

additional hour. The mixture was then poured into 600 cc. of water and the mixture was extracted with ether. The ether solution was washed with water, bicarbonate solution, then water and concentrated. The solid product IVab was worked up as described in part as in the previous section. The results and conditions are listed in Table IV.

Optical Rotatory Dispersion Data Relating the Configuration of (-)-I and (-)-V.—The optical rotatory dispersions

of derivatives of (-)-I and (-)-V were performed in the Laboratory of Professor Carl Djerassi.¹⁴ The derivatives, prepared by Dr. B. Sjöberg,¹⁹ are shown in Fig. 1, together with the optical rotatory dispersion curves which exhibit like Cotton effects.

(19) For details see B. Sjöberg, A. Fredga and C. Djerassi, *J. Am. Chem. Soc.*, **81**, 5002 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY, STANFORD, CALIF.]

The Vapor Phase Reaction of 2,3-Dimethyl-2-butene and Ozone¹

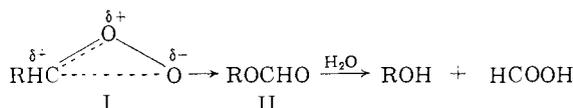
BY HOWARD E. SMITH² AND RICHARD H. EASTMAN

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In the vapor phase reaction of 2,3-dimethyl-2-butene and ozone the complex mixture of products was found to contain formic acid, formaldehyde, acetone, methanol, carbon dioxide, esters, and either acetic acid or a substance yielding acetic acid on hydrolysis. On the basis of the stoichiometry of the reaction, slightly more than two moles of olefin being required for the complete reaction of one mole of ozone, and the analysis of the mixture of products, it is suggested that two reactions, ozonolysis and allylic oxidation of the olefin, occur simultaneously.

Introduction

The recent appearance^{3,4} of work dealing with the reaction of olefins and ozone in the vapor phase prompts us to report the results of some experiments performed some time ago. This work was a continuation of that reported in a previous communication⁵ concerning the vapor phase ozonolysis of cyclohexene, from which there was obtained an ozonide with different properties from those formed in condensed systems, and which in turn gave the normal product, adipic acid, and the abnormal products, formic acid and *trans*-1,2-cyclohexandiol. It was proposed that the formic acid may be formed through a mechanism suggested by Criegee⁶ in which the intermediate I⁷ rearranges to a formate ester II. Alternatively, there may have been an



ozone-catalyzed allylic oxidation of cyclohexene leading to the formation of cyclohexen-3-ol, the ozonolysis of which would lead to formic acid.⁸

Now we report the vapor phase ozonolysis of 2,3-dimethyl-2-butene. It was chosen as most suitable in that it has no hydrogen attached to the doubly-bonded carbon atoms, is easily prepared in a very pure state, and has a relatively high vapor pressure.

(1) This material is taken from the thesis of Howard E. Smith offered in partial fulfillment of the requirements for the degree of Master of Science, Stanford University, 1954.

(2) Department of Chemistry, Vanderbilt University, Nashville 5, Tenn.

(3) A. E. Heath, S. J. Broadwell, L. G. Wayne and P. P. Mader, *J. Phys. Chem.*, **64**, 9 (1960).

(4) T. Vrbaski and R. J. Cvetanovic, *Can. J. Chem.*, **38**, 1053, 1063 (1960).

(5) R. H. Eastman and R. M. Silverstein, *J. Am. Chem. Soc.*, **75**, 1493 (1953).

(6) R. Criegee, 120th Meeting of the American Chemical Society, New York, N. Y., September 7, 1951, Abstract 22M; *Rec. Chem. Progr.*, **13**, 111 (1957).

(7) The mechanism for the initial attack of ozone at the double bond and the structure and rearrangement of I have recently been discussed by P. S. Bailey, *Chem. Revs.*, **58**, 926 (1958). For Criegee's zwitterion, Bailey suggests the resonance hybrid I.

(8) J. E. Leffler, *Chem. Revs.*, **45**, 400 (1949).

Method and Results

The 2,3-dimethyl-2-butene was prepared by dehydration⁹ of pinacolyl alcohol, and was purified by careful fractional distillation. The correctness of its assigned structure and its purity were demonstrated by comparison of its infrared absorption spectrum with that of 2,3-dimethyl-1-butene, the side product in the dehydration reaction.

The ozonization apparatus was that described⁵ previously. The olefin, as the vapor from a calibrated, thermostated bubbler, was introduced in a metered stream of dry nitrogen to the top of a 10 cm. \times 8 mm. vertically oriented reaction tube, the rate being varied by changes in the flow of nitrogen through the bubbler. The ozone was introduced by passing a metered stream of dry oxygen through a voltage variable, iodometrically calibrated,¹⁰ corona discharge ozonizer and thence into the reaction tube.

At the confluence of the olefin and ozone containing gas streams reaction took place immediately and, as measured by an iron-constantan thermocouple in the reaction tube, the steady-state temperature was 240° at a distance of 0.5 cm. below the point of mixing decreasing to 166° at 5 cm. In addition, as was observed previously in the gas phase ozonolysis of cyclohexene⁵ and 1-hexene,¹¹ an aerosol was produced a short distance down the reaction tube. In order to get complete consumption of ozone it was necessary to use slightly more than twice the molar equivalent of olefin, a stoichiometry similar to that found¹² in the vapor phase ozonolysis at room temperature of 1-hexene, cyclohexene and ethylene.

The reaction conditions under which our observations were made and during which a convenient amount of products could be collected in a reasonable length of time were: nitrogen flow rate, 250

(9) F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, **55**, 1106 (1933).

(10) C. M. Birdsall, A. C. Jenkins and E. Spadinger, *Anal. Chem.*, **24**, 662 (1952).

(11) R. D. Cadle, *Air Pollution Foundation*, Rept. **2**, No. 3, 27 (1956); *C. A.*, **51**, 9984c (1957).

(12) R. D. Cadle and C. Schadt, *J. Am. Chem. Soc.*, **74**, 6002 (1952)

TABLE I
STABLE PRODUCTS FROM THE VAPOR PHASE REACTION OF 2,3-DIMETHYL-2-BUTENE AND OZONE^a

		Cold trap ^b			Precipitator ^c		
		Meq./g. condensate	Mole ratio	Yield, ^d %	Meq./g. condensate	Mole ratio	Yield, ^d %
Acids before saponification	A	3.98 ± 0.01	1.7	..	4.88 ± 0.01	1.7	..
	B	2.38 ± .01	1.2	..			
Acids after saponification	A	5.04 ± .01	2.2	..	8.29 ± .01	2.9	..
	B	5.03 ± .01	2.5	..			
Formic acid	A	2.38 ± .18	1.0	2.4	4.17 ± .31	1.5	1.3
Acetic acid	A	2.66 ± .27	1.2	5.4	4.12 ± .41	1.4	2.6
Formaldehyde	A	3.60 ± .07	1.6	3.6	3.36 ± .07	1.2	1.1
	B	2.40 ± .03	1.2	2.4			
Acetone	A	4.6 ± .9	2.0	13.9	5.7 ± 1.2	2.0	5.4
	B	4.1 ± .9	2.0	12.4			

^a In addition to the products listed in the table both methanol and carbon dioxide were detected as products of the reaction. Based on 2,3-dimethyl-2-butene the yield of carbon dioxide in the exhaust gas was 5.7%. ^b Two different samples of condensate (A and B) were analyzed. The quantitative analysis of A accounts for 65 ± 8% of the condensate material, calculated without regard to hydrolysis and without including methanol. ^c Only one sample of condensate was analyzed. The quantitative analysis accounts for 87 ± 11% of the condensate material, calculated as in *b*. ^d Percentage yield based on 2,3-dimethyl-2-butene.

ml./min.; oxygen flow rate, 517 ml./min.; amount of olefin reacting, 0.53 mM/min. (45 mg./min.); amount of ozone reacting, 0.25 mM/min. (12 mg./min.).

Much of the reaction products condensed on the wall of the reaction tube, and was collected in a trap cooled to -78° at the bottom of the tube. The aerosol which passed through the trap was condensed with an electrostatic precipitator. The products were thus separated into three portions: those collected in the cold trap (32 mg./min.), those condensed by the precipitator (10 mg./min.), and those still entrained in the precipitator exhaust gas.

The material which collected in the cold trap was a homogeneous, water-soluble, greenish-yellow oil, which on standing at room temperature or on dilution with solvents lost its color, the bleaching being accompanied by the evolution of an unidentified gas. The infrared absorption spectrum of the bleached material using a capillary film showed only one band of interest, and this at 5.8 μ, while in the region above 7.6 μ there was only general absorption with no bands highly resolved. The material was not peroxidic,¹³ and isothermal distillation at 58° resulted in a series of impure fractions. The vapor phase infrared absorption spectra of these fractions revealed the presence of methanol, acetone and formic acid, and possibly methyl acetate and acetic acid. Fresh material was diluted with water and aliquots of this solution were quantitatively analyzed for total acids, formic acid,¹⁴ formaldehyde,¹⁵ acetic acid¹⁶ and acetone.¹⁷

The aqueous solution was acidic (pH 3.5), and it could be titrated with aqueous sodium hydroxide using phenolphthalein as indicator. The acid number could be increased on saponification by as much as 110%, and on boiling the aqueous solution

for an hour it was increased by about 30%, suggesting the presence of an ester.

The amount of formic acid was determined after saponification by the usual oxidative method,¹⁴ and after oxidation of the formic acid with mercuric oxide a serial steam distillation¹⁶ of the saponified solution showed that it contained, besides formic acid, mainly acetic acid.

Formaldehyde was determined before basic hydrolysis of the aqueous solution by precipitation of the dimedone derivative,¹⁵ and a pure derivative, m.p. 189–191°, was obtained directly in all experiments, indicating that this aldehyde was the only one present in detectable amounts.

Acetone was determined by precipitating¹⁷ the 2,4-dinitrophenylhydrazones of both acetone and formaldehyde and then calculating the amount of acetone by correcting the weight of precipitate for that of formaldehyde. In one experiment the formaldehyde was oxidized with basic potassium permanganate in the cold, and then the 2,4-dinitrohydrazone of acetone precipitated. Its purity, m.p. 123–125, and its amount, in excellent agreement with that estimated by the procedure outlined above, showed that acetone was the only ketone present in appreciable amounts.

A complete summary of the analyses is collected in Table I. Estimations of the uncertainties in the respective analyses were made on the basis of experiments not only with solutions of each component, but also with a standard mixture of all four components.

The second portion of products, the aerosol, which was condensed by the precipitator, was a colorless, water-soluble oil that on standing also evolved a small amount of gas. The infrared absorption spectrum of the condensate was similar to that of the material from the cold trap, and preliminary tests indicated the same components. By the same methods of quantitative analysis, formic acid, acetic acid, formaldehyde and acetone were found to be present, as is shown in Table I, in roughly the same mole ratios.

When the exhaust gas from the precipitator was subjected to vapor phase infrared analysis, bands assignable to acetone and to carbon dioxide were

(13) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 100.

(14) "Methods of Analysis of the Association of Official Agricultural Chemists," Fifth Edition, 1940, p. 466.

(15) J. H. Yoe and L. C. Reid, *Ind. Eng. Chem., Anal. Ed.*, **13**, 238 (1941).

(16) T. E. Friedemann, *J. Biol. Chem.*, **123**, 161 (1938).

(17) H. A. Iddles and C. E. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454 (1934).

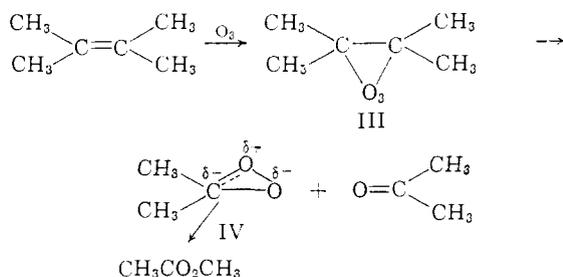
observed. Washing of this gas stream with water, treatment of the resulting aqueous solution with sodium hydroxide, acidification and isolation of the acidic components revealed, with the use of gas phase infrared analysis, the presence of only formic and acetic acid. Only the amount of carbon dioxide was determined quantitatively, and it was found that it accounted for about 6% of the olefin substrate.

As seen from the percentage yields in Table I, the high rate of gas flow (767 ml./min.) caused much of the reaction products to be swept through the cold trap and precipitator. Except for carbon dioxide, the amounts of these products were not estimated, but, nevertheless, the mole ratios of products as shown in the table give some indication of the relative amounts of three-, two- and one-carbon compound formed in the reaction.

Discussion

The requirement of slightly more than two moles of hydrocarbon for complete reaction of one mole of ozone suggest that two reactions were occurring simultaneously, attack of ozone at the carbon-carbon double bond and attack of oxygen at the allylic position¹⁸ of the olefin.

The ozonolysis evidently follows the course proposed by Criegee⁶ and leads to acetone and methyl acetate, the latter on saponification being detected as acetic acid. This sequence may be outlined as¹⁹

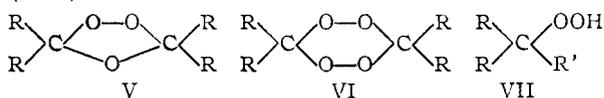


Evidence is accumulating^{6,7} that in condensed systems classical ozonides (V), dimeric (VI) and polymeric peroxides and hydroperoxides (VII) arise from intermediates such as IV by their additions to carbonyl compounds, by their dimerizations and

(18) E. H. Farmer and A. Sundralingam, *J. Chem. Soc.*, 121 (1942).

(19) For a discussion of the detailed structure of III see ref. 7.

polymerizations and by their reactions with solvents (R'H).



If these processes occurred to any extent in the vapor phase reaction, the mixture of products would be peroxidic. This, in fact, was not found in this work or in a similar reaction with 1-hexene,¹¹ and it would appear that rearrangement of IV is more important in the vapor phase. The mixture of products from the vapor phase ozonolysis of cyclohexene⁶ contained some traces of peroxidic oxygen, due perhaps to the presence of an ozonide (V) formed by an intramolecular addition reaction.

For the competing reaction, attack of oxygen at the allylic position of the olefin, this work does not suggest the details of the reactions which subsequently lead to three-, two- and one-carbon fragments. Considering the data in Table I and the detection of methanol in the unhydrolyzed mixture of products, it is likely that, in addition to formic acid, formaldehyde and carbon dioxide, both acetone and methanol are products in these processes.

Experimental²⁰

2,3-Dimethyl-2-butene.—Pinacolyl alcohol was heated with oxalic acid under a Hahn distilling head²¹ (b.p. 73°), and dehydration to charring took 40 hours. On fractional distillation of the product there was obtained 2,3-dimethyl-1-butene (5.9%), b.p. 55.0–55.9°, n_D^{20} 1.3900, d_4^{20} 0.8669, and 2,3-dimethyl-2-butene (55.8%), b.p. 72.0–73.5°, n_D^{20} 1.4128, d_4^{20} 0.707, similar in properties to those previously reported.^{8,22,23}

For final purification, the 2,3-dimethyl-2-butene was redistilled and that fraction with b.p. 73.1–73.2° was used in all ozonolysis experiments. The correctness of its assigned structure was confirmed by its vapor phase infrared absorption spectra, path length 10 cm. For the unsymmetrical olefin, 2,3-dimethyl-1-butene, there was a strong band at 6.05 μ , the strongest band occurring at 11.2 μ , while that of 2,3-dimethyl-2-butene showed only two weak bands in the region 6–8 μ and these at 6.8 and 7.2 μ . In addition, this material showed no absorption at 11.2 μ indicating the complete absence of 2,3-dimethyl-1-butene.

(20) Melting and boiling points are uncorrected. Infrared spectra were obtained using a model 21 Perkin-Elmer double beam spectrophotometer with rock salt optics.

(21) F. Arndt, *Org. Syntheses*, **20**, 27 (1940).

(22) N. Zelinsky and J. Zelikow, *Ber.*, **34**, 3249 (1901).

(23) B. Nybergh, *Hyllningskrift Tillagnad Ossian Aschan*, 98 (1920); *C. A.*, **16**, 2110 (1922).