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NOTES

Mass Spectrometric Observation of Allyl Radicals During the Interaction of Propene with Some Oxides at Low Pressures

Free radicals formed on the surface of catalysts have been assumed to play a role in the homogeneous oxidation of propylene [see, for example, Margolis (*1*) and Daniel and Keulks (*2*)]. The only direct experimental evidence for the presence of allyl radicals in the gas phase was presented by Hart and Friedli (*3*) in the interaction of propylene with manganese oxide at pressures of 10^{-6} Torr using a mass spectrometer. We have repeated the experiment of Hart and Friedli in order to check our experimental arrangement for sensitivity to detect free radicals. We have extended the studies to include the interactions of propylene with ZnO, with mixed oxides Mo–Mn–O and Bi–Mo–O and with MnO_2. These oxides are catalysts for three different types of reaction: (a) dehydrodimerization and of aromatization, (b) unsaturated aldehyde formation, (c) deep oxidation. We concentrated our aim on the possible presence of allyl radicals in the gas phase in these systems.

We have used a 60° sector field mass spectrometer equipped with an ion multiplier, allowing detection of ion currents of the order of magnitude of 10^{-16} A. A "low pressure" thermal reactor was coupled to the mass spectrometer. The reactor, similar to the one used by Pottie *et al.* (*4*) consisted of a quartz tube, 4 mm i.d., whose final 25 mm was surrounded by a 0.2 mm Pt furnace element encased in a quartz sheath. About 15 mm of the tube was filled with catalyst granules of 0.5 mm average diameter. The granules were held on both sides with a plug formed from a minimum amount of quartz wool. The reactant gases, after passing through the reactor at pressures of about 10^{-3} Torr, entered directly into the ionization chamber through a 5 mm aperture in the top plate. The distance between the top plate and the end of the furnace was 9 mm. A Pt/Pt–Ir thermocouple was located inside the reactor 17 mm from the end of the tube. Ionization by electrons of low energies was used for detection of free radicals in the presence of other components. However, when looking for free radicals using a standard electron impact ion source without special homogenization of electron kinetic energies, we were unable to suppress completely the ionization and fragmentation of propene because of its large excess in concentration.

Mn(II)–Mn(III)–O was prepared as in Ref. (*3*); X-ray analysis showed a mixture of Mn_3O_4 and Mn_2O_3 and the BET surface area was 23 m^2/g. ZnO and MnO_2, both commercial, had surface areas of 20 and 80 m^2/g, respectively. Bi–Mo–O on silica gel and Mo–Mn–O on Aerosil were industrial catalysts, with surface areas of 93 and 36 m^2/g, respectively. Propene and diallyl were from Fluka and Light Co. purified by repeated freezing and evacuation only. All experiments were carried out in the absence of oxygen.

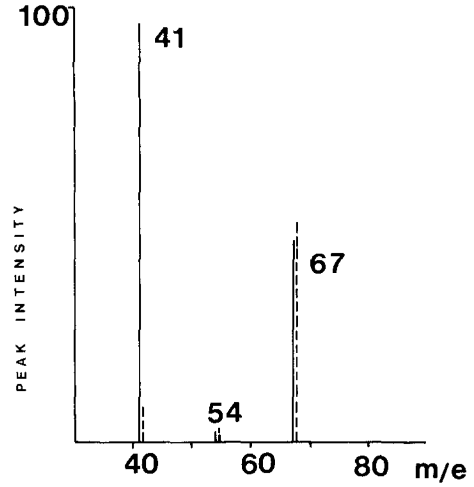

FIG. 1. Mass spectrum obtained after passing diallyl through the reactor at 200°C (----) and 840°C (—) with 11 eV electron beam energy.

The results were as follows:

a. Reactor without a catalyst. Diallyl vapor at 10^{-3} Torr was passed through the reactor filled with quartz wool at 200°C. The spectrum corresponds to 1,5-hexadiene (Fig 1, broken line). The spectrum obtained at 800°C (Fig. 1, solid line) shows a significant increase at mass 41, corresponding to the appearance of the allyl radical. Ion currents of the $C_3H_5^{\cdot}$ species of 2–3 orders of magnitude above the detection limit of the instrument were easily obtained with electrons of kinetic energies 1–2 eV above the threshold of ionization. This experiment shows that our device is comparable in sensitivity with similar devices used for free radical studies.

b. Reactor with Mn(II)-Mn(III)-O and propylene. The presence of allyl radicals in the interaction of propylene with manganese oxide was established from the dependence of the 41/42 peak intensities ratio on the temperature of the reactor. Peak *m/e* 42 represents the molecular ion of propylene, while *m/e* 41 belongs partly to the fragment ion of propylene, partly to the allyl radical. With increasing temperature of the reactor, the ratio of 41/42 peak intensities increases with catalyst Mn(II)-Mn(III)-O present (Fig. 2, open triangles), but no change was observed without the catalyst, i.e., with the reactor filled with quartz wool only (Fig. 2, open circles). The increasing value of the ratio suggests the presence of allyl radicals. Two facts confirm this assumption. First, no other peak except *m/e* 41 increases or newly appears in the spectrum after the temperature rise. Second, the observed dependence of the 41/42 ratio on temperature holds only for ionization with electrons close to threshold energies. For ionizing energies only ⩾ 2 eV above this region, the dependence on the reaction temperature changes, the ratio of peak intensities remaining constant. Further identification of the $C_3H_5^{\cdot}$ species through the measurement of the ionization potential would lead to doubtful results because of the very low concentrations of the radical.

We were particularly interested whether the appearance of the allyl radical in the system propylene Mn(II)-Mn(III)-O at

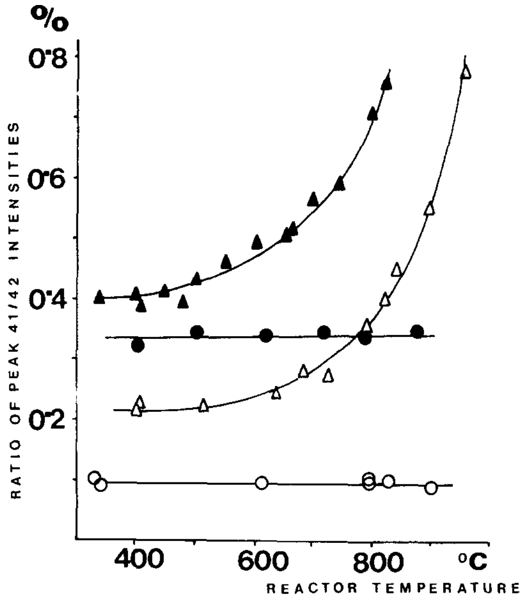

FIG. 2. Ratio of the 41/42 peak intensities against the reactor temperature at 13.5 eV electron beam energy: propene as reactant and reactor filled with: quartz wool (○), Mn(II)-Mn(III)-O (△), ZnO (▲), and mixed Bi-Mo-O (●).

high temperatures is followed by the appearance of 1,5-hexadiene as a product. No peak 67, which is significant for this compound, was observed (Fig. 1). This confirms that the allyl radical is desorbed directly from the surface of the catalyst. Since we were unable to detect diallyl as a product in our experiments with a simple low vacuum reactor at pressures of 10^{-3} Torr, we carried out one more experiment using the external reactor, which was connected to a mass spectrometer by an 18 μm molecular leak. 1,5-Hexadiene as a product was observed at pressures of 0.2 Torr in the reactor.

c. Reactor filled with ZnO, mixed Mo–Mn–O, mixed Bi–Mo–O and propylene. These catalysts were checked for the presence of allyl radicals at pressures comparable to those used with Mn(II)–Mn(III)–0, i.e., about 10^{-3} Torr in the reactor. Whereas ZnO showed a behavior similar to Mn(II)–Mn(III)–O, yielding allyl radicals (Fig. 2, solid triangles), the two mixed catalysts Bi–Mo–O (Fig. 2, solid circles) and Mo–Mn–O (not shown in the figures) showed no dependence of the ratio 41/42 on the reaction temperature within the temperature range measured.

Similarly to Mn(II)–Mn(III)–O, ZnO gave no detectable amount of diallyl as product. A relatively good yield of benzene as a product was found with ZnO, but only a little with Mn(II)–Mn(III)–O. Because of experimental difficulties caused by the high volatility of Zn from the ZnO catalyst it was difficult to give more accurate comparisons of products in the propene/ZnO or propene/Mn(II)–Mn(III)–O reactions. Nevertheless, the relatively good yield of benzene compared to the absence of diallyl in the propene/ZnO reaction suggests that the mechanisms leading to diallyl and benzene formation are different. The other two catalysts, Bi–Mo–O and Mo–Mn–O, where the allyl radicals were not detected in the reaction of propene, gave on the contrary easily measurable amounts of acrolein, even at pressures of 10^{-3} Torr.

d. Reactor filled with MnO_2. Using the same conditions as in previous experiments, the reaction of MnO_2 with propene and propene-*d*-6 was studied. The decrease of the propene peak *m/e* 42 with increase of the reaction temperature was much more remarkable than in the experiments previously described, the peak falling to 75% of its original value. Products of deep oxidation (CO_2, CO, H_2O or HDO and D_2O) were observed even at low reaction temperatures of about 200°C. The catalyst itself started to release oxygen at temperatures above 240°C. No allyl radicals were detected.

It can be concluded that in the reactions of propylene with the five oxides at pressures of 10^{-3} Torr, studied under comparable conditions, the allyl radical was detected in the gas phase only in the case of Mn(II)–Mn(III)–O and ZnO. Both these catalysts exhibit basic properties and according to the classifications of Seiyama *et al.* (*5*) and Weiss *et al.* (*6*) the formation of free radicals on the surface should be expected. With the catalysts leading to incomplete oxidation products (mixed Mo–Mn–O and mixed Bi–Mo–O) and with the catalyst of deep oxidation (MnO_2), no radicals were detected. Also this result agrees with the mentioned classification. The allyl intermediate formed on the relatively acid surface is cationic and easily excepts oxygen from the surface, leading to unsaturated aldehydes as products.

Our note represents the extension of the Hart and Friedli paper to several typical catalytic systems. It has been shown that the appearance of allyl radicals in the gaseous phase during the reaction of propylene with oxides is not typical for all systems. The search for allyl oxy- and allylperoxy-radicals was so far unsuccessful. Nevertheless, further studies are needed for estimation of the part which allyl radicals are playing in the catalytic mechanism. Measurements in which concentrations of free radicals and of reaction products are followed simultaneously are needed, and a flow reactor working at pressures about 10^{-1} Torr of propylene seems to be most suitable. However, the low concentrations of free radicals present make this task rather difficult.

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