160. *The Competitive Oxidation of Propene and Alkanes.*

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The relative rates of removal of propene and ethane in the oxidation of mixtures has been determined at 383° and 449°, and the limiting rate constant ratio $k_{\text{ethane}}/k_{\text{propene}}$ found for zero extent of reaction. With the value known for this ratio, the ratio $k_{\text{propane}}/k_{\text{propene}}$ is found. The values obtained agree well with those deduced from studies of the oxidation of propane alone.

IN the oxidation of an alkane above 320°C the major initial product is the alkene with the same number of carbon atoms.[1-4] In the later stages of the reaction the concentration of the alkene passes through a maximum owing to its own oxidation and it is possible to derive the relative reactivities of the alkane and the alkene in the prevailing free-radical mixture from their concentrations at this maximum. As a check on the mechanism for the formation and removal of the alkene it is important to show that the relative reactivities

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[1] Falconer and Knox, *Proc. Roy. Soc.*, 1959, *A*, **250**, 493.
[2] Knox, *Trans. Faraday Soc.*, 1960, **56**, 1225.
[3] Bickel and Zeelenberg, *J.*, 1961, 4014.
[4] Knox and Wells, unpublished results on the oxidation of ethane and ethylene.

obtained in this way agree with those obtained from competitive oxidations such as those previously carried out on alkanes.[5,6]

In the present work we have oxidised mixtures of ethane, propene, and oxygen in order to obtain the rate constant ratio $k_{\text{ethane}}/k_{\text{propene}}$, that is, the ratio of the rate constants of reactions (1) and (2):

$$C_2H_6 + X = C_2H_5 + XH \quad (1)$$

$$C_3H_6 + X = C_3H_5 + XH \text{ or } C_3H_6X \quad (2)$$

where X is the single free radical or a mixture of free radicals which removes the two hydrocarbons.

The apparatus was similar to that previously described.[5,6] Oxidations were carried out in the gas phase at 383° and 449° in a 100-ml. cylindrical Pyrex vessel. The reactions were taken nearly to completion and the products were analysed for unchanged hydrocarbons by gas chromatography by the Janak technique. An experimental ratio R was obtained for each oxidation:

$$R = \log\{[RH]_i/[RH]_f\}/\log\{[A]_i/[A]_f\}, \quad (A)$$
$$(RH = C_2H_6;\ A = C_3H_6)$$

where the subscripts " i " and " f " refer to initial and final concentrations of hydrocarbons. Initial concentrations were determined from standardisation experiments in which mixtures were removed from the reaction vessel for analysis before the end of the induction period. The reproducibility of the standardisation experiments was about $\pm 1\%$ but, since the evaluation of R depends essentially upon differences in concentrations, values of R are less precise; duplicate oxidations gave values of R which were generally within 5%.

When X is a single species, R is equal to the rate constant ratio $k_{\text{ethane}}/k_{\text{propene}}$,[5] the relation being true even when [X] changes throughout the reaction. If, however, X represents a mixture, as is likely in a hydrocarbon oxidation, the interpretation of R is more difficult and three situations must be considered:

(1) X is a mixture whose composition depends only on temperature but not on the composition of the mixture. R is then still a ratio of rate constants $k_{\text{RH}}/k_{\text{A}}$, but k_{RH} and k_{A} are now linear sums of elementary rate constants. Any activation energies derived from plots of log R against $1/T$ will then be complex and may not have a simple interpretation.

(2) The composition of X may depend upon the ratio of the two hydrocarbons RH and A. Except above 500° or when the oxygen is nearly exhausted, X will be made up of oxygenated radicals. If these radicals reflect the structure of RH and A (*e.g.*, RO, AOH, RO_2, AO_2H), R might be expected to depend upon [RH]/[A], and for each mixture R would be equal to a ratio of complex rate constants such as the linear sums mentioned under (1). If the oxygenated radicals do not reflect the structure of the hydrocarbons (*e.g.*, OH, CH_3O, HO_2, CH_3O_2, CHO), then R should be independent of [RH]/[A]. With alkane mixtures[5,6] and with the ethane–propene mixtures used here, where the ratio [ethane]/[propene] was varied over a factor of four at 383°, the ratio R was independent of hydrocarbon ratio. In view of the range of hydrocarbons which has now been studied it is probable that X consists of simple radicals which do not reflect the structure of the original hydrocarbons.

(3) X may change in composition throughout the oxidation with the extent of reaction. There is substantial evidence that this does happen. The extent of reaction can be varied simply by controlling the initial oxygen concentration, since studies of the oxidation of single hydrocarbons[1-4] have shown that the concentration has little effect on the yields

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[5] Knox, Smith, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1958, **54**, 1509.

[6] Falconer, Knox, and Trotman-Dickenson, *J.*, 1961, 782.

of products at a given stage in the reaction (measured by, say, the quantity of oxygen used). The major effect of increasing the initial oxygen pressure is simply to increase the final extent of reaction. When analysis for residual hydrocarbon is made towards the end of the reaction, the values of R might be expected to vary with [oxygen]/[total hydrocarbon]. When the composition of X changes and so produces a variation of R with extent of reaction, the value of R cannot be simply interpreted but must be in the nature of an average rate constant ratio.

Dependence of R upon [oxygen]/[hydrocarbon] has been found for alkane mixtures, the dependence being more pronounced at higher temperatures.[6] Fig. 1 shows a similar dependence for ethane–propene mixtures. Interpretable values of R can be obtained only when the extent of reaction is so low that the composition of X may be regarded as constant. Such values are obtained by extrapolation of R to zero [oxygen]/[hydrocarbon], that is, to zero extent of reaction. There is evidence that under these conditions the major radical which removes the hydrocarbons is HO_2.[1-4,7]

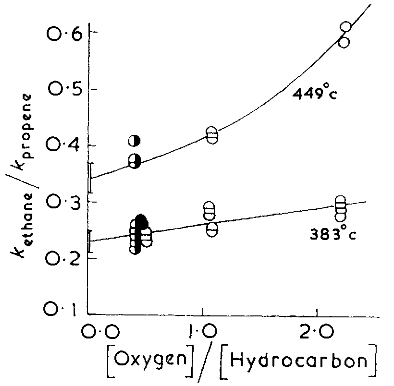

FIG. 1. Effect of oxygen : hydrocarbon ratio on $k_{ethane}/k_{propene}$ for ethane : propene ratios as follows: ○ = 1 : 1; ◑ = 1 : 1·5; ● = 3 : 1.

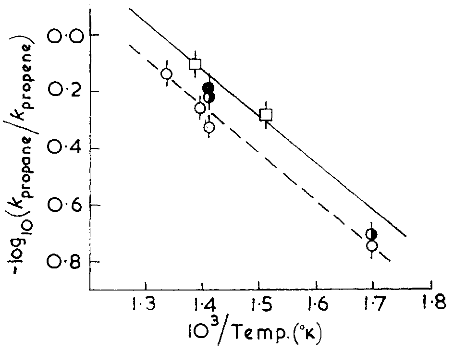

FIG. 2. Effect of temperature on $k_{propane}/k_{propene}$.

□ This work. Oxidation of (○) pure propane, (◑) propane (90%) + propene (10%), and (●) propane (80%) + propene (20%). Broken line through points for oxidation of pure propane. Full line through points extrapolated to start of reaction.

The extrapolated values of R at 383° and 449° are 0·23 ± 0·02 and 0·34 ± 0·03, respectively. These values are now identified with $k_{ethane}/k_{propene}$. Using the value of $k_{ethane}/k_{propane}$ of 0·44 which is independent of temperature[5] we obtain 0·52 ± 0·05 and 0·77 ± 0·08 for $k_{propane}/k_{propene}$ at 383° and 449°, respectively. These values may be compared with those derived directly from the oxidation of propane (Fig. 2).

The maximum in the yield of alkene in the oxidation of an alkane may be considered to arise from the following reactions:

$$RH + X = R + XH \tag{1}$$

$$R + O_2 = A + HO_2 \tag{3}$$

$$= \text{Other products} + X' \tag{4}$$

$$A + X = \text{Products} + X'' \tag{2}$$

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[7] Cullis and Newitt, *Proc. Roy. Soc.*, 1956, *A*, **237**, 530; 1960, *A*, **257**, 402.

The fraction, f, of alkyl radicals which react with oxygen to give the alkene can be determined by analysis of the products from the early stages of the reaction when oxidation of the alkene is negligible: $f = k_3/(k_3 + k_4)$. Since the rate of formation and of destruction of the alkene must be equal when its concentration is a maximum, we obtain

$$k_1/k_2 = k_{\mathrm{RH}}/k_{\mathrm{A}} = f^{-1}[\mathrm{A}]_{\mathrm{max.}}/[\mathrm{RH}]_{\mathrm{max.}}, \qquad \text{(B)}$$

where the subscript " max." implies concentrations of RH and A when the yield of the alkene is a maximum. Since the maxima do not occur at the start of the reaction, the results obtained in this way are not strictly comparable with those obtained in competitive experiments by extrapolation to low oxygen mole fractions. However, the point in the reaction at which the maximum occurs for any hydrocarbon can be considerably advanced by oxidising alkanes which are somewhat contaminated with the appropriate alkene, for example, propane containing 10—20% of propene.[1,2] The more propene that is initially present the earlier the maximum occurs and, as shown in Fig. 2, the higher is the ratio $k_{\mathrm{propane}}/k_{\mathrm{propene}}$ derived from equation (B). The agreement between the two methods of determining this rate constant ratio is satisfactory if attention is confined to the early stages of the reaction (□ and ● in Fig. 2), and it provides a good confirmation that the oxidation mechanism which we have assumed, and the competitive experiments, are basically reliable.

The strong temperature-dependence of the rate constant ratio may be expressed by the relation

$$k_{\mathrm{propane}}/k_{\mathrm{propene}} = 120 \exp(-7000 \text{ cal. mole}^{-1}/\boldsymbol{R}T).$$

The extreme Arrhenius parameters suggest that the simple interpretation in terms of two competing free-radical reactions may not be correct. There are two obvious alternatives: (1) While the composition of X may be constant at any one temperature it may vary with temperature and so contribute to E. (2) Reaction 2 may involve an equilibrium and the rate-determining step may be the slow decomposition of the addition product of X to A. One possible such scheme is

$$\mathrm{A} + \mathrm{HO_2} = \mathrm{AO_2H} \qquad (5), (-5)$$

$$\mathrm{AO_2H} = \text{Products} + \mathrm{X''} \qquad (6)$$

Since the initial products of oxidation of olefins[4,8] appear to demand a four-membered ring transition-state complex, reaction (6) may well have the very low A factor required for such a scheme to explain the unusual Arrhenius parameters.

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[8] Cullis, Fish, and Turner, *J.*, 1961, 318.