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The Exchange of Oxygen between Benzil and Water and the Benzilic Acid Rearrangement

BY IRVING ROBERTS AND HAROLD C. UREY

A recent kinetic study by Westheimer¹ has shown that the conversion of benzil to benzilic acid is first order with respect to both benzil and hydroxyl ion, but that the reaction does not exhibit general base catalysis. This can be explained only on the assumption originally made by Ingold² that the rearrangement takes place through an intermediate ion of the formula



As indicated by Westheimer, there are three possible mechanisms which will give kinetics in accord with the above. (1) Rapid, reversible hydration and ionization of the hydrate, followed by the rate-controlling step, the rearrangement of the ion



(2) Slow bimolecular reaction between benzil and hydroxyl ion, followed by rapid rearrangement of the ion



- (1) Westheimer, THIS JOURNAL, 58, 2209 (1936).
- (2) Ingold, Ann. Rep. Chem. Soc., 25, 124 (1928).

(3) Rapid, reversible addition of hydroxyl ion, followed by rate-controlling rearrangement of the ion



All three mechanisms should give the same rate equation, $-d(\text{benzil})/dt = k(\text{benzil})(\text{OH}^{-})$, and are therefore kinetically indistinguishable.

They can be distinguished, however, by determining whether benzil exchanges its oxygen with water containing an increased concentration of H_2O^{13} . If benzil undergoes a rapid reversible hydration as in mechanism (1), it should immediately exchange both its oxygen atoms; on the other hand, if mechanism (2) were correct, no change in the isotopic composition of the water should take place. With mechanism (3), if hydroxyl ion is present, the possibility of migration of the proton from one oxygen atom to the other in the negative ion will determine whether or not the benzil will exchange.

We have therefore performed exchange experiments on benzil in both neutral and alkaline solutions. Since benzil is insoluble in water, a mutual solvent, methanol, was used; the resulting mixture was homogeneous at 70° . Experiments showed that methanol gives no measurable exchange with heavy oxygen water in alkaline solution.

Experimental

Materials and Analyses.—Heavy oxygen water, prepared by fractional distillation,³ was refluxed with alkaline permanganate for one hour, fractionated, and distilled from chromic acid. Benzil, an Eastman Kodak chemical, was recrystallized once from carbon tetrachloride and once from methanol; m. p. 94–95° (corr.). Methanol was purified by the method of Lund and Bjerrum.⁴ Sodium

(3) Huffman and Urey, Ind. Eng. Chem., 29, 531 (1937).

(4) Lund and Bjerrum, Ber., 64, 210 (1931).

hydroxide was used in the form of a 50% solution, from which sodium carbonate had been allowed to settle.

The mass spectrograph was of the type described by Bleakney⁵; the procedure for analysis was that of Cohn and Urey,⁶ the great advantage of the use of this method being its insensitivity to small amounts of impurity. In the present work, the water recovered from the exchange experiments was shaken with 26 cc. of ordinary carbon dioxide at atmospheric pressure for five hours. The precision of the analyses was generally 1% or better.⁷

Exchange Experiments .- All operations were carried out in all-glass apparatus fitted with interchangeable ground joints. A mixture of 8.75 g. (0.0833 equivalent) of benzil and 20 cc. of methanol was heated to boiling. For Expts. 3 and 4, 0.030 cc. of 50% sodium hydroxide was also added initially. Into the resulting solution was pipetted 1.50 cc. (0.0833 mole) of heavy oxygen water containing 0.509% of H2O18. The mixture was again heated at the boiling point until complete solution took place, and immediately chilled under the tap, causing most of the solid to precipitate. The time of the second heating was recorded for each experiment. To recover the water for analysis, all liquid was distilled from the benzil in vacuo at room temperature, and the distillate was fractionated either in vacuo or at atmospheric pressure, the latter giving the better recovery.

Under the conditions of these exchange experiments, rearrangement took place to a negligible extent. The addition of sodium hydroxide to Expts. 3 and 4 reduced the initial isotopic composition of the water to 0.503% H₂O¹⁸. Benzil was assumed to contain 0.200% O¹⁸, the formal concentration of the heavy isotope.

Results and Discussion

In Table I are given the results obtained from the four experiments performed. It is evident that mechanism (2) can be eliminated immediately, since exchange takes place in all experiments. Mechanism (1) cannot be the only mechanism since Expts. 1 and 2 show a comparatively slow exchange in neutral solution, whereas Expts. 3 and 4 give complete exchange in the presence of 0.02 N sodium hydroxide within four minutes, the shortest time in which the experiments could be performed. The exchange which does take place in neutral solution may be the result of

TABLE	Ι
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0.0833 equivalent of benzil, 0.0833 mole of 0.509% H_2O^{18} , and 20 cc. of methanol at 70°. Calculated for complete exchange 0.352% H_2O^{18} .

Expt.	NaOH	Time, min.	H2O re- covered, cc.	$\% H_2O^{18}$	% exchange
1		2.5	0.61	0.484	16 ± 7
2		4	. 10	.442	43 ± 6
3	0.02 N	4	.22	.352	100 = 6
4	0.02 N	4	.62	.348	102 ± 6

(5) Bleakney, Phys. Rev., 40, 496 (1932).

(6) Cohn and Urey, THIS JOURNAL, 60, 679 (1938).

(7) Mass spectrograph analyses done by Dr. John E. Gorham.

maction of benzil with the small amount of hyd oxyl ion present, or, in part, the result of reaction with water molecules. Even if the latter is true, the hydroxyl ion reaction is a much more in pid one, leaving little doubt that the most probable initial step in the rearrangement is that represented in mechanism (3).

This picture is in complete accord with organic evidence. Scheuing⁸ has shown that the potassium hydroxide addition compound of benzil in benzene or pyridine solution forms within two to three minutes, whereas the rearrangement itself is a comparatively slow process. Evans and Dehn⁹ have allowed one mole of potassium hydroxide to react with one mole of benzil in anhydrous ether solution and have obtained 81% yield of potassium benzilate, demonstrating that the presence of water is not necessary for the rearrangement.

Mechanism (3) is also in agreement with the theory of reactivity as a function of electron displacements. According to Ingold,² the true, unstable intermediate is formed by a shift of electrons so that ten surround one carbon atom



This carbon atom will then tend to lose an electron pair in the form of any one of the three possible residues, OH^- , $C_6H_5^-$ or $C_6H_5CO^-$, leaving a stable resonance structure in each case. Of these, we would expect the OH⁻ to dissociate most readily, since the C-OH linkage is probably the weakest of the three. This is but a restatement of the above conclusion that the initial step in the rearrangement is a reversible The much slower dissociation of $C_6H_5^-$ will one. be followed by its addition to the adjacent carbon atom, an electron-attracting center; this should be succeeded by rapid addition and removal of a proton to and from the appropriate oxygen atoms in order to give the resulting benzilate ion. Dissociation of the third organic residue is observed in alcoholic solution where the only products are benzaldehyde and ethyl benzoate.¹⁰

The fact that reversible addition of hydroxyl ion to benzil results in exchange implies that a proton shifts rapidly from one oxygen atom to

(8) Scheuing, Ber., 56B, 253 (1923).

(9) Evans and Dehn, THIS JOURNAL, 52, 252 (1930).
(10) Lachman, *ibid.*, 45, 1509 (1923); 46, 779 (1924).

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the other in the intermediate ion. This may occur intramolecularly or with the aid of the solvent; the present data give no means of distinguishing between the two. A similar problem has arisen previously in the mechanism of acetone exchange, which is both general acid and hydroxyl ion catalyzed.⁶

Summary

1. From experiments demonstrating that benzil exchanges with heavy oxygen water much more rapidly in alkaline than in neutral solution, it is concluded that the first step in the benzilic acid rearrangement is a rapid, reversible addition of hydroxyl ion to benzil, the rate-controlling step being rearrangement of the ion thus formed.

2. This mechanism is entirely consistent with organic evidence and with the theory of reactivity of organic compounds as a function of electron displacements developed by English workers.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Coördination Compounds of Palladous Chloride¹

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Coördination compounds of ethylene derivatives with platinous chloride of the type (Un- $PtCl_2$)₂, where Un represents an ethylene derivative, have been described by Anderson² and by Kharasch and Ashford.⁸ Anderson prepared the compound of ethylene by refluxing ethylene with sodium chloroplatinate, and has recently succeeded in exchanging the bound ethylene for ethylene derivatives. Kharasch and Ashford prepared similar compounds by treating ethylene derivatives with platinic chloride. Their paper reviews briefly the previous work in the field and proposes a new structure for such compounds.

For reasons which will be discussed in a later publication, we became interested in ascertaining whether similar compounds with palladium are possible. Kondakov, Balăs and Vít⁴ claim to have prepared an addition compound of trimethylethylene and palladous chloride by allowing these substances to react in a sealed tube at room temperature in the presence of a trace of a basic substance. They consider the compound to have the formula Un PdCl₂.

Preparation of Palladous Chloride Compounds.—We were unable to obtain any compound of palladous chloride by direct interaction with the following unsaturated compounds: ethylene, isobutylene, cyclohexene, styrene, camphene. Numerous changes in procedure were of little avail. In some cases, the components were kept in a sealed tube for twenty-four hours. At all times a large excess of the unsaturated component was used. Neither acidic (hydrogen chloride) nor basic substances (pyridine, triethylamine) were effective in bringing about a combination. Solvents such as benzene, ether, and acetone did not appear to promote the reaction. Water was not used for it is claimed by Phillips⁵ that in its presence palladous chloride is reduced to palladium by olefins.

It was quite obvious that a new approach to the problem was necessary. The preparative method indicated by the following equations was then found to be successful

 $\begin{array}{rcl} PdCl_{2} + 2C_{6}H_{6}CN \longrightarrow (C_{6}H_{6}CN)_{2} \cdot PdCl_{2} & (1) \\ 2(C_{6}H_{6}CN)_{2} \cdot PdCl_{2} + 2Un \longrightarrow \\ & (Un \cdot PdCl_{2})_{2} + 4C_{6}H_{6}CN & (2) \end{array}$

The nitrile palladous chloride compounds are not described in the literature. For our study, we prepared the dibenzonitrile palladous chloride in 88–95% yield by heating palladous chloride in benzonitrile until solution took place. The method is the same as used by Kharasch and Ashford⁶ to obtain the dibenzonitrile platinous chloride compound. Incidentally, this method of preparing the nitrile compounds of platinous chloride is superior to that of Hofmann and Bugge,⁷ who treated benzonitrile in ether with an aqueous solution of potassium chloroplatinite

- (6) Kharasch and Ashford, unpublished work.
- (7) Hofmann and Bugge, Ber., 40, 1772 (1907).

⁽¹⁾ Abstracted from a dissertation submitted by Ralph C. Seyler to the Faculty of the Division of the Physical Sciences of the University of Chicago in 1937, in partial fulfilment of the requirements for the degree of Master of Science.

⁽²⁾ Anderson, J. Chem. Soc., 971 (1934); 1042 (1936).

⁽³⁾ Kharasch and Ashford, THIS JOURNAL, 58, 1733 (1936).

⁽⁴⁾ Kondakov, Balás and Vit, Chem. Listy, 23, 579 (1929); 24, 1, 26 (1930); C. A., 24, 3454 (1930).

⁽⁵⁾ Phillips, Am. Chem. J., 16, 265 (1894).