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Desorption of Allyl Radicals in the Heterogeneously-catalysed Oxidation of Propene: Mass Spectrometric Study

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Summary Mass spectrometric techniques have been used to detect and identify desorbing allyl radicals during the heterogeneously-catalysed oxidation of propene.

IT is generally accepted that allyl radicals are intermediates in the homogeneous gas-phase oxidation of propene.[1] Various authors[2] have suggested participation of adsorbed allyl radicals as intermediates in the heterogeneous oxidation of propene over solid oxide catalysts. Recent work on the oxidative dehydrodimerization of propene over oxide catalysts in this laboratory[3] also indicates the participation of allyl radical intermediates. However, in all of these studies the evidence for the presence of allyl radicals is of an indirect nature. Other authors *e.g.* ref. 4 have postulated other active intermediates for heterogeneous propene oxidation. We present direct evidence for the desorption of allyl radicals in certain heterogeneously-catalysed propene oxidation reactions.

Gaseous free radicals can be detected and identified using mass spectrometric techniques.[5] The apparatus used in this work was essentially the same as that of Hipple and Stevenson[6] except that an Al_2O_3 thermocouple well was mounted in the hot zone of the reaction tube to measure reaction temperatures and to act as the catalyst support. A Granville–Phillips quadrupole residual gas analyser (Spectrascan 750®) was used as the spectrometer. A 4–1 mixture of propene–oxygen or pure propene was passed through the reaction tube directly into the ion source of the spectrometer. The flight time for allyl radicals from the end of the reaction tube to the electron beam was approximately 18 μsec. The catalyst was manganese oxide prepared from manganese acetate by heating in air at 900°. The reaction temperature was 600—650° (the temperature of the oxidative dehydrodimerization reaction[3]), and the total pressure was 10^{-6} to 10^{-7} torr.

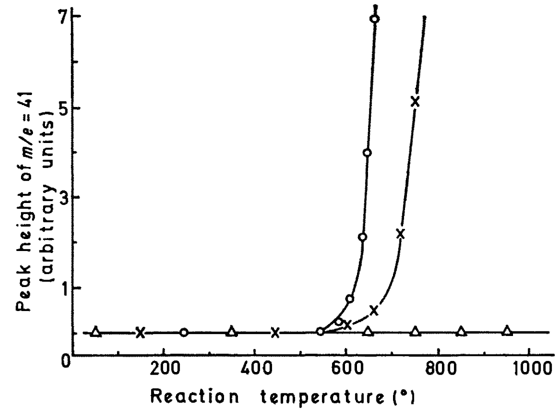

FIGURE. *Peak height of* m/e = 41 *against reaction temperature with the electron beam energy set at* 9·0 ± 1 ev; × : *hexa*-1,5-*diene*; ○: *propene–oxygen mixture or pure propene with the manganese oxide catalyst present*; △: *propene–oxygen mixture or pure propene with no catalyst present*; $C_3H_5\cdot + e^- \rightarrow C_3H_5^+ + 2e^-$, A. P. $\geqslant$ 8·16 ev; $C_3H_6 + e^- \rightarrow C_3H_5^+ + H\cdot + 2e^-$, A. P. $\geqslant$ 12·0 ev; $C_6H_{10} + e^- \rightarrow C_3H_5^+ + C_3H_5\cdot + 2e^-$, A. P. $\geqslant$ 10·9 ev.

The ability to detect allyl radicals in this system was proven by thermally decomposing hexa-1,5-diene at 4×10^{-7} torr. A peak at $m/e = 41$ ($C_3H_5^+$) was detected at reaction temperatures above about 600° with the electron beam energy set at 9·0 ev. The Figure indicates the increase in the $m/e = 41$ peak with increasing temperature. The degree of decomposition of the hexadiene to allyl radicals was rate limited at any temperature since the residence time was only 0·1 msec. The maximum degree of decomposition of hexadiene and thus the maximum partial pressure of allyl radicals has been estimated for various temperatures (see Table). The calculation assumes the applicability of the first-order rate constant (k_∞) for the unimolecular decomposition of hexadiene for this system.[7] The value of the constant was calculated from Benson's data,[8] and it has been assumed that the rate of recombination of the radicals was negligible and that no radicals were lost by wall collisions, *etc.*

*Maximum % hexa-*1,5*-diene decomposed and maximum partial pressure of allyl radicals produced by the thermal decomposition of hexa-*1,5*-diene at various reaction temperatures*

Temperature (°)	% Hexadiene decomposition	Maximum partial pressure of allyl radicals (torr)
600	0·01	6×10^{-11}
700	0·25	2×10^{-9}
800	8·7	4×10^{-8}

When a propene–oxygen mixture or pure propene was passed through the reaction tube, allyl radicals were detected above 600° when the manganese oxide catalyst was present. Under the same conditions, but without the catalyst, no allyl radicals were detected at temperatures to 800° (Figure). No other active intermediates (radicals or positive ions) were detected under any of the conditions used in this study.

Since allyl radicals were produced from propene at the same rate over the manganese oxide catalyst whether or not gaseous oxygen was present and since no radicals were produced in the absence of the catalyst, it is clear that the catalyst surface is responsible for radical formation. The surface probably acts as a hydrogen atom abstracting agent to produce radicals which "desorb" into the gas phase where they are detected. Homogeneous gas phase reactions are not important at these low pressures because of the very low collision frequencies.

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