2.25 g. (80%) of XV having b.p. 61.5–62° at 0.55 mm., n^{25}D 1.4476, d^{25} 0.923.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.9; H, 12.1. Found: C, 71.9; H, 12.0.

The virtual absence of a carbonyl band in the infrared spectrum of XV indicates that it exists mainly as the hemiketal XVa. Distillation of XV at 100° resulted in partial dehydration as evidenced by the appearance of carbon-carbon double bond band in the infrared spectrum.

α-*t*-Butyl-γ,γ,γ-trimethyllevulinic Acid (VI).—In a 125-ml. bottle equipped with a gas inlet tube which reached nearly to the bottom, and a suitable outlet, was placed 50 ml. of distilled water, 1.6 g. (0.008 mole) of XV and 1.70 g. (0.011 mole) of potassium permanganate. A slow stream of carbon dioxide was passed into the bottle while it was shaken until the permanganate had been consumed (9 days). The manganese dioxide was removed by treatment with oxalic acid and, after the solution had been made alkaline, it was extracted with three 20-ml. portions of pentane. Evaporation of the solvent gave 0.5 g. (31%) of unreacted starting material.

The alkaline solution was acidified with 20% sulfuric acid and then extracted with three 25-ml. portions of pentane. After drying over anhydrous sodium sulfate, the pentane solution was evaporated giving 0.51 g. (30%) of VI, m.p. 73–78°. Sublimation afforded pure VI, m.p. 81–82.5°.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.3; H, 10.4; neut. equiv., 214. Found: C, 67.1; H, 10.6; neut. equiv., 216.

Synthetic VI was found to be identical with the acid formed by reaction of III with methanolic hydrogen chloride.

Lactonization of α-*t*-Butyl-γ,γ,γ-trimethyllevulinic Acid.—In a glass tube was sealed 28 mg. of VI which was then heated to 180° for three days. The product was dissolved in pentane and washed with 5% sodium hydroxide solution. Evaporation of the solvent gave a solid which sublimed at 10 mm. and 80° to give 20 mg. (78%) of α,γ-di-*t*-butyl-$\Delta^{\alpha,\beta}$-butenolide (IV), m.p. 92.5–94°, identical with the material obtained by treatment of III with base. III was found to be converted quantitatively to IV on heating under similar conditions.

2,2,6,6-Tetramethyl-4-heptenone-3 (II).—The low-boiling fraction obtained from the irradiation of diazomethyl *t*-butyl ketone was redistilled through a 12-inch wire gauze packed column. The pure material had b.p. 87° at 29 mm., n^{25}D 1.4368, d^{25} 0.855 λ_{max} 228 mμ, ω_{max} (ethanol).

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.5; H, 12.0. Found: C, 78.6; H, 11.8.

The 2,4-dinitrophenylhydrazone was obtained as a yellow solid, m.p. 145–146° after recrystallization from ethanol. The ultraviolet spectrum had λ_{max} 365 mμ, ϵ_{max} 29,000 (ethanol).

Anal. Calcd. for $C_{17}H_{24}O_4N_4$: C, 58.6; H, 6.9. Found: C, 58.6, 58.7; H, 6.8, 6.9.

2,2,6,6-Tetramethylheptanone-3,2,4-dinitrophenylhydrazone.—The reduction of 0.166 g. (0.99 mmole) of II was carried out in 15 ml. of absolute ethanol using Adams catalyst. In 25 minutes, 0.81 equivalent of hydrogen had been used. A solution of 0.32 g. (1.6 mmoles) of 2,4-dinitrophenylhydrazine in alcohol was added to the hydrogenated material. After concentration to 20 ml. and cooling, 0.203 g. of the 2,4-dinitrophenylhydrazone was obtained, m.p. 98–103°. The crude material was dissolved in 3:1 hexane-benzene and chromatographed through alumina giving 0.200 g. of material having m.p. 127–128° which could be raised to 129–129.3° after recrystallization from ethanol. Water was added to the original filtrate which was then continuously extracted with hexane. The hexane solution was chromatographed giving an additional 0.023 g. of the dinitrophenylhydrazone (total 65%). It had λ_{max} 363 mμ, ϵ_{max} 22,000 (ethanol).

Anal. Calcd. for $C_{17}H_{26}O_4N_4$: C, 58.3; H, 7.5. Found: C, 58.2; H, 7.7.

A sample of 2,2,6,6-tetramethylheptanone-3 was kindly supplied by Dr. Bartlett.[10] The 2,4-dinitrophenylhydrazone of this ketone was identical with the above derivative by m.p., infrared and ultraviolet spectra.

Photolysis of Diazoacetophenone.—Diazoacetophenone was prepared in the conventional manner from benzoyl chloride and diazomethane. After recrystallization from hexane, it had m.p. 46–46.5°.

In a 250-ml. flat-bottom quartz flask was placed 6.0 g. (0.041 mole) of diazoacetophenone which was irradiated for five days. The dark product was triturated with 50 ml. of acetonitrile and the cream-colored solid was filtered. There was obtained 0.42 g. (8.6%) of material having m.p. 255–258°. On recrystallization from anisole, dimethylformamide and anisole, the m.p. was raised to 268–270°.

The α,γ-diphenylbutenolide was prepared from benzylidene acetophenone by the method of Hann and Lapworth.[13] After recrystallization, it had m.p. 268–270°. The material obtained in the photolysis was shown to be identical with this material by mixed m.p. and infrared spectrum. The butenolide was reported to have m.p. 288°[11,12] and it was noted that if the temperature of the melting point block was raised rapidly to 285° and then slowly raised, the butenolide had m.p. 287–288°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Deuterium Isotope Effect of Some Ionic Reactions of Benzaldehyde

BY KENNETH B. WIBERG

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The chromic acid oxidation, Cannizzaro reaction and benzoin condensation have been studied using benzaldehyde-d_1. The chromic acid oxidation was found to have a deuterium isotope effect, k_H/k_D, of 4.3, indicating that the cleavage of the carbon-hydrogen bond of the aldehyde is the rate-determining step. Since the reaction is acid catalyzed, the formation of an ester intermediate similar to that in the permanganate oxidation of benzaldehyde is suggested. The Cannizzaro reaction was found to have an isotope effect of 1.8. The observation of an isotope effect is in accord with the currently accepted mechanism, but the value is unusually low for an ionic reaction. The benzoin condensation appeared to give an isotope effect which evidenced itself as an induction period with the labeled aldehyde. It was also shown that exchange of the aldehyde hydrogen with the solvent occurred during the reaction at about the same rate as the condensation. These observations are not in agreement with the Lapworth mechanism.

Introduction

The deuterium isotope effect has proved to be of value in the elucidation of the mechanisms of a number of reactions,[1,2] particularly oxidation processes.[2] Unfortunately, little is known concerning the magnitude of the effect for different types of reactions, and of the effect of substituents. It is therefore planned to measure the deuterium isotope effect for a number of reactions of benzaldehyde, toluene and their ring-substituted derivatives. The results of a study of the chromic acid oxidation, the Cannizzaro reaction and the benzoin condensation of benzaldehyde and benzaldehyde-c_1 are described herein.

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[1] P. D. Bartlett and F. A. Tate, THIS JOURNAL, **75**, 91 (1953); R. P. Bell, "Acid-Base Catalysis," Oxford University Press, New York, N. Y., 1941, p. 146.

[2] (a) F. H. Westheimer and N. Nicolaides, *ibid.*, **71**, 25 (1949); F. A. Loewus, F. H. Westheimer and B. Vennesland, *ibid.*, **75**, 5018 (1953); (b) K. B. Wiberg and R. Stewart, Abst. 124th Meeting, A.C.S., Chicago, Ill., 1953, p. 67.

These reactions were chosen since they are presumably ionic in nature. Furthermore, a comparison of the isotope effect in the chromic acid oxidation with that previously determined for permanganate oxidation of benzaldehyde[2b] was of interest. The Cannizzaro reaction probably involves a hydride transfer, and thus would give data on a type of reaction for which no information is presently available. The benzoin condensation also was investigated since some features of the commonly accepted mechanism have not been satisfactorily explained.

Experimental

Benzaldehyde-d_1.—To a mixture of 1 g. (0.025 mole) of lithium aluminum deuteride[3] in 50 ml. of anhydrous ether[4] was added with stirring a solution of 10 g. (0.05 mole) of benzil in the minimum volume of ether (about 100 ml.). After one hour, the solution was treated with 30% Rochelle salt solution. The ether layer was separated, and the residue was extracted with warm ether. The combined ether solutions were dried with anhydrous sodium sulfate and then evaporated to give 10 g. of dihydrobenzoin-d_2, sufficiently pure for the following reaction.

To 6 g. (0.028 mole) of dihydrobenzoin-d_2 in 150 ml. of benzene was added 13 g. (0.29 mole) of lead tetraacetate, followed by shaking. After one hour, water was added, the solution was filtered and the benzene layer was separated. Most of the benzene was removed by distillation and the residue was converted to the bisulfite addition compound with 40% sodium bisulfite solution. After filtration and washing with ether, 9 g. (75%) of the air-dried bisulfite addition compound was obtained. This was converted to benzaldehyde-d_1 with 10% sodium carbonate solution immediately before use. Material having b.p. 178–179° was used in the subsequent experiments.

The benzaldehyde-d_1 was analyzed *via* the mass spectrometer cracking pattern and the infrared absorption spectrum.[5] The peak intensities for the significant mass numbers of benzaldehyde and benzaldehyde-d_1 are

Mass	C_6H_5CDO (p = 32 μ)	C_6H_5CHO (p = 35 μ)
105	1872 ($C_6H_5C^+{=}O$)	1998 ($C_6H_5C^+{=}O$)
106	154 (isotope)	1992 (parent)
107	1836 (parent)	204 (isotope)
108	147 (isotope)	13.2 (isotope)

It is apparent that the benzaldehyde-d_1 contained little if any ordinary benzaldehyde. In the infrared spectrum (Fig. 1), benzaldehyde has two aldehyde carbon–hydrogen stretching bands, at 3.58 and 3.68 μ. In the labeled aldehyde, these bands are shifted to 4.76 and 4.83 μ.[6] The spectra confirm the isotopic purity of the aldehyde. These bands are useful in analyzing for the relative amounts of the labeled and unlabeled aldehyde in a mixture. Unfortunately, the use of the ratio of transmission of the two aldehydes is not always satisfactory since the bands of the ordinary aldehyde overlap the strong hydroxyl band of benzoic acid, which is formed quickly by autoöxidation of the aldehyde. It is therefore more convenient to plot the log of the transmission for the labeled aldehyde against concentration (Fig. 2) under constant conditions (0.100 ml. of the aldehyde made up to 1.00 ml. with carbon tetrachloride and run in a 0.1-mm. cell, correction being made for cell absorption).

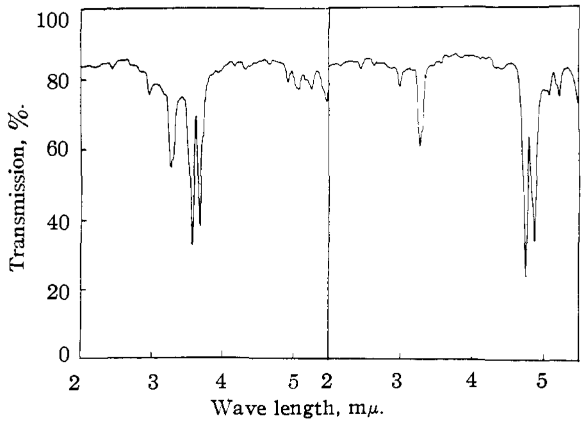

Fig. 1.—Infrared spectrum of benzaldehyde (left) and of benzaldehyde-d_1 (right).

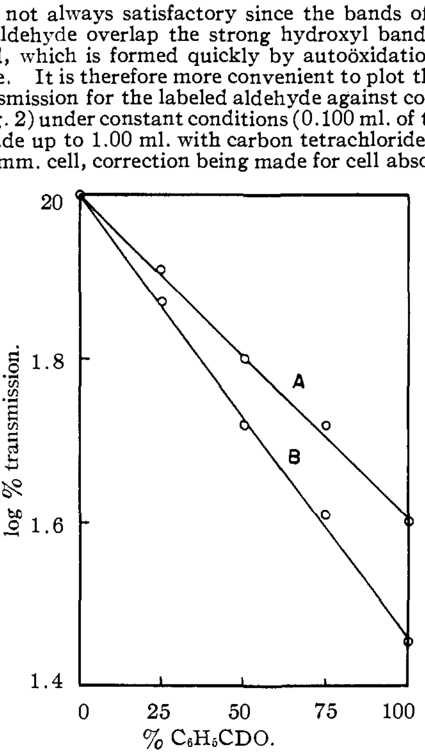

Fig. 2.—Calibration curve for infrared analysis of benzaldehyde and benzaldehyde-d_1 mixtures: curve A, λ 4.83μ; curve B, λ 4.76μ.

Chromic Acid Oxidation.—The solvent, 90% acetic acid, was prepared by mixing 360 ml. of glacial acetic acid with 40 ml. of distilled water. Solutions of chromic acid (0.100 *M*), chromic acid containing sodium acetate (0.100 *M* each) and benzaldehyde (0.150 *M*) in 90% acetic acid were prepared. Fifty ml. of the chromic acid solution was mixed with 50 ml. of the benzaldehyde solution at 25.0°. Five-ml. aliquots were removed at regular intervals and added to a solution of 1 g. of potassium iodide in 20 ml. of water containing 0.5 ml. of 18 *N* sulfuric acid. The iodine formed was titrated with 0.1 *N* sodium thiosulfate solution. The rate of reaction decreased with increasing time, and thus rate constants were not calculated, but rather comparisons were made of the times required for a given fraction of complete reaction. Since both reactions are of the same order, the ratio of these times will be inversely proportional to the ratio of the rate constants. The decrease in rate was due probably to the formation of acetate ion as the addition of sodium acetate markedly slowed the reaction (Fig. 3). The observed isotope effect, k_Hk_D, was 4.3 ± 0.2.

Cannizzaro Reaction.[7]—To a solution of 40 ml. of methanol, 10 ml. of 1.00 *N* sodium hydroxide solution and 10 ml. of distilled water was added 2.00 ml. of freshly distilled benzaldehyde. Five-ml. aliquots were sealed under reduced pressure in tubes having a total capacity of about 7 ml. These tubes were placed in a boiling water-bath, and at regular intervals, one was removed, added to 10 ml. of 0.1 *N* hydrochloric acid and back-titrated with 0.1 *N* sodium hydroxide to *p*H 8. The rate constant was determined by plotting the reciprocal of the square of the hydroxyl ion con-

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(3) Obtained from Metal Hydrides, Inc., on allocation from the Atomic Energy Commission.

(4) The ether was distilled from sodium hydride immediately before being used.

(5) The mass spectra were obtained using a Consolidated Engineering Corp. Model 21-103 spectrometer, and the infrared spectra were obtained using a Perkin-Elmer model 21 spectrometer.

(6) The two carbon–hydrogen stretching bands are characteristic of the formyl group of most aldehydes. The reason for two bands is not clear, and this problem is being studied by Dr. D. F. Eggers of these laboratories.

(7) The procedure used was essentially that of E. L. Molt, *Rec. trav. chim.*, **56**, 233 (1937).

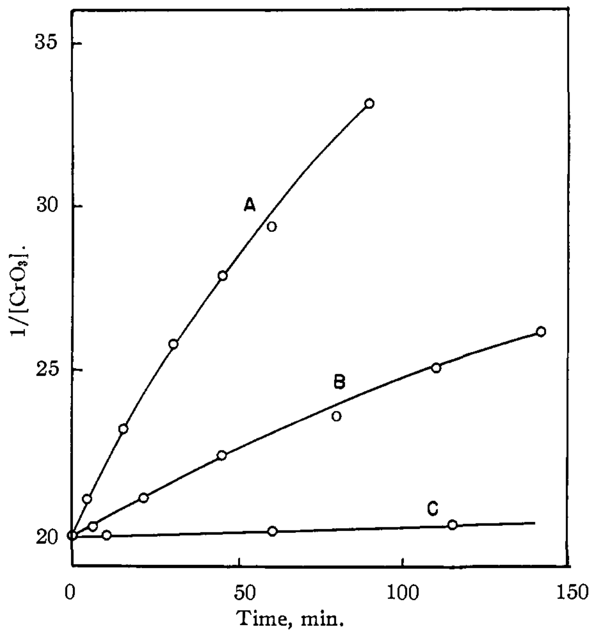

Fig. 3.—Chromic acid oxidation of benzaldehyde: curve A, benzaldehyde; curve B, benzaldehyde-*d*$_1$; curve C, benzaldehyde with sodium acetate.

centration against time (Fig. 4), the slope being eight times the rate constant. The third-order rate constants were: C_6H_5CHO, 1.33 ± 0.06 × 10^{-2} l.^{2} mole^{-2} min.$^{-1}$,[8] C_6H_5-CDO, 0.73 ± 0.05 × 10^{-2} l.^{2} mole^{-2} min.$^{-1}$. The isotope effect, k_H/k_D, was 1.8 ± 0.2.

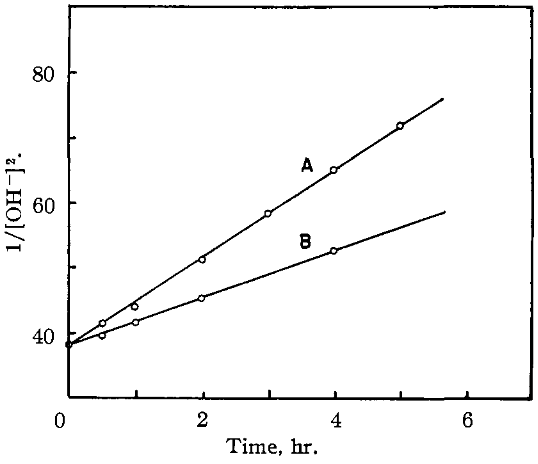

Fig. 4.—Cannizzaro reaction of benzaldehyde (curve A) and benzaldehyde-*d*$_1$ (curve B).

Benzoin Condensation.[9]—The solvent, 66% ethanol, was prepared by mixing 210 ml. of 95% ethanol and 90 ml. of distilled water. To a 0.100 *N* solution of potassium cyanide in 66% ethanol at 64.5° and in an atmosphere of nitrogen (vapor thermostat using methanol) was added 2.00 ml. of freshly distilled benzaldehyde (resultant concentration 0.30 *M*). Five-ml. aliquots were removed at regular intervals and added to 5 ml. of Fehling solution A and 8 ml. of 50% ethanol in a 50-ml. erlenmeyer flask. Five ml. of Fehling solution B was added quickly, and the resultant solution was heated to near boiling for 20 min. The solution was cooled, transferred to a beaker containing 1 g. of potassium iodide and treated with 4 ml. of 18 *N* sulfuric acid with ice-bath cooling. The liberated iodine was titrated with 0.1 *N* sodium thiosulfate solution. Some trial experiments indicated that this method was satisfactory and that benzaldehyde did not interfere. The observed second-order rate constant for benzaldehyde (Fig. 5) was 1.06 × 10^{-1} l. mole^{-1} min.$^{-1}$, in satisfactory agreement with the value 8.9 × 10^{-2} obtained by Stern[9] at a slightly lower temperature, 60°, in a solvent of approximately the same composition. An induction period was noted in the benzaldehyde-*d*$_1$ reaction, after which the reaction proceeded at essentially the same rate as the unlabeled case.

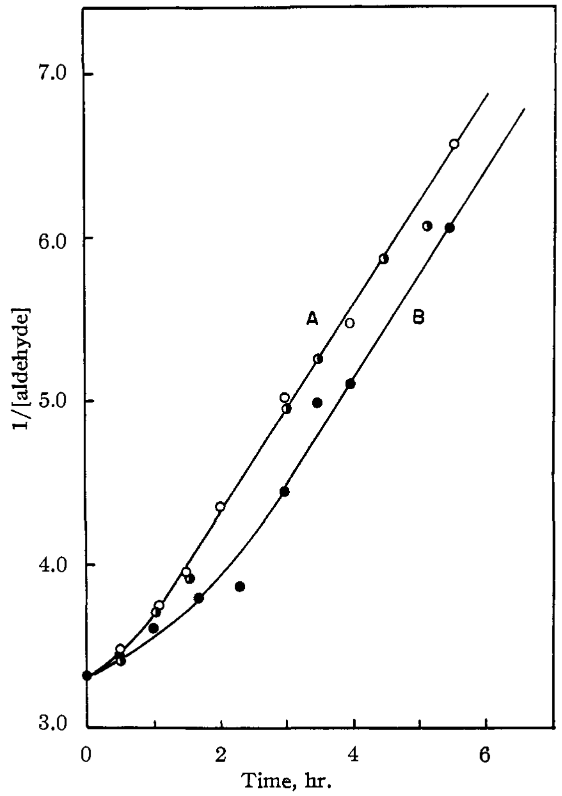

Fig. 5.—Benzoin condensation of benzaldehyde (curve A, open circles are run 1, half-closed circles are run 2) and benzaldehyde-*d*$_1$ (curve B).

Formation of Benzoin in the Presence of Deuterium Oxide.—To 20 ml. of absolute ethanol was added 4 ml. of deuterium oxide[10] (99.8%) and 130 mg. of potassium cyanide. The solution was placed in a thermostat at 40.0° and 2.00 ml. of redistilled benzaldehyde was added ([C_6H_5CHO] = 0.80 *M*, [KCN] = 0.08 *M*). After a given period of time, the solution was cooled and added to a mixture of 20 ml. of ether, 10 ml. of water and 4 ml. (a twofold excess) of 1 *N* hydrochloric acid. The ether layer was separated and the aqueous layer was extracted with another 20-ml. portion of ether. The combined ether solutions were dried over anhydrous sodium sulfate and distilled, the fraction boiling at 177–179° being collected. The relative amounts of benzaldehyde and benzaldehyde-*d*$_1$ were determined using the infrared spectrum and the curve in Fig. 2. The results are

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[8] E. L. Molt, ref. 7, obtained the rate constant 1.43 × 10^{-2} in 50% methanol, and noted that the rate decreased somewhat as the methanol concentration was increased. The solution used in this investigation was 67% methanol, by volume.

[9] The procedure used was essentially that of E. Stern, *Z. physik. Chem.*, **50**, 513 (1905). He treated the reaction solutions with acid, and steam distilled to remove benzaldehyde and hydrogen cyanide before analyzing them with Fehling solution. This procedure appeared to cause some loss of benzoin in the hands of the present investigator. Since some independent experiments showed that benzaldehyde did not react with Fehling solution, the above procedure was found to be more convenient. The cupric ion quickly removes the cyanide ion, thus quenching the reaction. The extent of the reaction with Fehling solution was determined volumetrically rather than using the tedious gravimetric procedure of Stern.

[10] Obtained from The Stuart Oxygen Co. on allocation from The Atomic Energy Commission.

Time, min.	C_6H_5CDO, % ±2	Benzoin condensation, % ±2
15	0	4
75	10	11
120	16	16

Results and Discussion

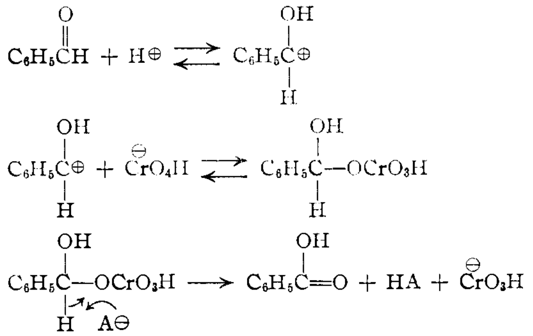
a. Chromic Acid Oxidation.—The only previous work on the chromic acid oxidation of aromatic aldehydes is that of Lucchi.[11] He measured the rate of oxidation of a series of aldehydes in about 70% acetic acid containing a large excess of sulfuric acid. He found that electron-attracting groups accelerated the reaction, but the nature of the effect is not clear since, for example, *p*-methyl-, *p*-chloro- and *p*-bromobenzaldehyde have higher activation energies for reaction than does benzaldehyde. He unfortunately did not study the effect of sulfuric acid concentration on the rate of reaction.

In the present work, the reaction was studied in 90% acetic acid with no added mineral acid. It was noted that the rate of oxidation decreased with increasing time, when plotted as a second-order reaction (Fig. 3). The decrease in rate is probably due to the formation of acetate ion required by the stoichiometry, since the addition of sodium acetate caused a marked drop in rate. A comparison of the

$$3C_6H_5CHO + 2HCrO_4^- + 2H^+ + 6HOAc = 3C_6H_5COOH + 2Cr^{+3} + 5H_2O + 6OAc^-$$

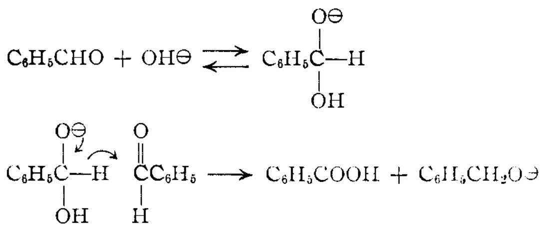
times required for a certain fraction of complete reaction for benzaldehyde and benzaldehyde-d_1 gave a value for the isotope effect, k_H/k_D, of 4.3 ± 0.2. This definitely indicates that the cleavage of the aldehyde carbon–hydrogen bond is the rate-controlling step. The value obtained is somewhat smaller than that observed in the permanganate oxidation of benzaldehyde, where a value of six was obtained.[2b]

Since the reaction is acid catalyzed, and involves the carbon–hydrogen bond of the aldehyde in the rate-controlling step, one is tempted to suggest a mechanism similar to that found in the permanganate oxidation of benzaldehyde,[2b] involving an ester intermediate. A detailed kinetic investigation is now in progress.

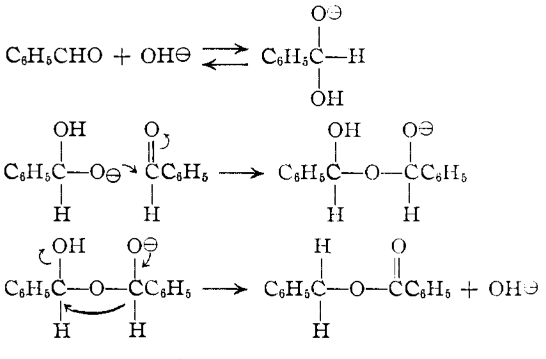


b. Cannizzaro Reaction.—The details of the Cannizzaro reaction have received numerous investigations, and as a result, two mechanisms have been proposed for the homogeneous reaction[12]

(A)



(B)



No definitive experiment has been devised which would distinguish between the two possibilities. In mechanism A, an isotope effect would be expected since the second step must be rate controlling in order to fit the observed rate law. In mechanism B, if the second step were rate controlling, no isotope effect would be expected, whereas if step three were the slow step, an isotope effect should be observed.

The isotope effect obtained in this work was 1.8 ± 0.2, which is unusually low for an ionic reaction, where the values usually range from four to ten.[1] However, all the ionic reactions of carbon–hydrogen bonds which have been studied have involved the removal of a proton, whereas the Cannizzaro reaction involves a hydride ion. The only hydride transfer which has been studied is the hydrolysis of triphenylsilane. The original investigators[13] found a reverse isotope effect, with the deuterium containing isomer reacting six times as fast as the ordinary silane. A reinvestigation has, however, shown that the reaction has a normal isotope effect of slightly more than one.[14] The mechanism of this reaction[13,14] is quite different from that of the Cannizzaro reaction, and therefore the low value which was observed cannot be extrapolated to the present case.

There are several possible causes of the low isotope effect. First, this may be a characteristic of hydride transfer reactions. Second, if the mechanism is represented by B, a small isotope effect might be observed if step two were rate controlling, since attack occurs at a carbon directly attached to the deuterium. This possibility will be examined by comparing the rates of reaction of benzaldehyde and benzaldehyde-d_1 with 2,4-dinitrophenylhydrazine. The third possibility is that a reaction in which the driving force is the push of the hydrogen away from the carbon might have a lower isotope effect than one in which the hydrogen is pulled away, as in most of the cases which have been

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[11] E. Lucchi, *Boll. sci. facolta chim. ind. Balogna*, **208**, 333 (1940); **2**, 165, 176 (1941); *Gazz. chim. ital.*, **71**, 729, 752 (1941).

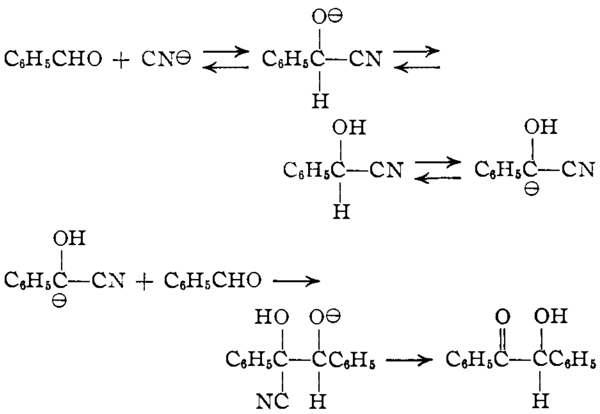
[12] *Cf.* the discussion of the mechanism of the Cannizzaro reactions by T. A. Geissman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 96, and L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 350.

[13] H. Gilman, G. E. Dunn and G. S. Hammond, This Journal, **73**, 4499 (1951).

[14] L. Kaplan and K. E. Wilzbach, *ibid.*, **74**, 6152 (1952).

studied. The last possibility is that the reaction may be free radical, although this is not likely.[15]

c. Benzoin Condensation.—Previous work in the benzoin condensation has shown that the rate of reaction is proportional to the square of the benzaldehyde concentration and the first power of the cyanide ion concentration.[9] Furthermore, added base did not accelerate the reaction.[9] On the basis of this and other evidence,[16] the Lapworth[17] mechanism has become generally accepted. Since base catalysis was not observed, the mechanism requires that very little mandelonitrile exist in equilibrium with the anions, and thus mandelonitrile must be about as acidic as hydrogen cyanide (k 8×10^{-10}).[18] It is convenient to compare the acidity of mandelonitrile with that of phenol (k 1×10^{-10})[19] rather than with hydrogen cyanide, the latter two compounds having similar dissociation constants. If the mechanism is correct, mandelonitrile should have about the same acidity as phenol. This does not appear entirely reasonable since phenol has the possibility of resonance stabilization of the anion which does not appear in mandelonitrile.



The rates of reaction of benzaldehyde and benzaldehyde-d_1 were determined by a modification of the method of Stern.[9] The data are shown in Fig. 5. The ordinary benzaldehyde appeared to give a small induction period and then gave good pseudo second-order kinetics. The induction period may be an artifact caused by the analytical method and will not be considered further at this time. The benzaldehyde-d_1, however, gave a relatively long induction period before giving the same rate as the unlabeled compound. This result would not be anticipated on the basis of the Lapworth mechanism, as it is currently formulated.

In order to obtain further data concerning the reaction, it was carried out in a solvent containing 58 mole % deuterium, and the rate of deuterium exchange was compared with the rate of reaction. It was found that the two processes occurred at about the same rate with a benzaldehyde concentration of 0.80 *M*. Since the rate of deuterium exchange is probably first order with respect to benzaldehyde whereas the condensation is second order, the rate of exchange would be somewhat faster than the rate of condensation at a benzaldehyde concentration of 0.30 *M* which was used in the kinetic investigation. If one assumes that the reaction shows an isotope effect, then the induction period observed with the labeled aldehyde may easily be explained as a slow condensation of benzaldehyde-d_1 coupled with the deuterium being transferred to the solvent giving ordinary benzaldehyde which then reacted at the normal rate.

These results are clearly at variance with the Lapworth mechanism since it predicts no deuterium isotope effect, and a very rapid exchange of the aldehyde hydrogen with the solvent. In order to obtain further data, it is now planned to study both the deuterium exchange and the condensation over a range of aldehyde concentration and of temperature for benzaldehyde and several ring-substituted derivatives. This should indicate whether the exchange is caused by a side reaction or is a consequence of the condensation mechanism, and should also give the magnitude of the isotope effect. A further discussion of the mechanism will be postponed until the completion of this study.

Finally, it might be mentioned that although knowledge of the C^{14} isotope effect would probably be of value in elucidating the mechanism of the reaction, the recent study[20] of this isotope effect is of no value. The benzoin formed by the condensation of benzaldehyde-C^{14} was cleaved and the benzaldehyde and benzoic acid obtained were analyzed for their radioactivity. It is not surprising that no difference was observed, since it is known that the less stable unsymmetrical benzoins are converted to their more stable isomer by treatment with alcoholic potassium cyanide,[21] and also that optically active benzoins are easily racemized in alkaline solution.[22] This indicates that the two carbons carrying the functional groups are interconverted easily.

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[15] A free radical mechanism has been suggested (J. Weiss, *Trans. Faraday Soc.*, **37**, 782 (1941)), for the reaction, largely on the basis of the observation by M. S. Kharasch and M. Foy, THIS JOURNAL, **57**, 1510 (1935), that the heterogeneous Cannizzaro reaction is catalyzed by peroxides. However, a later investigation by E. R. Alexander, *ibid.*, **69**, 289 (1947), showed that this was not the case in the homogeneous Cannizzaro reaction.

[16] *Cf.* the review of the benzoin condensation by W. S. Ide and J. S. Buck, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 273.

[17] A. Lapworth, *J. Chem. Soc.*, **83**, 995 (1903); **85**, 1206 (1904).

[18] J. A. Cranston and H. F. Brown, *J. Roy. Tech. Coll.*, **4**, 54 (1937); H. F. Brown and J. A. Cranston, *J. Chem. Soc.*, 578 (1940).

[19] G. J. Tiessens, *Rec. trav. chim.*, **48**, 1068 (1929).

[20] W. H. Stevens and R. W. Attree, *J. Chem. Phys.*, **18**, 574 (1950).

[21] S. S. Jenkins, THIS JOURNAL, **53**, 3115 (1931).

[22] A. Weissberger, A. Dörken and W. Schwarze, *Ber.*, **64B**, 1200 (1931).