buted to a primary act of efficiency nearly 0.5. Mechanism II as written similarly gives $f_r = f_1'$ and meets the same difficulty. However, if it is supposed that at low acid, reaction 2 takes place as

$$O^* + OOH^- = O^*O + OH^-$$

the necessary degree of freedom to account for the change in f_r is introduced. An analogous change in mechanism does not appear as reasonable with HO as the reactant. The fractionation data tend to disqualify mechanism I, and favor II as a means of explaining all the observations.

The transition from the limiting decomposition to the chain decomposition has been discussed by Lea.[5] The slight trend in ϕ with concentration of hydrogen peroxide (Table I, experiments 1–4 and 5–7) is presumably due to a residual chain decomposition, which diminishes as the peroxide concentration decreases. It is by no means certain that the chain decomposition which sets in is carried by HO and HO_2. The difficulty that has been experienced in obtaining reproducible data when the chain lengths are long makes it questionable to assume that the chain carriers are these radicals in any particular case. The fractionation factors f_0 and f_r should be useful in characterizing the intermediates in future work. They have the advantage over rate measurements that they are independent of chain length, and are affected only by changing the identity of the intermediates. Thus an accidental inhibitor that acts only by breaking chains will affect the quantum yield but not the values of f_0 and f_r. It is assumed in these remarks that the chains are long enough so that the principal path for decomposition of H_2O_2 is by the chain mechanism.

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[CONTRIBUTION FROM STANFORD RESEARCH INSTITUTE]

Kinetics of the Gas Phase Reaction of Olefins with Ozone

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A rapid gas phase reaction occurs between ozone and various olefins. The over-all reactions are quite complicated, more olefin disappears than ozone on a mole basis, and the stoichiometry varies with reactant pressures. By extrapolating rates back to initial conditions, a relatively simple second-order rate law was observed. The initial rate was mostly homogeneous and independent of foreign gas pressure. Within experimental error the rates are also independent of temperature. Certain aspects of a mechanism are discussed.

The reaction of ozone and olefins has been studied in the liquid phase, especially with respect to reaction products.[1]

The present paper reports a study of the kinetics of the gas phase reaction of olefins with ozone. Another group in this Laboratory has been investigating the products of the gas phase reaction between olefins and ozone,[2] and this study will be reported separately. This work was part of a broad program to investigate reactions which may occur in contaminated atmospheres, and thus particular emphasis has been placed on low concentrations.

Experimental

The olefins investigated were 1-hexene, ethylene, cyclohexene and (very briefly) 1-decene, 1-octene, 1-heptene, 1-pentene and propylene. They were obtained from commercial sources. The liquid hydrocarbons were purified by distillation. The ethylene was condensed in a trap cooled with liquid nitrogen. Gaseous ethylene was produced as needed by allowing the trap to warm slightly. Ozone was prepared from cylinder oxygen by a corona discharge ozonizer.

Two techniques were used to follow the course of the reactions. One involved mixing the reactants in the air of a galvanized iron chamber of 10 m.^{3} volume. Samples of the air in the chamber were withdrawn periodically and analyzed chemically for oxidant using a modification of the method of Crabtree and Kemp.[3] This method had the advantage that very low concentrations of reactants could be employed.

The other technique employed the cell of a recording infrared spectrometer as the reaction vessel. This cell was 10 cm. long and 3 cm. in inside diameter. The chemical reaction was followed by measuring absorption at a fixed wave length. The gas handling system was similar to that used by Mills and Johnston for reactions at intermediate pressures.[4]

The reaction cell, mixing cell and double stopcock were immersed in a thermostated oil-bath. Each of the lines leading to the gas-handling system included a coil immersed in the oil-bath which aided in bringing the gases to bath temperature. A run was started by evacuating the reaction cell, closing the stopcock between cell and pump, and admitting reactants through the double stopcock. This technique required higher concentrations of reactants than the chamber technique, but temperature and total pressure were more easily controlled.

The rates of decomposition of ozone in the two types of equipment were investigated. The rate of disappearance of ozone in the chamber was about 15% per hour. No observable decomposition of ozone occurred in the cell of the spectrometer during two minutes which was longer than most of the runs.

Results

1-Hexene.—The gas phase reaction of 1-hexene with ozone was studied entirely with the chamber technique. Two sets of runs were made to determine the order and stoichiometry of the reaction.

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(1) R. Criegee, "The Ozonolysis of Olefins and Acetylenes," paper presented before the Division of Organic Chemistry, 120th Meeting of the American Chemical Society, Sept., 1951.

(2) R. H. Eastman and R. M. Silverstein, private communication.

(3) J. Crabtree and A. R. Kemp, *Ind. Eng. Chem., Anal. Ed.*, **18**, 769 (1946).

(4) R. L. Mills and H. S. Johnston, THIS JOURNAL, **73**, 938 (1951).

One set involved maintaining the initial ozone concentration at 1 μatm. (microatmosphere or atm. $\times$ 10^{-6}) and varying the initial concentration of 1-hexene. The other involved maintaining the initial concentration of 1-hexene at 10 μatm. and varying the initial concentration of ozone. The results were plotted as oxidant concentration *vs.* time curves. The slopes of each curve (reaction rates) were measured at several different points and plotted against the corresponding oxidant concentrations on log paper. Examination of these curves revealed approximately straight lines, but the slopes varied from run to run so that the over-all reaction had no particular order. More 1-hexene disappeared than ozone on a mole basis. Initial rates were estimated by extrapolating the logarithmic plots back to initial conditions. The order of the initial reaction was estimated by plotting log initial rates against log initial concentrations of one reactant when the initial concentration of the other reactant was held constant (Figs. 1 and 2). The slopes of the straight lines fitted to the points by the method of least squares were the orders with respect to the variable reactant. These were 0.90 with respect to ozone and 0.99 with respect to 1-hexene. Thus the order of the reaction was essentially two, and one with respect to each reactant. The average second-order velocity constant calculated from these data was 0.013 μatm.$^{-1}$ min.$^{-1}$ with a standard deviation of 0.002.

The relative amounts of 1-hexene and of ozone consumed during the reaction are shown by Table I. More 1-hexene was used than ozone, and the relative amounts consumed varied with the concentration.

TABLE I

AMOUNT OF OXIDANT CONSUMED

Initial ozone concentration was varied and initial 1-hexene concentration was 10 μatm.

Original ozone concentration, μatm.	Oxidant consumed, %	Original ozone concentration, μatm.	Oxidant consumed, %
10	60	5	76
8	57	2.5	100
6	67	1.0	100

The effect of temperature on the rate of reaction of 1 μatm. of ozone with 10 μatm. of 1-hexene was investigated by changing the temperature of the room which houses the chamber. Runs were made at 8, 16, 21 and 27°, measured within the chamber. The curves obtained were identical within the limits of experimental error.

Ethylene.—The gas phase reaction of ethylene and ozone was studied using the infrared spectrometer supplemented by a few experiments using the chamber technique. The concentrations of ethylene and ozone in the reaction cell varied from 185 to 4500 μatm. These data were treated in the same manner as the data from the chamber experiments. The plot of log rate *vs.* log ethylene for a given run did not give a straight line, and thus the over-all reaction had no definite order. However, the initial reaction was first order with respect to both ozone and ethylene and was thus second order. Most of the runs were made at 30°. Variations in the total pressure (mainly oxygen and nitrogen) from 150 to 650 mm. produced no significant change in the velocity constants. Varying the ratio of the initial concentrations of ozone to ethylene from 0.95 to 11.0 produced no significant change. The average of 37 velocity constants was 5.2 $\times$ 10^{-3} μatm.$^{-1}$ min.$^{-1}$ with a standard deviation of 2.0 $\times$ 10^{-3}.

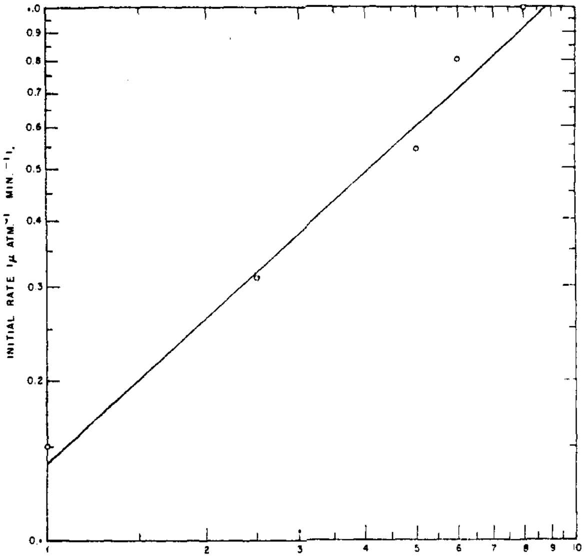

Fig. 1.—Initial rate *vs.* initial concentration of ozone. Initial 1-hexene concentration maintained at 10 μatm

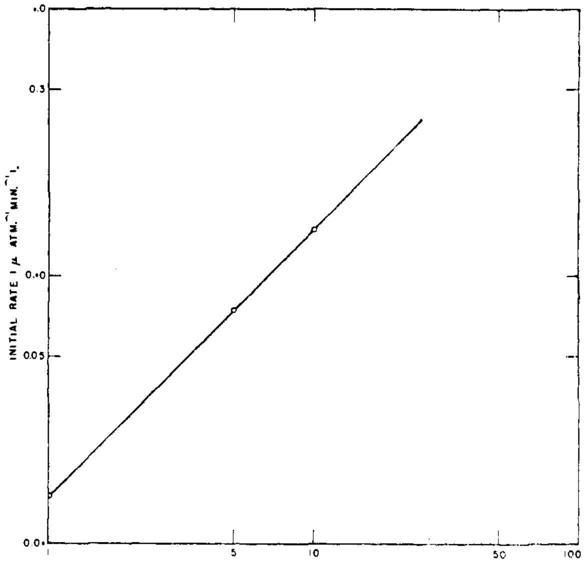

Fig. 2.—Initial rate *vs.* initial concentration of 1-hexene. Initial ozone concentration maintained at 1μatm.

The effect of temperature was investigated by making 6 runs each at 40 and 50° in addition to the runs at 30°. The change in temperature produced no significant change in the velocity constant.

The stoichiometry was studied by determining the amounts of ethylene and ozone consumed during the two sets of experiments (Table II).

Apparently considerably more ethylene was consumed than ozone. An attempt was made to determine whether at any wave length in the

TABLE II

RELATIVE AMOUNTS OF OZONE AND ETHYLENE CONSUMED

Original ethylene concn., μatm.	Original ozone concn. = ozone consumed, μatm.	Ratio ethylene consumed to ozone consumed
4350	540	3.2
4160 Set 1	520	2.1
3670	450	1.9
3700	690	3.1
3400 Set 2	620	1.9
3300	590	2.0

infrared, absorption would increase and then decrease during the reaction indicating an intermediate reaction product which accumulated to an appreciable extent. The spectrum was examined from about 2.5 to 15 μ at intervals of 0.2 μ but no such product was found.

For purposes of comparison four runs were made using the chamber technique. The average initial second-order velocity constant was 3.3×10^{-3} μatm.$^{-1}$ min.$^{-1}$. Again more ethylene than ozone was consumed.

Other Olefins.—The reaction of ozone with cyclohexene was studied briefly because the location of the double bond in the interior of the molecule would give the double bond somewhat different properties. The chamber technique was used. The average initial second-order velocity constant was 0.087 μatm.$^{-1}$ min.$^{-1}$. Again, more olefin than ozone, on a mole basis, was consumed.

In order to determine the effect of chain length on the reaction rate, a number of terminal olefins other than 1-hexene were studied using concentrations of 10 and 20 μatm. of olefin and 1 μatm. of ozone in the chamber. The olefins studied were 1-decene, 1-octene, 1-heptene, 1-pentene and propylene. The oxidant concentration *vs.* time curves for all of these at each concentration were almost identical to that of 1-hexene, although the reactions involving 1-pentene and propylene may have been slightly slower than the others. The reaction involving ethylene was much slower than the rest (Table III).

TABLE III

INITIAL SECOND-ORDER VELOCITY CONSTANTS FOR THE REACTION OF SEVERAL TERMINAL OLEFINS

Concentrations used were 1 μatm. of ozone and 10 μatm. of olefins

Olefin	Second-order velocity constant, μatm.$^{-1}$ min.$^{-1}$	Olefin	Second-order velocity constant, μatm.$^{-1}$ min.$^{-1}$
Decene	0.016	Pentene	0.0078
Octene	.012	Propene	.0092
Heptene	.012	Ethylene	.0040
Hexene	.015		

Discussion

These experimental results show that a rapid gas phase reaction occurs between ozone and various olefins. The over-all reactions are quite complicated, more olefin than ozone disappears on a mole basis, and the stoichiometry varies with reactant pressures. By extrapolating rates back to initial conditions, a simple second-order rate law was observed. The initial rate was essentially independent of foreign gas pressure. A great change in surface (chamber to small infrared cell for ethylene) made a negligible change in the initial rate constant. Temperature had very little or no effect. Thus the empirical energy of activation was zero within experimental error for both 1-hexene and ethylene.

If the velocity constant is written as $k = Ae^{-E/RT}$ it is found that the pre-exponential factor A is 5.6×10^6 cc. mole^{-1} sec.$^{-1}$ for 1-hexene and 3.5×10^5 cc. mole^{-1} sec.$^{-1}$ for ethylene. The normal value for the pre-exponential factors for simple bimolecular reactions is about 10^{11} to 10^{13} cc. mole^{-1} sec.$^{-1}$. Thus for these reactions, even the initial second-order part of the reaction is not a normal bimolecular process. This low pre-exponential factor presents the interesting possibility that the first step may involve a forbidden electronic transition[5] where ozone donates an oxygen atom to the olefin.

However, there are other explanations of the lack of effect of temperature. Ozone and olefin might be in equilibrium with a chemical complex (1). The empirical initial rate constant would then be the product of an equilibrium constant and rate constant. If the complex formation is sufficiently exothermic, the product of the equilibrium constant and rate constant would be temperature independent.

The over-all reaction of ozone and olefins in the gas phase is very complex as evidenced by a variety of products,[2] by the absence of a constant order to the over-all reaction, and by the variable stoichiometry. This study establishes, however, that the initial step is simply a second-order process, but even the relatively simple initial rate is quantitatively anomalous.

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(5) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950.