by Allen, Eliot and Bell.[3] 2,3-Diphenylbutanediol-2,3 (56 g.) containing 0.03 g. of phenyl-β-naphthylamine was placed in a 500-ml. flask cooled in an ice–salt-bath and 170 ml. of acetyl bromide was added slowly. After the vigorous reaction was over (thirty minutes), the reaction mixture was heated on a water-bath for three hours, when no more evolution of hydrogen bromide was observed. The excess of acetyl bromide was removed under reduced pressure and the oily residue was cooled, dissolved in ether, and washed with sodium carbonate solution and with water. After drying over sodium sulfate the ether was distilled and 17 ml. of bromine in 50 ml. of dry chloroform was added dropwise with continuous shaking to a solution of the oily residue in 100 ml. of dry chloroform. The chloroform was removed under reduced pressure and the solid mass obtained on cooling the residue was filtered, washed with cold hexane and crystallized from ethyl alcohol; yield 34 g. (40%) of dibromide, m. p. 147–148°. I was prepared from the dibromide by the procedure described previously.[3]

Reaction of 2,3-Diphenylbutadiene with Picric Acid.—A solution of 2.5 g. (0.012 mole) of (I) and 1.5 g. (0.006 mole) of picric acid in 50 ml. of benzene was heated under slow reflux in a nitrogen atmosphere under a positive pressure of 7 cm. of mercury for seven days. The benzene was distilled under reduced pressure and the reddish-brown residue was extracted with two 50-ml. portions of ether. The ether solution was washed several times with aqueous sodium bicarbonate, then with water, and dried over sodium sulfate. The ether was distilled and a solution of the residue in 15 ml. of hexane was cooled in a freezing mixture. The colorless crystals which separated (0.9 g.) were recrystallized from methyl alcohol; m. p. and mixed m. p. with known samples of cis-dimethylstilbene[2,3] 67–68°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.3; H, 7.7. Found: C, 92.3; H, 7.8.

In a similar experiment in which 50 ml. of xylene was the solvent, after seven days refluxing 0.75 g. (30%) of crude (II) was isolated, which after recrystallization melted at 66°.

Structure of cis-Dimethylstilbene Derived from I.—II prepared from I by the above procedure (0.83 g.) was added to a solution of 5 ml. of 30% hydrogen peroxide in 15 ml. of 88% formic acid with stirring and heated at 45–50° for forty minutes. The mixture was allowed to stand overnight at room temperature and poured into 100 ml. of ice water. The oily product was separated and crystallized on standing for several hours. After filtering and washing with cold water, 0.4 g. of crude 2,3-diphenylbutanediol-2,3 was obtained, m. p. 114–116°. After two recrystallizations from benzene–petroleum ether the yield was 0.29 g. (30%), m. p. and mixed m. p. with an authentic sample[4] 117–118°.

2,3-Diphenylbutanediol-2,3 prepared in this way (0.4 g.) in 5 ml. of glacial acetic acid was oxidized by portionwise addition of 0.5 g. of chromic anhydride during ten minutes. The mixture was heated on a water-bath for one hour and poured into cold water. The product was isolated by extraction with ether, which was washed with sodium carbonate solution and dried over sodium sulfate, and then distilled at atmospheric pressure, It was proved to be acetophenone by conversion to the semicarbazone, m. p. and mixed m. p. with a known sample 202°.

cis-Dimethylstilbene prepared from I was also identified by oxidation to acetophenone (identified as the semicarbazone) by direct treatment with chromic acid in acetic acid according to the procedure by Lévy[7] for oxidizing trans-dimethylstilbene.

Reaction of 1,4-Diphenyl-1,3-butadiene with Picric Acid.—These reactants formed a deep red solution on heating in benzene or xylene solution under the conditions described for 2,3-diphenylbutadiene. Red crystals separated from the solutions, which on exposure to air and on treatment with alcohol became yellow and yielded 1,4-diphenyl-1,3-butadiene and picric acid. Formation of an unstable molecular compound from 1,4-diphenyl-1,3-

butadiene and s-trinitrobenzene has been described by Briegleb and Kambeitz.[8]

Acknowledgment.—The author expresses his gratitude to Dr. Arthur C. Cope for his interest in this investigation.

(8) Briegleb and Kambeitz, *Z. physik. Chem.*, **32B**, 305 (1936).

On the Nature of the Reaction between Ascorbic Acid and Formaldehyde[1]

BY F. J. REITHEL AND R. P. WITHER

In a recent publication[2] evidence was presented to show that mixtures of ascorbic acid and formaldehyde solutions yield carbon dioxide as a reaction product. Under the proper conditions one mole of carbon dioxide is produced per mole of ascorbic acid.

Previous workers[3] studying the reaction between ascorbic acid and formaldehyde ascribed the disappearance of the reducing properties of ascorbic acid to an addition reaction with formaldehyde. It occurred to us that the phenomena observed might be explained more fully by postulating the oxidation of ascorbic acid by formaldehyde. It has been shown[4] that solutions of dehydroascorbic acid liberate carbon dioxide under conditions similar to those employed by us.

In the following experiments the rates of carbon dioxide evolution from dehydroascorbic acid and ascorbic acid–formaldehyde solutions were compared using the Warburg apparatus. All solutions were saturated with carbon dioxide before use. After gas and temperature equilibration the contents of the side arm were tipped into the body of the flask and the carbon dioxide evolution followed manometrically. The results are summarized in Table I. The data indicate that the rate of evolution of carbon dioxide from the ascorbic acid–formaldehyde mixture is nearly identical with that from the solution of dehydroascorbic acid. Similar data exist for other reaction mixtures in which the concentration of ascorbic acid was varied from 4.8×10^{-2} to 4.8×10^{-3} M and the formaldehyde concentration was varied from 0.2 to 1.8 M. In all cases the rate of carbon dioxide evolution was similar to controls containing dehydroascorbic acid. The use of iodine as an oxidizing agent also yielded results similar to those presented.

In addition to this evidence it has been found that the effect of temperature on the rate of car-

(2) Reithel and West, THIS JOURNAL, **70**, 898 (1948).
(3) Snow and Zilva, *Biochem. J.*, **37**, 630 (1943).
(4) West and Rinehart, *J. Biol. Chem.*, **146**, 105 (1942).

(7) Lévy, *Bull. soc. chim. France*, [4] **29**, 889 (1921).

TABLE I

EVOLUTION OF CARBON DIOXIDE FROM DEHYDROASCORBIC ACID AND ASCORBIC ACID–FORMALDEHYDE SOLUTIONS

Molar acetate buffer, pH 5.4, was used; ascorbic acid 9.65×10^{-2} M in buffer; cupric acetate (oxidant) 0.193 M in buffer; formaldehyde 10% in buffer; temperature 40°

Minutes	Dehydroascorbic[a] acid		Formaldehyde[b] ascorbic acid	
	Microliters of carbon dioxide			
30	90	95	34	34
60	138	144	121	116
90	219	225	222	222
120	282	290	298	296
270	543	547	593	586
450	752	759	798	795
720	964	973	940	937

[a] 1.0 ml. of buffer plus 0.5 ml. of cupric acetate in body of Warburg flask; 0.5 ml. of ascorbic acid in sidearm. [b] 0.5 ml. of buffer plus 1.0 ml. of formaldehyde in body; 0.5 ml. of ascorbic acid in sidearm.

bon dioxide evolution is similar in both systems. As shown previously[2] ascorbic acid and formaldehyde react to yield carbon dioxide at 32 and 40°, evolution beginning at zero time. However, at 25° there is a two hour delay in the evolution of carbon dioxide. The same phenomenon has been noted with solutions of dehydroascorbic acid prepared in the same way and at the same concentrations as described above.

These experiments strongly suggest that formaldehyde is reduced by ascorbic acid and that the resultant dehydroascorbic acid slowly forms carbon dioxide as one of its decomposition products.

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Solvolytic Reactivities of Some Secondary Alkyl Chlorides

BY JOHN D. ROBERTS[1]

Despite numerous comparisons of the reactivities of saturated organic halides toward nucleophilic reagents[2] relatively few investigations have been made of solvolytic reactivities of saturated halides under comparable conditions except for the series: methyl, ethyl, isopropyl, and t-butyl.[2] Dostrovsky and Hughes[3] have measured the solvolytic reaction rates of several alkyl bromides in aqueous alcohol and formic acid while Bartlett and Swain[4] and Brown and Johanneson[5] have reported relative reactivities for tertiary chlorides.

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(2) For many references see Evans, "The Reactions of Organic Halides in Solution," The Manchester University Press, Manchester, 1946, and Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940.

(3) Dostrovsky and Hughes, J. Chem. Soc., 164 (1946).

(4) Bartlett and M. Swain, unpublished work, presented by P. D. Bartlett at the Organic Symposium, Boston, 1947.

(5) H. C. Brown and Johanneson, paper presented at the Atlantic City meeting of the American Chemical Society, April, 1946.

In the present investigation the solvolytic reaction rates of four saturated secondary alkyl chlorides were measured in 50% water–50% alcohol by volume at 90–100° and are summarized in Table I.

TABLE I

SOLVOLYTIC REACTION RATE CONSTANTS OF SATURATED ALKYL CHLORIDES

Chloride	$k_1{}^{90°}$, hr.$^{-1}$	$k_1{}^{95°}$, hr.$^{-1}$	$k_1{}^{100°}$, hr.$^{-1}$	$\Delta H^{\neq}$, kcal.[a]	(95°) % olefin
Isopropyl	0.0582	0.0934	0.135	22.8	..
s-Butyl	.0539	.0891	.139	25.6	..
Diethylcarbinyl[b]	.0539	.0825	.122	22.1	15
Methylisopropylcarbinyl[c]	.159	.253	.386	24.3	24

[a] Average over 90–100°, obtained graphically. [b] Prepared by the method of Hass and Weber, Ind. Eng. Chem., Anal. Ed., 7, 231 (1935). [c] Prepared by the method of Whitmore and Johnston, Ref. 6.

The reactivities of the first three compounds given in Table I are very similar as might be expected from their structures. The somewhat greater reactivity of methylisopropylcarbinyl chloride may be related to the rearrangement which probably takes place in the hydrolysis of this substance.[6] The difference in reactivity is hardly due to bimolecular elimination (E2) involving solvent molecules since no significant difference in the extent of olefin formation is noted between diethylcarbinyl and methylisopropylcarbinyl chlorides. No noticeable trend in the values of $\Delta H^{\neq}$ is apparent for this series of chlorides. It is probable that further elucidation of the relative reactivities of secondary halides will depend on whether or not quantitative determination of the relative fractions of ionization (S_N1) or direct (S_N2) mechanisms involved in solvolysis reactions can be made by methods such as proposed by Grunwald and Winstein.[7]

Experimental

The rate determinations were carried out in 50% water–50% alcohol (by volume) as previously described[8] using an oil-thermostat with a mercury–toluene regulator. Temperatures were accurate to $\pm0.1°$. The extent of olefin formation was measured by quantitative hydrogenation of larger scale runs than were used in the rate experiments. In each case the reactions were carried to a calculated 95% or more of complete solvolysis before determination of olefin. The procedure was as follows. A solution of the alkyl halide in 100 ml. of 50% alcohol was placed in a 250-ml. distilling flask along with a thin-walled bulb containing a weighed quantity of platinum oxide and a number of 3–4 mm. glass beads. The contents of the flask were degassed and the flask sealed in vacuo. After the solvolytic reaction was complete, the tip of the seal-off of the flask was scratched and inserted in a short plastic tube leading to a hydrogen buret. The line was evacuated and the tip broken by carefully flexing the plastic tube. Hydrogen was admitted from the buret, the catalyst bulb broken by vigorous shaking, and the reduction

(6) Whitmore and Johnston, THIS JOURNAL, 55, 5020 (1933).

(7) Grunwald and Winstein, ibid., 70, 846 (1948).

(8) Roberts, Urbanek and Armstrong, paper submitted for publication in THIS JOURNAL.