Velocity Constants for the Reactions of Alkyl Radicals with Oxygen

By R. R. BAKER, R. R. BALDWIN,* and R. W. WALKER
(*Chemistry Department, The University, Hull, Yorkshire*)

Summary Velocity constants have been evaluated for the reactions of alkyl radicals with oxygen to give the conjugate olefin.

THE major initial product in the gas-phase oxidation of C_2—C_4 alkanes in the temperature range 300° to 550°C is the conjugate olefin. It is generally accepted that the olefin is produced by the reaction of the alkyl radical with oxygen, although it is not clear whether the reaction proceeds through a peroxy-radical[1—3] or through a bimolecular hydrogen-atom transfer.[4]

TABLE

Reaction	Temp. °C	$k_{\text{olefin}}/k_{\text{decomp}}$ mm. Hg^{-1}	k_{olefin} l. mole^{-1}sec.$^{-1}$
$C_2H_5 + O_2 = HO_2 + C_2H_4$	440		$8{\cdot}2 \times 10^7$
	623		$1{\cdot}0 \times 10^8$
$C_3H_7{}^n + O_2 = HO_2 + C_3H_6$	480	0·0300	$3{\cdot}5 \times 10^7$
$C_4H_9{}^i + O_2 = HO_2 + C_4H_8{}^i$	480	0·0190	$2{\cdot}3 \times 10^7$
$C_4H_9{}^n + O_2 = HO_2 +$ but-1-ene	480	0·0335	$2{\cdot}8 \times 10^8$
$C_4H_9{}^s + O_2 = HO_2 +$ *cis*-but-2-ene	480	0·0115	$1{\cdot}2 \times 10^8$
$C_4H_9{}^s + O_2 = HO_2 +$ *trans*-but-2-ene ..	480	0·0205	$2{\cdot}1 \times 10^8$

$$C_nH_{2n+1} + O_2 \rightleftharpoons C_nH_{2n+1}O_2 \qquad \text{(A)}$$

$$C_nH_{2n+1}O_2 \rightarrow C_nH_{2n} + HO_2 \qquad \text{(B)}$$

$$C_nH_{2n+1} + O_2 \rightarrow C_nH_{2n} + HO_2 \qquad \text{(C)}$$

If both routes occur, the overall velocity constant for the formation of olefin is,

$$k_{\text{olefin}} = k_C + k_A k_B/(k_B + k_{-A} + k_{\text{OX}}),$$

where k_{OX} is the overall velocity constant for the reaction (assumed to be a first-order process) of alkylperoxy-radicals giving products other than the conjugate olefin. Virtually no estimates of k_{olefin} are currently available.

From studies involving the addition of traces of hydrocarbon to slowly reacting mixtures of hydrogen and oxygen in aged boric-acid-coated reaction vessels at 480°C, information has been obtained on the reactions of alkyl radicals in an oxidising environment. With propane, n-butane, and isobutane as additives, the initial yields of conjugate olefins are 82 ± 2%, 65 ± 2%, and 81 ± 1%, respectively, of the alkane consumed, for hydrogen/oxygen ratios varying from 6/1 to 1/5 at a total pressure of 500 mm. Hg. The remaining products result almost equally from radical pyrolysis and from radical oxidation reactions. Competition between the reaction forming the conjugate olefin and the decomposition of the alkyl radical by C–C homolysis introduces an oxygen dependence into the relative rate of formation of conjugate olefin and decomposition products. With propane and isobutane, the rates of decomposition of the s-propyl and the t-butyl radicals are negligible relative to those of the primary propyl and isobutyl radicals under the conditions used. With n-butane, the decomposition products of the two butyl radicals differ, and thus allow the reactions to be distinguished. Thus, for the three alkanes, the following decomposition reactions are important,

$$CH_3CH_2CH_2 = CH_3 + C_2H_4 \qquad (1)$$

$$(CH_3)_2CHCH_2 = CH_3 + CH_3CH{=}CH_2 \qquad (2)$$

$$CH_3CH_2CH_2CH_2 = C_2H_5 + C_2H_4 \qquad (3)$$

$$CH_3CHCH_2CH_3 = CH_3 + CH_3CH{=}CH_2 \qquad (4)$$

By measuring the variation of the initial ratio of conjugate olefin to the appropriate decomposition product over a ten-fold range of oxygen pressure, values of $k_{\text{olefin}}/k_{\text{decomp}}$ consistent to ±15% have been obtained for particular radicals, and these are shown in the Table. To obtain absolute values of k_{olefin}, the value of k_{decomp} is required, and for the present purpose, the values of A and E for these reactions given by Kerr and Lloyd[5] will be used. The resulting values of k_{olefin} are also shown in the Table, together with independent values for the ethyl radical of $8{\cdot}2 \times 10^7$ l. mole^{-1}sec.$^{-1}$ obtained from the oxidation of propionaldehyde,[6] and $1{\cdot}0 \times 10^8$ obtained from the oxidation of ethane.[7] The values of k_{olefin} vary by an order of magnitude, and a critical examination of the values for k_{decomp} will be necessary before significance can be attached to this variation, which is rather greater than the variation of $k_{\text{olefin}}/k_{\text{decomp}}$. In particular, the values of A and E given by Kerr and Lloyd for reactions (2) and (3) are not consistent with the corresponding values for the back reaction, and the entropy and enthalpy changes in the reaction.

Slater and Calvert[8] have estimated that k_{olefin} for the isobutyl radical is $2{\cdot}6 \times 10^5$ l. mole^{-1}sec.$^{-1}$ at 40°C, assuming that the velocity constant for the recombination of two isobutyl radicals is $2{\cdot}2 \times 10^{10}$ l. mole^{-1}sec.$^{-1}$. Combination of the values of k_{olefin} for isobutyl radicals at 40° and 480°C gives Arrhenius parameters for the reaction of $E = 4{\cdot}7$ kcal.mole^{-1} and $\log A = 8{\cdot}7$ (litre mole sec. units). It is believed that these are the first parameters to be quoted for this type of reaction.

This work was supported by the United States Office of Scientific Research through the European Office of Aerospace Research (OAR), United States Air Force.

(*Received, October 13th*, 1969; *Com.* 1555.)

---

[1] N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," Pergamon Press, London, 1959.

[2] A. Fish, *Quart Rev.*, 1964, **18**, 243.

[3] J. H. Knox, in "Advances in Chemistry," No. 76, vol. 2, ed. R. F. Gould, Amer. Chem. Soc., Washington, 1968, p. 1.

[4] S. W. Benson, ref. 3, p. 143.

[5] J. A. Kerr and A. C. Lloyd, *Quart. Rev.*, 1968, **22**, 549.

[6] R. R. Baldwin, R. W. Walker, and D. H. Langford, *Trans. Faraday Soc.*, 1969, **65**, 806.

[7] R. J. Sampson, *J. Chem. Soc.*, 1963, 5095.

[8] D. H. Slater and J. G. Calvert, ref. 3, p. 58.