The Mechanism of Oxidation of Alkanes in the Gas Phase

By JOHN H. KNOX
(*Department of Chemistry, University of Edinburgh*)

RECENT work on the slow gas-phase oxidation of simple alkanes (ethane, propane, isobutane)[1] above 300° C has shown that olefins (ethylene, propene, isobutene, respectively) form about 80% of the total product in the initial stages. Later in the oxidations the olefins are consumed and yield mainly carbonyl compounds.

Although the initial formation of olefin can be explained by reactions 1 and 2, the later stages

$$\mathrm{RH} + \mathrm{HO_2} = \mathrm{R} + \mathrm{H_2O_2} \quad (\mathrm{RH} = \text{Alkane}) \qquad (1)$$

$$\mathrm{R} + \mathrm{O_2} = \mathrm{AB} + \mathrm{HO_2} \quad (\mathrm{AB} = \text{Olefin}) \; .. \qquad (2)$$

of the reaction must involve the co-oxidation of the olefin and alkane.

The reactivity of HO_2 in abstraction reactions may be estimated from D[H–OOH][2] and the rates of known reactions involving HO_2:[3] it appears to be low. Reaction 1 is then unlikely to be the main remover of RH in the intermediate stages of oxidation since, when the rate is high, it cannot compete effectively with reaction 3.

$$\mathrm{HO_2} + \mathrm{HO_2} = \mathrm{H_2O_2} + \mathrm{O_2} \quad .. \qquad (3)$$

After the initial stages a more reactive radical than HO_2 appears to take over as the main chain-propagator. This is supported by co-oxidation studies with alkane mixtures,[4,5] which point to a decline in radical selectivity as the reaction proceeds. Since the only reasonable alternative to HO_2 as chain-propagator is OH, and since reaction 2 must occur at all stages in the oxidation, there must be a mechanism for effecting the overall conversion 4

$$2\,\mathrm{HO_2} \rightsquigarrow 2\,\mathrm{OH} + \mathrm{O_2} \qquad \Delta H = +8 \text{ kcal. mole}^{-1} \qquad (4)$$

Above about 450° C the conversion can be effected by reaction 3 followed by homogeneous dissociation of hydrogen peroxide as suggested by Sampson,[6] but below 400° C hydrogen peroxide is stable and reaction 3 is chain-terminating. Any low-temperature conversion must bypass reaction 3 and must involve an alternative reaction of HO_2 with the accumulating olefin. The addition of HO_2 to AB to form ABOOH is only 15 kcal. mole^{-1} exothermic and the equilibrium 5 lies far to the left at 300° C. Nevertheless, in the presence of oxygen, the ABOOH radical may be stabilized by reaction 6 to give OOABOOH. D[OO–ABOOH] is[7] about 29 kcal. mole^{-1}. A conversion is then possible *via* reactions 5—8, and the chain is completed by reactions 2 and 9.

$$\mathrm{AB} + \mathrm{HO_2} = \mathrm{ABOOH} \quad .. \qquad (5)$$

$$\mathrm{ABOOH} + \mathrm{O_2} = \mathrm{OOABOOH} \quad .. \qquad (6)$$

$$\mathrm{OOABOOH} + \mathrm{HO_2} = \mathrm{HOOABOOH} + \mathrm{O_2} \qquad (7)$$

$$\mathrm{HOOABOOH} = \mathrm{NO} + \mathrm{AO} + \mathrm{BO} + \mathrm{OH} \qquad (8)$$

$$\mathrm{OH} + \mathrm{RH} = \mathrm{R} + \mathrm{H_2O} \; .. \quad .. \qquad (9)$$

---

[1] J. H. Knox, *Ann. Reports*, 1962, **59**, 18.
[2] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, 1962, **36**, 2681.
[3] R. R. Baldwin and L. Mayor, *Trans. Faraday Soc.*, 1960, **56**, 80, 93, 103.
[4] W. E. Falconer, J. H. Knox, and A. F. Trotman-Dickenson, *J.*, 1961, 782.
[5] J. H. Knox and J. M. C. Turner, *J.*, 1965, in the press.
[6] R. J. Sampson, *J.*, 1963, 5095.
[7] S. W. Benson, *J. Chem. Phys.*, 1964, **40**, 1007.

Reaction 8 is regarded as a three-stage process:

$$\mathrm{HOOABOO\dot{H} = HO + OABOOH} \quad .. \quad (8a)$$

$$\mathrm{OABOOH = OA + BOOH} \quad .. \quad (8b)$$

$$\mathrm{BOOH = BO + OH} \quad .. \quad .. \quad (8c)$$

where reactions 8b and 8c follow inevitably on 8a. Since it can occur[8] above about 300° c to give free radicals, the suggested conversion mechanism can operate in the typical low-temperature oxidation regime.

Since the mechanism converts $2HO_2$ into 2OH radicals for each AB molecule consumed, some "wastage" of AB can be tolerated; indeed an additional sequence of reactions similar to 5—8 starting with the addition of OH to AB must be added to those already suggested.

The mechanism requires reactions 5—8 to occur at identical rates: therefore [AB]/[OOABOOH] = k_7/k_5. Reasonable values are $k_5 = 2 \times 10^8 \exp[-5000/1{\cdot}99T]$ mole^{-1} l. sec.$^{-1}$ and $k_7 = 10^9$ mole^{-1} l. sec.$^{-1}$. The ratio k_7/k_5 is then about 300 at 600° and indicates a high concentration of OOABOOH radicals. Nevertheless, at moderately high reaction rates, peroxy-radicals will preferentially react with HO_2 if the activation energy for H-abstraction is greater than about 10 kcal. mole^{-1}.

The complete scheme explains many of the major features of alkane and olefin oxidation in the gas phase:

(1) The slow increase in the rate of acceleration of alkane oxidations observed by Knox[9] and by Zeelenberg and Bickel[10] is due to the increasing importance of the olefin-catalysed conversion of HO_2 into OH.

(2) The change in radical selectivity as the reaction proceeds is due to the change from HO_2 to OH as predominant attacking radical.

(3) The formation of the carbonyl compounds AO and BO as the major oxidation products from olefins is predicted.

(4) The low-temperature limit for alkane combustion is identified as the temperature at which homogeneous pyrolysis of alkyl hydroperoxides can compete effectively with their heterogeneous decomposition. The kinetic effects of surfaces at the lower limit are related to their ability to destroy peroxides.

(5) The negative temperature coefficient results from the increasing instability of ABOOH as the temperature rises. Above about 380° c reaction 6 can no longer compete effectively with reaction -5 and the conversion mechanism begins to fail about this temperature: HO_2 radicals are forced to accumulate and undergo the chain-termination reaction 3. The rate of oxidation thus declines with rise of temperature until the homogeneous decomposition of hydrogen peroxide becomes important at about 425—450° c.

(*Received, February 12th,* 1965.)

---

[8] A. D. Kirk and J. H. Knox, *Trans. Faraday Soc.*, 1960, **56**, 1296.
[9] J. H. Knox, *Trans. Faraday Soc.*, 1959, **55**, 1362; 1960, **56**, 1225.
[10] A. P. Zeelenberg and A. F. Bickel, *J.*, 1961, 4014.