Exchange Reaction of Biacetyl with Deuterium Oxide

By W. D. WALTERS

In connection with a recent photochemical investigation in which deutero-biacetyl was used,[1] it became of interest to attempt to measure the rate at which the hydrogen atoms of biacetyl are exchanged in the presence of deuterium oxide. The rates of racemization, halogenation and, recently, isotope exchange have been used in correlating the differences in the reactivities of various carbonyl compounds with differences in structure. Therefore, the rate of exchange might prove useful in comparing biacetyl with other ketones.

Experimental Method

Samples were prepared by distilling the desired amount of biacetyl into a tube containing a weighed amount of deuterium oxide solution of known acid content. The sample tube was sealed off under vacuum, warmed quickly and placed in a thermostat. In this work the 99.6% deuterium oxide, obtained from Norway, was distilled twice under vacuum to remove traces of non-volatile basic material, and the biacetyl was purified as in a previous study.[2] In the experiments at 25° the temperature was controlled to within ±0.02°, in those at 56°, to within ±0.1°. After exchange had occurred, the deutero-biacetyl was separated from the aqueous solution in the manner already described.[1] The method of separation used for the experiments in Tables I and II was tested with a sample of deutero-biacetyl of known deuterium content. No noticeable exchange occurred during the separation. Several experiments were also performed in which an attempt was made to stop the exchange during the separation process by the addition of a buffer of $Na_2HPO_4-Na_2HPO_4$. Although the results were similar to those in Table II, the buffer was not satisfactory since in its presence exchange occurred at an appreciable rate. After separation the sample of deutero-biacetyl was further dried with anhydrous copper sulfate and then burned in a stream of oxygen over heated platinum foil, as described by Geib.[3] The deuterium content of the water from the combustion was determined according to the method of Harteck.[4]

Quantitative results for the exchange were obtained only for experiments in the presence of hydrochloric acid. As had been expected, even very dilute solutions of sodium hydroxide brought about a rapid disappearance of biacetyl at room temperature. The product, which, presumably, is 1,4-dimethylcyclohexanediol-1,4-dione-2,5,[5] is probably formed by a base-catalyzed aldol condensation. A sample kept for three days at 56° in the presence of a sodium acetate–acetic acid buffer yielded no biacetyl on separation. In the presence of distilled water at 25° for six

(1) Herr, Matheson and Walters, THIS JOURNAL, 63, 1464 (1941).
(2) Walters, THIS JOURNAL, 62, 880 (1940).
(3) Geib, Z. physik. Chem., A180, 211 (1937).
(4) Harteck, Z. Elektrochem., 44, 3 (1938).
(5) Diels, Blanchard and Heyden, Ber., 47, 2356 (1914).

days the loss of biacetyl amounted to about 1%. In neutral deuterium oxide, the loss of biacetyl may have some effect on the results, and increasing the reaction time to secure more exchange would increase the loss. Moreover, with only a small amount of exchange, the experimental error in the deuterium measurement is appreciable. Therefore, the rate obtained for exchange in pure deuterium oxide is only an approximate value. In the presence of dilute acid biacetyl was relatively stable. In experiments with 1 N hydrochloric acid for reaction times similar to those used for exchange there was no noticeable loss of biacetyl at 25° and less than 0.2% at 56°. The loss in the acid solution at 56° is so small compared to the amount of exchange that any error from this cause should be insignificant.

Results

The data from the exchange experiments are shown in Tables I and II. The percentage of

TABLE I

Expt.	Sample, g.	Ac₂, wt. %	Soln., % D before exchange	Acid concn. meq./g.	Soln. % D, av.
9	0.5917	11.0	99.6	0.00	99.6
3	.6183	7.88	98.2	1.27	97.0
4	.6230	9.92	98.5	0.941	97.3
5	.6199	11.0	98.8	.692	97.8
11	1.1411	9.69	98.8	.705	98.0
12	0.5423	9.75	99.5	.147	98.3

TABLE II
RATE OF THE EXCHANGE

Expt.	Temp., °C.	Time, min.	% D in Ac₂	k min.$^{-1} \times 10^5$	k' min.$^{-1} \times 10^5$
9	25.0	8069	0.5	0.06	..
3	25.0	20970	39.6	2.40	1.67
4	25.0	21065	31.6	1.80	1.70
5	25.0	21395	24.0	1.28	1.66
11	55.7	439	21.0	53.7	69
12	55.8	2967	30.1	12.1	75

deuterium in the aqueous solution before exchange, given in the fourth column in Table I, does not include the hydrogen atoms of biacetyl. As the exchange proceeds, the percentage of deuterium in the water decreases since some of the atoms of deuterium are replaced by hydrogen atoms from biacetyl. Therefore, the average deuterium content during the reaction is also given. Since the molarities but not the activities of the deuterium ion in aqueous solutions of biacetyl were known, the rate of exchange, k', was calculated for 1 M hydrochloric acid. To obtain k' at 56°, it was assumed that the variation in the specific volume of the solution with temperature was the same as that of deuterium oxide.

Discussion

The fact that the exchange in the presence of acid is rapid in comparison with the rate in deu-

terium oxide alone would indicate that the exchange is catalyzed by oxonium ions. Within the limits of experimental error, the rate of exchange is proportional to the acid concentration over a fivefold change in the concentration of hydrochloric acid. The values in the above experiments with a deuterium content of about 98% will be somewhat lower than the rates that would be obtained if it were possible to keep the solution 100% with respect to deuterium. However, the difference is probably within the experimental error. From the rates at the two temperatures, the activation energy for the exchange reaction would appear to be about 23.9 kcal.

The rate constant for the acid catalyzed exchange reaction of biacetyl can be compared with the rate of exchange for acetone measured by Reitz[6] in 90% deuterium oxide. At 25° the rate of the exchange reaction for acetone was found to be about 5×10^{-4} min.$^{-1}$ for 1 M hydrochloric acid. It is apparent that with two carbonyl groups in the molecule the acid catalyzed exchange reaction is considerably slower than the reaction for a molecule with one carbonyl group. It may be assumed that the rate of the acid catalyzed deuterium exchange for biacetyl is determined by the rate of enolization, as was demonstrated in the case of acetone.[6] In the acid catalyzed enolization the first step involves the transfer of a proton from the oxonium ion to the ketone and the second step is the removal of a proton from the intermediate ion to form the enol. For a number of ketones it has been shown that the second process is the rate determining step for enolization and that the first step is an equilibrium reaction.[7] Therefore, a change in structure of the ketone can affect the rate of enolization by shifting the equilibrium point of the first step, with the resultant change in concentration of the intermediate ion, and by altering the rate of removal of the proton from the intermediate ion. However, the present results alone do not permit an exact evaluation of the effect of change in structure upon the separate processes. Of interest in this connection, particularly with regard to the first step, are the recent spectroscopic results of Gordy and Stanford[8] which show no significant difference in the proton-attracting powers

(6) Reitz, Z. physik. Chem., **A179**, 119 (1937).

(7) Zucker and Hammett, THIS JOURNAL, **61**, 2785 (1939); Cohn and Urey, ibid., **60**, 679 (1938); Bonhoeffer and Reitz, Z. physik. Chem., **A179**, 135 (1937).

(8) Gordy and Stanford, J. Chem. Phys., **9**, 204, 215 (1941).

of acetone and biacetyl, within the limits of experimental error of the method.

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The Isolation of Some Compounds from North Dakota Lignite

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Two years ago extracts of a lignite, originating in Hungary, were submitted to chromatographic analysis and small quantities of two crystalline compounds were isolated: a triterpene (m. p. 244–247°) and the potassium salt of a strongly reducing organic acid.[1] Recently North Dakota lignite (from the Velva district, Truax–Traer camp area) was investigated by similar methods. While we were unsuccessful in finding the compounds mentioned, some other crystalline, fluorescing substances were isolated in the following way.

Thirty kilos of lignite were shaken with 30 liters of 90% acetone. After twofold dilution, the filtrate was extracted with 3×600 ml. of petroleum ether (b. p. 60–70°). The extracts were concentrated in vacuo to 75–100 ml. and chromatographed on five slaked-lime columns (25×5 cm.). The chromatograms were developed with petroleum ether until several sharply bordered and strongly fluorescing zones were visible under a quartz lamp. About 11 cm. below the top a greenish, fluorescent line appeared. The next lower 5-cm. section was heterogeneous and ended with a fluorescing blue line, about 1.5 cm. thick. This whole section, including the latter zone, was cut from each column. The combined fractions were eluted with a 1:1 alcohol–petroleum ether mixture, the alcohol was washed out, the upper layer dried and evaporated. White crystals appeared, contaminated with some yellowish oil. The substance was recrystallized repeatedly from hot petroleum ether in which it is slightly soluble; yield, 12 mg., m. p. 328–330° (cor., slight decomp.). The compound shows chromatographic homogeneity; it is free from nitrogen and ash.

Anal. Calcd. for $(C_{10}H_{16}O)_n$: C, 78.88; H, 10.60. Found: C, 79.13 and 79.18; H, 10.33 and 10.35.

Due to difficulties in the micro-molecular weight determination the value of n could not be definitely established. Probably $n = 3$.

(1) L. Zechmeister and O. Frehden, Nature, **144**, 331 (1939).