[CONTRIBUTION FROM THE TUFTS COLLEGE DEPARTMENT OF CHEMISTRY]

STUDIES IN OZONOLYSIS. II.[1] QUANTITATIVE STUDY OF THE OZONATION OF 3-OCTENE[2]

FRED L. GREENWOOD AND MICHAEL G. WOLKOWICH

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Little work of a quantitative nature has been carried out on the ozonation reaction. The first experiments were reported by Brus and Peyresblanques (1). The course of the ozonation was followed by determining unabsorbed ozone coming from the reaction flask at various intervals during the ozonation, and by plotting these values against the volume of ozonized oxygen led into the reaction mixture. Chloroform was used as the solvent, and periodic additions of solvent were made to replace the solvent entrained by the gas stream. The loss of unsaturated compound by entrainment and possible reaction of the solvent with ozone were ignored. Harries (2) has pointed out that chloroform is attacked appreciably by ozone and is not a particularly satisfactory solvent for ozonation. We (3) also found chloroform to be quite sensitive to attack by ozone. In those cases where the reaction of unsaturated compound and ozone is not a rapid and complete one, chloroform would appear to be a poor solvent for ozonation reactions.

Noller, *et al.* (4) have used the technique of Brus and Peyresblanques, but they endeavored to compensate for the effect of the reaction mixture on ozone by plotting an "adjusted" percent of unabsorbed ozone against the equivalents of ozone entering the reaction mixture. This "adjusted" percent was arrived at by conducting the ozonation until the concentration of ozone coming from the reaction flask was approximately constant. This value, which was always less than the ozone concentration produced by the ozonizer, was given a value of 100% and the other unabsorbed ozone values were adjusted on this basis. These workers made the comment that their method was "rather crude" and that attempts were being made to refine the procedure. However, no reports of further work have appeared. The data showed that other functional groups in a molecule affected the rate of addition of ozone to the carbon-carbon double bond. The addition of ozone to oleic acid, elaidic acid, and methyl oleate did appear to be approximately quantitative. Tits and Bruylants (5) have ozonized a series of α,β-unsaturated amides by the technique described by Noller, *et al.*

Pummerer, Matthäus, and Socias-Vinals (6) studied the course of the ozonation reaction by titrating aliquots of the reaction mixture at regular intervals with bromine-carbon tetrachloride. With 3-ethyl-2-pentene they found a regular diminution in bromine titration as the ozonation proceeded. The experimental data are quite sketchy, and it is impossible to calculate quantitatively the course of the reaction. Carbon tetrachloride was the solvent used, and this solvent is attacked by ozone (3).

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[1] Paper I, Greenwood, *J. Org. Chem.*, **10**, 414 (1945).

[2] We wish to express our gratitude to the Research Corporation for their support of a portion of this work.

The reaction of solvent and ozone could be disregarded by using a solvent which is completely resistant to ozone. We have found specially purified *n*-pentane to be completely resistant to 2% (vol.) ozone at −35°. At 0° the pentane was attacked by ozone of this concentration. Ozonides are oxidizing agents, and there is the possibility that during an ozonation the ozonide may be reacting with alkene which has not yet been transformed to the ozonide. To answer this question and to follow quantitatively the course of an ozonation, solutions of 3-octene in purified *n*-pentane were reacted with definite amounts of ozone. Unreacted 3-octene in the reaction mixture was determined by titration with bromine-acetic acid. The results of the experiments are indicated in Table I.

TABLE I

Ozonation of 100 mM. of 3-Octene with Various Increments of Ozone and Determination of Unreacted Alkene in the Reaction Mixture
(*n*-Pentane solvent; temp. −40°)

OZONE PRODUCTION		TIME OZONE WAS LED INTO REACT. MIXTURE (Hours)	mM. OF OZONE ADDED TO REACT. MIXTURE	mM. OF 3-OCTENE UNREACTED IN REACT. MIXTURE CALC'D. FROM OZONE USED	mM. OF 3-OCTENE UNREACTED IN REACT. MIXTURE DETERMINED BY BROMINE TITRATION
Vol.-% of Ozone	Mg. Ozone per hour				
.9	217	2.13	9.6	90.4	88.3
.8	202	4.70	19.8	80.2	77.8
1.1	272	5.33	30.2	69.8	68.6
1.0	237	7.90	39.0	61.0	58.9
.8	205	11.57	49.4	50.6	50.0
1.2	284	10.22	60.5	39.5	38.0
.9	225	14.68	68.8	31.2	29.9
1.1	259	15.18	81.9	18.1	16.9
1.1	279	15.47	89.9	10.1	9.1
1.0	265	18.13	100.1	None	None

These data show that under the experimental conditions used the reaction of 3-octene and ozone is a quantitative one, and that the ozonide does not react with the alkene.

EXPERIMENTAL

Ozonizer. The ozonizer used in these experiments was that described previously (7). The voltage on the transformer primary was constant at 114 and the secondary was delivering 7150 volts. The flow of oxygen through the apparatus was kept constant at 11.5 liters per hour. Under these conditions the ozone concentration for different experiments varied from 0.8 to 1.2% (vol.) (202–284 mg. ozone per hour); however, during any one experiment the ozone concentration was checked every two or three hours and it remained constant.

Ozonation apparatus. The apparatus in which the ozonations were carried out consisted of a reaction flask fitted with a thermometer well, a gas disperser, and a spiral reflux condenser which was cooled with Dry Ice-alcohol. A flow meter filled with pentachloroethane between the ozonizer and ozonation flask enabled one to maintain a constant gas flow through the apparatus at all times. By means of a system of three-way stopcocks the stream of gas flowing through the apparatus could be diverted and analyzed for ozone before entering the reaction flask or after passing through the reaction flask and the reflux condenser.

Ozone concentrations were determined by bubbling 0.05 cu. ft. of the gas through neutral potassium iodide and titrating the liberated iodine with standard thiosulfate in the usual way. The time necessary for the 0.05 cu. ft. of gas to flow through the meter was clocked with a stopwatch. In this way it was possible to calculate the rate of gas flow each time an analysis was made.

Chemicals. n-Pentane was employed as a solvent. As purchased, the *n*-pentane (Phillips Petroleum Company, pure grade) was not satisfactory, for it reacted with ozone, even at −40°. The pentane was purified by placing 750 ml. of it in the ozonation flask, cooling the liquid to −40° and passing 1% (vol.) ozone at a rate of 11.5 liters per hour through the liquid for eight hours. The treated material was transferred to a flask fitted with a gas inlet and a reflux condenser which was filled with ⅛ inch helices. The pentane was entrained with nitrogen, and the helix-filled condenser was cooled just enough to maintain a slight reflux. The entrained pentane was caught with a Dry Ice-alcohol condenser and, after warming sufficiently, was washed successively with aqueous potassium iodide, aqueous sodium thiosulfate, and water. The material was then forced through a layer of phosphorus pentoxide which was supported on a fritted glass funnel. In this way *n*-pentane was obtained which was completely resistant to ozone under our reaction conditions.

The *3-octene* was prepared by a Boord synthesis essentially as described by Wibaut and Gitsels (8). The 3-octene was distilled through an 18 plate, Fenske column; the material had b.p. 121.4°/776 mm. and n_D^{25} 1.4109.

Ozonation of 3-octene and determination of unreacted alkene. In the ozonation flask was placed 11.22 g. (0.1 mole) of 3-octene and 150 ml. of purified *n*-pentane. This solution was cooled to −40 to −35° and kept at this temperature during the ozonation. The desired amount of ozone was introduced into the reaction flask by passing ozonized oxygen through it for the proper length of time. In the first experiment 0.01 mole of ozone was introduced into the reaction flask, and in succeeding experiments increasing amounts of ozone were used until in the final experiment 0.1 mole of ozone was introduced. During each ozonation the gas was passed through aqueous potassium iodide after it had passed through the reaction flask. No ozone escaped from the reaction flask except in the case when 0.1 mole of ozone was used. In this latter experiment 18.13 hours were required to introduce the 0.1 mole of ozone, and even here the first perceptible yellow color did not appear in the potassium iodide solution until just 0.18 hour before the required time. After the ozonation the reaction flask was left attached to the ozonation apparatus and nitrogen was bubbled through the cold (−40°) reaction mixture at a rate of 11.5 liters per hour for one-half hour to entrain dissolved oxygen.

The pentane-ozonide solution was warmed to 0° and transferred to a 200-ml. volumetric flask which was immersed in ice-water. The solution was brought to 200 ml. with cold, purified pentane. Aliquots (50 ml.) of the ozonide solution were transferred to a 250-ml. Erlenmeyer flask which was immersed in ice-water. The Erlenmeyer flask was kept in ice water during the titration of the alkene with bromine-acetic acid solution. The titer of the bromine-acetic acid solution was determined by adding 5.00 ml. of the solution to excess potassium iodide solution and titrating the liberated iodine with standard thiosulfate. One ml. of the solution was found to contain 0.46 mM. of bromine.

Resistance of purified n-pentane to ozone attack. To make certain that ozone was not attacking the pentane solvent and that nothing was formed by the interaction of ozonized oxygen and pentane which would interfere with the bromine titration for alkene, the following experiment was carried out. The apparatus and experimental conditions were those described earlier for an ozonation. In the reaction flask was placed 150 ml. of purified *n*-pentane and ozone of 1.4% (vol.) concentration was bubbled through the liquid for eight hours. The ozonizer was producing ozone at the rate of 330 mg. per hour. Within 15 min. after admitting ozone to the reaction flask ozone was coming through the pentane at a rate of 298 mg. per hour. After half an hour ozone was coming through the pentane at a rate of 328 mg. per hour. The fact that the ozone coming through the pentane did not immediately become equal to that entering the solvent is explained by ozone dissolving in the liquid until a saturated solution was reached. Several times during the next eight hours the gas stream was analyzed for ozone before and after passing through the pentane, and in each case the values checked.

After eight hours the ozonized oxygen was replaced by nitrogen, and this gas was bubbled through the pentane for one hour at a rate of 11.5 liters per hour to entrain dissolved ozone. The pentane was now warmed to 0° and a 50-ml. aliquot was titrated with bromine-acetic acid solution as described previously. Three drops of the bromine solution sufficed to impart a definite color to the liquid.

A 5-ml. portion of the ozonized pentane was shaken with aqueous potassium iodide and a barely perceptible yellow color was imparted to the aqueous layer.

Non-reaction of 3-octene with oxygen. In any ozonation there is much more oxygen than ozone passed through the reaction mixture. To be certain that no interfering reaction of oxygen with 3-octene could be occurring, the following experiment was conducted. For 12 hours oxygen was passed through a solution of 11.22 g. of 3-octene in 150 ml. of purified *n*-pentane under the same conditions as employed for an ozonation. The solution was then diluted to 200 ml. with pentane and a 25-ml. aliquot was titrated with bromine-acetic acid solution as described earlier. A second solution of 3-octene (5.61 g.) in 100 ml. of purified *n*-pentane (volumetric flask in ice-water) was prepared. This solution was not treated with oxygen, and a 25-ml. aliquot was titrated with bromine-acetic acid solution. Both 3-octene solutions required the same volume of bromine solution for titration. These titrations show that there was no reaction of oxygen with the 3-octene and no loss of 3-octene by entrainment. Calculation of the bromine number of the 3-octene in each solution gave a value of 141 (theory 142.4).

SUMMARY

Properly purified *n*-pentane is completely resistant to low concentrations, 2% (vol.) or less, of ozone at −40°, but not at 0°.

The reaction of 3-octene and ozone at −40° proceeds in a quantitative manner and no side reactions are in evidence.

MEDFORD 55, MASSACHUSETTS

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