

Interaction of Oxygen with Propene Adsorbed on Zinc Oxide

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Summary Propene adsorbed on zinc oxide was oxidized to surface formate and acetate species as well as OH groups *via* an unidentified precursor.

THE i.r. spectra of propene adsorbed on zinc oxide which we have obtained are essentially the same as those reported by Dent and Kokes (Figure).¹ After adsorption of the propene the temperature of the zinc oxide was increased in the presence of oxygen. At room temperature no spectral change was observed. At 70 °C the band at 3590 cm^{-1} due to OH groups formed on adsorption of the propene, as well as bands at 3050, 2966, 2945, 2907 and 1200 cm^{-1} which are attributable to π -allyl species,¹ disappeared. Simultaneously, new bands appeared at *ca.* 3500, 2900, and 1500–1300 cm^{-1} . The broad band at *ca.* 3500 cm^{-1} is attributed to surface OH groups. On raising the temperature from 150 to 230 °C the bands at 2870, 1574, and 1365 cm^{-1} decreased in intensity while the intensity of the bands at 2980, 2920, 1548, and 1432 cm^{-1} hardly changed. This suggests that these bands form two groups, which can be attributed to two different adsorbed species. According to the work of Tamaru and his co-workers,² formate ions on ZnO show bands at 2870, 1590, and 1360 cm^{-1} attributable to C–H stretching, and O–C–O antisymmetric and symmetric stretching vibrations, respectively. Further, since acetate ions show absorptions at 2983, 2925, 1556, and 1420 cm^{-1} , we assign these two groups of the bands to surface formate and acetate ions, respectively.³ Essentially the same spectra were obtained by Kugler and Kokes⁴ who attributed the observed bands to adsorbed acrolein. Their assignment of the band at 1580 cm^{-1} seems questionable. Our assignment of the bands in the 1500–1300 cm^{-1} region was checked by deuteration, when no shift was observed. Thus, we conclude that the oxygen uptake around 80 °C observed with ZnO containing adsorbed propene described previously⁵ is attributable to formation of surface formate and acetate ions as well as OH groups.

Since the observed oxygen uptake was about twice as great as the amount of propene adsorbed,⁵ in addition to

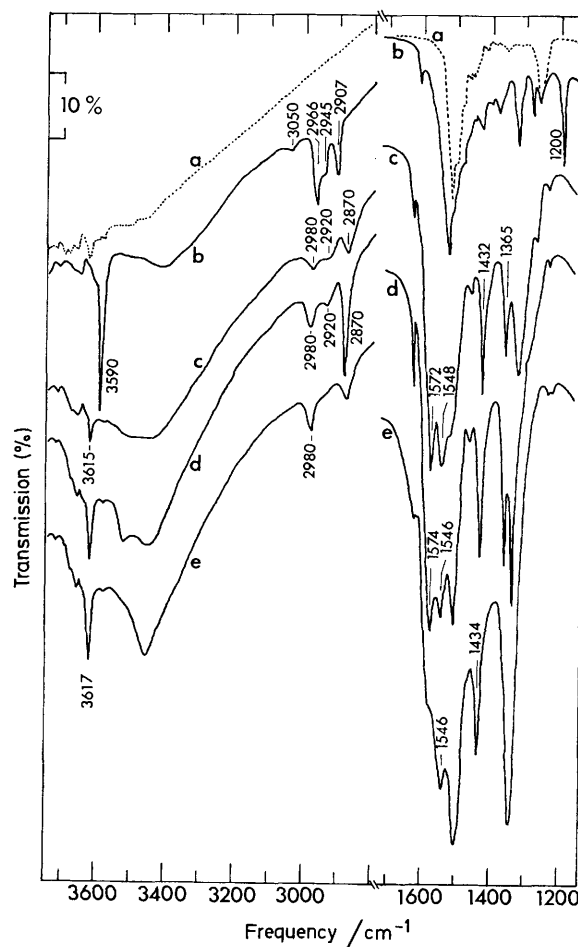


FIGURE. I.r. spectra of propene adsorbed on ZnO. (a) Background (origin and pretreatment of the ZnO were the same as in ref. 1); (b) after 1 h adsorption of propene followed by 5 min evacuation at 25 °C; (c) followed by 1 h at 70 °C in oxygen; (d) 1 h at 150 °C in oxygen; (e) 1 h at 230 °C in oxygen.

gaseous oxygen, lattice oxygen is expected to participate in the formation of the carboxylate species or the OH groups, although details of this are unclear. The ratio of the intensity of the band at 1432 cm^{-1} to that at 1365 cm^{-1} was always constant below $80\text{ }^{\circ}\text{C}$. This suggests that the carboxylate ions are both formed simultaneously on oxidation of the propene.

As already described, at $70\text{ }^{\circ}\text{C}$ the π -allyl species disappeared completely while carboxylate species were formed slowly in the range $70\text{--}230\text{ }^{\circ}\text{C}$, suggesting that the carboxylate species are not formed directly from π -allyl species, but probably *via* a precursor, which could not be identified by the i.r. spectra.

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³ K. Itoh and H. J. Bernstein, *Canad. J. Chem.*, 1956, **34**, 170.

⁴ B. L. Kugler and R. J. Kokes, *J. Catalysis*, 1974, **32**, 170.

⁵ Y. Kubokawa, T. Ono, and N. Yano, *J. Catalysis*, 1973, **28**, 471.