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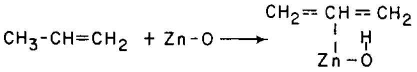
Intermediates in the Oxidation of Propylene Over Zinc Oxide

Oxidation of propylene to acrolein over cuprous oxide (*1*) and bismuth molydate (*2*) appears to occur via a slow step involving hydrogen abstraction from the propylene to form an allylic species, which then undergoes subsequent reaction with an oxygen species to form acrolein. Although it seems certain that an allyl species is an intermediate, the nature of the oxygen species has been the subject of considerable speculation. Recently, we inaugurated a study of the oxidation of propylene over zinc oxide in the hopes of shedding some light on this question. Although we recognized that the mechanism over zinc oxide is likely to differ from that over more effective catalysts, we felt that the fact that both oxygen species (*3*) (observable by ESR) and olefin species (*4*) (observable by infrared) were well-characterized on this surface might offset this disadvantage. We have presented elsewhere a synopsis of a few preliminary experiments (*5*). In this note we present new evidence that suggests that an O_2^- oxygen species reacts with a π-allyl species to form adsorbed acrolein.

Oxygen adsorbs on activated zinc oxide to give a strong ESR signal, which is assigned (with some confidence) to an O_2^- radical (*3*). This species is stable at room temperature for a period of at least 2 yr, does not desorb on evacuation, and does not react with either hydrogen or ethylene (*6*). If a sample of the activated catalyst is exposed to oxygen at room temperature and degassed briefly, a stable O_2^- signal appears with an intensity corresponding to a surface concentration of the order of 10^{-3} cm^3/g. If the sample is then exposed to propylene and degassed briefly, about 0.4 cm^3/g of propylene is retained by the catalyst as the π-allyl species (as judged by the ir spectrum). The O_2^- signal then slowly decays and disappears within 1 day.* Reexposure to oxygen and evacuation brings about the immediate reappearance of the O_2^- signal followed by its slow disappearance. This cycle can be repeated at least three times; since the π-allyl concentration greatly exceeds the O_2^- concentration, the cycling can probably be repeated many times. No new radical is observed to be formed by this reaction.

Although alternative explanations are possible, these observations are consistent with the view that the reaction sequence involves the radical–radical surface combination indicated below:

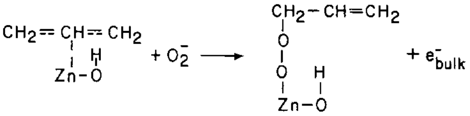
1)



$$CH_3\text{-}CH\text{=}CH_2 + Zn\text{-}O \longrightarrow \begin{array}{c} CH_2\text{=}CH\text{=}CH_2 \\ \vdots \quad H \\ Zn - O \end{array}$$

2) $O_2 + e^-_{bulk} \longrightarrow O_2^-$

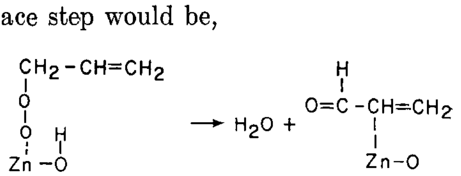
3)



$$\begin{array}{c} CH_2\text{=}CH\text{=}CH_2 \\ \vdots \quad H \\ Zn - O \end{array} + O_2^- \longrightarrow \begin{array}{l} CH_2\text{-}CH\text{=}CH_2 \\ | \\ O \\ | \\ O \quad H \\ | \quad\; | \\ Zn - O \end{array} + e^-_{bulk}$$

If this adsorbed allyl peroxide undergoes subsequent reactions akin to those found for alkyl peroxides in solution, decomposition should occur via dehydration, since this is the expected pathway in the presence of Lewis acids and bases (*8*) and since the active sites have been assigned such properties (*9*). Accordingly, the next surface step would be,

4)



$$\begin{array}{l} CH_2\text{-}CH\text{=}CH_2 \\ | \\ O \\ | \\ O \quad H \\ \vdots \quad\; | \\ Zn - O \end{array} \longrightarrow H_2O + \begin{array}{l} \;\;H \\ \;\;| \\ O\text{=}C\text{-}CH\text{=}CH_2 \\ \qquad\;\; | \\ \qquad\; Zn\text{-}O \end{array}$$

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* Decay of the O_2^- signal in the presence of olefins containing allylic hydrogens has been noted by others (*7*).

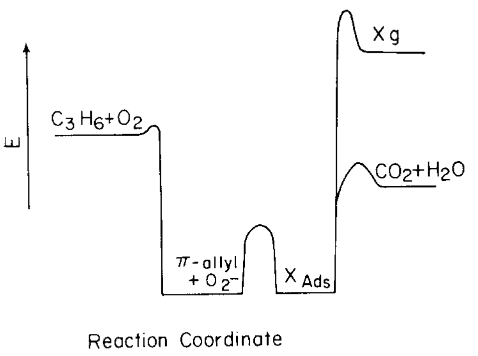

FIG. 1. Potential energy diagram (schematic).

Studies of oxygen uptake by the preadsorbed π-allyl confirm that a surface complex is formed. Such oxygen uptake proceeds at a reasonable rate until the uptake is about 1.2 oxygen molecules/π-allyl and then the reaction slows down appreciably, whereas, in the absence of π-allyl, the uptake of oxygen is very small (0.003 cm^3/g in 24 hr).† Attempts to desorb the reaction product by raising the temperature failed in that when the temperature is raised to the point where desorption is possible, reaction of the complex with the catalyst itself occurs with the production of primarily carbon dioxide or monoxide and water.

Several pieces of evidence suggest that a partially oxygenated complex is indeed formed and that it is so tightly held that it reacts before it desorbs. Such might be expected to be the case for a conjugated system (like acrolein) in view of the strong interaction of zinc oxide with unsaturated species. Accordingly, we have taken the view that the observed reaction sequence may be represented by the diagram in Fig. 1. For such a sequence it may be impossible to form gaseous X from adsorbed X because formation of CO_2 and H_2O is so highly favored kinetically. We may, however, still subject the proposed surface sequence to experimental test. The X formed by reaction (plus H_2O and any CO_2 formed by a side reaction) should yield a characteristic infrared spectrum. If the spectra of a variety of adsorbed gases are examined and one of these produces a spectrum the same as X (except for CO_2 and H_2O), then we may *tentatively* conclude that this adsorbed gas is the surface complex. Such a study was carried out.

Studies of the spectrum formed by reaction of adsorbed π-allyl with oxygen at 40°C suggest that there may be additional reaction of π-allyl with the reaction complex if the surface is saturated with π-allyl; hence, reaction was carried out with about 0.2 cm^3/g of adsorbed propylene, corresponding to about 50% of the saturation π-allyl coverage. Adsorbed pro-

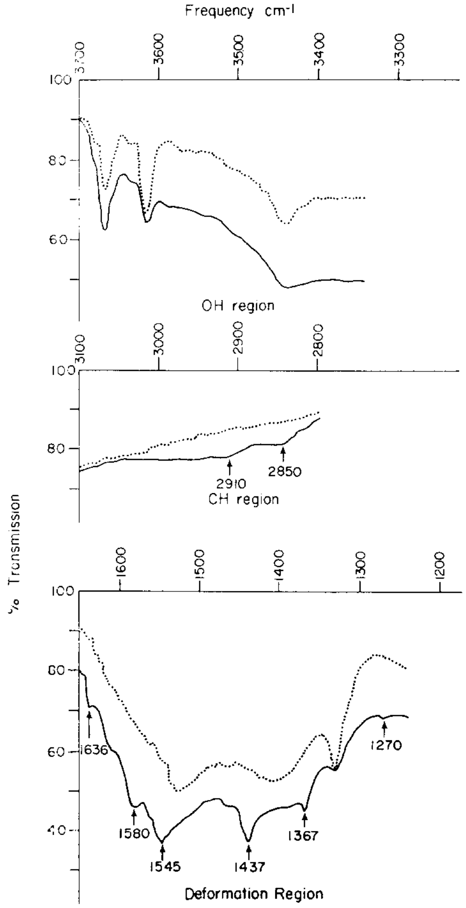

FIG. 2. Infrared spectrum of reaction product X. (....) Background; (—) reaction product X.

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† Similar complex formation by oxygen–olefin interaction has also been detected by Kubokawa, Ono and Yano (*10*). In this study, however, it is not assured that the reaction was with only the π-allyl.

pylene at these lower coverages yields the same bands reported earlier except for one weak band (at 1443 cm^{-1}), which is no longer evident at the lower coverage. Even under these conditions, however, the OH band formed by dissociation is strong and can be used to monitor the reaction with oxygen. When, during the course of the reaction, this band is no longer evident, the reaction is assumed to be complete.

The solid lines in Fig. 2 show the spectrum of the reaction product in the OH, CH and deformation regions. The dotted lines show the background spectrum of the freshly activated ZnO surface. In the OH region the band at about 3590 cm^{-1}, ascribed to dissociated propylene, is completely gone and the background band at about 3620 cm^{-1} shows the distortion we have found to be characteristic of hydrogen bonding. This hydrogen bonding could be due to the surface complex but the increase in intensity in the 3450 cm^{-1} region leads us to believe that water is also present. The CH region shows some absorption, with broad maxima centered at about 2910 and 2850 cm^{-1} but is not very well defined. The deformation region shows a host of bands superimposed on a rather broad background spectrum.‡ Bands showing up as maxima at positions not found in the background are listed in Table 1 together with those previously listed for propylene.

TABLE 1

Observed Bands (cm^{-1}) for Adsorbed Species

π-Allyl (*4*)	X^a	Adsorbed[a] acrolein	Gas-phase acrolein (*11*)
3593			
3055			3103 m
2970	2910 w	2915 w	3000 m
2947	2850 w	2847 w	2800 s
2915			
2868			
1545	1636 w	1632 w	1724 vs
1443	1580 m		1625 m
1390	1545 s	1540 s	
1288	1437 s	1437 s	1420 s
1258	1367 w	1365 m	1360 m
1203	1270 vw	1267 vw	1275 w

[a] Relative intensities are based on classifying the 1545 and 1540 bands as strong and all others relative to that. Band positions are accurate to approximately 5 cm^{-1} except for the broad bands between 2847 and 2915 cm^{-1} which could be in error by 10 cm^{-1}.

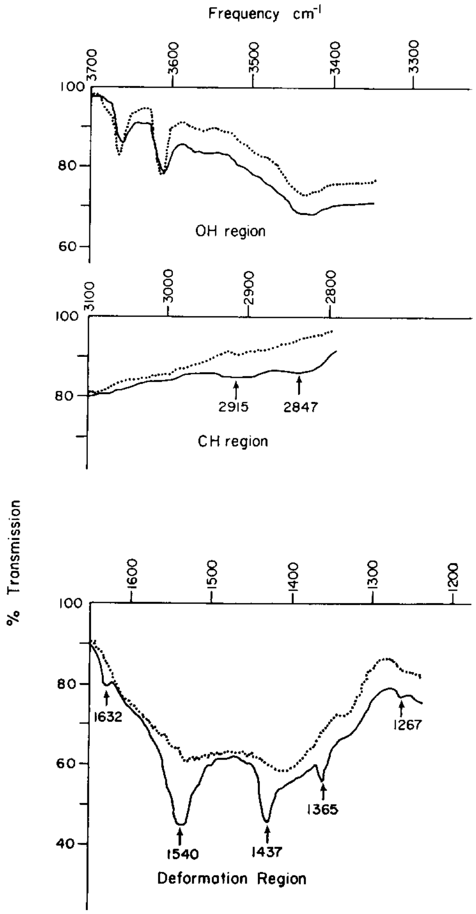

Fig. 3. Infrared spectrum of adsorbed acrolein. (....) Background; (—) adsorbed acrolein.

The solid lines in Fig. 3 show the spectrum of adsorbed acrolein on this same catalyst sample after reactivation. The dotted lines show the background spectrum of the freshly activated ZnO surface. The decrease in background intensity in the deformation region shows some sintering has

‡ The background spectrum in these runs is broader and interferes more with the spectrum than that shown earlier (*4*). This reflects differences from one zinc oxide batch to another rather than differences in pretreatment.

occurred. Once again, the OH region shows evidence of hydrogen bonding but the increase in intensity near 3450 cm^{-1} is not as great as in Fig. 2 suggesting that water formation, if it occurs on adsorption, is not extensive. Bands are also apparent in the CH and deformation region. These are listed in Table 1 together with the positions of relevant fundamentals (*11*) reported for acrolein.

The spectrum of X is strikingly similar to that for adsorbed acrolein except for the moderately strong band at 1580 cm^{-1}. In separate experiments we have established that small amounts of adsorbed carbon dioxide yield a band in this region together with some growth of the background bands. Thus, the reaction product yields a spectrum very close to that for adsorbed acrolein plus some carbon dioxide. (There may also be a band in the spectrum for X at 1610 cm^{-1}, which appears as a shoulder and is not listed in Table 1. This band could be due to product water; since, however, such a shoulder was perceptible for the unreacted propylene, we assume, if it is really a band, that it does not stem from the reaction product.)

We have examined the spectra of a number of species, other than acrolein, that could reasonably stem from partial oxidation of propylene: allene, propanol, 2-propanol, propionaldehyde, acetone, propionic acid, acetic acid and acetaldehyde. Only the spectrum of adsorbed acrolein resembles that of the species X. Accordingly, we believe X is the same as that formed by adsorption of relatively small amounts of acrolein. We should like to emphasize, however, that comparison of the spectrum of X with that for gaseous acrolein suggests that the structure is modified significantly by adsorption. More specific structural assignments must await work currently in progress; in this note we wish only to show that, at low temperature, the adsorbed π-allyl reacts with the O_2^- radical to produce a surface species very much like adsorbed acrolein plus carbon dioxide and water.

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REFERENCES

1. Voge, H. H., and Adams, C. R., *in* "Advances in Catalysis and Related Subjects" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 17, p. 151. Academic Press, New York, 1967.
2. Sachtler, W. M. H., and de Boer, N. H., *in* "Proceedings of the Third International Congress on Catalysis (Amsterdam, 1964)" (W. M. H. Sachtler, J. C. A. Schuit, and P. Zweitering, Eds.), Vol. 1, p. 252. Wiley, New York, 1965.
3. Lunsford, J. H., *Catal. Rev.* **8**, 135 (1973).
4. Kokes, R. J., and Dent, A. L., *in* "Advances in Catalysis and Related Subjects" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 22, p. 1. Academic Press, New York, 1972.
5. Kokes, R. J., *Catal. Rev.* **6**, 1 (1972).
6. Kokes, R. J., *in* "Proceedings of the Third International Congress on Catalysis (Amsterdam, 1964)" (W. M. H. Sachtler, J. C. A. Schuit, and P. Zweitering, Eds.), Vol. 1, p. 484. Wiley, New York, 1965.
7. Van Hooff, J. H. C., PhD thesis, Technische Hogeschool Te Eindoven, 1968.
8. March, J., "Advanced Organic Chemistry: Reactions, Mechanisms and Structure." McGraw-Hill, New York, 1968.
9. Kokes, R. J., *Intra-Sci. Chem. Rep.* **6**, 77 (1972).
10. Kubokawa, Y., Ono, T., and Yano, N., *J. Catal.* **28**, 471 (1973).
11. Harris, R. K., *Spectrochim. Acta* **20**, 1129 (1964).

B. L. Kugler
R. J. Kokes

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

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