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Investigation of the Mechanism of Propylene Oxidation on Zinc Oxide

BLANCA L. KUGLER[1] AND JOHN W. GRYDER

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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Infrared studies of the products of propylene oxidation on zinc oxide as a function of time show the buildup and decay of an intermediate. Comparison of the infrared spectra of partially oxidized propylene with the spectra of adsorbed three-carbon compounds, partially oxidized perdeuterio propylene, and propylene partially oxidized by $^{18}O_2$ permits the intermediate to be identified as glycidaldehyde and/or glycidol. A possible mechanism is proposed consistent with the infrared spectra and with the observation that under oxygen-poor conditions, propylene is converted to acrolein with a stoichiometry of two propylenes to one oxygen. Individual steps of the mechanism are verified by direct observation; and hydrogen and glycidaldehyde, predicted by the mechanism, are indicated in the reaction products by mass peaks at 2 and 72.

INTRODUCTION

In a previous publication from this laboratory (*1*), preliminary results of an investigation of propylene oxidation on the surface of zinc oxide at room temperature were reported. It was determined by ESR and infrared spectroscopy that the reaction occurs between π-allyl and O_2^- species. The π-allyl is formed when propylene chemisorbs on zinc oxide and has been characterized by Kokes and Dent (*2, 3*). It has been established by Lunsford and others (*4, 5*) that oxygen adsorbs on zinc oxide at room temperature as an O_2^- species. Infrared spectroscopy was used to follow the course of the reaction, and acrolein was identified as the major product. However, the reaction products could not be desorbed without raising the temperature high enough to cause reactions yielding primarily carbon dioxide or monoxide and water. This is in agreement with the work of Daniel and Keulks (*6*), which showed that no acrolein is formed in the high-temperature oxidation of propylene on zinc oxide. Thus, the formation of acrolein on zinc oxide is a surface reaction and not a true catalytic process.

A simple mechanism which was proposed for this process (*1*) involves the combination of the adsorbed O_2^- and π-allyl species to form a hydroperoxide species on the zinc oxide surface. This is followed by the dehydration of the hydroperoxide to yield adsorbed water and acrolein. Further results of a continuing study of this reacting system which are presented here have shown, however, that the stoichiometry required by this mechanism does not agree with volumetric measurements of the amount of oxygen uptake by a sample with preadsorbed propylene. Evidence for the formation of epoxide intermediates has also been found. A more complex mechanism is proposed to explain the new information which has been obtained on this reaction.

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[1] Current address: Department of Chemistry, Lafayette College, Easton, Pa. 18042.

EXPERIMENTAL

Materials. The zinc oxide used was Kadox-25, a product of the New Jersey Zinc Co.

Research grade propylene from the Phillips Petroleum Co. was purified by condensation in a liquid nitrogen trap followed by distillation with the center cut retained as purified gas. Perdeuteriopropylene was obtained from Merck, Sharp, and Dohme. The purity, checked by mass spectrometry, was 93.4%. It was purified by freezing and pumping.

$^{18}O_2$ was obtained from Miles Laboratories. It was manufactured by Yeda Research and Development Co., Rehovoth, Israel. It was certified by the manufacturer to be 94.262 atom % ^{18}O and 0.366 atom % ^{17}O and was used without further purification.

Tank oxygen and carbon dioxide were purified in the same manner as the propylene. Tank hydrogen and deuterium, which was obtained from the Matheson Scientific Co., were purified by passage through a degassed charcoal trap at $-195°C$.

Acrolein was obtained from the Eastman Kodak Co., and glycidaldehyde and glycidol were obtained from Aldrich Chemical Co. Their purity was checked by gas chromatography.

Infrared and mass spectrometry studies. Approximately 0.7 g of zinc oxide were pressed into a disc (20 mm in diameter) in a stainless steel ring at 5500 psi. The ring containing the disc was then placed in the center of the infrared cell.

The infrared cell is a section of glass tubing about 10 cm long and 3 cm in diameter, fitted at each end with a NaCl window. The windows are held on by removable brass end pieces with O-ring seals. Cooling of the windows is accomplished by water flowing through copper tubing which is wrapped around the cell next to the end pieces. Nichrome wire was wrapped around the sample area on the outside of the cell to provide heating. The sample temperature was measured by means of a Chromel–Alumel thermocouple resting directly on the zinc oxide disc. Tubulations, with stopcocks, connected to the cell on either side of the sample area, permitted gases to be circulated over the sample when the cell was attached to the vacuum system with ball joints.

Infrared spectra were recorded with a Perkin–Elmer 521 grating double-beam spectrometer with a spectral slit width varying from 5 cm^{-1} at 3600 cm^{-1} to 2 cm^{-1} at 1200 cm^{-1}.

A matched path length cell containing no sample was evacuated to 10^{-6} Torr and placed in the reference beam of the spectrometer. The cells maintained a vacuum for a period much longer than the time of an experiment. To offset the background adsorption of the degassed zinc oxide, a series of several calibrated screens was also inserted in the reference beam. In each case, prior to adsorption of any gases, a background scan of the degassed zinc oxide was made and is shown in all infrared spectra as a dotted line. All infrared spectra were recorded at room temperature. The equipment and methods are essentially the same as those employed by Dent and Kokes (*3*).

Mass spectra were recorded on a Hitachi–Perkin–Elmer RMU 6 mass spectrometer. Because only extremely small amounts of reaction products were desorbed from the zinc oxide surface, the sample in an infrared cell was connected directly to the gas inlet apparatus of the spectrometer, so that, when the spectra were recorded, the sample was directly exposed to the analyzer of the spectrometer. Thus, the same samples were used for both infrared and mass spectra. A background mass spectrum of the degassed zinc oxide was also run before each experiment.

Adsorption studies. A 9.9 g sample of zinc oxide was pressed into discs as described for the infrared samples and then broken up. The pieces were placed in a U-shaped sample tube designed to fit inside a cylindrical furnace.

The activation procedure was the same as for the infrared samples, except that the period of oxygen circulation was increased from 3 to 6 hr.

The vacuum system was a conventional BET system equipped with a circulating pump, gas buret, and mercury manometer. The pressure was maintained by an oil diffusion pump at 10^{-6} Torr, as measured by a McLeod gauge.

Activation procedure. The sample was first degassed at room temperature. The temperature was slowly increased to 450°C, and degassing was continued for 1 hr. Then oxygen at about 160 Torr was circulated over the sample for 3 hr at 450°C with a liquid nitrogen trap in the circulation loop. The circulation was continued while the sample cooled to room temperature. The sample was then degassed briefly. This oxygen treatment, which results in samples with excellent infrared transmission, is essentially the same as that used in previous studies of propylene adsorption (*3*) and produces a sample with a BET surface area of about 6 m^2/g.

In the experiments where perdeuteriopropylene was used, in addition to the above activation procedure, a mixture of 10 Torr of oxygen and 150 Torr of deuterium was circulated over the sample for 2 hr at 300°C. After degassing 0.5 hr at 300°C, the sample was degassed at 450°C for 1 hr. Following this, oxygen circulation over the sample through a liquid nitrogen trap was carried out at 450°C for 2 hr. After cooling to room temperature with the oxygen circulating, the sample was degassed briefly.

RESULTS AND DISCUSSION

In earlier experiments (*1*), the reaction between adsorbed propylene and oxygen was carried out at 40°C with about 0.28 cm^3/g of propylene, corresponding to about 50% of the saturation π-allyl coverage, and an oxygen pressure of 150 Torr. However, further investigation has shown that it is not necessary to have gas-phase oxygen present throughout the reaction in order for it to go to completion. When a zinc oxide sample with about 0.28 cm^3/g of adsorbed propylene is exposed to 150 Torr of oxygen for 1 hr at 40°C, the infrared spectrum shows that the reaction is not complete, in that the bands due to the π-allyl still have significant intensity, and the bands due to the reaction product are not yet fully developed. However, if the gaseous oxygen is pumped out and the sample allowed to sit overnight at room temperature without reintroduction of any oxygen, the reaction will proceed to completion. The bands due to the π-allyl disappear, and the reaction product bands grow until they reach a stable intensity. The final spectrum is virtually identical to that obtained when the reaction is run with gaseous oxygen present throughout. However, when an infrared sample with the same amount of adsorbed π-allyl is allowed to sit at room temperature without any exposure to oxygen, the infrared spectrum remains unchanged for several days, indicating that gas-phase oxygen is necessary to initiate the reaction.

The amount of oxygen uptake by a sample with preadsorbed π-allyl has been measured, and the results are plotted in Fig. 1 as the ratio of the volume of oxygen to that of propylene versus time since exposure to oxygen. An adsorption sample weighing 9.9 g was used, and about 2.8 cm^3 of propylene were adsorbed, so that the propylene surface coverage is the same as for the infrared sample described above, and the measurements were also carried out at 40°C. It can be seen from Fig. 1 that in 1 hr, which was the time of exposure of the infrared sample to gaseous oxygen, the ratio of moles of oxygen reacted to moles of propylene preadsorbed is only about 1:2. A ratio of 1:1 is not reached until 10 hr of expsoure to oxygen. It should be noted that, under the conditions of the infrared experiment, no significant amount of oxygen remains adsorbed on the surface after evacuation. Therefore, it must be concluded that any mechanism, such as the one proposed earlier (*1*), which requires a clear-cut 1:1 stoichiometry, must be ruled out, or, at the least, cannot be the only mechanism operating. Thus, it becomes necessary to investigate the possibility of other, more complex mechanisms, involving the participation of as yet unidentified intermediates.

There is one band in the infrared spectrum of the reaction which behaves as if it belongs to an intermediate species. It is a weak but sharp band located at 1237 cm^{-1}. It appears in the course of the reaction about 30 min after introduction of oxygen, as the π-allyl bands begin to decrease in intensity and the acrolein bands begin to appear. It remains at a constant intensity for about 1 hr, and then slowly disappears overnight, whether or not gas-phase oxygen is present. It is never present in the final reaction product spectrum, and it is the only band in the reaction spectrum which behaves in this way. The intensity of the 1237 cm^{-1} band increases with increasing propylene surface coverage and with increasing oxygen pressure, indicating that the species which gives rise to this band is an adduct of propylene and oxygen. When more propylene is added to an infrared sample which shows the 1237 cm^{-1} band, it disappears rather rapidly, and no new bands in addition to the reaction product bands already present are observed. This suggests that the species which is responsible for this band is capable of reacting with propylene to form acrolein.

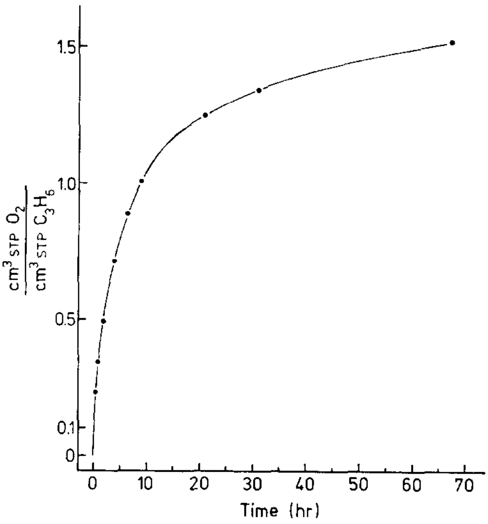


FIG. 1. Plot of oxygen uptake by a sample with adsorbed propylene against time since exposure to oxygen.

When the oxidation reaction is run using perdeuteriopropylene, C_3D_6, a band appears in the infrared spectrum at 1217–1222 cm^{-1} which exhibits the same unique behavior as the 1237 cm^{-1} band does when perhydropropylene is used. The fact that the 1237 cm^{-1} band shifts only 15–20 cm^{-1} to lower frequency upon deuterium substitution indicates that the vibration which produces this band does not involve any hydrogen atoms directly. One vibration which meets this requirement and is also known to produce a band in the vicinity of 1237 cm^{-1} is the ring breathing vibration of epoxides (*7*).

A calculation of the expected isotopic shift with deuterium substitution for this vibration in ethylene oxide, using the force constants and equations derived by Bonner (*8*), yields a value of 52 cm^{-1}. While this is somewhat larger than the observed shift of the 1237 cm^{-1} band, it is at least the right order of magnitude. The smaller shift may

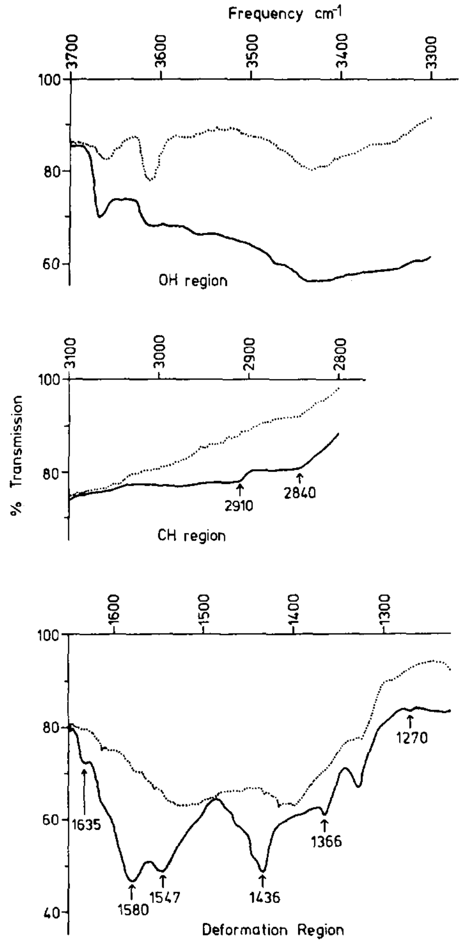
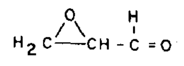


FIG. 2. Infrared spectrum of the products of reaction between glycidaldehyde and propylene. (· · · ·), Background; (——), reaction products.

well be accounted for by the fact that the species which gives rise to the 1237 cm^{-1} band is tied down on the surface, so that the ethylene oxide model is not accurate.

Assuming, then, an adduct of propylene and oxygen containing three carbon atoms and two oxygen atoms, with an infrared spectrum which is only distinguishable from that of adsorbed acrolein by a band at 1237 cm^{-1}, the most likely possibility is the epoxide of acrolein



commonly known as glycidaldehyde.

When approximately 0.2 cm^3 of glycidaldehyde vapor are adsorbed on a clean infrared sample at room temperature, the only band in the spectrum which can be distinguished from the background bands occurs at 1242 cm^{-1} and is similar in size and shape to the band at 1237 cm^{-1} which is observed during the reaction between propylene and oxygen. When about 0.2 cm^3 of propylene are added to the sample with adsorbed glycidaldehyde at room temperature, first the π-allyl bands appear, and then the 1242 cm^{-1} band of the glycidaldehyde and the π-allyl bands disappear, and a new spectrum is produced, which is shown in Fig. 2.

This spectrum should be compared with the one shown in Fig. 3, which results from the reaction of propylene and oxygen and was reported previously (*1*). To aid in the comparison of these spectra, the positions of the bands in Figs. 2 and 3 at positions other than those of the background bands, as well as the band positions from the spectrum of adsorbed acrolein, are listed in Table 1.

An examination of Figs. 2 and 3 and Table 1 clearly shows that not only will glycidaldehyde react with the π-allyl on the zinc oxide surface, but the spectrum of the resulting products is identical to that obtained when propylene is reacted directly with oxygen.

The band at 1580 cm^{-1}, which is the one band in Figs. 2 and 3 which cannot be assigned to adsorbed acrolein, was previously thought to be due to adsorbed CO_2 from further oxidation of propylene (*1*). However, analysis of the infrared spectrum of adsorbed CO_2 has shown that, while it does have a band at about 1580 cm^{-1}, it has much more intense bands at 1525 and 1327 cm^{-1}. Since these two bands are not present in Fig. 3, this assignment of the 1580 cm^{-1} band must be abandoned. This conclusion is in agreement with the results of another study of propylene oxidation on zinc oxide, by Kubokawa, Ono, and Yano (*9*), in which essentially no CO_2 formation was observed below 100°C.

When about 0.3 cm^3 of glycidaldehyde are adsorbed on a clean infrared sample at room temperature and allowed to sit overnight, the spectrum shown in Fig. 4 develops. Only the deformation region is shown because the OH and CH regions show no distinguishable bands. The same spectrum develops whether or not gas-phase oxygen is present.

The most prominent feature of this spectrum is a very strong band at 1585 cm^{-1}, which agrees within the experimental error of 5 cm^{-1} with the position of the 1580 cm^{-1} band in the reaction product spectrum. There is also a medium, slightly broad band at 1437 cm^{-1}, which is identical to the position of one of the adsorbed acrolein bands. The band at 1327 cm^{-1} occurs at a position where there is also a maximum in the background absorption. However, it is sharper

TABLE 1

OBSERVED BANDS (CM^{-1}) FOR ADSORBED SPECIES

Glycidaldehyde + propylene	Propylene + O_2	Adsorbed acrolein (*1*)
2910w	2910w	2915w
2840w	2850w	2847w
1635w	1636w	1632w
1580s	1580m	—
1547s	1545s	1540s
1436s	1437s	1437s
1366w	1367w	1365m
1270vw	1270vw	1267vw

Note. Relative intensities are based on classifying the 1547, 1545 and 1540 cm^{-1} bands as strong and all others relative to that. Band positions are accurate to approximately 5 cm^{-1}, except for the broad bands between 2840 and 2915 cm^{-1}, which could be in error by 10 cm^{-1}.

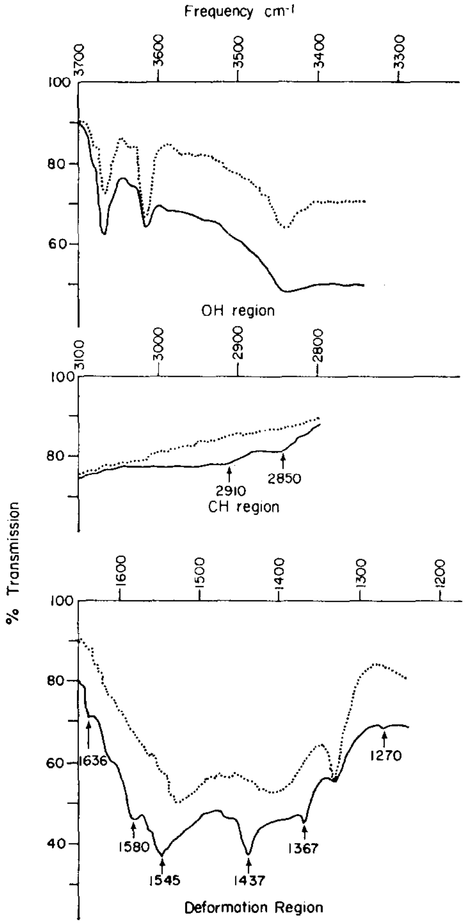


FIG. 3. Infrared spectrum of the products of reaction between propylene and oxygen. (····), Background; (——), reaction products.

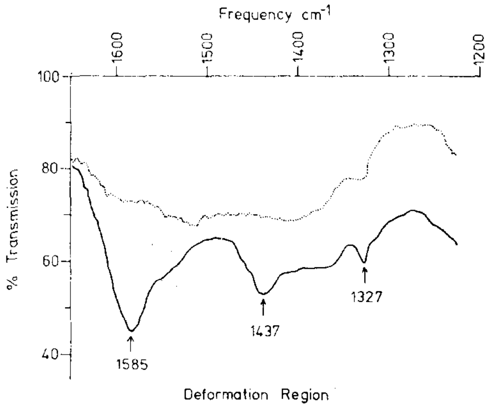
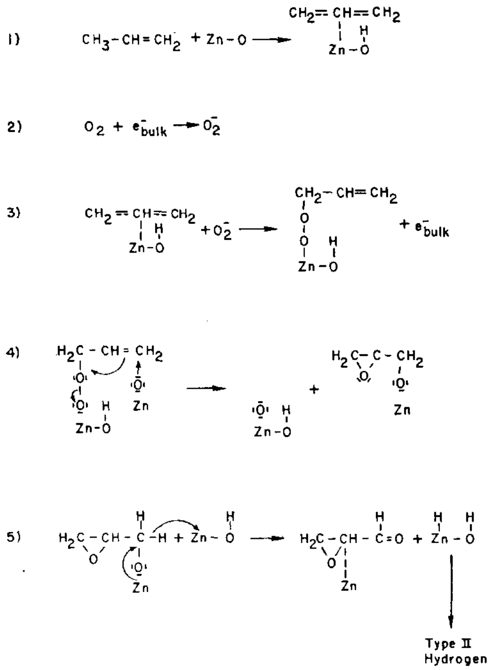


FIG. 4. Infrared spectrum of species formed from adsorbed glycidaldehyde. (····), Background; (——), adsorbed species.

and stronger than in the case of the background, and, hence, probably does belong to the spectrum of the adsorbed species. It is also present in Fig. 2 in the spectrum of the reaction product of glycidaldehyde and propylene. However, since it is the weakest band in the spectrum in Fig. 4, it is not surprising that it shows up only weakly in the spectrum of the reaction product of propylene and oxygen (Fig. 3), where the 1580 cm^{-1} band itself is weak. Thus, the only band in the spectrum resulting from glycidaldehyde (Fig. 4) which is distinguishable from that of adsorbed acrolein is the 1585 cm^{-1} band, and this is precisely the band in the reaction product spectrum (Fig. 3) which is not assignable to adsorbed acrolein. Although no attempt was made to identify the species responsible for this band, presumably glycidaldehyde isomerizes on the surface to form some other substance which gives rise to it. Zinc oxide has been found to catalyze several isomerization reactions. For example, when about 0.2 cm^3 of propylene oxide are adsorbed on a clean infrared sample, after 2 days the infrared spectrum changes to that of adsorbed propionaldehyde.

Thus, it appears that glycidaldehyde could be an intermediate species formed by the reaction of propylene and oxygen which is responsible for the 1237 cm^{-1} band, and which can react with more propylene to give acrolein. Some of the glycidaldehyde could react independently to give a species which produces the 1580 cm^{-1} band. If all the bands in Fig. 3 except the 1580 cm^{-1} band are assigned to adsorbed acrolein, and the 1580 cm^{-1} band is assigned to a species formed from glycidaldehyde, a complete assignment of the reaction product spectrum is now possible.

It is possible to write a reasonable mechanism for the formation of glycidaldehyde from propylene and oxygen on the surface of zinc oxide:



The first three steps are the same as those in the simple mechanism proposed earlier (*1*), and involve adsorption of oxygen as an O_2^- species, adsorption of propylene as the π-allyl, and reaction of the O_2^- and the π-allyl to form a hydroperoxide species. Unfortunately, no direct physical evidence for this third step has been obtained. The O–O stretch, which would be characteristic, occurs around 900 cm^{-1} (*7*), which is below the point at which zinc oxide becomes opaque in the infrared. However, it is known that hydroperoxides are formed in solution by the autoxidation of olefins by atmospheric oxygen, if radical species are present or can readily be formed (*10*). Since both the π-allyl and the O_2^- species have radical character, the formation of a hydroperoxide intermediate seems likely.

Formation of glycidaldehyde from the hydroperoxide species is shown in steps 4 and 5. Step 4 shows the formation of glycidol, the alcohol analogous to glycidaldehyde. Precisely this step occurs as part of the mechanism of the homogeneous oxidation of α,β-unsaturated ketones by alkaline hydroperoxide (*10*). Furthermore, in a study of a heterogeneous system by Lyons (*11*), hydroperoxide species were found to form epoxy alcohols in high yield over zeolite catalysts exchanged with vanadium.

In the presence of oxygen, glycidol should be easily oxidized to glycidaldehyde. However, even without oxygen present, step 5 shows how this could occur as glycidol loses hydrogen to the zinc oxide surface to form glycidaldehyde.

Although as stated earlier the products of the reaction do not readily desorb from the surface, so that conventional methods of product analysis cannot be used, it has been possible to analyze the products by mass spectrometry because of the very high sensitivity of this technique. The mass spectrum of the reaction products shows a small, but distinct and reproducible, peak at $m/e = 2$, indicating the formation of molecular hydrogen.

Dent and Kokes (*12*) have shown that zinc oxide has a rather large capacity for hydrogen adsorption. There are two types of adsorption at room temperature. Type I gives rise to Zn–H and O–H bands in the infrared. Type II, which is infrared inactive, is irreversible, and the capacity of the surface for this type of adsorption is at least 0.25 cm^3/g. Since no Zn–H or O–H bands appear in the infrared in the course of the reaction between propylene and oxygen (indicating that no Type I hydrogen is present), presumably significant quantities of Type II hdyrogen are formed, as shown in step 5. The fact that Type II hydrogen is not easily removed from the surface by evacuation is consistent with the observation that only small quantities of hydrogen are detected in the reaction products, and only when pumping on the sample with the diffusion pump of the mass spectrometer.

It should also be mentioned that the mass spectrum of the reaction products shows a small peak at $m/e = 72$, indicating the presence of some species which has the same molecular weight as glycidaldehyde. Thus, the evidence from mass spectrometry strongly indicates that a reaction such as that shown in step 5 is quite plausible as part of the overall mechanism. The mass spectrum also contains several peaks, including the parent peak at $m/e = 56$, which are characteristic of the mass spectrum of acrolein, which is further confirmation of the identification of acrolein as the major product.

Since step 4 suggests the participation of glycidol as a reactive intermediate, several experiments have been performed to see if this is reasonable. The infrared spectrum obtained when 0.2 cm^3 of glycidol are adsorbed on a clean zinc oxide surface at room temperature is virtually indistinguishable from that of adsorbed glycidaldehyde. The only band which can be distinguished from the background bands occurs at 1242 cm^{-1}. This supports the suggestion that this band is the result of an epoxide ring vibration, since both compounds contain this functional group. Although this result means that it is impossible to distinguish glycidol from glycidaldehyde by their infrared spectra, it also means that both compounds have infrared spectra which are compatible with the reaction product spectrum, and, thus, both compounds could be reaction intermediates.

When the zinc oxide sample with adsorbed glycidol is allowed to sit overnight, the infrared spectrum shown in Fig. 5 results. Apparently, glycidol dehydrates on the surface to form acrolein and water. Figure 5 clearly shows the spectrum of adsorbed acrolein (see Table 1 for the band positions). There is also a very large increase in the intensity of the background band at 3670 cm^{-1} which is characteristic of

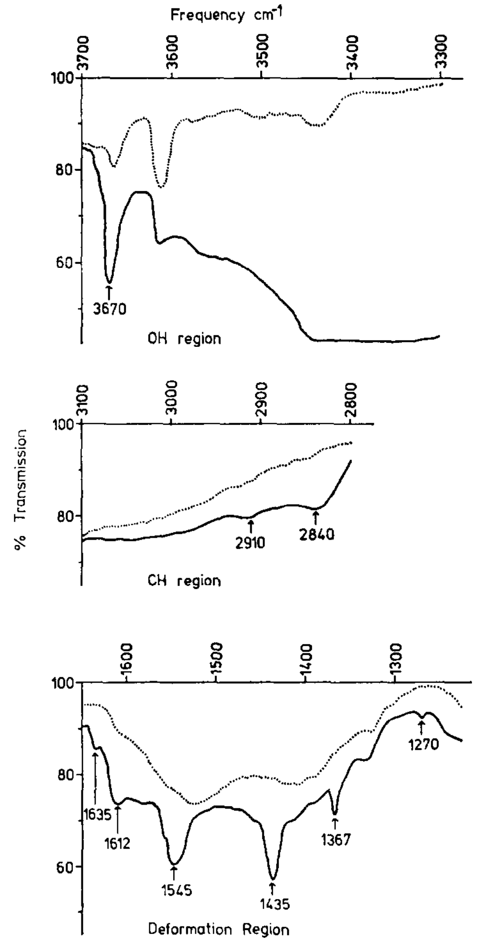


FIG. 5. Infrared spectrum of species formed from adsorbed glycidol. (····), Background; (——), adsorbed species.

adsorbed water. The bands at 3620 and 3450 cm^{-1} show the distortion which indicates hydrogen bonding. The band at 1612 cm^{-1} is also present in the spectrum of adsorbed water.

The dehydration of adsorbed glycidol presents another pathway for the formation of acrolein. However, this pathway has a 1:1 stoichiometry, and, thus, is presumably not the major pathway in the absence of excess oxygen. Indeed Fig. 5 shows an increase in the background bands due to water formation that is much more significant than in the case of the reaction product spectrum (Fig. 3). However, if glycidol is formed in the course of the reaction, this pathway should occur to some extent.

Step 5 in the proposed mechanism postulates the formation of glycidaldehyde from glycidol by incorporation of lattice oxygen. While some evidence for this step has been found in the detection of hydrogen among the reaction products, the evidence from the infrared spectra is inconclusive. It is not possible to tell whether or not there is a very weak band in Fig. 5 at 1580 cm^{-1}, which would indicate the presence of the species formed from glycidaldehyde. However,

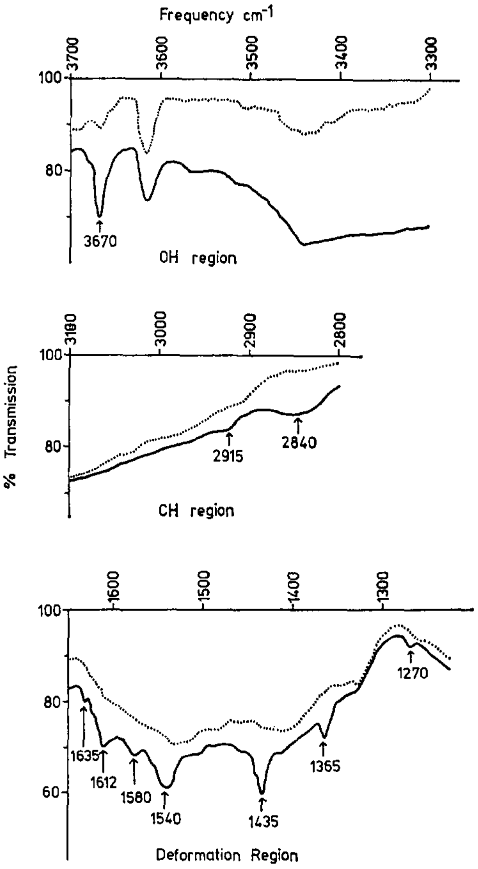


FIG. 6. Infrared spectrum of species formed from adsorbed glycidol in the presence of oxygen. (····), Background; (——), adsorbed species.

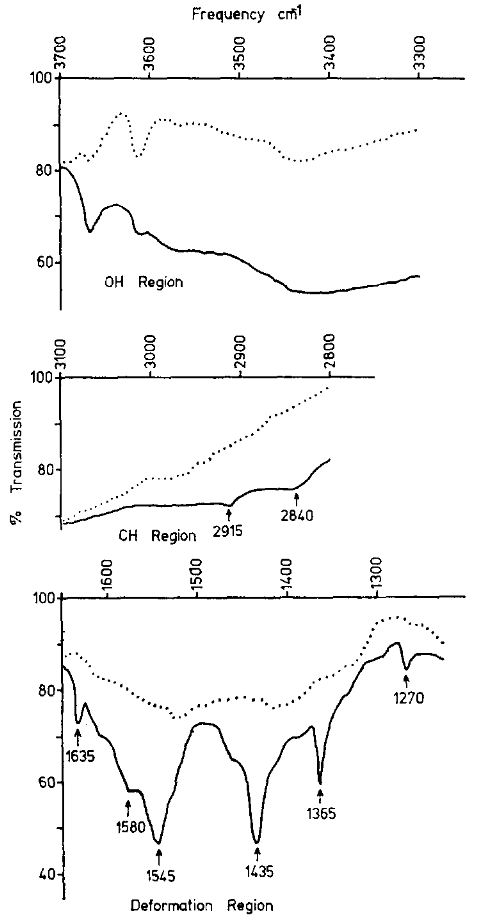
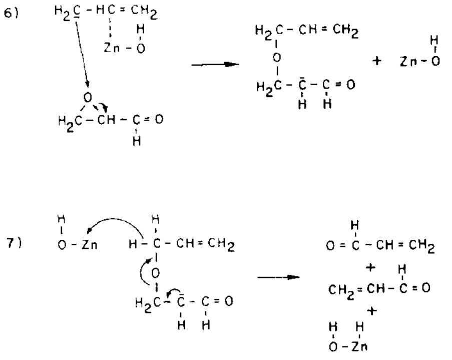


FIG. 7. Infrared spectrum of the products of reaction between glycidol and propylene. (····), Background; (——), reaction products.

when 0.2 cm^3 of adsorbed glycidol are allowed to sit overnight at room temperature in the presence of 150 Torr of oxygen, the infrared spectrum shown in Fig. 6 results. In this spectrum, a band at 1580 cm^{-1} is clearly present, indicating that, in the presence of oxygen, some of the glycidol has been oxidized to glycidaldehyde, since it has been established that glycidaldehyde reacts to form the species responsible for the 1580 cm^{-1} band. Comparison of Figs. 5 and 6 shows that the dehydration of glycidol to form water and acrolein has also taken place in the presence of oxygen.

When 0.3 cm^3 of propylene is added to a sample with 0.35 cm^3 of preadsorbed glycidol at room temperature, the infrared spectrum shown in Fig. 7 results. A comparison of this spectrum with those shown in Figs. 2 and 3 shows that glycidol can also react with propylene to produce acrolein. It is possible to tell that the glycidol is reacting with the propylene, rather than just dehydrating, because in this experiment the acrolein bands appear immediately after addition of the propylene, whereas when glycidol sits alone on the surface, it takes several hours for the acrolein bands to appear. In addition to this, the 3670 cm^{-1} band which is characteristic of adsorbed water is not nearly as intense as it is in the spectrum resulting from the dehydration (Fig. 5). It is particularly important to note that there is a band present at 1580 cm^{-1} in Fig. 7. which could indicate that some glycidaldehyde has been formed.

Thus, it appears that glycidol can react with propylene, but, for reasons which will be discussed more fully later, it probably reacts by forming glycidaldehyde first. The glycidaldehyde could then react with the propylene by the following mechanism.



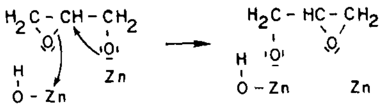
Step 7 calls for formation of hydrogen as in Step 4, and produces 2 moles of acrolein.

One of the most significant points to be made about this mechanism is that it requires only a 1:2 oxygen-to-propylene stoichiometry, which is consistent with the results of the adsorption measurements. The overall reaction is

$$2C_3H_6 + O_2 \rightleftarrows 2CH_2{=}CH{-}CHO + 2H_2.$$

Obviously, there is not direct evidence for the precise nature of each step in the mechanism, and indeed it is proposed only as a possible mechanism which is consistent with the experimental evidence and with what is known about the mechanisms of similar reactions in solution. This mechanism best explains the results in the absence of excess oxygen. In the presence of excess oxygen, other mechanisms such as the one proposed earlier (*1*) may also be important.

It should be pointed out that glycidol is a symmetric intermediate if it can isomerize on the surface as shown below.



In an attempt to determine whether or not lattice oxygen does participate in the reaction as shown above and in Step 4, the reaction was carried out at 40°C with 0.3 cm^3 of preadsorbed propylene and 180 Torr of $^{18}O_2$ and the infrared spectrum examined. [There is no exchange of gas-phase oxygen with the zinc oxide lattice below about 250°C (*13*).] When this is done, the band at 1237 cm^{-1} which has been assigned to the epoxide group remains essentially unshifted, but at about half of the intensity which it has when $^{16}O_2$ is used. As in the case of the experiment using perdeuteriopropylene, the 1237 cm^{-1} band was identified by its unique behavior. If the glycidol species does isomerize as shown above, then when $^{18}O_2$ is used, the epoxide oxygen in the species on the left would come from the gas phase and would be an ^{18}O atom, and the epoxide oxygen in the species on the right would come from the lattice and would be a ^{16}O atom. A calculation of the expected isotopic shift with ^{18}O substitution was carried out in the same way as in the case of deuterium substitution (*8*), and a value of 24 cm^{-1} was obtained. Thus, the 1237 cm^{-1} band should split into two bands, one unshifted and the other shifted to lower frequency by approximately this amount. The fact that about half the original intensity of the 1237 cm^{-1} band remains unshifted when $^{18}O_2$ is used indicates that oxygen from the lattice is participating in the reaction, if the assignment of the 1237 cm^{-1} band to the epoxide group is correct. However, no new band at lower frequency than the 1237 cm^{-1} band could be located with any certainty. The location of the band may be obscured because the band is very weak, because it is hidden by another band in this frequency range, or because of the increasing absorption by zinc oxide in this region. Unfortunately the attempts to locate the band were unsuccessful. Further experimentation is needed to investigate the participation of lattice oxygen and the possible isomerization of the glycidol species.

Although it appears from the results shown in Figs. 2 and 7 that both glycidaldehyde and glycidol can react with propylene, it seems likely that glycidol reacts by forming glycidaldehyde first, as shown in step 4. It is difficult to propose a mechanism where propylene reacts directly with glycidol to form only acrolein, without at some point oxidizing the alcohol to the aldehyde. Furthermore, the formation of some glycidaldehyde would explain the presence of the 1580 cm^{-1} band in the infrared spectrum of the reaction products and in Fig. 7 where the reaction is between glycidol and propylene.

Step 4 is very probably an equilibrium process, with the equilibrium lying mostly on the side of glycidol. This is suggested by the behavior of the 1580 cm^{-1} band which arises from glycidaldehyde. If glycidol is adsorbed on the zinc oxide surface alone, the 1580 cm^{-1} band is extremely weak, if indeed it is present at all, indicating that very little glycidaldehyde is formed. The 1580 cm^{-1} band is also very weak, but definitely present, when glycidol is reacted with propylene. When glycidol sits on the surface in the presence of oxygen, the 1580 cm^{-1} band is significantly stronger than when oxygen is absent. When propylene is reacted directly with oxygen, and the oxygen is pumped out after 1 hr, this band is definitely present, but still weak. When propylene is reacted with oxygen, and the oxygen is not pumped out, the band is stronger than when it is pumped out. When glycidaldehyde is reacted with propylene, the 1580 cm^{-1} band is the strongest of all of these cases. These results indicate that when oxygen is present, glycidol is easily oxidized to glycidaldehyde. When oxygen is absent, glycidaldehyde can be formed in small amounts by step 4. If the glycidaldehyde is removed by reaction with propylene, however, more will be formed from glycidol, which in turn can react with more propylene. However, the possibility that the reaction of glycidol with propylene is a concerted process rather than a stepwise one cannot be ruled out.

Although zinc oxide is far from an effective catalyst for acrolein production, a comparison of the mechanism indicated over zinc oxide with what is known about the mechanism on other, more effective catalysts may prove useful. However, it must be kept in mind that reaction over zinc oxide takes place at room temperature, while the reaction over other catalysts is run at much higher temperatures (300–500°C). This difference may prove to be significant.

The mechanism proposed by Adams and Jennings and others (*14–16*) for cuprous oxide and bismuth molybdate catalysts involves a symmetric allyl species, which is analogous to the π-allyl on zinc oxide. All of the data obtained on the reaction over these catalysts indicate that it must go through some symmetric intermediate. However, Sachtler (*16*) has questioned whether a π-allyl complex with a transition metal ion would be stable enough to permit a sufficient steady-state concentration at the high temperatures at which these catalysts are used. He proposes rapid formation of a carbon–oxygen bond resulting in an asymmetric σ-allyl species.

The mechanism proposed in this study offers an alternative possibility in that it involves another kinetically symmetric intermediate in addition to the π-allyl. This intermediate is glycidol, which is effectively symmetric if it can isomerize on the surface as indicated above, and if this isomerization is fast compared to further steps in the mechanism. This is a species in which the symmetry is preserved after oxygen incorporation. If an analogous species were formed on cuprous oxide and bismuth molybdate, Adams and Jennings' (*14*) conclusion that the second hydrogen abstraction takes place before oxygen incorporation would not be mandated by their results. That is, if the symmetry is preserved after the oxygen incorporation, it is not necessary to require that the second hydrogen abstraction occur before incorporation in order to explain the discrimination isotope effect which they observed. In this case, the mechanism which is detailed above over zinc oside, where the second hydrogen abstraction takes place after oxygen incorporation, would be entirely consistent in this respect with all of the data on cuprous oxide and bismuth molybdate.

CONCLUSIONS

The stoichiometry of the reaction between propylene adsorbed on zinc oxide and oxygen under oxygen-poor conditions is shown to be approximately two propylenes for one oxygen even though the reaction product is acrolein. This observation requires that another product be formed. Mass spectroscopic evidence and the properties of adsorbed hydrogen on zinc oxide suggest that the other product is irreversibly adsorbed hydrogen.

The reaction takes place with at least one intermediate which has an infrared absorption band at 1237 cm^{-1} that grows and decays during the progress of the reaction. The spectra are consistent with glycidol or glycidaldehyde being the intermediate. Both of these compounds, when adsorbed on zinc oxide, react with adsorbed propylene to yield a product having the infrared spectrum of acrolein; and the mass spectrum shows a peak at mass 72, consistent with glycidaldehyde being an intermediate. The infrared spectra of partially oxidized perdeuteriopropylene and of propylene partially oxidized with $^{18}O_2$ are in agreement with the assumption that the intermediate contains an epoxide ring and that some of the epoxide oxygens come from the zinc oxide lattice.

A plausible mechanism is presented which is consistent with all of the experimental observations. It should also be noted that a kinetically symmetric intermediate-containing oxygen is proposed in the mechanism. An intermediate of this sort would negate the conclusion made by others from disciminative isotope studies that two hydrogens must be removed from propylene before oxygen is inserted.

Although comparison of our surface reaction with effective catalysts is presumptuous, our results, including the observation that some of the oxygen in the product acrolein may arise from the lattice, are in agreement with observations made for the oxidation of propylene over bismuth molybdate and cuprous oxide catalysts.

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