348. *The Reaction of Hydrogen Atoms with Oxygen and with Ethane.*

By R. R. Baldwin and A. Melvin.

Values of the Arrhenius parameters for the reaction $H + O_2 = OH + O$ have been obtained by combining estimates from shock tube studies at $1650°K$, from flame studies at $1100°K$, from studies of the $H_2 + O_2$ reaction at about $800°K$, and from atomic reaction studies at $300°K$. Statistical treatment gives

$$\log_{10} k_2 = 11 \cdot 313 \pm 0 \cdot 28 - (16,490 \pm 700)/4 \cdot 576T$$

in l. mole^{-1} sec.$^{-1}$ units. Similar treatment of values for the reaction $H + C_2H_6 = H_2 + C_2H_5$ from flame studies at $1100°K$, from the inhibiting action of ethane on the $H_2 + O_2$ at $813°K$, and from low-temperature studies of the reaction of H or D atoms with ethane gives

$$\log_{10} k_{14} = 11 \cdot 117 \pm 0 \cdot 25 - (9710 \pm 580)/4 \cdot 576T$$

One of the difficulties in determining the activation energies and pre-exponential factors of free-radical reactions is that considerable accuracy in individual determinations is required to obtain reasonably accurate activation energies if high temperatures are involved and if the investigation is restricted to a narrow temperature range. For example, if an activation energy of 20 kcal./mole is determined by measurements of velocity constants at two temperatures $100°K$ apart and around $1000°K$, an error of 10% in each k causes an error of 5 kcal./mole in E. With limited experimental accuracy, accurate activation energies and pre-exponential factors can only be determined by extending the range of temperature. This paper gives two cases where reasonably accurate parameters have now been obtained by correlating investigations over a very wide range of temperatures.

Reaction of Hydrogen Atoms with Oxygen.—Reaction (2) has long been of importance, since it decides the explosive region of the $H_2 + O_2$ reaction and of the water-sensitised

$$H + O_2 = OH + O \tag{2}$$
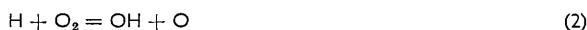
oxidation of carbon monoxide. Recent interest in the significance of chemical kinetics in flame phenomena has re-emphasised the need for reliable kinetic data. Four sets of estimates at widely differing temperatures are now available.

(1) *At temperatures around* $500°c$. Studies of the second limit of the $H_2 + O_2$ reaction provided the earliest estimates of k_2. Lewis and von Elbe [1] obtained a value * of $5 \cdot 3 \times 10^3$ l. mole^{-1} sec.$^{-1}$ at $520°c$, the second limit being used to obtain k_2/k_4; k_4 was obtained [2] by combining the results obtained by Farkas and Sacchse [3] on the hydrogen-atom concentrations in the mercury-photosensitised $H_2 + O_2$ reaction with the value for the velocity constant of $H + H + M \longrightarrow H_2 + M$, obtained by Steiner.[4]

$$H + O_2 + M \longrightarrow HO_2 + M \tag{4}$$

Baldwin and Simmons [5] obtained a value of $6 \cdot 6 \times 10^5$ by using the inhibiting action of

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* All velocity constants are given in l. mole^{-1} sec.$^{-1}$.

[1] Lewis and von Elbe, " Combustion, Flames and Explosions of Gases," Academic Press, New York, 1951.
[2] Lewis and von Elbe, *J. Chem. Phys.*, 1939, **7**, 710.
[3] Farkas and Sacchse, *Z. phys. Chem. B.*, 1934, **27**, 111.
[4] Steiner, *Trans. Faraday Soc.*, 1935, **31**, 623.
[5] Baldwin and Simmons, *Trans. Faraday Soc.*, 1957, **53**, 964.

ethane on the second limit to determine the ratio k_{14}/k_2, and extrapolating Berlie and LeRoy's data [6] to obtain k_{14} at 520°c.

$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \qquad (14)$$

Although valuable in suggesting that the figure given by Lewis and von Elbe was too low by a factor of 10^2—10^3, this value is only approximate, since the extrapolation is uncertain by a factor of about five. Three more reliable estimates have recently been tabulated.[7]

(*a*) Semenoff [8] obtained a value of $6\cdot7 \times 10^6$ at 520°c by using Kowalski's measurements [9] of the rate of the $H_2 + O_2$ reaction within the explosion peninsula at pressures just above the first limit. An activation energy of 17 kcal./mole being assumed, this corresponds to $k_2 = 8\cdot8 \times 10^6$ at 540°c.

(*b*) Baldwin [10] obtained a value of $3\cdot5 \times 10^6$ at 540°c from first-limit measurements of the $H_2 + O_2$ reaction. On the assumption that the only termination process is surface destruction of hydrogen atoms, the first limit is given by $2k_2[O_2] = k_H$. If the destruction is efficient, then $k_H = 23D/d^2$ for a cylindrical vessel of diameter d, D being the diffusion coefficient for hydrogen atoms. By measuring the first limit over a range of mixture composition, allowance was made for the gas-phase termination process (4), for the surface destruction of OH radicals, and for the fact that $k_H < 23D/d^2$ because the surface is only moderately efficient. The value obtained has been confirmed [11] by measurements with a surface coated with potassium hydroxide, which is extremely efficient for the destruction of hydrogen atoms. The limitations in accuracy with this method arise from the calculation of diffusion constants from the Stefan–Maxwell equation, and from the estimate of the collision diameter of the hydrogen atom.

(*c*) Baldwin and Cowe [7] studied the inhibiting action of formaldehyde on the $H_2 + O_2$ reaction at 540°c and obtained the ratio k_{14a}/k_2. This was combined with a number of independent estimates of k_{14a} to obtain k_2.

$$H + HCHO \longrightarrow H_2 + HCO \qquad (14a)$$

Depending on the method used to estimate k_{14a}, values from $3\cdot0$ to $10\cdot5 \times 10^6$ were obtained for k_2, the lower figure being probably less accurate.

These three estimates give a mean figure of $6\cdot0 \times 10^6$ which is probably accurate to within $\pm50\%$. This figure is in good agreement with the value of $5\cdot3 \times 10^6$ at 540°c obtained by Karmilova, Nalbandyan, and Semenoff [12] using an improved version of Kowalski's method.

(2) *At temperatures around* 1100°K. Fenimore and Jones [13] obtained an estimate of k_2 by measuring the rate of oxygen consumption in a hydrogen–oxygen–nitrogen flame by traversing the flame with a quartz probe; the hydrogen-atom concentration in the flame was estimated by addition of heavy water and following the rate of formation of HD. A value of $1\cdot5 \times 10^8$ was obtained at 1100°K.

(3) *At temperatures around* 1650°K. Schott and Kinsey [14] measured the induction period of the $H_2 + O_2$ reaction in shock-tube experiments, the hydroxyl absorption being used to follow the reaction. The evaluation of k_2 required log $[OH]_i/[OH]_0$, where $[OH]_i$ is the OH concentration at the end of the induction period and $[OH]_0$ is the initial concentration. $[OH]_i$ could be measured directly, but as $[OH]_0$ was too small to be measured

[6] Berlie and LeRoy, *Discuss. Faraday Soc.*, 1953, **14**, 50.
[7] Baldwin and Cowe, *Trans. Faraday Soc.*, 1962, **58**, 1768.
[8] Semenoff, *Acta Physicochim.*, 1942, **20**, 290.
[9] Kowalski, *Physik. Z. Sowjet.*, 1933, **4**, 723.
[10] Baldwin, *Trans. Faraday Soc.*, 1956, **52**, 1344.
[11] Baldwin and Melvin, unpublished work.
[12] Karmilova, Nalbandyan, and Semenoff, *Zhur. fiz. Khim.*, 1958, **32**, 1193.
[13] Fenimore and Jones, *J. Phys. Chem.*, 1959, **63**, 1154.
[14] Schott and Kinsey, *J. Chem. Phys.*, 1958, **29**, 1177.

by light absorption, it had to be calculated from an assumed initiation process, $H_2 + O_2 \longrightarrow 2OH$, and the velocity constant for $OH + H_2 \longrightarrow H_2O + H$.

(4) *At room temperature.* Kaufman and Greco [15] studied the reaction $O + OH \longrightarrow O_2 + H$, reaction (−2), producing oxygen atoms by $N + NO \longrightarrow N_2 + O$ and OH radicals by $H + NO_2 \longrightarrow NO + OH$. They obtained a value for k_{-2} of $1 \cdot 1 \pm 0 \cdot 4 \times 10^{10}$ at 310°K. Clyne [16] produced hydroxyl radicals by the reaction $H + NO_2 \longrightarrow NO + OH$, and measured the stationary concentration of oxygen atoms resulting from reactions (−2) and $OH + OH \longrightarrow H_2O + O$. A value of $k_{-2} = 3 \pm 1 \times 10^{10}$ was obtained at 293°K. By using the equilibrium constant k_2/k_{-2} given by Kaufman and Greco,[15] values for k_2 of 0·328 at 310°K and 0·183 at 293°K can be obtained.

The various values for k_2 are summarised below and plotted in Fig. 1.

	Temp. (°K)	k		Temp. (°K)	k
Clyne	293	0·183	Fenimore and Jones †	1100	$1 \cdot 60 \times 10^8$
Kaufman and Greco	310	0·328		1500	$1 \cdot 44 \times 10^9$
Baldwin and Cowe	813	$6 \cdot 0 \times 10^6$	Schott and Kinsey	1650	$1 \cdot 43 \times 10^9$
Karmilova, Nalbandyan,	733	$1 \cdot 88 \times 10^6$			
and Semenoff *	873	$9 \cdot 76 \times 10^6$			

* The extremes of the temperature range investigated are given.   † The extremes of the temperature range quoted by Fenimore and Jones.[17]

The best straight line drawn by inspection of the points gives the Arrhenius parameters as $\log_{10} A = 11 \cdot 33$, $E = 16 \cdot 55$ kcal./mole. A possible 50% error being assumed at the two
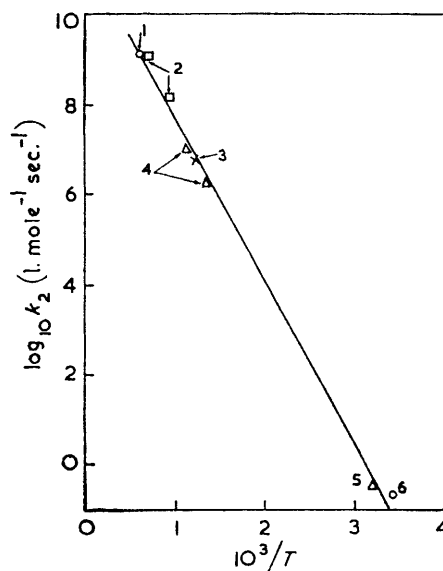

Fig. 1. Data for reaction $H + O_2 = OH + O$.
1, Schott and Kinsey; 2, Fenimore and Jones; 3, Baldwin and Cowe; 4, Karmilova *et al.*; 5, Kaufman and Greco; 6, Clyne.

extreme temperatures investigated, the possible error in $\log_{10} A$ is $\pm 0 \cdot 27$ and in E is $\pm 0 \cdot 80$ kcal./mole. Statistical treatment gave the 95% confidence limits of A and E in close agreement with these values. Interpretation by the Arrhenius equation has been adopted since more elaborate treatments in which the pre-exponential factor was assumed proportional to $T^{\frac{1}{2}}$, and to T, did not noticeably reduce the statistical error. Moreover, a temperature-independent pre-exponential factor is obtained from transition-state theory

[15] Kaufman and Greco, 9th Internat. Combustion Symposium, Cornell, 1962, Academic Press, New York, 1963.
[16] Clyne, 9th Internat. Combustion Symposium, Cornell, 1962, Academic Press, New York, 1963.
[17] Fenimore and Jones, 9th Internat. Combustion Symposium, Cornell, 1962, Academic Press, New York, 1963.

on the assumption that the vibration partition function is independent of temperature; if the vibration energy is classical, the pre-exponential factor is proportional to T. The statistical analysis for the three types of expression are given below.

TABLE 1.

	$\log_{10} A$	E(kcal./mole)
$k = Ae^{-E/RT}$	$11{\cdot}313 \pm 0{\cdot}28$	$16{\cdot}49 \pm 0{\cdot}70$
$k = AT^{\frac{1}{2}}e^{-E/RT}$	$9{\cdot}680 \pm 0{\cdot}25$	$15{\cdot}93 \pm 0{\cdot}64$
$k = ATe^{-E/RT}$	$8{\cdot}047 \pm 0{\cdot}23$	$15{\cdot}37 \pm 0{\cdot}58$

The value of studies over a wide range of temperature is shown by the fact that omission of the two points at room temperature gives the Arrhenius parameters as $\log_{10} A = 11{\cdot}739 \pm 0{\cdot}42$, $E = 18{\cdot}45 \pm 1{\cdot}83$. From these parameters, k (at $300°$K) $= 0{\cdot}02$. The discrepancy between this value and results given by Clyne and by Kaufman and Greco is very much greater than the errors admitted by these workers, suggesting that these parameters are much less likely than the values in Table 1.

Second-limit measurements show that $k_2/k_4 = 36$ mm. Hg (M $=$ H$_2$) at $540°$c. Taking the value of $k_2 = 7{\cdot}6 \times 10^6$ from the analysis above, $k_4 = 1{\cdot}07 \times 10^{10}$ l.^{2} mole^{-2} sec.$^{-1}$ at $540°$c (M $=$ H$_2$). Since second-limit measurements [18] show that k_4 (argon)$/k_4$(H$_2$) $= 0{\cdot}20$, k_4(M $=$ A) $= 0{\cdot}214 \times 10^{10}$ at $540°$c. The corresponding value found by Clyne [16] at room temperature is $1{\cdot}2 \pm 0{\cdot}3 \times 10^{10}$. $k_4 = Ae^{-E/RT}$ being assumed, this corresponds to a negative activation energy of 1570 cal./mole. If it is assumed that $A \propto T$, the negative value becomes 2500 cal./mole.

The Reaction of Hydrogen Atoms with Ethane.—Despite repeated investigations, precise values for the pre-exponential factors and activation energies in the reaction of hydrogen atoms with hydrocarbons have been difficult to establish. Steacie [19] reviews values for H $+$ CH$_4$ ranging from $E = 15{\cdot}6$ kcal./mole with a steric factor nearly unity, to $E = 4{\cdot}1$ kcal./mole with a steric factor of 10^{-5}. Although the earliest estimates favoured the higher E, the more recent work of LeRoy [20] supports the lower value. A similar situation exists in the reaction of hydrogen atoms with ethane:

$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \tag{14}$$

Berlie and LeRoy [6] produced hydrogen atoms by dissociating molecular hydrogen on a tungsten filament, and determined the concentration of hydrogen atoms by their catalytic recombination on a platinum surface. In the range 80—163°c, they obtained an activation energy of $6{\cdot}8$ kcal./mole and a pre-exponential factor of $3{\cdot}4 \times 10^9$, equivalent to a steric factor of 5×10^{-3}. This low steric factor was used to argue support for the low factor suggested for H $+$ CH$_4$. Darwent and Roberts,[21] however, producing deuterium atoms by the photolysis of D$_2$S, obtained an activation energy for D $+$ C$_2$H$_6$ of $9{\cdot}0$ kcal./mole and a steric factor of $0{\cdot}6$, in the temperature range 31—306°c.

These estimates of k_{14} were originally used [5] to obtain k_2 by combining them with the value of k_{14}/k_2 obtained from studies of the inhibiting action of ethane on the second limit of the H$_2$ $+$ O$_2$ reaction. Considerable extrapolation of k_{14} was necessary and since a number of independent estimates of k_2 are now available, it seems more realistic to use the value of k_{14}/k_2 at 540°c to obtain k_{14} at 540°c. Since Fenimore and Jones [17] have obtained an estimate of k_{14} at flame temperatures, four sets of values over a wide temperature range can be combined.

(1) *At 80—163°c.* Berlie and LeRoy [6] measured k_{14} at four temperatures in the

[18] Lewis and von Elbe, *J. Chem. Phys.*, 1942, **10**, 366.
[19] Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1954.
[20] LeRoy, *Discuss. Faraday Soc.*, 1953, **14**, 120.
[21] Darwent and Roberts, *Discuss. Faraday Soc.*, 1953, **14**, 55.

range 80—163°c. The extreme values from the mean line through these points are plotted in Fig. 2.

(2) *At* 31—306°c. The procedure adopted by Darwent and Roberts [21] gives the ratio $k_{14'}/k_D$.

$$D + C_2H_6 \longrightarrow C_2H_5 + HD \qquad (14')$$

$$D + D_2S \longrightarrow D_2 + DS \qquad (D)$$

By photolysing D_2S in the presence of H_2, they showed that the ratio $[HD]/[D_2]$ produced was independent of temperature, so that reactions (D) and (C) have the same activation energy, the ratio $k_C/k_D = 0.099$ being independent of temperature.

$$D + H_2 \longrightarrow HD + H \qquad (C)$$

Darwent and Roberts adopted the rather arbitrary figure of 5 kcal./mole for E_c, and the steric factor of 0.07 given by Farkas and Farkas.[22] k_D, and hence $k_{14'}$, can be obtained
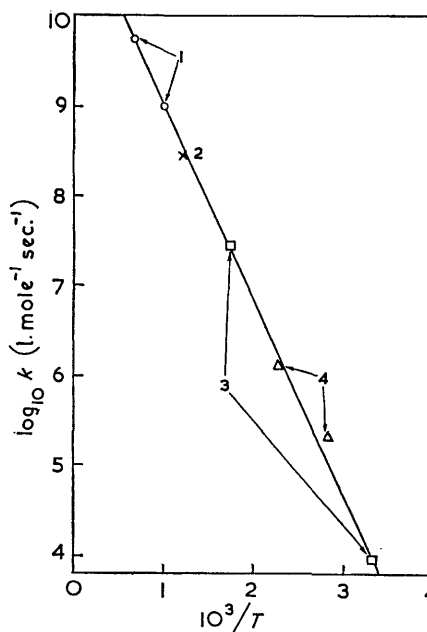
FIG. 2. Data for reaction $H + C_2H_6 = C_2H_5 + H_2$.
1, Fenimore and Jones; 2, Baldwin and Melvin; 3, Darwent and Roberts; 4, Berlie and LeRoy.

more reliably, however, from the recent values for k_C given by Shavitt.[23] Since McNesby, Scheer, and Klein,[24] using the treatment given by Bigeleisen [25,26] for a loosely bound activated complex, find that the activation energy and pre-exponential factors of $H + HCHO$ and $D + HCHO$ are the same, it has been assumed that $k_{14} = k_{14'}$. The values obtained at the extremes of the temperature range are given in Table 2 and plotted in Fig. 2.

(3) *At* 540°c. From studies of the inhibiting action of ethane on the second limit of $H_2 + O_2$ mixtures, Baldwin and Simmons [5] obtained a value of $k_{14}/k_2 = 64$ at 540°c. This value was obtained by using the second limit mechanism suggested by Lewis and von Elbe,[1] involving reactions (1)—(6).
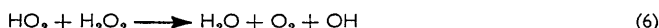
[22] Farkas and Farkas, *Proc. Roy. Soc.*, 1935, *A*, **152**, 124.
[23] Shavitt, *J. Chem. Phys.*, 1959, **31**, 1359.
[24] McNesby, Scheer, and Klein, *J. Chem. Phys.*, 1960, **32**, 1814.
[25] Bigeleisen, *J. Chem. Phys.*, 1949, **17**, 675.
[26] Bigeleisen, *J. Chem. Phys.*, 1953, **21**, 1333.

3 N

$$OH + H_2 \longrightarrow H_2O + H \tag{1}$$
$$H + O_2 \longrightarrow OH + O \tag{2}$$
$$O + H_2 \longrightarrow OH + H \tag{3}$$
$$H + O_2 + M \longrightarrow HO_2 + M \tag{4}$$
$$HO_2 \longrightarrow \tfrac{1}{2}H_2O_2 + \tfrac{1}{2}O_2 \tag{5}$$
$$HO_2 + H_2O_2 \longrightarrow H_2O + O_2 + OH \tag{6}$$

Recent evidence [27,28] has indicated that reaction (6) plays no detectable part at temperatures around 500°c, and that HO_2 radicals are probably destroyed completely at the surface in vessels coated with potassium chloride. Re-interpretation of Baldwin and Simmons's data by using a simplified scheme involving reactions (1)—(4), (5a), (14), and (15) gives $k_{14}/k_2 = 42$ at 540°C.

$$HO_2 \longrightarrow \tfrac{1}{2}H_2O + \tfrac{3}{4}O_2 \tag{5a}$$
$$H + C_2H_6 \longrightarrow H_2 + C_2H_5 \tag{14}$$
$$OH + C_2H_6 \longrightarrow H_2O + C_2H_5 \tag{15}$$

Evidence [29] has been given that effectively all the ethyl radicals are removed without continuing the chain.

Baldwin and Simmons used vessels which had been lightly coated with potassium chloride, and allowed one minute for mixing in the vessel before withdrawal. To minimise any possible reaction during this period, their experiments have been repeated with heavily coated vessels and using mixing periods of only 20 sec. The extent of inhibition is conveniently assessed in terms of $i_{\frac{1}{2}}$, the mole fraction of inhibitor required to halve the second limit. With the above mechanism

$$1/i_{\frac{1}{2}} = k_{14}/k_2 y + 2k_{15}/(k_1 x + k_{15} i_{\frac{1}{2}})$$

The values of k_{14}/k_2 and k_{15}/k_1 which give the closest agreement between observed and calculated values of $i_{\frac{1}{2}}$ can be determined. Table 2 shows the results, over a wide range of mixture composition, based on $k_{14}/k_2 = 38\cdot4$, $k_{15}/k_1 = 12\cdot4$. The observed values have been corrected for surface destruction of H and OH as described earlier.[5] The r.m.s. deviation of observed and calculated values is 2·6%. From k_2 at 540°C (Fig. 1), $k_{14} = 2\cdot93 \times 10^8$.

TABLE 2.

Comparison of observed and calculated values of $i_{\frac{1}{2}}$.

Mole fraction		$10^2 i_{\frac{1}{2}}$		Mole fraction		$10^2 i_{\frac{1}{2}}$		Mole fraction		$10^2 i_{\frac{1}{2}}$	
H_2	O_2	Obs.	Calc.	H_2	O_2	Obs.	Calc.	H_2	O_2	Obs.	Calc.
0·28	0·07	0·151	0·158	0·07	0·14	0·188	0·184	0·07	0·56	0·341	0·344
0·28	0·10	0·210	0·215	0·10	0·14	0·217	0·212	0·10	0·56	0·428	0·432
0·28	0·14	0·292	0·283	0·14	0·14	0·233	0·237	0·14	0·56	0·535	0·528
0·28	0·28	0·466	0·474	0·28	0·14	0·292	0·283	0·28	0·56	0·757	0·739
0·28	0·56	0·757	0·739	0·56	0·14	0·333	0·317	0·43	0·56	0·869	0·871
0·28	0·71	0·815	0·838								

Baldwin and Simmons showed that a consistent value for k_{14}/k_2 could also be obtained from studies of the first limit in vessels coated with potassium chloride. Gorban and Nalbandyan [30,31] have extended this approach by using a potassium tetraborate surface

[27] Baldwin and Mayor, *Trans. Faraday Soc.*, 1960, **56**, 80, 93, 103.
[28] Baldwin and Brattan, 8th Internat. Combustion Symposium, Pasadena, 1960, Wilkins and Williams, 1962.
[29] Baldwin and Simmons, *Trans. Faraday Soc.*, 1955, **51**, 680.
[30] Gorban and Nalbandyan, *Doklady Akad. Nauk, U.S.S.R.*, 1960, **132**, 1335.
[31] Gorban and Nalbandyan, *J. Phys. Chem. (Russia)*, 1962, **36**, 941.

that is extremely inefficient for radical destruction, so that very low first limits (*ca.* 0·1 mm. of Hg) are obtained. Their published treatment is not entirely satisfactory, since they provide no evidence for their assumption that destruction of hydrogen atoms is the sole surface termination process, and they also ignore reaction (15). Moreover, their two published papers appear to use two different formulæ to interpret the same set of results, and each paper also appears internally inconsistent, so that a reliable evaluation of k_{14}/k_2 is not possible.

(4) *At temperatures around* 1100°K. Fenimore and Jones [17] examined the disappearance of ethane in a hydrogen–oxygen–argon flame containing ethane, and showed that the ethane was consumed in hydrogen-rich flames by reaction (14), and in lean flames by reaction (15). To obtain k_{14}, the value of k_2 previously determined [13] at flame temperatures was used.

These various values for k_{14} are summarised below and plotted in Fig. 2.

	T(°K)	k		T(°K)	k
Berlie and LeRoy	353	$2·1 \times 10^5$	Baldwin and Melvin	813	$2·9 \times 10^8$
	436	$1·3 \times 10^6$	Fenimore and Jones	1000	$1·0 \times 10^9$
Darwent and Roberts ...	300	$8·9 \times 10^3$		1500	$5·4 \times 10^9$
	579	$2·9 \times 10^7$			

The best line drawn by inspection of the points gives the Arrhenius parameters as $\log_{10} A = 11·170$, $E = 9·93$ kcal./mole; possible errors of 50% in both low and high temperature values being assumed, the possible errors in $\log_{10} A$ and E are $\pm 0·230$ and $\pm 0·53$, respectively. Statistical treatment gives $\log_{10} A = 11·117 \pm 0·25$, $E = 9·71 \pm 0·58$; if Berlie and LeRoy's results are omitted, $\log_{10} A = 11·165 \pm 0·065$, $E = 9·90 \pm 0·17$.

Transition-state theory would give a pre-exponential factor proportional to $T^{-\frac{1}{2}}$ if vibrational partition functions are independent of temperature. The parameters in $k = A T^{-\frac{1}{2}} e^{-E/RT}$ then become $\log_{10} A = 12·745 \pm 0·26$, $E = 10·29 \pm 0·55$.

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