REACTIONS OF OXYGEN ACTIVATED BY ELECTRICAL DISCHARGE WITH BUTENE-1[1]

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ABSTRACT

Reactions of oxygen activated by electrical discharge with butene-1 have been studied in a "spherical diffusion" reaction zone. When small concentrations of oxygen are passed through the discharge tube in helium as the carrier gas, and the concentration of butene-1 in the reaction zone is sufficiently high, the observed products are entirely explainable by an interaction of the ground-state oxygen atoms with butene-1. With large deviations from these conditions considerable complexities arise, and under some conditions α-butylene ozonide and its decomposition products become important and the products are then explainable without any significant participation of oxygen atoms in the process.

INTRODUCTION

The number of methods available for the production of oxygen atoms in the laboratory is limited. One of the earliest methods employed for the production of oxygen atoms was the gaseous electrical discharge in oxygen molecules (1). The other methods frequently used are the mercury-photosensitized decomposition of nitrous oxide and the photodecomposition of nitrogen dioxide, and both these methods have been used extensively in this laboratory to study reactions of oxygen atoms. With the use of the nitrous oxide technique the main features of the reactions of oxygen atoms with olefins have now been established (2). In the present work one of the olefin reactions with oxygen atoms produced by electrical discharge was studied in order to compare this method for producing oxygen atoms with the nitrous oxide and the nitrogen dioxide methods. The relatively simple reaction of oxygen atoms with butene-1 was chosen for this purpose. An experimental arrangement incorporating the usual features of a "diffusion flame technique" (3, 4) was adopted in order to minimize any tendency for the occurrence of surface reactions, and to find out at the same time whether the application of the Garvin–Kistiakowsky "Temperature Pattern Method" (5) for the determination of rate constants is suitable for this reaction.

In the reaction of oxygen atoms with butene-1, two principal products are formed, α-butylene oxide and *n*-butyraldehyde, together with smaller amounts of methyl ethyl ketone and traces of some other compounds (2). The addition products possess excess energy when formed because of the high heats of reaction and decompose if not deactivated collisionally. This fragmentation is essentially suppressed at a pressure of about 10 mm (6) and the course of the reaction is then relatively simple. In the present work, on the other hand, considerable complexities are observed, especially under certain conditions. At the same time the electrical discharge technique is widely used to generate oxygen atoms and study their reactions. It is therefore essential to emphasize its potentially complex character. The latter is due to several factors. The technique is restricted to relatively quite low pressures, and as a result the concentration of the primary reactant is also low so that secondary attacks by oxygen atoms on the products may and indeed very frequently do take place. Also, when "hot" products are formed in the primary step, as is the case in the addition of oxygen atoms to olefins, they will tend to decompose

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into free radicals at the low pressures, leading thus to further secondary reactions. An additional potential disadvantage of the low pressures is the difficulty of establishing whether any surface reactions occur. (In the present work any surface reactions in the reaction zone have been disregarded: it is likely that at least under some experimental conditions employed they are unimportant.) Another factor contributing to the observed complexities is the frequent presence, in addition to oxygen atoms, of other reactive or potentially reactive species, including here excess molecular oxygen when present. The object of the present work is to illustrate on the example of a reaction, the mechanism of which has been previously established by more convenient methods, some of the complexities which may be encountered in the application of the electrical discharge technique. The discussion of the obtained results is consequently more extensive than would be otherwise justifiable in view of its largely qualitative character.

EXPERIMENTAL

Apparatus

The apparatus used was an all-glass flow system. The gas flows were controlled by capillaries and needle valves (Edwards and Co.) with a constant pressure head. The pressure in the reactor was varied by means of internal capillaries of various dimensions. Helium and oxygen were passed through a liquid nitrogen trap before the discharge to remove any grease or mercury vapor in the gases, as these gave inconsistent results due to coating of the surface of the discharge tube (a quartz tube, 10 mm i.d.). An electrodeless discharge was used at microwave frequencies, supplied from a Raytheon Diatherm unit with the use of a 90% power output. The two probes were of copper wire, each a $\frac{1}{4}$ wavelength. These were placed at a distance of 22 cm from the nozzle through which the gases were discharged into a wide pyrex tube in which the reaction was carried out. The nozzle projected some distance into the reaction zone and had an orifice 0.5 mm in diameter. Butene-1 was introduced directly into the wide tube, but at a point below the nozzle to assure uniform distribution before the reaction zone was reached.

The products were frozen out in two liquid nitrogen traps and were transferred to a LeRoy still (7) at $-120°$ C and fractionated to obtain the products free of unreacted butene-1 and of any products of equal or greater volatility.

Attempts were made to measure the concentration of oxygen atoms at the nozzle by measuring the heat of recombination on a hot platinum wire, on a hot platinum wire coated with either silver or cobalt, and a silver-plated glass tip probe. It was found that all these methods gave inconsistent results so the direct measurement of the oxygen atom concentration was abandoned.

Materials

Research grade butene-1 (Phillips Petroleum Co.) was transferred to a storage volume at liquid nitrogen temperature and degassed at dry ice temperature. This was repeated several times until a pressure of 10^{-5} mm Hg was obtained.

Oxygen (People's Gas Co., Ottawa) was used without further purification. In some of the experiments extra-dry and pure oxygen (Matheson Co.) was used and it was found that the results obtained were identical with those obtained with the ordinary cylinder oxygen.

Helium (Air Reduction Co.) was passed through a liquid nitrogen trap to remove any water and was used without any further purification.

Analysis of Products

The products of the reaction after the removal of the unreacted butene-1 and of any products of equal or greater volatility in the low-temperature fractionation still were passed through a gas–liquid chromotographic (GLC) column. The GLC apparatus used was modelled on that used by Callear and Cvetanović (8). The column consisted of 7.5-ft glass tubing (4 mm i.d.) packed with glass spheres passing 270 mesh with dinonyl phthalate as the liquid phase (4 g of dinonyl phthalate per 100 g of glass spheres). The column was maintained at room temperature. For some analyses a high resolution 50-ft column of $\frac{1}{4}$-in. copper tubing was used. It contained, as the stationary phase, 40 g of tricresyl phosphate per 100 g of firebrick (30–60 mesh). The products eluted from the column could be collected at liquid nitrogen temperature, and thus analyzed also by infrared and mass spectrometer.

The products of the reaction identified by these means were propionaldehyde, acetaldehyde, methyl alcohol, ethyl alcohol, *n*-butyraldehyde, α-butylene oxide, methyl ethyl ketone, and α-butylene ozonide. A sample of α-butylene ozonide was kindly prepared by Dr. T. Vrbaški using the method of Harries (9, 10).

RESULTS

The reaction of butene-1 with oxygen atoms produced by microwave discharge was found to be more complex than the corresponding reaction with oxygen atoms formed by mercury-photosensitized decomposition of nitrous oxide (2) or by photolysis of nitrogen dioxide (6). In the last two reactions *n*-butyraldehyde, α-butylene oxide, and small amounts of methyl ethyl ketone, acetaldehyde, and propionaldehyde are formed. In the present case, in addition to these compounds, ethanol and methanol and under certain conditions α-butylene ozonide and formaldehyde are also produced, and propionaldehyde is frequently formed in large amounts.

In order to obtain some insight into the mechanism of formation of these products, the pressure of butene-1, oxygen, and helium and the total pressure were varied.

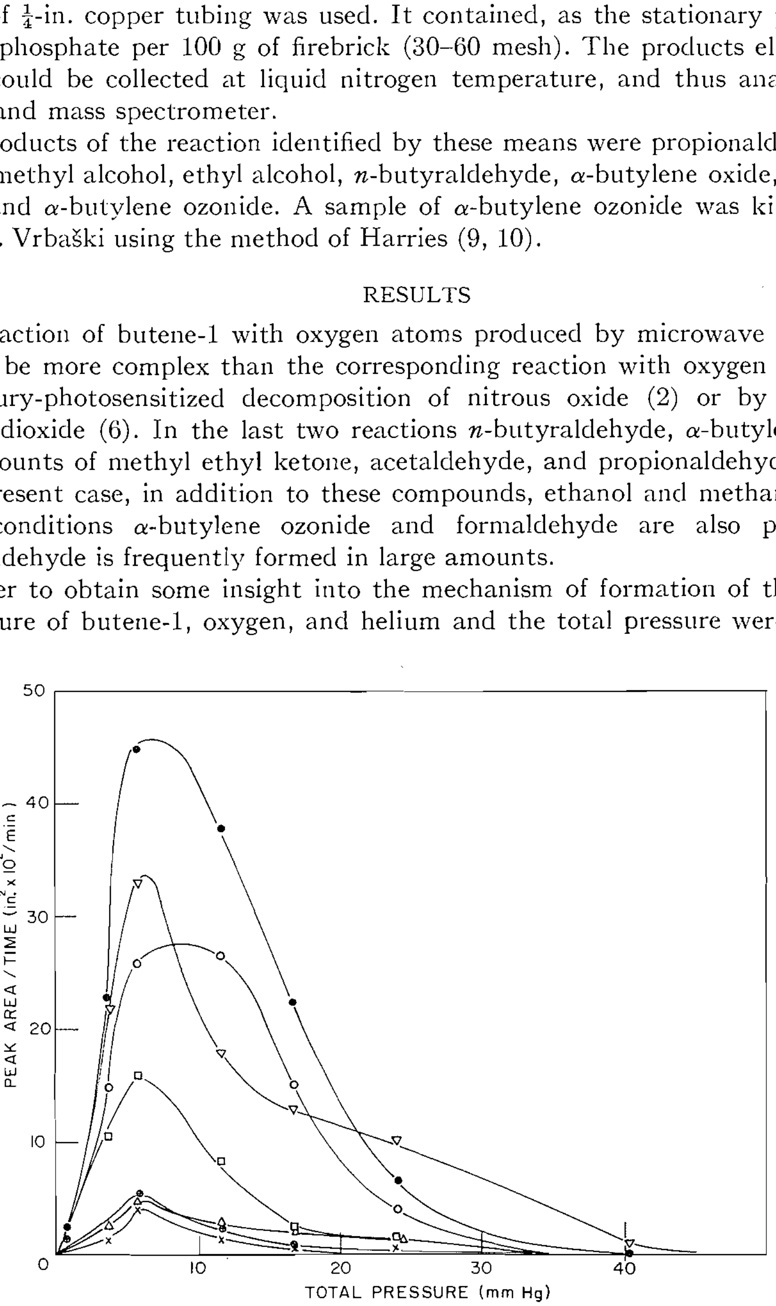


FIG. 1. Variation in the amounts of products formed per unit time with total pressure at low butene-1 flow. Oxygen flow 2.54 ml/min, helium flow 54.0 ml/min, butene-1 flow 0.75 ml/min: × methanol, △ methyl ethyl ketone, ⊕ acetaldehyde, □ ethanol, ○ *n*-butyraldehyde, ▽ propionaldehyde, ● α-butylene oxide.

Variation of Total Pressure

The total pressure was varied from 0 to 40 mm for both high and low butene-1 flows, using constant flows of the reactants in each case. In Fig. 1, the results obtained for the amounts of the products formed (measured as peak area per unit time from the GLC data) as a function of total pressure are shown for low butene-1 flow (0.75 ml/min). The main products are α–butylene oxide, propionaldehyde, ethanol, and *n*-butyraldehyde with smaller amounts of methyl ethyl ketone, acetaldehyde, and methanol. All the products show maxima at around 6.5 mm. It is understandable that there would be, at low pressure, a decrease in the amounts of the products formed due to recombination of the oxygen atoms on the walls of the discharge tube. However, at high pressure there was a gradual decrease in the amounts of products until at 40 mm there were essentially no products detectable on GLC. It was noted that during this gradual decrease the light intensity of the discharge appeared to decrease also. The light intensity of the discharge was therefore measured as a function of the pressure and it was found that the photocell readings showed a similar decrease to that observed above. Since the light intensity probably parallels in an approximate and qualitative manner the amount of dissociation of the molecules into atoms, it would appear that as the pressure is increased the energy available for dissociation of the molecules is reduced.

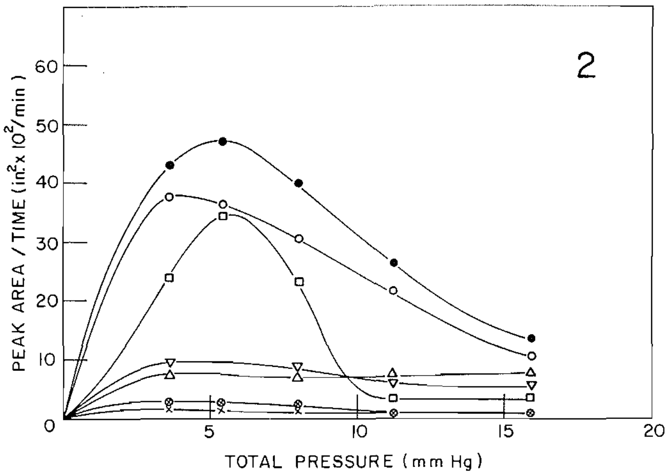
The experiments with high butene-1 flow (40 ml/min) showed the same general trends as found for low butene-1 flow and the maxima in the amounts of products were again at around 6 mm (Fig. 2). There was, however, an important difference: the amount of propanal formed remained in this case quite small, while it is one of the major products at low butene-1 flow.

Variation of Oxygen : Helium Ratio

The ratio of oxygen to helium was varied at constant pressure (3.5 mm) and constant butene-1 flow (0.75 ml/min). A plot of percentage oxygen against peak area of the products per unit time is shown in Fig. 3. The results obtained showed the same trends as before, with α-butylene oxide, propionaldehyde, *n*-butyraldehyde, and ethanol as the main products and smaller amounts of acetaldehyde, methyl ethyl ketone, and methanol. Up to about 7% oxygen there was an increase in the peak areas of each of the products, but as the percentage oxygen was still further increased (and at the same time the percentage of helium was correspondingly decreased) there was a general decrease in the amounts of the products. Since this is observed with all the products, it would appear that this effect is concerned with the initial formation of the oxygen atoms in the discharge. A possible explanation of this effect is that the efficiency of oxygen for the capture of electrons is less than that of helium, so that at high oxygen percentages the concentration of oxygen atoms is reduced.

Variation of Oxygen in the Absence of Helium

The flow of oxygen was varied from 0.80 ml/min to 25.6 ml/min in the absence of helium at a constant butene-1 flow (0.75 ml/min). The total pressure for this range of oxygen flows varied from 0.19 mm to 2.60 mm. Since the butene-1 flow was small compared to the oxygen flow, the total pressure was essentially the partial pressure of oxygen. Under these conditions it was found that the results were not reproducible. However, it was possible to note certain trends in the results. As the pressure of oxygen increased, there was an increase in the amounts of α-butylene oxide, propionaldehyde, and a small increase in the amount of acetaldehyde and methyl ethyl ketone, while amounts of ethanol and methanol decreased. Under these conditions, however, *n*-butyraldehyde was not found in the products.



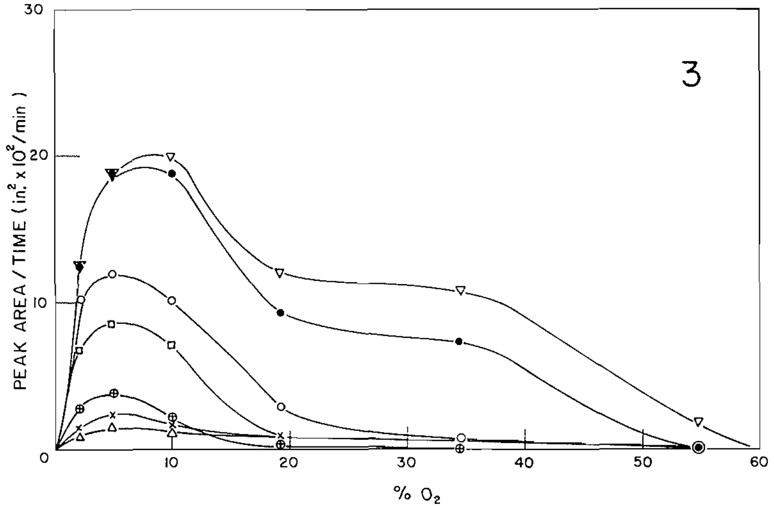


FIG. 2. Variation in the amounts of products formed per unit time with total pressure at high butene-1 flow. Oxygen flow 2.54 ml/min, helium flow 54.0 ml/min, butene-1 flow 40.1 ml/min: × methanol, △ methyl ethyl ketone, ⊗ acetaldehyde, □ ethanol, ○ *n*-butyraldehyde, ▽ propionaldehyde, ● α-butylene oxide.

FIG. 3. Plot of per cent oxygen in discharge gas against the amount of product formed per unit time. Total pressure 3.4 mm, butene flow 0.75 ml/min: × methanol, △ methyl ethyl ketone, ⊕ acetaldehyde, □ ethanol, ○ *n*-butyraldehyde, ▽ propionaldehyde, ● α-butylene oxide.

In all these experiments it was noted that a large diffuse GLC peak appeared at an elution time of about 200 minutes. This peak was collected and analyzed by infrared and mass spectra. It was found to be identical with a synthetic sample of α-butylene ozonide. Some observations on the stability and the manner of decomposition of a synthetic sample of α-butylene ozonide suggested that this compound was probably the main initial product in these experiments. It was probably formed directly from ozone and butene-1 while α-butylene oxide, acetaldehyde, and methyl ethyl ketone were formed in the course of the same reaction or together with propionaldehyde in the subsequent decomposition of the α-butylene ozonide. The absence of *n*-butyraldehyde suggested that a reaction of oxygen atoms with butene-1 was unimportant under these conditions.

Variation of Oxygen in the Presence of Helium

The partial pressure of oxygen was varied at constant total pressure (3.5 mm), constant helium flow (54.0 ml/min), and constant butene-1 flow (0.75 ml/min). The results obtained have been plotted in Fig. 4. Below 0.05 mm it was not possible to observe any products, perhaps because the small amounts of oxygen atoms formed recombined before they reached the nozzle. Above this pressure there was a steep increase in the amount of products to a maximum, and at higher partial pressures of oxygen there was a gradual decline in the amount of products formed. As was found above, propionaldehyde, α-butylene oxide, *n*-butyraldehyde, and ethanol were the main products with smaller amounts of acetaldehyde, methanol, and methyl ethyl ketone.

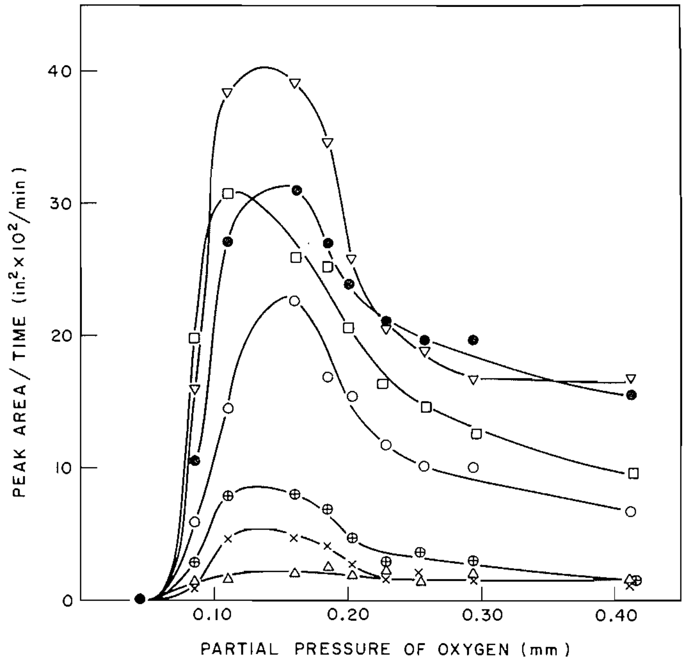


FIG. 4. Plot of oxygen pressure against the amount of products formed per unit time. Butene-1 flow 0.75 ml/min, helium flow 54.0 ml/min, total pressure 3.5 mm: × methanol, △ methyl ethyl ketone, ⊕ acetaldehyde, □ ethanol, ○ *n*-butyraldehyde, ▽ propionaldehyde, ● α-butylene oxide.

Variation of Butene-1

The flow rate of butene-1 was varied from 0.56 ml/min to 40 ml/min at constant flows of helium (54.0 ml/min) and oxygen (2.54 ml/min) and constant pressure (3.5 mm). A plot of the partial pressure of butene-1 against the GLC peak area per unit time is shown in Fig. 5. It is apparent from this graph that the compounds formed fall into two classes. The first class of compounds (α-butylene oxide, *n*-butyraldehyde, ethanol, and methyl ethyl ketone) show a steady rise in the amount formed at lower partial pressures of butene-1 and finally reach a constant value, while with the second class (propionaldehyde, acetaldehyde, and methanol) after an initial sharp increase in the amounts formed there is a gradual decrease to constant values. In order to determine whether these effects were due to a change in the discharge intensity, photocell readings were taken of the light intensities of the discharge and it was found that these remained constant. Thus, under these conditions the change in the amount of product formed is directly connected with the partial pressure of butene-1. At very low butene-1 flow (0.56 ml/min) a relatively large amount of water was formed, probably due to secondary attack on the compounds initially formed by excess oxygen atoms. This effect was not noted at higher concentrations of butene-1.

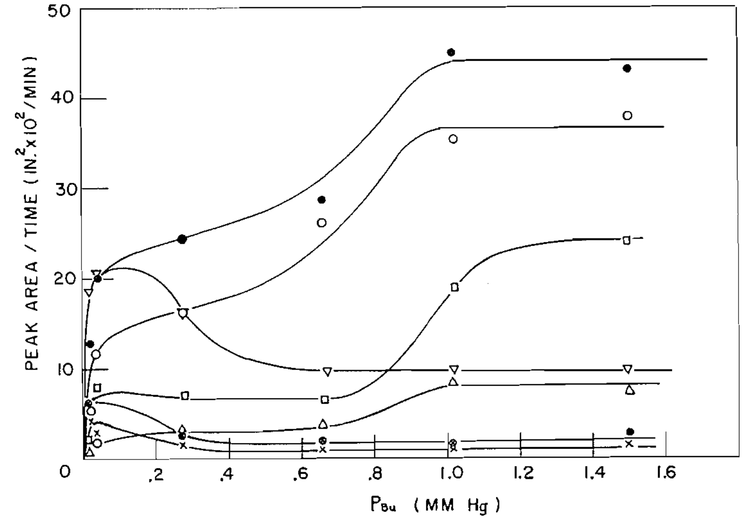


FIG. 5. Plot of butene-1 pressure against the amount of products formed per unit time. Total pressure 3.5 mm, oxygen flow 2.54 ml/min, helium flow 54 ml/min: × methanol, △ methyl ethyl ketone, ⊗ acetaldehyde, □ ethanol, ○ *n*-butyraldehyde, ▽ propionaldehyde, ● α-butylene oxide.

DISCUSSION

Since discharge is passed through oxygen and helium some distance from the nozzle, it is convenient to treat the reactions occurring in the discharge tube separately from those occurring at the nozzle, i.e. in the reaction zone where butene-1 is present as well. The proposed reactions which are likely to occur in the discharge tube are the following:

$$\mathrm{He} + e \rightarrow \mathrm{He}^* \qquad [\phi_1]$$

$$\mathrm{O_2} + e \rightarrow 2\mathrm{O} \qquad [\phi_2]$$

$$\mathrm{O_2} + e \rightarrow \mathrm{O_2}^* \qquad [\phi_3]$$

$$\mathrm{He}^* + \mathrm{O_2} \rightarrow 2\mathrm{O} + \mathrm{He} \qquad [\mathrm{I}]$$

$$\mathrm{He}^* + \mathrm{O_2} \rightarrow \mathrm{O_2}^* + \mathrm{He} \qquad [\mathrm{II}]$$

$$\mathrm{He}^* + \mathrm{He} \rightarrow 2\mathrm{He} \qquad [\mathrm{III}a]$$

$$\mathrm{O_2}^* + \mathrm{He} \rightarrow \mathrm{O_2} + \mathrm{He} \qquad [\mathrm{III}b]$$

$$\mathrm{O} + \mathrm{O} + \mathrm{W} \rightarrow \mathrm{O_2} + \mathrm{W} \qquad [\mathrm{IV}]$$

$$\mathrm{O} + \mathrm{O} + \mathrm{M} \rightarrow \mathrm{O_2}^* + \mathrm{M} \qquad [\mathrm{V}]$$

$$\mathrm{O} + \mathrm{O_2}^* + \mathrm{M} \rightarrow \mathrm{O_3} + \mathrm{M} \qquad [\mathrm{VI}]$$

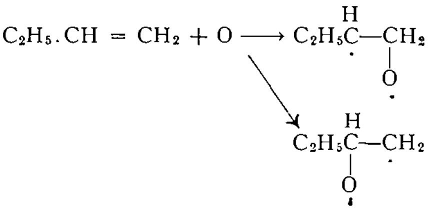
$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{O_3} + \mathrm{M} \qquad [\mathrm{VII}]$$

$$\mathrm{O} + \mathrm{O_3} \rightarrow 2\mathrm{O_2}. \qquad [\mathrm{VIII}]$$

Reaction $[\phi_1]$ is probably the initiation reaction in the discharge since the efficiency for electron capture is greater in the case of helium than oxygen. When no helium is present, reactions [ϕ_2] and [ϕ_3] take place giving oxygen atoms and excited oxygen molecules. Reactions [I] and [II] form oxygen atoms and excited oxygen molecules by transfer of energy from the excited helium. The quenching of the excited helium and excited oxygen are shown in reactions [III*a*] and [III*b*]. Reactions [IV] and [V] recombine oxygen molecules by third-body collision with the wall and other molecules, respectively. To account for the formation of ozone, reactions [VI] and [VII] are proposed. Reaction [VIII] re-forms oxygen molecules by the attack of oxygen atoms on ozone.

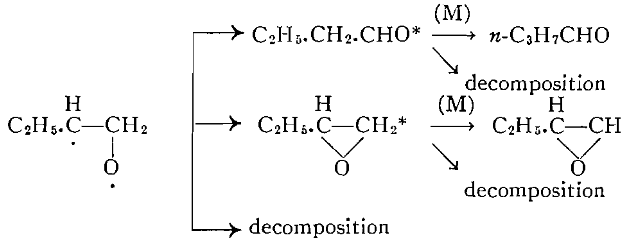
Of the products formed in the discharge tube the only ones which may reach the nozzle and eventually react with butene-1 in the reaction zone are: oxygen atoms, ozone, and excited oxygen molecules.

The general mechanism of reaction of oxygen atoms with butene-1 is as follows (2):



[1*a*]

[1*b*]



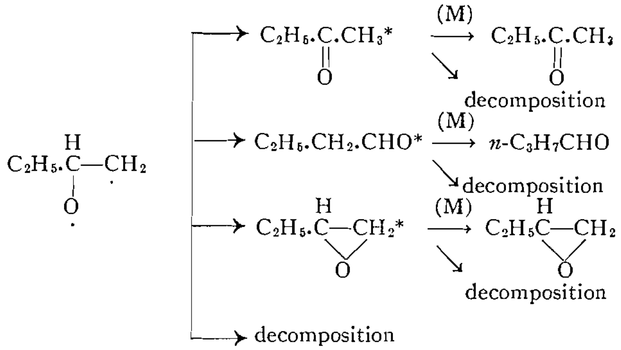
[2*a*]

[2*b*]

[3*a*]

[3*b*]

[4]



[5*a*]

[5*b*]

[6*a*]

[6*b*]

[7*a*]

[7*b*]

[8]

where [1*a*], addition to the less substituted carbon atom of the double bond, largely predominates over [1*b*] so that considerably more *n*-C_3H_7CHO is formed than $C_2H_5.CO.CH_3$. There is reason to believe that pressure-independent decomposition processes, reactions [4] and [8], are not very important in this reaction (2). At pressures higher than about 10 to 30 mm the collisional deactivations in [2*a*], [3*a*], [5*a*], [6*a*], and [7*a*] are essentially complete, so that the main products are α-butene oxide, *n*-butyraldehyde, and a smaller amount of methyl ethyl ketone. In addition to these, even at the higher pressures, very small amounts of acetaldehyde and propionaldehyde are also formed (2, 6) and the mechanism of their formation is not yet known, although they may be due then to some pressure-independent fragmentation. At lower pressures the pressure-independent fragmentation processes begin to be of importance, especially so below about 10 mm. This leads to an increase in the amounts of acetaldehyde and propionaldehyde and to a decrease in the addition products (α-butene oxide, n-butyraldehyde, and methyl ethyl ketone) (6).

Disregarding for the moment methanol and ethanol, which are observed in the present work in addition to the above compounds, it is evident that under conditions of the experiments plotted in Fig. 5 (total pressure 3.5 mm, helium to oxygen ratio approximately 20) and when the partial pressure of butene-1 is sufficiently high the products formed are within the limits of experimental accuracy, quantitatively, such as would be expected to be formed in the reaction of the ground state oxygen atoms with butene-1 at the actual total pressure (3.5 mm). At such a low total pressure the pressure-dependent fragmentation is quite important and appreciable amounts of free C_2H_5 radicals and smaller amounts of free CH_3 radicals could be expected to be produced. The formation of ethanol and methanol is then explained by the interaction of these free radicals with the molecular oxygen present, as is frequently observed. Thus, in the reaction of butene-2 with oxygen atoms from the mercury-photosensitized decomposition of N_2O, the relatively large amounts of free CH_3 radicals form large amounts of methanol when some molecular oxygen is added (2). The same reaction with oxygen atoms from photolysis of NO_2 gives large amounts of CH_3NO_3 and CH_3NO_2 instead (11), because of the presence of excess NO_2. In the reaction of butene-1 with oxygen atoms from NO_2 photolysis some $C_2H_5NO_3$ has indeed been identified, suggesting the presence of free C_2H_5 radicals (the elution time of $C_2H_5NO_2$ is considerably larger than that of $C_2H_5NO_3$ and $C_2H_5NO_2$ would, therefore, not be observed in small amounts at the GLC column temperature used) (6). Similarly in the isobutene reaction very small amounts of CH_3NO_3 and CH_3NO_2 are found, suggesting formation of some free CH_3 radicals, as would be expected in this case. All this supports the proposed explanation for the formation of ethanol and methanol in the present work. The absence of these two compounds in the same reaction with oxygen atoms formed from N_2O, even when molecular oxygen is present (2), is explained by the much higher total pressures used and the consequent suppression of the pressure dependent fragmentation. In the NO_2 work, the excess NO_2 acted as free radical scavenger as already indicated, so that even at low pressures no alcohols were detected.

As the butene-1 pressure is decreased in Fig. 5, ethanol and the direct oxygen atom addition products, α-butene oxide, n-butyraldehyde, and methyl ethyl ketone, begin to decrease while propionaldehyde, acetaldehyde, and methanol increase. This suggests that under conditions of these experiments butene-1 pressure has to be relatively quite high before secondary processes are suppressed and that propionaldehyde, acetaldehyde, and methanol result at least to a large extent from secondary processes, especially so propionaldehyde. The trend in ethanol is consistent with the mechanism of its formation suggested in the preceding paragraph. It shows at the same time that the effect of decreasing butene pressure is not due (at least not predominantly so) to a decreasing efficiency of the gaseous mixture for collisional deactivation as butene concentration is lowered, since the trend in ethanol would be expected then to be the same as that of propionaldehyde, acetaldehyde, and methanol.

The foregoing explanations are supported by the difference in the composition of the products at various pressures for a low and a high butene flow as shown in Figs. 1 and 2, respectively. In this case again, propionaldehyde, acetaldehyde, and methanol are much smaller, especially so propionaldehyde, at the high butene flow.

Relatively high butene-1 pressures necessary to suppress secondary processes even when the partial pressure of oxygen is small, as in Fig. 5, would seem to preclude quantitative use of the Garvin–Kistiakowsky's Temperature Pattern Method for this reaction, at least under conditions of the present experiments. At small butene-1 pressures, such as would be anticipated to be necessary in order not to confine the reaction to a very small region around the nozzle, considerable complexities arise. The results of the experiments at such low partial pressures of butene are shown in Figs. 1, 3, and 4. The observed complexities are difficult to explain in detail, but are likely to be of general occurrence under certain experimental conditions and may seriously affect both quantitative and qualitative studies of oxygen atom reactions. For this reason a discussion of these results may be in order.

The reasons for the general trend in the amounts of products formed with varying pressure, as shown in Fig. 1, have already been discussed. The gaseous mixture in these experiments consisted mainly of helium which is probably not too efficient as a collisional deactivator and there are no drastic changes in the character of the products formed. At higher pressure the relative increase in propionaldehyde is conspicuous. This is probably due to the simultaneous increase in the partial pressure of oxygen (the composition of the gases was kept constant while the pressure was varied). The effect of the increasing concentration of oxygen is shown better in Figs. 3 and 4. Here again the reasons for the general decline in the amounts of products formed as oxygen concentration is increased have already been discussed. Attention should now be focussed on the variation in the relative amounts of the products, and it is evident that at higher percentages of oxygen in the mixture propionaldehyde becomes relatively more important while *n*-butanal and ethanol tend to be suppressed. Roughly similar trend was observed when oxygen pressure was varied in the absence of helium. As the oxygen pressure was increased from 0.2 to 2.6 mm the amounts of α-butylene oxide and propionaldehyde increased, ethanol decreased, and *n*-butyraldehyde was not found in the products under these conditions. In these last experiments, however, the reproducibility was poor and also α-butylene ozonide was identified as an important product. This compound is unstable and the lack of reproducibility was almost certainly largely due to the varying extent of its decomposition.

The formation of α-butylene ozonide suggests an important participation of ozone in the process under these conditions. When ozone reacts at room temperature with butene-1 in the gas phase (in the presence of excess oxygen) propionaldehyde and formaldehyde appear to be the main products (12). The largely increased formation of propionaldehyde at low butene-1 and larger oxygen concentrations is probably due to this reaction. In agreement with this, under these conditions large amounts of polymerized formaldehyde were found in the liquid nitrogen trap for the collection of the products, from where samples of the polymer were directly withdrawn for qualitative identification.

The manner in which ozone is formed is uncertain. There are two general possibilities: it may be formed in and after the discharge but predominantly before the gases reach the nozzle, or it may result from the reactions which take place after the stream of gas containing oxygen atoms meets butene-1 in the reaction zone. The first possibility depends on the efficiency of reaction [VII] which competes with [VIII] and with the reverse of [VII]. Depending on the pressure of the gas and its efficiency as the "third body", a certain steady-state concentration of ozone should establish itself. It is not possible at present to predict with certainty whether this concentration should in a particular case be negligible compared with the concentration of oxygen atoms. The problem has been recently discussed by Herron and Schiff (13), who could not detect ozone mass spectrometrically in oxygen subjected to electrical discharge, although calculations based on literature values of rate constants of the above reactions (but for a different "third body") suggested detectable steady-state concentrations of ozone. Such calculated steady-state concentrations of ozone would be of the correct order of magnitude to be of importance under conditions of some of the present experiments.

The established formation of α-butylene ozonide cannot be regarded as a proof that ozone results directly from the discharge, since it may be, perhaps, equally well formed in the reaction zone. It is well known that under certain conditions in the atmosphere (and these conditions were simulated in the laboratory) ozone is formed in a chain reaction following an initial interaction of oxygen atoms with hydrocarbons (14). The detailed mechanism of this chain process is not known, although it appears reasonably certain that it involves initially an interaction of free radicals with molecular oxygen to form a hydroperoxy free radical. The latter, perhaps, reacts with another molecule of oxygen to give ozone. In agreement with these views it was possible to initiate ozone formation by generating free radicals in an oxygen atmosphere (14). Similar conditions can be readily envisaged in some of the experiments in the present work. Hydroperoxy radicals appear to be able also to react in some instances directly with olefins to form epoxides (15). It is evident then that explanations can be suggested for the results of some experiments in the present work, in particular to explain the formation of the ozonide, propanal, and the epoxide and the significant absence of *n*-butanal, as outlined before, without assuming any significant participation of oxygen atoms in the process (except, perhaps, in the initiation stage). Further substantial progress has to be made in this general field before a more reliable and quantitative discussion can be undertaken.

Substantial quantities of excited molecules of oxygen have been detected (13) mass spectrometrically in oxygen subjected to electrical discharge, the excited state being probably the $^1\Delta_g$ electronic state. What effect, if any, such molecules would have on butene-1 is not known. The increased formation of propanal at lower butene-1 concentrations, as shown in Fig. 5, cannot be due to excited molecules of oxygen since in this case no suppression with increasing butene-1 pressure would be expected. Under conditions of these experiments (low oxygen concentration in helium) no evidence was detected for any significant reaction of eventually present excited oxygen molecules with butene-1. Whether such molecules play a role in the experiments in which the concentration of oxygen in the discharge tube is large cannot be said at present because it is not possible to treat the results in a quantitative manner.

In conclusion, it ought to be stressed that the present work shows that under appropriate conditions oxygen atoms produced from molecular oxygen by electrical discharge lead to the same type of reaction as obtained with ground state oxygen atoms produced by mercury-photosensitized decomposition of nitrous oxide or by photolysis of nitrogen dioxide. The observed differences are understandable in view of the low over-all pressures and the excess molecular oxygen present. At the same time, considerable caution has to be exercised in the choice of the appropriate conditions when this technique is employed in order to avoid secondary processes which can sometimes completely mask the primary reactions of the oxygen atoms.

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