by so much as 4%) for that which reacted before zero time (and also for acidic impurities). Subsequent samples were titrated analogously with the results shown in Table II.

TABLE II

REACTION OF BENZIL WITH NaOH IN 66²/₃% DIOXANE-33¹/₃% H₂O AT 49.5°

[Benzil] ₀ = 0.05686 M; [NaOH] ₀ = 0.03201 M		
Time, sec.	[NaOH]	10 ³ k, l. mole ⁻¹ sec. ⁻¹
80,340	0.02283	8.12
101,820	.02083	8.34
167,280	.01678	8.06
188,340	.01561	8.08
201,360	.01514	7.93

Av. 8.11 ± 0.10

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(18) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., p. 285.