MOLECULAR REARRANGEMENTS IN THE REACTIONS OF OXYGEN ATOMS WITH OLEFINS[1]

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ABSTRACT

Reactions of oxygen atoms with propylene, butene-1, *iso*-butene, *cis*-butene-2, *trans*-butene-2, *cis*-pentene-2, and tetramethyl ethylene have been studied at room temperature and at pressures between 50 and 600 mm. The following generalizations can be made. The oxygen atom adds predominantly to the "less-substituted" carbon atom of the olefinic double bond to form a short-lived biradical which rapidly rearranges into isomeric epoxy and carbonyl compounds. Rearrangements involve migration of radicals (including H atoms) from the carbon atom to which oxygen is attached to the other carbon atom of the original double bond. Partly inhibited rotation around the original double bond also takes place. Migration of H atoms is exclusively internal. Migration of larger radicals, such as CH_3, is only partly internal: a large fraction of these radicals become completely detached from the rest of the molecule and the particular carbonyl compound is produced both by radical combination and by internal migration. The fragmentation resulting from the splitting off of a migrating radical is pressure independent. The final addition products formed are "hot" as a result of high heats of reaction and undergo decomposition if the excess energy is not removed by collisions. This second type of fragmentation is, therefore, pressure dependent. It is very extensive in the case of ethylene and appears to be completely suppressed in the investigated pressure range in the case of more complex olefins (possessing a greater number of degrees of freedom) such as butenes and higher homologues. Propylene exhibits an intermediate behavior. For orientation of addition of oxygen atoms a carbon atom of an olefinic double bond to which CH_3 is attached is "less substituted" than a corresponding carbon atom to which C_2H_5 is attached.

INTRODUCTION

In a previous publication (1) some preliminary results of a study of the reactions of oxygen atoms with a number of butenes have been briefly reported. This investigation has two distinct objectives: (1) to establish the general mechanism and the type of products formed, and (2) to obtain information on the rates of these reactions. In the present paper the first of the two aspects of the investigation is presented in detail and is extended to some further olefins studied in the meantime.

This work is a part of a more extensive study of the reactions of oxygen atoms with different organic compounds. The reactions with ethylene (2) and acetaldehyde (3) have already been described, while the results obtained with some other types of compounds will be published at a later date. Oxygen atoms are generated by mercury-photosensitized decomposition of nitrous oxide (4) and are probably in their ground, triplet $O(^3P)$, state. The amount of nitrogen formed gives a direct quantitative measure of the oxygen atoms generated and serves as an internal actinometer.

EXPERIMENTAL

A conventional-type high-vacuum apparatus was used. It incorporated a cylindrical silica reaction cell, 5 cm. in diameter and 10 cm. long, an all-glass circulating pump supported on teflon bearings, a LeRoy still (5), and a constant volume burette with a copper oxide tube and outlets for sampling tubes connected with it. Two low-pressure mercury lamps were placed one at each end of the reaction cell and were used singly or simultaneously as the source of mercury resonance radiation.

For the analysis of products use was made of the LeRoy still (for a preliminary separation into fractions), the copper oxide tube in conjunction with the constant-volume

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burette (for the analysis of the non-condensables), gas–liquid chromatography (GLC), infrared and mass spectroscopy. An attempt was made, whenever possible, to verify the qualitative identification of the products by directly comparing the GLC relative elution times (6) and the infrared and mass spectra for the unknown product (after separation on GLC) and for a standard sample of the corresponding compound. In one or two cases a standard sample was not available and the identification was based on the comparison of the mass and infrared spectra with the existing literature data. In the early stages of the investigation, before the type of products formed was established, relative elution times were determined for a number of different C_4H_8O isomers and, thus, several possibilities were readily ruled out. A 10 ft. column of dinonyl phthalate on glass spheres (passing 270 mesh) was used, and the GLC apparatus differed from the one previously described (7) in that the low pressure (*ca.* 30 mm.) at the outlet of the column was maintained constant by inserting a suitable *internal* capillary in the lead to the high-vacuum pump and not by an external leak. A better stability was obtained in this manner and a gradual deterioration in the performance of the high-vacuum pump was prevented. The inlet pressure was maintained at 14 p.s.i. and the column temperature varied from 25° to 110° C. depending on the volatility of the products.

Best available grades of reactants were used after thorough degassing and bulb-to-bulb distillation *in vacuo.* N.B.S. samples of *cis*-pentene-2 and 3-methylheptane were kindly supplied by the Stanford Research Institute. *cis*-C_4D_8-2 was prepared by Dr. L. C. Leitch of these laboratories. Molecular oxygen was produced by heating reagent grade $KMnO_4$.

In the experiments carried out a large excess of nitrous oxide was used (100 to 600 mm. N_2O and usually only a few millimeters of the olefin). The ratio of the over-all quenching efficiency of an olefin and nitrous oxide is about 2 (8). The quantum yield of decomposition of nitrous oxide, however, is quite high (3) while that of olefins is as a rule very low, especially at the high total pressures used (9). Experimental conditions, therefore, could be readily adjusted so as to eliminate complications from direct quenching decompositions of olefins. By not extending the reactions to too high conversions, secondary reactions involving the products could also be avoided. Actually no trends in the rates of formation of the products per oxygen atom consumed were observed, except at very high conversions, after most of the olefin was consumed.

RESULTS

Experiments carried out with a number of hydrocarbons have shown that in general three types of reactions may be expected between the ground-state oxygen atoms and olefins: (1) addition of atoms to the olefin to form addition products, (2) fragmentation of the initially produced addition products, and (3) hydrogen abstraction.

Hydrogen Abstraction

At room temperature at least, and with the olefins studied so far, no evidence was found of any direct hydrogen abstraction by oxygen atoms. This finding is in agreement with the observed much higher rates of addition of oxygen atoms to the olefinic double bond relative to the hydrogen abstraction from paraffins. Thus, for example, the addition of oxygen atoms to *cis*-pentene-2 was found to be 43 times faster than the reaction of oxygen atoms with 3-methylheptane. It is conceivable, however, that with certain olefins a small amount of direct hydrogen abstraction takes place even at room temperature and that at elevated temperatures the abstraction reaction might become quite important.

Reaction of Oxygen Atoms with Propylene

In the reactions reported in the present communication the observed addition compounds, isomeric epoxides and carbonyl compounds, are the major reaction products, although a certain amount of fragmentation occurs as well. In this respect propylene exhibits a behavior intermediate between that of ethylene on one side and higher alkenes on the other. In the case of ethylene (2) extensive fragmentation takes place (CO yield ≈ 0.5). At best very little ethylene oxide is formed, and while the remainder of the oxygen is recovered mainly in the form of aldehydes at least a large fraction of these results from free-radical reactions. There is, however, an indication of a pressure effect, although this is quite small: there is a slight increase in the yields of aldehyde and ethylene oxide and a decrease in CO with increasing pressure. In contrast to this, in the case of higher olefins, taking as an example butene-1, large amounts of α-butene oxide and *n*-butyraldehyde are formed by direct addition of oxygen atoms and subsequent molecular rearrangement, their yields are pressure independent between 100 and 600 mm. within the experimental error, and there is relatively little fragmentation. The main trends observed in the case of propylene are shown in Fig. 1. At higher pressures increasing amounts of propylene oxide and propionaldehyde are formed and the character of the reaction approaches the one exhibited by butene-1, while at lower pressures fragmentation becomes more important and the reaction in many respects resembles that of ethylene. The pronounced pressure effect in the case of propylene is of particular interest and will be further discussed in the following section. With the chromatographic column used acetone could not be resolved from propionaldehyde, and total peak areas for the two compounds are plotted in Fig. 1. Infrared and mass spectra indicated large predominance and perhaps exclusive formation of the aldehyde. One separation was carried out on a 50 ft. tricresyl phosphate on firebrick column (120°) on which the two compounds completely resolved, and the ratio of the peak area of the aldehyde to that of acetone was about 9:1.

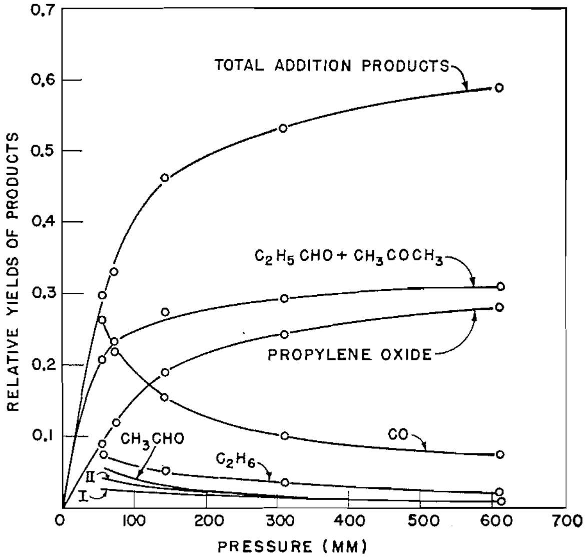


FIG. 1. Products observed in the room-temperature reaction of oxygen atoms with propylene at various total pressures. Curve I gives the yields of H_2 and also those of C_2H_4. Curve II gives the yields of CH_4. (For H_2, C_2H_4, CH_4, and CH_3CHO experimental points are not shown because of the mutual proximity and partial overlapping of the curves.)

Formation of Addition Products

The addition products formed in the different reactions studied are summarized in Table I. The fractions of the addition products given in the table are based on GLC peak areas, taking the sum of the peak areas of all the addition products observed as unity. In some cases, as, for example, *cis*-β-butene oxide and *iso*-butanal as well as for *cis*-β-pentene oxide and 2-methylbutanal, the peaks partially overlapped and were approximately resolved graphically to obtain the individual peak areas. The last column in Table I gives the sum of the peak areas of all the fragmentation products observed by GLC analysis as a fraction of the total peak area of all the products (both addition and fragmentation). No attempt was made to identify the very small amounts of these fragmentation products in the cases where they were observed. In the case of butene-1 they seemed to consist largely of acetaldehyde and propionaldehyde.

TABLE I

PRODUCTS OBSERVED BY GLC ANALYSIS

(After removal of the unconsumed reactants and of any products of the same or greater volatility)

	Addition products[a]				Fragmentation products[b]
Reactant	Epoxides		Carbonyl compounds		
Propylene	Propylene oxide	0.50[c]	Propanal Acetone	0.50[c,d]	
Butene-1	α-Butene oxide	0.53	*n*-Butanal Methylethyl ketone	0.43 0.04	0.06
iso-Butene	*iso*-Butene oxide	0.54	*iso*-Butanal Methylethyl ketone	0.43 0.03	0.00
cis-Butene-2	*cis*-β-Butene oxide *trans*-β-Butene oxide	0.25 0.26	*iso*-Butanal Methylethyl ketone	0.23 0.26	0.02
trans-Butene-2	*cis*-β-Butene oxide *trans*-β-Butene oxide	0.15 0.33	*iso*-Butanal Methylethyl ketone	0.21 0.31	0.02
cis-Pentene-2	*cis*-β-Pentene oxide *trans*-β-Pentene oxide	0.23 0.31	2-Methylbutanal Methyl-*n*-propyl ketone Diethylketone	0.21 0.25[e]	0.06
Tetramethyl ethylene	Tetramethyl ethylene oxide	0.52	Pinacolone	0.48	0.08

[a] *The fractions are calculated from GLC peak areas taking the total area of all* addition *products as unity.*

[b] *The fractions are calculated from the total GLC peak area of the observed compounds other than the addition products taking the total peak area of* all *the products observed as unity.*

[c] *Extrapolated values for infinite pressure.*

[d] *Predominantly propanal (about 90%).*

[e] *Predominantly methyl-n-propyl ketone; some diethylketone is probably also formed (a small peak of the same elution time is observed; infrared and mass spectra, however, indicate a very low upper limit and perhaps absence of diethylketone).*

Formation of a restricted number of principal products in these reactions, mutually isomeric and of a molecular weight equal to that of the olefin used plus an oxygen atom, suggested strongly a direct addition of the atoms followed mainly by a molecular rearrangement rather than a free-radical process. This was substantiated by experiments in which two olefins were used simultaneously. In these experiments no new products were found but only those observed with the same two olefins when used singly, and their respective amounts were approximately proportional to the concentrations of the olefins used. Further information on the nature of these processes was obtained by studying the effect of additions of molecular oxygen.

Effect of Additions of Molecular Oxygen

Several experiments were carried out with *iso*-butene, butene-1, *cis*-butene-2, and tetramethyl ethylene in the presence of molecular oxygen. Initial pressures of 500 mm. N_2O, 7 to 15 mm. olefin, and 3 to 30 mm. O_2 were used.

In the case of *iso*-butene and butene-1 there was no or at best very little inhibition of the formation of the addition products even when the partial pressure of molecular oxygen was relatively quite high. The yields of aldehydes appeared to be slightly lowered and smaller amounts of some new products were also formed. In the case of *iso*-butene the latter amounted roughly to about 20% of the total product and probably were *tert*-butanol and acetone, although the identification was not certain. These two compounds were not found in the mercury-photosensitized reaction of *iso*-butene (60 mm.) in the presence of small amounts of O_2 but in the absence of N_2O. No attempt was made to study in detail these products or the mode of their formation.

In experiments with *cis*-butene-2 it was found that after a small amount of quenching by oxygen itself was taken into account approximately, the yields of *cis*- and *trans*-β-butene oxide and of methylethyl ketone were, within the analytical error, unaffected by the presence of molecular oxygen. On the other hand, the yield of ethane (produced normally in this reaction in small amounts, as discussed later) was rapidly suppressed and that of *iso*-butanal was reduced to about 20 to 25% of its value in the absence of oxygen and then remained independent of further oxygen additions. Simultaneously, appreciable amounts of methanol began to be formed. The effect of additions of O_2 on the composition of liquid products is shown in Table II. These results indicate that a large fraction of *iso*-butanal is formed by radical combination but that, nevertheless, a certain amount is produced by internal migration of CH_3 radicals. Similarly, one experiment with tetramethyl ethylene in the presence of about 40 mm. of O_2 showed a substantial reduction but not complete suppression of pinacolone while the yield of the epoxide appeared to be unaffected.

TABLE II

THE EFFECT OF MOLECULAR OXYGEN ON LIQUID PRODUCTS IN THE REACTION OF O ATOMS WITH *cis*-BUTENE-2 (500 mm. N_2O, 7 mm. *cis*-C_4H_8-2; irradiation time 30 min. Fractions of the sum of the observed GLC peak areas are given.)

Run	pO_2, mm.	*trans*-β-C_4H_8O	*cis*-β-C_4H_8O	$CH_3COC_2H_5$	*iso*-C_3H_7CHO	CH_3OH
264	–	0.26	0.23	0.26	0.25	–
266	3.2	0.27	0.24	0.25	0.095	0.15
265	14.6	0.27	0.22	0.24	0.052	0.21
267	41.7	0.26	0.23	0.27	0.052	0.19

Effects of Irradiation Time and of Pressure

Effects of time of irradiation and of the total pressure were checked with butene-1 and *cis*-butene-2 and, in a less systematic manner, with some of the other olefins used. Within the experimental error the rates of product formation were found to be independent of irradiation time up to relatively high conversions. The results of experiments with constant small amount of *cis*-butene-2 (about 5 mm.) and nitrous oxide varying from 80 to 600 mm. are given in Table III. There was at best only a very slight decline at low pressures in the yields per oxygen atom consumed of the addition products, and their ratios remained constant (in these experiments total peak areas of *iso*-butanal plus *cis*-β-butene oxide were measured). The yield of C_2H_6 showed a slight decline at first;

TABLE III

THE EFFECT OF PRESSURE ON THE YIELD OF PRODUCTS IN THE REACTION OF O ATOMS WITH *cis*-BUTENE-2

Pressure, mm.	Relative rates						
	CO^a	$CH_4{}^a$	$C_2H_6{}^a$	$C_2H_4{}^a$	*trans*-β-Butene oxide[b]	*iso*-C_3H_7CHO +*cis*-β-butene oxide[b]	$CH_3COC_2H_5{}^b$
82	0.041	Trace	0.097	0.009	0.19	0.39	0.18
105	0.035	Trace	n.d.[c]	n.d.[c]	0.18	0.36	0.18
205	0.035	Trace	0.094	0.005	0.22	0.41	0.21
406	0.038	Trace	0.073	0.004	0.20	0.39	0.20
608	0.046	Trace	0.072	0.002	0.19	0.41	0.20

[a] *Based on manometric measurements and mass spectrometer analyses.*
[b] *Based on GLC peak areas.*
[c] *Not determined.*

there was, however, a tendency for leveling off rather than for complete suppression of this product at still higher pressures. The nitrous oxide technique is not suitable for the study of these processes at quite low pressures because of the increasing importance of secondary phenomena. In the pressure range 50 to 600 mm. the ratio of the two major products from butene-1, α-butene oxide and *n*-butanal, remained constant—their absolute yields per oxygen atom consumed appeared also to be constant although a very slight pressure dependence might have been masked by a small random run-to-run variation in GLC response. With the other olefins occasional experiments with variable pressures did not show any significant pressure effects. Of the minor products, carbon monoxide seemed to show generally a slight pressure dependence; thus, with butene-1 its yield per oxygen atom consumed decreased from about 0.06 at a total pressure of 50 mm. to 0.03 at 600 mm.

The Extent of Fragmentation

The very small amounts of fragmentation products detected by GLC analysis (Table I) were thought at first (1) to indicate that fragmentation occurred only to the extent of a few per cent. Actually, it proved difficult to establish accurately the extent of fragmentation. A number of GLC calibrations showed that the observed addition products accounted only for about 70 to 80% of the oxygen atoms consumed and in some cases even less. The quantitative aspect of this result, however, is not entirely satisfactory. Apart from the likelihood that some hydrogen abstraction may occur, there is no certainty that all the addition products formed are quantitatively recovered, in spite of all the precautions. Also, it is somewhat difficult to obtain accurate GLC calibrations with the very small amounts involved, especially so with some of the substances formed in these reactions. An attempt was, therefore, also made to estimate the extent of fragmentation from the amount of other fragmentation products detectable.

The fragmentation products more volatile than nitrous oxide were separated on the LeRoy still into the non-condensables and the "C_2" fraction and then further analyzed. The results are given in Table IV and refer to experiments in which 300 mm. N_2O and small amounts of the olefin were used. No systematic analysis could be made for products of similar volatility to that of N_2O, such as C_3H_8, C_3H_6, etc. In some cases, infrared spectra were taken of the N_2O fraction and no additional peaks were observed; minor amounts of any substances present need not have been detected in this manner. Similarly, in the GLC analysis, minor amounts of substances eluting with the original olefin or of those much less volatile than the major products observed could have escaped detection.

TABLE IV

PRODUCTS MORE VOLATILE THAN NITROUS OXIDE
(non-condensables and "C_2" hydrocarbons)

Reactant	Rates per oxygen atom consumed		
	CO	CH_4	C_2H_6[a]
Butene-1	0.04	Trace	0.00
iso-Butene	0.03	Trace	0.00
cis-Butene-2	0.04	Trace	0.08
trans-Butene-2	0.04	Trace	0.08
cis-Pentene-2	0.03	Trace	0.015
Tetramethyl ethylene	0.02	Trace	0.15

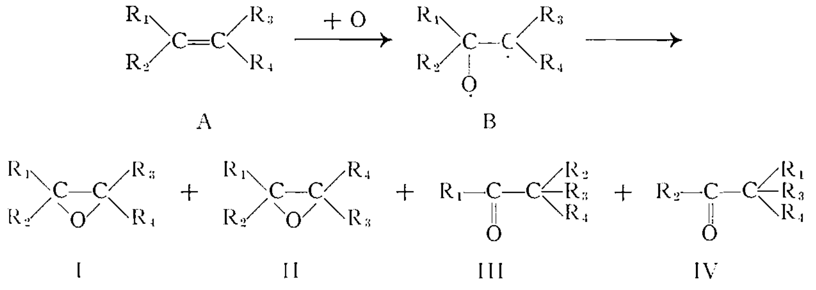
[a] *Mass spectrometer analyses of the* C_2H_6 *fraction indicated at best only trace amounts of* C_2H_4.

The appreciable amounts of ethane formed in some cases, as shown in Table IV, indicate that at least in some of the studied reactions the fragmentation is not negligible even when appreciable pressure effects are absent. With *cis*-butene-2, for example, an experiment in which a mixture of *cis*-C_4H_8-2 and a smaller amount of *cis*-C_4D_8-2 was used no C_2D_6 was formed but only CH_3CD_3 and C_2H_6. Ethane is, therefore, formed by combination of free methyl radicals. The results obtained in the presence of O_2 also showed that ethane and a large fraction of *iso*-butanal were formed by combination of free radicals, as already pointed out. On the basis of these results, the extent of fragmentation into free radicals at higher pressures can be estimated at about 30 to 35% (based on the consumption of oxygen atoms) for *cis*-butene-2 and in the case of tetramethyl ethylene probably as much as 60%. Such large fragmentation at higher pressures appears to take place when rearrangements which follow the addition of oxygen atoms involve migration of methyl radicals, but not (or at best only to a small extent) when H atoms migrate. It is significant that even when large fragmentation of this kind occurs the greater part of the free radicals recombine to form the same compound as produced by direct internal migration. Thus it would seem that the fragmentation involves entirely (or predominantly) only the splitting off of the migrating radicals.

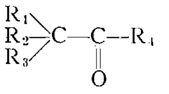
DISCUSSION

On the basis of the comparison of the addition products formed with butene-1, *cis*-butene-2, and *iso*-butene, the mechanism of addition of oxygen atoms to a CC double bond in alkenes was generalized in the preliminary communication (1) in the form of two rules. In view of the additional information available, these rules can now be amplified. The consistency of the results obtained in all the reactions of alkenes with oxygen atoms studied so far indicates that the addition products formed can in general be explained and predicted by assuming that: (1) an oxygen atom adds to one carbon atom of the double bond to form a biradical and this addition takes place in the case of unsymmetrical alkenes predominantly at the less-substituted carbon atom, and (2) the triplet thus formed degrades to the ground-state compounds in two ways: (*a*) by forming the corresponding epoxides without any internal rearrangement except a partially restricted rotation about the original double bond, and (*b*) by forming carbonyl compounds through migration of a particle (either a hydrogen atom or a radical) attached to the carbon atom carrying the oxygen atom to the other carbon atom of the original double bond. Migrating radicals may in the course of this process become to a smaller or greater extent detached from the molecule, as will be discussed later.

The following scheme for the reaction of oxygen atoms with a generalized olefin (A) illustrates the above rules. R_1, R_2, R_3, and R_4 are alkyl radicals or hydrogen atoms. The first C atom of the double bond is assumed to be "less substituted".



Each of the compounds I to IV is produced in substantial quantities: these four compounds are the main and may be the exclusive addition products formed. (Compounds III and IV will be identical if $R_1 = R_2$, and similarly I and II if either $R_1 = R_2$ or $R_3 = R_4$.) It is possible also that some addition of oxygen atoms may take place at the "more-substituted" carbon atom, in which case minor quantities of carbonyl compounds V and VI will also be formed. In all the cases studied so far, addition to the "more-substituted" carbon atom has been of minor importance inasmuch as it occurred at all.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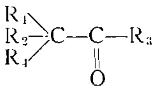
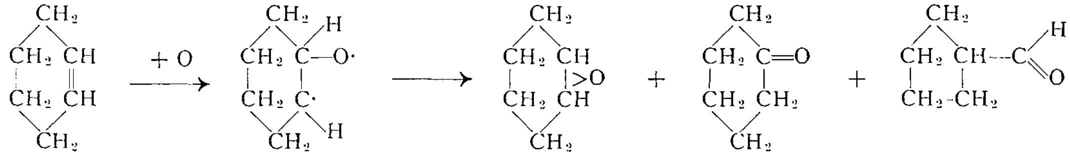

VI

This reaction scheme has been illustrated in the preliminary communication (1) by the example of *cis*-butene-2, a symmetrical olefin. The predicted and observed addition products in this case are *cis*- and *trans*-2,3-epoxybutane, methylethyl ketone (formed through migration of an H atom) and *iso*-butanal (formed through migration of a CH_3 radical). The same products are to be expected and have been observed with *trans*-butene-2. In the case of *iso*-butene the main addition products are *iso*-butene oxide and *iso*-butanal and, therefore, oxygen atoms add predominantly to the "less-substituted" carbon atoms of the double bond. Addition to the "more-substituted" carbon atom of the double bond would require formation of some methylethyl ketone as well; some methylethyl ketone appears to be formed but its amount is extremely small. In the case of butene-1, small amounts of methylethyl ketone besides the main addition products, 1,2-epoxybutane and *n*-butanal, indicate that minor addition to the *more*-substituted carbon atom of the double bond might be also taking place. The same is true for propylene where small amounts of acetone seem to be formed, besides the expected main addition products, propylene oxide and propanal. With tetramethyl ethylene the addition products are tetramethyl ethylene oxide and pinacolone, as expected.

The case of *cis*-pentene-2 is of particular interest since it shows that in terms of the above rules the carbon atom to which the methyl radical is attached is "*less* substituted" than the other carbon atom of the double bond to which an ethyl radical is attached. Addition of an oxygen atom to the former would lead to the formation of methyl-*n*-propyl ketone besides 2-methylbutanal and the two isomeric epoxides, *cis*- and *trans*-2,3-epoxypentane, while the addition to the latter would result in diethylketone and the same aldehyde and epoxides. Methyl-*n*-propyl ketone is definitely the predominant ketone formed although, perhaps, small amounts of diethylketone are formed as well.

Cycloölefins represent an interesting special case. For cyclohexene, for example, the same reaction scheme would require the formation of the following compounds:



C VII VIII IX

In addition to cyclohexene oxide (VII), two carbonyl compounds would be expected to be formed: cyclohexanone (VIII) through migration of an H atom and cyclopentyl formaldehyde (IX) through migration of the "radical" attached to the carbon atom to which oxygen is attached in the biradical (C). These compounds are actually formed and no other products have been detected.*

There are indications that the intermediate biradical (B) is very short-lived. This is suggested by the difference in the ratios of *cis*- and *trans*-2,3-epoxybutane formed in the reactions of oxygen atoms with *cis*- and *trans*-butene-2, respectively. The lack of appreciable effects of the presence of molecular oxygen on the amounts of the addition products formed also supports this conclusion. It appears, therefore, that the initially formed biradical isomerizes extremely rapidly into the final addition compounds. Since these reactions, however, are very exothermic, the addition compounds carry a large excess of energy when formed (carbonyl compounds about 115 kcal./mole and epoxides probably about 90 kcal./mole). The probability of decomposition of these compounds before dissipation of the excess energy can take place will depend largely on their complexity (the number of "degrees of freedom"). The simplest olefin, ethylene, appears to undergo almost exclusive decomposition on reacting with oxygen atoms. Propylene exhibits a pronounced collisional stabilization of the addition products formed (Fig. 1), while pressure effects appear to be absent with higher alkenes in the investigated pressure range. There is, however, a certain amount of decomposition even when no pressure effects are observed, which suggests that there is an intrinsic probability of a certain fraction of the initially formed biradical undergoing fragmentation. In view of the extremely short life of the biradical, it is not surprising that this fragmentation process is pressure independent.

The nature of the two types of fragmentation processes occurring in the reactions of oxygen atoms with olefins should now be briefly discussed. The pressure-dependent fragmentation, as observed in the case of propylene (and previously with ethylene), is characterized by the formation of products which could be expected from thermal decomposition of the major addition products and is consistent with the assumption that these are initially formed in an energy-rich state. The excess energy is in most cases readily removed by collisions in the gas phase. An inspection of the data given in Tables II and IV shows that the initial act (or part of the initial act) of the pressure-independent decomposition is probably the splitting off of a radical attached to the same carbon atom to which oxygen initially adds. In other words, the same particles which migrate in the rearrangement processes may become detached from the molecule.

**Details of the experiments performed with cyclohexene and cyclopentene will be published elsewhere.*

Thus, ethane is formed only in those cases where CH_3 is a migrating particle and then a great part of the resulting product is inhibited by the additions of O_2. The remaining fraction of the molecule would probably dimerize and the amount of the dimer formed should be comparable with that of ethane. Such dimers are likely to be of too low volatility to be readily detectable by the analytical techniques employed. Their formation could explain the low material balances observed. The pressure-independent fragmentation in the case of butene-2 appears, therefore, to be similar to the pressure-independent decomposition induced in 2,3-epoxybutane by mercury photosensitization (10). It is not certain whether migrating H atoms split off to a small extent. Thus, in the case of *iso*-butene, in spite of considerable effort no products other than the addition products already described could be isolated and identified. Any free H atoms which might be produced by splitting off from the initially formed biradical would readily add to excess *iso*-butene and the tertiary butyl radicals formed would be largely converted to compounds of low volatility.

The data in Fig. 1 for the propylene reaction can be treated kinetically. Thus, a plot of the reciprocal rates of the production of propanal (plus small amounts of acetone) against reciprocal pressure gives a straight line (Fig. 2), indicating a single-stage collisional deactivation. A similar plot for propylene oxide shows a distinct curvature; a plot of the square root of the reciprocal rate against reciprocal pressure, on the other hand, is a straight line. Such a relationship should be expected for a two-stage collisional deactivation with decomposition occurring at both stages provided the lifetimes of the two forms are approximately equal. The following reaction scheme for the propylene reaction is probably, with minor modifications, representative of the general reaction scheme for the reactions of oxygen atoms with olefins, provided it is realized that with increasing number of degrees of freedom the energy-rich molecules formed become longer lived and the pressure-dependent fragmentation becomes less important under otherwise comparable conditions.

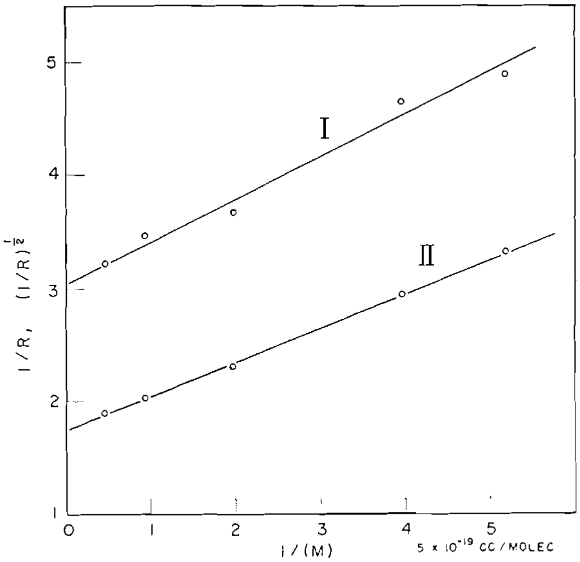
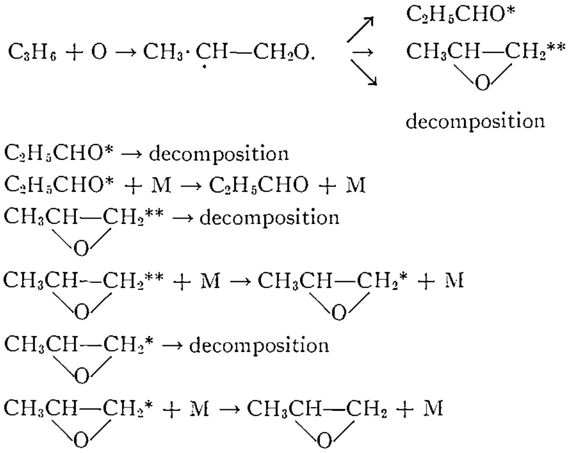


FIG. 2. I. Plot of the reciprocal relative rate $(1/R)$ of formation of propanal + acetone against the reciprocal concentration of reactants. II. Plot of the square root of the relative rate of formation of propylene oxide $(1/R)^{\frac{1}{2}}$ against the reciprocal concentration of reactants.



$$C_3H_6 + O \rightarrow CH_3\cdot\dot{C}H{-}CH_2O. \begin{cases} \nearrow C_2H_5CHO^* & [1] \\ \rightarrow \underset{\diagdown O \diagup}{CH_3CH{-}CH_2}{}^{**} & [2] \\ \searrow \text{decomposition} & [3] \end{cases}$$

$$C_2H_5CHO^* \rightarrow \text{decomposition} \qquad [1a]$$

$$C_2H_5CHO^* + M \rightarrow C_2H_5CHO + M \qquad [1b]$$

$$\underset{\diagdown O \diagup}{CH_3CH{-}CH_2}{}^{**} \rightarrow \text{decomposition} \qquad [2a]$$

$$\underset{\diagdown O \diagup}{CH_3CH{-}CH_2}{}^{**} + M \rightarrow \underset{\diagdown O \diagup}{CH_3CH{-}CH_2}{}^{*} + M \qquad [2b]$$

$$\underset{\diagdown O \diagup}{CH_3CH{-}CH_2}{}^{*} \rightarrow \text{decomposition} \qquad [2c]$$

$$\underset{\diagdown O \diagup}{CH_3CH{-}CH_2}{}^{*} + M \rightarrow \underset{\diagdown O \diagup}{CH_3CH{-}CH_2} + M \qquad [2d]$$

If, as assumed, $k_{2a}/k_{2b} = k_{2c}/k_{2d}$, the steady-state treatment leads to the relationships

$$1/R_{1b} = (1/\alpha_1)(1+k_{1a}/k_{1b}(M))$$

and

$$(1/R_{2d})^{\frac{1}{2}} = [1/(\alpha_2)]^{\frac{1}{2}}(1+k_{2a}/k_{2b}(M)),$$

where R_{1b} and R_{2d} are the rates of production of propanal and propene oxide per oxygen atom consumed, and α_1 and α_2 are the fractions of O atoms consumed in reactions (1) and (2) respectively. Taking approximately $k_{1b} = k_{2b} = k_{2d} = 10^{-10}$ cc./molec. sec., the plots in Fig. 2 indicate that the lifetimes of the energy-rich molecules $C_2H_5CHO^*$, $\underset{\diagdown O \diagup}{CH_3.CH{-}CH_2}{}^{**}$, and $\underset{\diagdown O \diagup}{CH_3.CH{-}CH_2}{}^{*}$ are between 10^{-8} and 10^{-9} second. It ought to be stressed, however, that the good straight-line plots in Fig. 2 are considerably better than should be expected in view of the likely experimental errors, and their quantitative implications should be taken with some reserve. Reaction (3) in the above scheme represents the pressure-independent fragmentation process.

The chemical reactions of oxygen atoms with olefins and the molecular rearrangements following the initial addition of the atoms exhibit certain regularities which have to be considered in the light of hyperconjugation and inductive effects. These regularities embrace: (1) systematic variation of reaction rates with the structure of the olefin, (2) specificity with respect to the position of addition of the atoms, and (3) nature of internal rearrangements which take place. These effects can best be discussed simultaneously and it is, therefore, convenient to defer their discussion until further results of the present investigations are published, particularly the relative rate constants of these reactions.

Oxygen atoms produced by the technique employed in the present study are probably in their ground, $O(^3P)$ state. This conclusion is valid provided the spin conservation rule is obeyed in the mercury-photosensitized decomposition of nitrous oxide. In this connection it is of interest that investigations now carried out in this laboratory (11) show that the course of the reaction of butene-1 with $O(^3P)$ atoms produced by photolysis of NO_2 is the same as observed in the present work.

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