

Rate Constants for Hydrogen+Oxygen System, and for H Atoms and OH Radicals+Alkanes

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Rate constants at 500°C for the elementary steps in the $\text{H}_2 + \text{O}_2$ reaction have been revised to take into account self-heating of the reaction mixtures, reaction of O atoms with H_2O_2 , and other refinements in the mechanism. By combination with independent data at lower temperatures, Arrhenius parameters for the reactions have been obtained.

Rate constants for $\text{OH} + \text{RH}$ [reaction (21)] and $\text{H} + \text{RH}$ [reaction (22)] for C_2 – C_5 alkanes have been revised to allow for self-heating, and for reaction of O atoms and HO_2 radicals with the additive. Combination with data at lower temperatures has given Arrhenius parameters for the reactions. The results indicate that, to a first approximation, rate constants for an unknown alkane can be obtained by the relationships

$$k_{21}/k_1 = 0.214n_p \exp(1070/T) + 0.173n_s \exp(1820/T) + 0.273n_t \exp(2060/T)$$

$$k_{22} = 2.2 \times 10^{10} n_p \exp(-4715/T) + 4.9 \times 10^{10} n_s \exp(-4005/T) + 5.1 \times 10^{10} n_t \exp(-3030/T),$$

where n_p , n_s , n_t are the number of primary, secondary and tertiary C–H bonds, and k_1 is the rate constant for the reaction $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}(1)$.

Previous studies of the addition of small amounts (0.1 % or less) of C_2H_6 ,^{1, 2} C_3H_8 ,³ n- and i- C_4H_{10} ,³ and neopentane⁴ to slowly reacting mixtures of $\text{H}_2 + \text{O}_2$ have enabled rate constants at 480–500°C to be obtained for the reaction of H atoms and of OH radicals with the alkane (RH). The basic principle of the method, given elsewhere,^{1–5} can be illustrated by assuming (a) a simplified mechanism for the $\text{H}_2 + \text{O}_2$ reaction, (b) that H_2 is only removed by reaction (1) and (c) that RH is only removed by reactions (21) and (22). In this case the relative rate of consumption of RH and H_2 is given by eqn (i).†

$$d[\text{RH}]/d[\text{H}_2] = \frac{k_{21}[\text{RH}]}{k_1[\text{H}_2]} + \frac{k_{22}[\text{RH}]}{k_4[\text{O}_2][\text{M}]} \quad (\text{i})$$



Because of the difficulty in measuring accurately the initial slope of the $[\text{RH}]$ against ΔP plot, the experimental parameter used initially^{2, 3} was ΔP_{20} , the pressure change corresponding to 20 % loss of RH. Integration of eqn (i), with $[\text{H}_2]$ effectively constant, gives eqn (ii).

$$\frac{[\text{O}_2][\text{M}]}{\Delta[\text{H}_2]_{20}} = \frac{k_{21}[\text{O}_2][\text{M}]}{0.223 k_1[\text{H}_2]} + \frac{k_{22}}{0.223 k_4} \quad (\text{ii})$$

† Reaction numbers have been chosen to maintain consistency with previous papers.

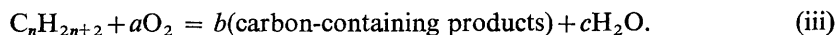
By measuring the consumption of RH gas-chromatographically, and by using the pressure change ΔP_{20} to obtain $\Delta[H_2]_{20}$, the rate constants k_{21}/k_1 and k_{22}/k_4 can be obtained by a suitable graphical treatment^{1-3, 5} of results obtained over a wide range of mixture composition.

To refine this treatment, allowance has to be made for the following additional factors. (1) The pressure change resulting from the formation of H_2O_2 , and from the oxidation of the hydrocarbon and its oxidation products, which becomes even more important if the pressure change corresponding to 50 % consumption (ΔP_{50}) is used so as to increase the accuracy of measurement of ΔP . (2) In the full mechanism for the $H_2 + O_2$ reaction in aged boric-acid-coated vessels, reaction (1) is not the sole source of H_2O ; moreover, the ratio $[H]/[OH]$ is not as simple as that implicit in expressions (i) and (ii). (3) The pressure change does not give an accurate measure of the water formation and hydrogen consumption unless allowance is made for the slight self-heating of the reaction mixture. (4) Attack on the hydrocarbon by O atoms and by HO_2 radicals, although relatively unimportant, does influence the final values obtained for k_{21}/k_1 and k_{22}/k_4 .

The method of handling each of the factors is discussed below.

PRESSURE CHANGES RESULTING FROM OXIDATION OF ALKANE

For each of the alkanes studied,^{2, 6-12} detailed analyses of reaction products have been made for a certain number of mixtures up to an alkane consumption of over 60 %. Significant yields of carbon monoxide and other products are found, indicating substantial oxidation of the primary products. An overall oxidation equation of the form given by eqn (iii) can thus be written.



The value of b is calculated so that the sum of the carbon atoms in the products is equal to n , and c is obtained by assuming that all the $(2n+2)$ H atoms not found in

TABLE 1.—OVERALL EQUATIONS FOR HYDROCARBON OXIDATION AT 50 % CONSUMPTION
TEMPERATURE 480°C (ETHANE 500°C)

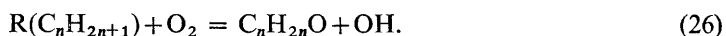
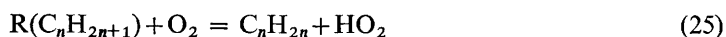
H ₂	mixture			RH							
	O ₂	N ₂	Torr		C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	i-C ₄ H ₁₀	neopentane	n-C ₅ H ₁₂	(CH ₃) ₃ C—C(CH ₃) ₃
140	70	285	5	<i>a</i>	0.85	0.91	1.21	1.31	1.79	1.27	1.28
				<i>b</i>	1.24	1.54	2.01	1.68	2.67	1.94	2.97
				<i>c</i>	1.23	1.16	1.37	1.31	1.71	1.60	1.20
140	355	0	5	<i>a</i>	0.92	1.17	1.76	1.51	2.63	1.91	2.27
				<i>b</i>	1.25	1.56	2.19	1.82	2.82	2.08	3.58
				<i>c</i>	1.32	1.42	1.90	1.68	2.61	2.32	2.67
425	70	0	5	<i>a</i>	0.84	0.76	0.94	0.96	1.79	1.24	2.00
				<i>b</i>	1.27	1.57	2.05	1.62	3.02	1.99	3.46
				<i>c</i>	1.17	0.96	1.04	1.11	1.62	1.60	2.22

the carbon-containing products are present as H_2O . Values of a , b and c , for all the alkanes studied at 50 % consumption are given in table 1 for each of the three main $H_2 + O_2 + N_2$ mixtures used in the analysis of reaction products.

The value of $(b+c-a-1)$ changes only slightly with mixture composition, so that by using these mixtures as a guide, the small pressure changes due to oxidation of the alkane and its products can be calculated with an accuracy such that the corrected

pressure change is accurate to within 2 %. No correction is made for the pressure change due to H_2O_2 formation, as this is included in the computer program used to interpret the experimental results.

ALLOWANCE FOR ALL REACTIONS REQUIRED IN THE MECHANISM OF $\text{H}_2 + \text{O}_2$ REACTION



Previous papers^{13, 14} have described a computer program which predicts the reaction profile for the full mechanism necessary to interpret the experimental features of the $\text{H}_2 + \text{O}_2$ reaction in aged boric-acid-coated vessels. Reactions (21)-(24) involving attack on RH by OH, H, O and HO_2 have been added to this scheme. Product analysis shows that the majority of alkyl radicals formed by this attack either undergoes reaction (25) to form the conjugate alkene and HO_2 , or forms an oxygenated compound and OH by the overall reaction (26). Because of the very low concentrations of RH used, the occurrence of reactions (21)-(24), and (25) and (26) does not significantly alter the relative concentrations of OH, H, O and HO_2 from their values in the absence of RH; this is confirmed by the absence of any effect of RH at these low concentrations on either maximum rate, or the induction period (expressed as the time to one-half maximum rate).

EFFECTS RESULTING FROM SELF-HEATING

The temperature rise in an exothermic reaction is given^{15, 16} by eqn (iv) :

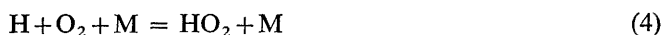
$$\rho C_v(dT/dt) = R_H - A\lambda(T - T_0)/d^2 \quad (\text{iv})$$

where ρ is the density, C_v is the molar heat capacity, R_H the rate of heat evolution. A is the constant in the equation $h = (A\lambda/d^2)V/S$ for the heat transfer coefficient, h , between the gas, volume V , and the vessel surface area, S . λ is the thermal conductivity of the gas, d the vessel diameter, and T_0 the initial temperature. Insertion of reasonable values shows that dT/dt is effectively zero within one second, so that with the rates involved in the present work, a stationary temperature rise $\Delta T = (T - T_0)$ given by $dT/dt = 0$ may be assumed.

For $\text{H}_2 + \text{O}_2 + \text{N}_2$ mixtures, the rate of heat evolution may be calculated either from the stoichiometric equations for the production of the stable products H_2O and H_2O_2 , or by summing the heat produced by each elementary step. In the presence of alkane, the latter procedure has been adopted because of possible uncertainties in the mode of formation of a product, though the contribution from alkane reactions is, in any case, small. The conductivity λ of the mixture was calculated using the Wassiljewa¹⁷ equation for a two-component system, one component being H_2 and the other being a gas of conductivity equal to the weighted mean of the remaining components; since the remaining components all have similar conductivities, this procedure is unlikely to introduce any appreciable error. From an analysis made by Tyler,¹⁸ based on a treatment by Boddington, Gray and Harvey,¹⁹ a value of $A = 32$ has been taken on the grounds that ΔT will be small,

rather than the value of $A = 21.6$ used by Foo and Yang.¹⁶ For the range of $\text{H}_2 + \text{O}_2 + \text{N}_2$ mixtures used in previous studies, which gave reaction rates in the range $0.05\text{--}0.3 \text{ Torr s}^{-1}$ pressure change at 500°C , the calculated values of ΔT were in the range $0.5\text{--}2.5^\circ\text{C}$. Attempts were made to measure these rises in temperature experimentally, but although values of the correct order were obtained, the experimental fluctuation with different thermocouples suggested that the calculated values were more accurate than the measured values.

EFFECT OF SELF-HEATING ON THE CONSTANTS OF $\text{H}_2 + \text{O}_2$ REACTION



Previous papers^{13, 14} have interpreted the induction period and maximum rate of the slow reaction, and the second explosion limit, in terms of a number of parameters. The values of these parameters at 500°C , if no allowance is made for self-heating, are listed in the first line of table 2, together with the r.m.s. deviation between observed and calculated values for the induction period, the maximum rate, and the second limit. Of the parameters required, k_7 can be obtained from a direct study^{14, 20} of the decomposition of H_2O_2 , k_2/k_4 from the second limit²¹ in KCl-coated vessels, and the ratio k_{14a}/k_{14} from studies²² of the decomposition of H_2O_2 in the presence of H_2 . k_{8a} , k_{13} and k_{13a} were assumed to be zero in this treatment.^{13, 14} Of the remaining parameters, the induction period is largely determined by k_{11}/k_{10}^\ddagger , which can thus be evaluated from measurements of induction periods over a wide range of mixture composition. The rate of the slow reaction is determined by k_2/k_4 , k_7 , k_{11}/k_{10}^\ddagger , k_{14}/k_2 , k_{14a}/k_2 and k_{15}/k_1 , so that by measuring the rate as a function of mixture composition, the unknown parameters k_{14}/k_2 and k_{15}/k_1 can be obtained. The remaining unknown parameter,* $k'_8/k_2k_{10}^\ddagger$ can be evaluated from measurements of the second limit in aged B_2O_3 -coated vessels over a wide range of mixture composition.¹⁴

As shown by previous analysis,²³ the maximum rate of the slow reaction is essentially the rate of decomposition of H_2O_2 which reaches a quasi-stationary concentration determined by reactions (14), (15) and (11). Self-heating increases

* k_8 and k_{8b} are effectively indistinguishable kinetically and k'_8 is used to denote $k_8 + k_{8b}$.

the reaction rate mainly because of the high value of E_7 ($\approx 190 \text{ kJ mol}^{-1}$), thus reducing the values of k_{14}/k_2 and k_{15}/k_1 . The value of $k_{11}/k_{10}^{\frac{1}{2}}$ is obtained from the induction period, defined as the time to one-half maximum rate, and since the maximum rate is increased by self-heating, $k_{11}/k_{10}^{\frac{1}{2}}$ increases, as shown in line 2 of table 2.

Since the original analysis,^{13, 14} an estimate of the rate constant for $\text{O} + \text{H}_2\text{O}_2$ has been given,²⁴ and it has also been found possible²⁵ to evaluate the ratio $k_{8a}/k_2k_{10}^{\frac{1}{2}}$ from second limit measurements, as well as $k'_8/k_2k_{10}^{\frac{1}{2}}$. Incorporation of reactions (8a) and (13) into the computer treatment affects slightly the values obtained for the other parameters, $\text{O} + \text{H}_2\text{O}_2$ having the greatest effect on k_{15}/k_1 , and reaction (8a) having the greatest effect on $k'_8/k_2k_{10}^{\frac{1}{2}}$. Both reactions (8) and (8a) play only a minor role in the slow reaction. Lines 2 and 3 in table 2 show the effect of introducing reaction (13) with $k_{13}/k_3 = 10.4$ on the assumption that the measured²⁴ rate constant for $\text{O} + \text{H}_2\text{O}_2$ is k_{13} . Line 4 gives the effect of introducing reaction (8a). Comparison of lines 4 and 5 indicates the effect of replacing reaction (13) by (13a). Since a choice between these reactions is not feasible, possible errors are minimised in the last line by taking $k_{13}/k_3 = k_{13a}/k_3 = 5.2$. Although, except for $k'_8/k_2k_{10}^{\frac{1}{2}}$, the changes from previously published values are almost within experimental error, the new figures given in line 6 now represent the most accurate values and supersede those given earlier.¹⁴

TABLE 2.—OPTIMUM PARAMETERS FOR $\text{H}_2 + \text{O}_2$ REACTION AT 500°C

self-heating	O + H ₂ O ₂		optimum values from slow reaction						optimum value from second limit		
			induction period		rate						
	<i>k</i> ₁₃ / <i>k</i> ₃	<i>k</i> _{13a} / <i>k</i> ₃	<i>k</i> ₁₁ / <i>k</i> ₁₀ ^½	r.m.s. deviation/%	<i>k</i> ₁₄ / <i>k</i> ₂	<i>k</i> ₁₅ / <i>k</i> ₁	r.m.s. deviation/%	<i>k</i> _{8a} / <i>k</i> ₂ <i>k</i> ₁₀ ^½	<i>k</i> ₈ / <i>k</i> ₂ <i>k</i> ₁₀ ^½	r.m.s. deviation/%	
no	0	0	0.0289	4.0	246	4.7	5.8	0	0.32	3.8	
yes	0	0	0.0360	4.8	287	5.04	3.8	0	0.32	3.7	
yes	10.4	0	0.0363	4.4	293	3.70	2.9	0	0.34	4.8	
yes	10.4	0	0.0363	4.3	280	3.73	2.8	0.088	0.55	1.2	
yes	0	10.4	0.0363	4.5	279	4.48	3.3	0.078	0.52	0.9	
yes	5.2	5.2	0.0366	4.5	281	4.06	3.1	0.081	0.53	1.0	

To evaluate k'_8 , k_{8a} , k_{11} , k_{14} and k_{15} from the ratios† in table 2, values of k_1 , k_2 and k_{10} are required. The line drawn by Baulch *et al.*²⁶ through the points for k_1 covering the temperature range 300–1200 K lies significantly above the point in the range 600–900 K. However, the results obtained by Greiner²⁷ (295–495 K), Eberius *et al.*²⁸ (476–1150 K) and Westenberg and de Haas²⁹ (298–745 K) lie on a well defined curve. Points taken from this curve over the range 300–900 K are described by eqn (v) with a r.m.s. deviation of 3.0 %. This gives $k_1 = (4.06 \pm 0.4) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 500°C .

$$k_1 = 1.28 \times 10^5 T^{\frac{1}{2}} \exp(-1480/T). \quad (\text{v})$$

In view of recent accurate measurements³⁰ of $k(\text{H} + \text{C}_2\text{H}_6) = 1.32 \times 10^{11} \exp(-4715/T) = 2.96 \times 10^8$ at 500°C , it is considered that combination of this value with $k(\text{H} + \text{C}_2\text{H}_6)/k_2 = 38.7$, given later, provides a more accurate estimate of $k_2 = 7.65 \times 10^6$ at 500°C than the value of 3.95×10^6 obtained from the expression recommended²⁶ by Baulch *et al.* A number of determinations^{31, 32} have given $k_{10} = 2.0 \times 10^9$, independent of temperature. From these values, $k_{8a} = 2.8 \times 10^{10}$, $k'_8 = 1.81 \times 10^{11}$, $k_{11} = 1.64 \times 10^3$, $k_{14} = 2.15 \times 10^9$, $k_{14a} = 2.6 \times 10^8$, $k_{15} = 1.65 \times 10^9$ at 500°C .

† All rate constants and ratios are given in $\text{dm}^3 \text{ mol s}$ units.

The change in the values of k'_8 and k_{8a} from those given in an earlier paper,²⁵ is almost entirely due to the new value taken for k_2 . No new measurements at other temperatures have been reported. Combination of the new values of $(k_8 + k_{8b})$ and k_{8a} with values²⁴ at lower temperatures, as in an earlier paper,²⁵ gives $A_8 = 5.4 \times 10^{11}$, $E_8 = 7.6 \text{ kJ mol}^{-1}$, $A_{8a} = 2.8 \times 10^{10}$, $E_{8a} = 0$, $A_{8b} = 5.5 \times 10^{10}$, $E_{8b} = 7.6 \text{ kJ mol}^{-1}$. With as assumed activation energy of 90 kJ mol^{-1} , the value of k_{11} gives $A_{11} = 1.97 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The value of $k_{15} = 1.65 \times 10^9$ at 500°C may be combined with earlier estimates over the range $300\text{--}460 \text{ K}$ ³³ and $298\text{--}666 \text{ K}$ ³⁴ to give $A_{15} = 3.7 \times 10^9$, $E_{15} = 4.8 \pm 0.6 \text{ kJ mol}^{-1}$.

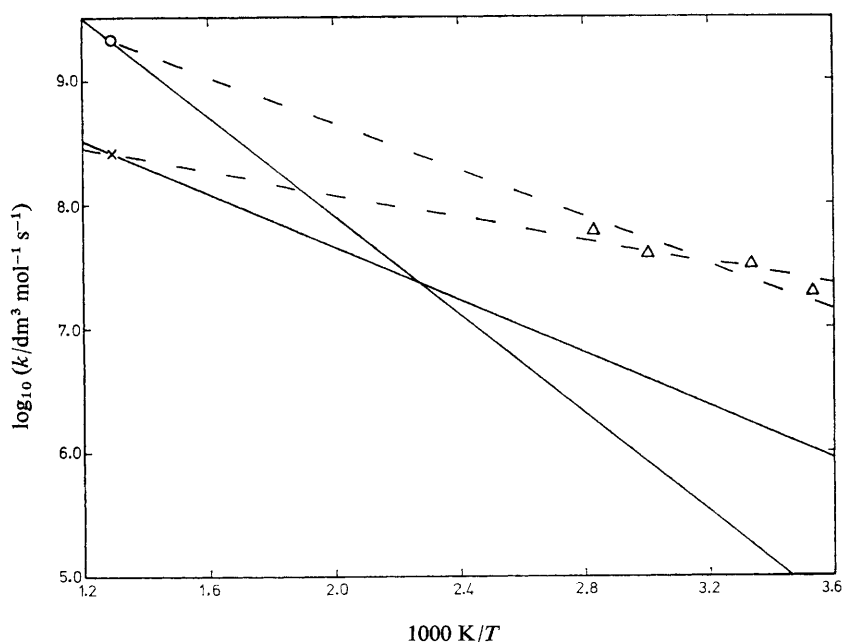


FIG. 1.—Variation with temperature of rate constant for $\text{H} + \text{H}_2\text{O}_2$. \circ , k_{14} , present work; \times , k_{14a} , present work; \triangle , $(k_{14} + k_{14a})$, from Klemm *et al.*,³⁵ —, lines using data of Albers *et al.*,²⁴ ---, lines using data of Klemm *et al.*,³⁵

In a previous paper,²⁵ the ratio k_{14a}/k_{14} at $440\text{--}480^\circ\text{C}$, obtained from studies of the $\text{H}_2 + \text{H}_2\text{O}_2$ system, was combined with a value obtained by Albers *et al.*²⁴ for k_{14aD}/k_{14D} , the corresponding ratio for D atoms reacting with H_2O_2 , to give $(E_{14} - E_{14a})$ and A_{14}/A_{14a} on the assumption that $k_{14a}/k_{14} = k_{14aD}/k_{14D}$. A better estimate is obtained by the use of $k_{14a}/k_{14} = 0.143$ at 450°C ,²² which gives $(E_{14} - E_{14a}) = 17.5 \text{ kJ mol}^{-1}$, $A_{14}/A_{14a} = 128$ on the assumption that the ratio $k_{14aD}/k_{14D} = 10$ given by Albers *et al.* refers to the lowest temperature used. (If their ratio refers to the mean temperature, A_{14} then becomes unreasonably high). Albers *et al.*²⁴ give $E_{14aD} = 17.6 \text{ kJ mol}^{-1}$, and a reasonable estimate³⁵ of $(E_{14a} - E_{14aD})$ is 3.0 kJ mol^{-1} , so that $E_{14a} = 20.6 \text{ kJ mol}^{-1}$ and $E_{14} = 38.1 \text{ kJ mol}^{-1}$. With these activation energies, the experimental value of $k_{14} = 2.1 \times 10^9$ at 500°C gives $A_{14} = 8.0 \times 10^{11}$ and hence $A_{14a} = 6.3 \times 10^9$.

However, a recent paper³⁵ has given values for $(k_{14} + k_{14a})$ in the temperature range $283\text{--}353 \text{ K}$ higher, by a factor of ≈ 10 , than those obtained by Albers *et al.*²⁴

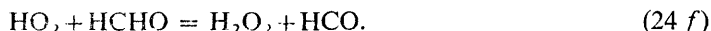
These results are shown in fig. 1, which also gives the lines corresponding to the above expressions for k_{14} and for k_{14a} , and which are derived by use of the low temperature results of Albers *et al.*

Klemm *et al.*³⁵ give reasons why the method used by Albers *et al.* might give low values for k_{14} and k_{14a} . If their own results are accepted, their points can be linked to the high temperature values of k_{14} and k_{14a} with almost equal scatter. The former case would give $A_{14} = 3.6 \times 10^{10}$, $E_{14} = 18.1 \text{ kJ mol}^{-1}$. Klemm *et al.* (fig. 5 of their paper) adopt this view and suggest a much higher value of $E_{14a} = 40 \text{ kJ mol}^{-1}$ based on our own studies of the $\text{H}_2 + \text{H}_2\text{O}_2$ system, but we do not believe the accuracy of those results is sufficient to justify this decision. Combination of the results of Klemm *et al.* with the value of k_{14a} at 500°C gives $E_{14a} = 8.9 \text{ kJ mol}^{-1}$, $A_{14a} = 1.05 \times 10^9$, and E_{14} would then have to be greater than E_{14a} .

There seems no way of resolving the discrepancies in the low temperature results. Use of the results of Albers *et al.* gives parameters consistent with those obtained for reactions (8) and (8a), as discussed earlier,²⁵ but further work is required.

EFFECT OF ATTACK BY O AND BY HO_2 ON RATE CONSTANTS $\text{H} + \text{RH}$ AND $\text{OH} + \text{RH}$

By adding reactions (21)–(24) to the mechanism already used for the slow reaction of $\text{H}_2 + \text{O}_2 + \text{N}_2$ mixtures, a computer program can be written to construct the relationship between the alkane consumption and the pressure change, including allowance for the effect of self-heating both on the rate constants and on the pressure change. By interpolation, the pressure change corresponding to 50 % consumption of alkane can be calculated, and the r.m.s. deviation between observed and calculated values obtained. By incorporating an optimisation procedure, the parameters k_{21}/k_1 and k_{22}/k_2 can be adjusted so as to give minimum r.m.s. deviation for a wide range of mixture composition* with $[\text{H}_2]/[\text{O}_2]$ ratios ranging from 12 to 0.075. To operate the program, values of k_{23}/k_3 and k_{24}/k_{10}^\ddagger must be supplied, but since reactions (23) and (24) play a relatively minor part in the consumption of alkane, approximate estimations of their value are sufficient. Values of k_{23} for the various alkanes were obtained using the expressions given by Heron and Huie³⁷ for attack at individual C—H bonds; the value of $k_3 = 1.74 \times 10^{10} \exp(-4755/T)$ was used.²⁶ The values used for k_{23}/k_3 at 480°C for the alkanes C_2H_6 , C_3H_8 , $n\text{-C}_4\text{H}_{10}$, $i\text{-C}_4\text{H}_{10}$, neopentane, $n\text{-C}_5\text{H}_{12}$ and 2,2,3,3-tetramethylbutane (TMB) were 9.4 (500°C), 61, 103, 87, 37, 129 and 52, respectively. The values of k_{24}/k_{10}^\ddagger were based on the preliminary estimates† of k_{24}/k_{24f} of 0.028, 0.080 and 0.13, for C_2H_6 , C_3H_8 and $i\text{-C}_4\text{H}_{10}$ respectively at $440\text{--}500^\circ\text{C}$, obtained from a study of the addition of these hydrocarbons to $\text{HCHO} + \text{O}_2$ mixtures in KCl-coated vessels. From the value at 500°C of $k_{24f}/k_{10}^\ddagger = 22.7 \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1})^\ddagger$, (18.9 at 480°C) and on the assumption of additivity of attack at the different types of C—H bond, values of k_{24}/k_{10}^\ddagger at 480°C for the above hydrocarbons, except TMB, were estimated as 0.70 (500°C), 1.8, 2.9, 2.8, 1.1 and 3.8, respectively. For TMB, an experimental determination³⁹ at 440°C was used, with a suitable activation energy to give $k_{24}/k_{10}^\ddagger = 0.67$ at 480°C . Preliminary experiments⁴⁰ with C_2H_6 added to $\text{TMB} + \text{O}_2$ mixtures confirm the similar values for C_2H_6 and TMB.

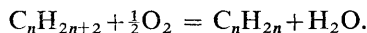


* The experimental data for most of the alkanes discussed here are given in ref. (2), (3), (10)–(12) and (36).

† The original estimates³⁸ have been reduced slightly in view of the contribution from OH attack on the RH, which preliminary calculations indicate to be of some significance.

RATE CONSTANTS FOR $H+RH$ AND $OH+RH$

The effects of the various corrections discussed are illustrated in table 3 for two hydrocarbons, C_3H_8 and $i-C_4H_{10}$. The original correction to the pressure change caused by reactions of the hydrocarbon was $\frac{1}{2}\Delta[RH]$, based on the overall reaction given below for the formation of the main primary products, namely conjugate alkenes.



The effect of the improved correction, based on product analysis, can be seen in lines 1 and 2 of table 3 for C_3H_8 , and in lines 6 and 7 for $i-C_4H_{10}$; k_{21}/k_1 is reduced by $\approx 10\%$ and k_{22}/k_2 by $\approx 5\%$. The effect is most marked for hydrocarbons with the highest values of k_{21}/k_1 , k_{22}/k_2 , since ΔP_{50} is small.

TABLE 3.—EFFECT OF CORRECTIONS ON VALUES OF k_{21}/k_1 AND k_{22}/k_2

RH	correction to ΔP	A	k_{23}/k_3	$k_{24}/k_{10}^{\frac{1}{2}}$	optimum values of		r.m.s. % deviation
					k_{21}/k_1	k_{22}/k_2	
1 C_3H_8	$\Delta[RH]/2$	0	0	0	18.2	145	4.2
2	analysis	0	0	0	17.8	144	4.5
3	analysis	0.0835	0	0	15.9	140	4.3
4	analysis	0.0835	54	0	13.4	143	5.8
5	analysis	0.0835	54	1.8	9.9	125	4.1
6 $n-C_4H_{10}$	$\Delta[RH]/2$	0	0	0	30.0	264	8.1
7	analysis	0	0	0	27.7	255	9.9
8	analysis	0.0835	0	0	24.1	242	8.5
9	analysis	0.0835	92	0	19.9	245	10.0
10	analysis	0.0835	92	2.9	13.2	217	7.2
11	analysis	0.0835	92	3.5	12.0	211	6.6

Comparison of lines 2, 3 for C_3H_8 and lines 7, 8 for $i-C_4H_{10}$ shows that the introduction of self-heating reduces k_{21}/k_1 by ≈ 10 – 15% and has a smaller effect ($< 5\%$) on k_{22}/k_2 . The effect will be significantly less for C_2H_6 because the values of ΔP_{50} are much larger.

Comparison of lines 3, 4 and 8, 9 shows that introduction of $O+RH$ reduces the value obtained for the kinetically equivalent $OH+RH$, the ratio k_{21}/k_1 decreasing by $\approx 15\%$ for all hydrocarbons as expected.

Comparison of lines 4, 5 for C_3H_8 , and lines 9, 10 for $n-C_4H_{10}$ shows that introduction of HO_2+RH reduces k_{21}/k_1 by ≈ 25 – 35% and k_{22}/k_2 by ≈ 10 – 15% , the effects being most marked for those hydrocarbons with the highest value of $k_{24}/k_{10}^{\frac{1}{2}}$. Comparison of lines 10, 11 for $n-C_4H_{10}$ shows that a small uncertainty in the value of $k_{24}/k_{10}^{\frac{1}{2}}$ has some effect on k_{21}/k_1 but much less effect on k_{22}/k_2 . Table 3 shows that the effect of all the corrections is to reduce the value of k_{21}/k_1 .

TABLE 4.—RATE CONSTANT RATIOS AT $480^\circ C$ FOR $H+RH$ AND $OH+RH$

hydrocarbon	C_2H_6 †	C_3H_8	$n-C_4H_{10}$	$i-C_4H_{10}$	neo- C_5H_{12}	$n-C_5H_{12}$	2,2,3,3-tetramethylbutane
k_{21}/k_1	5.7	9.9	13.2	12.6	10.2	18.1	8.0
k_{22}/k_2	39	125	217	223	52	309	112
number of mixtures used	28	27	27	29	17	13	12
r.m.s. % deviation	3.5	4.1	7.2	7.6	5.4	7.3	8.2

† Value at $500^\circ C$.

by a total factor of nearly 2, and that each correction makes a significant contribution. In contrast, the effect on k_{22}/k_2 is much less marked.

The optimum values of k_{21}/k_1 and k_{22}/k_2 for all the hydrocarbons studied are shown in table 4.

RATE CONSTANTS FOR $\text{OH} + \text{RH}$

Absolute values of the rate constants k_{21} for each hydrocarbon can be obtained if the value of k_1 is known. For comparison with Greiner's values⁴¹ for these hydrocarbons, however, it seems more logical to compare the present ratios of k_{21}/k_1

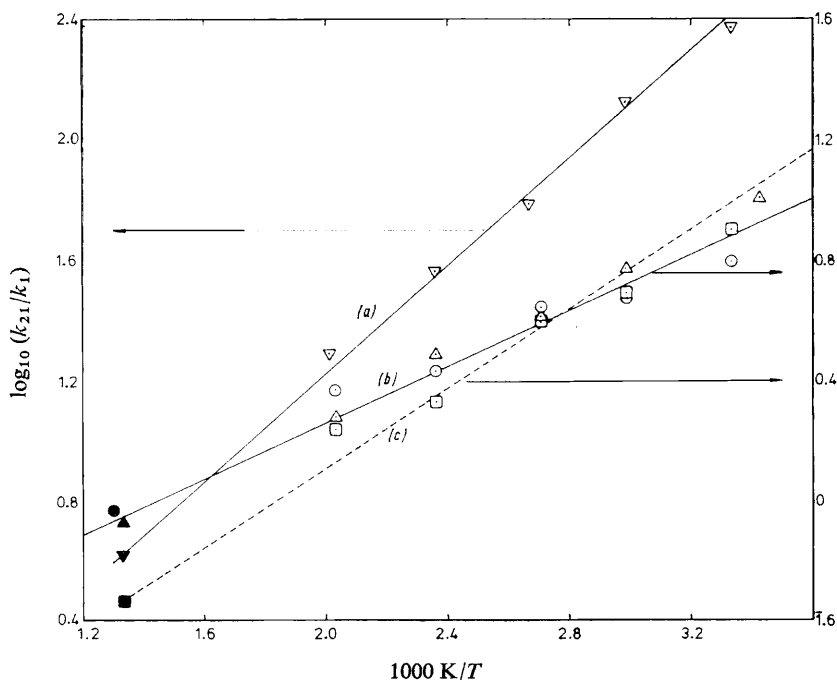


FIG. 2.—Variation of k_{21}/k_1 per CH bond with temperature.

	C_2H_6	neo- C_5H_{12}	TMB	$(\text{CH}_3)_3\text{CH}$
Greiner ⁴¹	○	△	□	▽
present work	●	▲	■	▼

(a) Tertiary C—H, (b) primary C—H for C_2H_6 , C_5H_{12} , (c) primary C—H for TMB.

with those obtained by Greiner using his values both for $\text{OH} + \text{RH}$ ⁴¹ and his expression $k_1 = 4.07 \times 10^9 \exp(-2023/T)$ for $\text{OH} + \text{H}_2$,²⁷ since in this way small experimental errors in Greiner's work, such as the calibration for OH concentration, may cancel out. A number of workers^{37, 41-43} have suggested that a reasonably accurate rate constant for the total radical attack on an alkane can be obtained by assuming additivity of attack at the three different types of bond, primary, secondary and tertiary, in the molecule. Fig. 2 shows a composite plot of k_{21}^p/k_1 per C—H bond*

* As in previous papers, subscripts e, p, nb, ib, pe, np and tb are used to indicate rate constants for C_2H_6 , C_3H_8 , n- C_4H_{10} , i- C_4H_{10} , n- C_5H_{12} , neopentane and 2,2,3,3-tetramethylbutane, respectively. Superscripts p, s and t are used to denote attack at primary, secondary and tertiary C—H bonds, respectively.

for hydrocarbons containing only primary C—H bonds over the range 0–500°C, obtained by combining the present results with those of Greiner.⁴¹ In view of the experimental scatter, particularly apparent in Greiner's data, the results for C₂H₆ and neo-C₅H₁₂ are considered to lie on a common line giving $k_{21}^p/k_1 = 0.214 \exp(1070/T)$. Although Greiner, from his data alone, considered that neo-C₅H₁₂ and tetramethylbutane lay on a common line with C₂H₆ having a different gradient, the high temperature point suggests that a separate line can be drawn through the points for tetramethylbutane giving $k_{21}^p/k_1 = 0.062 \exp(1520/T)$ per C—H bond.

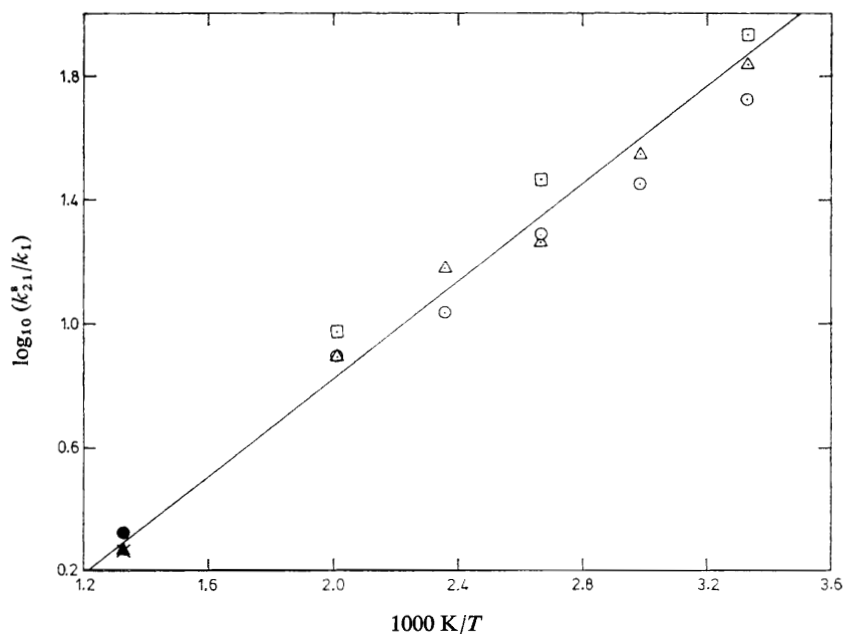


FIG. 3.—Variation of k_{21}^s/k_1 per CH bond with temperature.

	C ₃ H ₈	n-C ₄ H ₁₀	n-C ₅ H ₁₂	n-C ₈ H ₁₈
Greiner ⁴¹	○	△	—	□
present work	●	▲	×	—

Fig. 3 shows the plot for secondary C—H bonds. Using the mean value of k_{21}^p for C₂H₆ and neo-C₅H₁₂ at each temperature from fig. 2, the value for 6 primary C—H bonds has been subtracted from the values of k_{21}/k_1 for C₃H₈, n-C₄H₁₀, n-C₅H₁₂ (present results only) and n-C₈H₁₈ (Greiner's results only). The values per C—H bond again give a common plot with no significant trends, and the best straight line gives $k_{21}^s/k_1 = 0.173 \exp(1820/T)$.

Fig. 2 also shows the plot for a tertiary C—H bond, obtained by subtracting the value for 9 primary C—H bonds from the total rate constant ratio for i-C₄H₁₀. The straight line gives the expression $k_{21}^t/k_1 = 0.273 \exp(2060/T)$.

The overall rate constant k_{21} can thus be expressed by eqn (vi),

$$k_{21}/k_1 = 0.214n_p \exp(1070/T) + 0.173n_s \exp(1820/T) + 0.273n_t \exp(2060/T) \quad (\text{vi})$$

where n_p , n_s and n_t are the number of primary, secondary and tertiary C—H bonds. Although this equation provides the most useful general method of calculating the

relative proportions of the various radicals formed by OH attack on an alkane, its accuracy may be limited in specific special cases.

The only independent work appears to be that of Booth, Hucknall and Sampson,⁴⁴ who produced OH radicals in a mixture of two hydrocarbons by thermal decomposition of H_2O_2 and measured the yields of alkene produced. They obtained the rate constant ratios at 653 K given in table 5, which are in close agreement with the rate constant ratios given by eqn (vi) at 653 K. It would be useful to add the data obtained by Booth *et al.*⁴⁴ to fig. 2 and 3 to reinforce the higher temperature values, but this would require an accurate knowledge of $k(\text{OH} + \text{RH})/k_1$ for one of the hydrocarbons, preferably C_3H_8 . The uncertainty in this ratio is at least as great as the small discrepancies between the ratios obtained by Booth and those given by eqn (vi). The ratios given by Booth *et al.* for $\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ and for $(\text{n-C}_4\text{H}_{10})/\text{C}_3\text{H}_8$ require $k_{21s}/k_{21p} = 3.5$ at 653 K as compared with 2.5 from the plots in fig. 2 and 3. However, a line drawn through the experimental point for C_2H_6 in fig. 2 would reduce k_{21s}/k_{21p} below 2.5. The slightly higher selectivity required by the data of Booth *et al.* is within the experimental accuracy of their data, but may also be caused by some attack by the more selective HO_2 radical which, according to calculations given in their paper, will occur to some extent.

TABLE 5.—RATE CONSTANTS FOR OH ATTACK ON ALKANES AT 653 K

RH	k_{21p}/k_1 per C—H bond	k_{21s}/k_1 per C—H bond	k_{21t}/k_1 per C—H bond	$k_{21(\text{total})}/k_1$	$k_{21(\text{RH})}/k_{21(\text{C}_3\text{H}_8)}$ (calc)	$k_{21(\text{RH})}/k_{21(\text{C}_3\text{H}_8)}$ from Booth <i>et al.</i>
C_2H_6	1.12	—	—	6.72	0.54	0.46 ± 0.05
C_3H_8	1.12	2.80	—	12.32	(1.00)	(1.00)
$\text{n-C}_4\text{H}_{10}$	1.12	2.80	—	17.72	1.45	1.54 ± 0.13
$\text{i-C}_4\text{H}_{10}$	1.12	—	6.55	16.63	1.35	1.28 ± 0.07

Although only ratios of k_{21}/k_1 have been given, absolute values of k_{21} for primary, secondary, and tertiary bonds, and for the overall values for individual hydrocarbons, can be obtained by combining these ratios with the recommended expression (v) for k_1 over the range 300–900 K.

RATE CONSTANTS FOR $\text{H} + \text{RH}$

With $(E_2 - E_{22e}) = 31 \text{ kJ mol}^{-1}$, the ratio $k_{22e}/k_2 = 38.7$ at 500°C would become 44.0 at 480°C . From the expression³⁰ given earlier for k_{22e} , $k_2 = 5.73 \times 10^6$ at 480°C . The absolute values of $k(\text{H} + \text{RH})$ at 480°C can then be calculated from the data in table 4.

The ratios k_{22}/k_2 for C_2H_6 , neo- C_5H_{12} and 2,2,3,3-tetramethylbutane give values of k_{22}^p/k_2 per primary C—H bond of 7.3, 4.4 and 6.2, respectively, at 480°C . The discrepancy for neo- C_5H_{12} is well outside experimental error. A possible explanation of these results and the corresponding values for OH attack is that the C—H bond strength in neo- C_5H_{12} is rather higher than in the other two hydrocarbons (which would affect H attack more than OH attack), but that steric hindrance is greater with 2,2,3,3-tetramethylbutane in the case of OH attack.

Subtracting an average value of 7.0 per primary C—H bond from the ratios for C_3H_8 , $\text{n-C}_4\text{H}_{10}$ and $\text{n-C}_5\text{H}_{12}$ gives values of 41.5, 43.5 and 44.5 for k_{22}^s/k_2 per secondary C—H bond at 480°C , respectively. From the ratio for $\text{i-C}_4\text{H}_{10}$, $k_{22}^t/k_2 = 160$ per tertiary C—H bond. A reasonable estimate of the ratio k_{22}/k_2 for any alkane at 480°C is thus given by eqn (vii)

$$k_{22}/k_2 = 7.0n_p + 43n_s + 160n_t. \quad (\text{vii})$$

Absolute values of k_{22} can be obtained by use of the value of $k_2 = 5.73 \times 10^6$ given above.

Surprisingly, no new measurements of k_{22} for hydrocarbons other than C_2H_6 have appeared⁴⁵ since our earlier paper.⁴⁶ Two types of study at lower temperatures were then available.

(a) Kazmi, Diefendorf and Le Roy⁴⁷ produced H atoms by dissociation of H_2 on a heated tungsten wire. Recent discussion³⁰ indicates the difficulty of determining the stoichiometry in such a system, though evidence for a ratio (H atoms consumed)/(RH consumed) of 6 for C_3H_8 has been given.⁴⁷

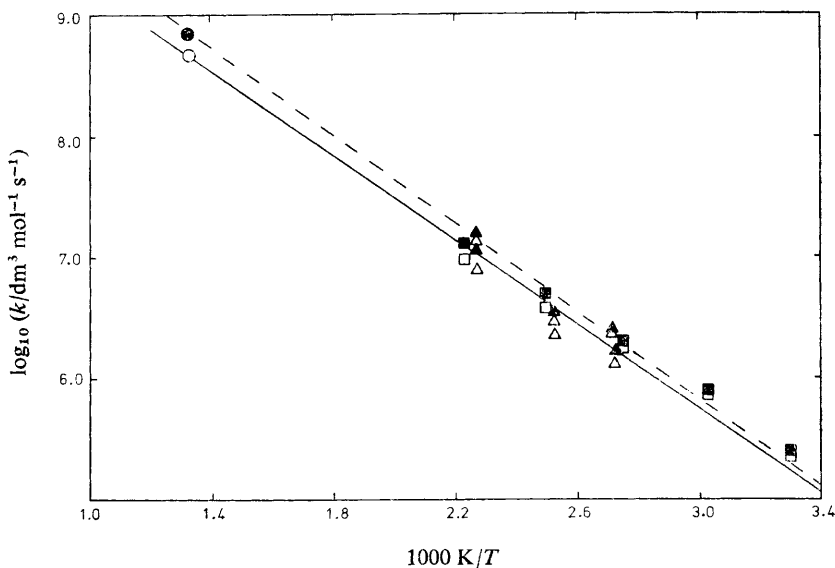


FIG. 4.—Variation with temperature of rate constant for $H + C_3H_8$.

	present work	Kazmi <i>et al.</i> ⁴⁷	Darwent and Roberts ⁴⁸
$k(\text{total})$ — — —	●	▲	■
k for s- CH_2 —	○	△	◻

(b) Darwent and Roberts⁴⁸ produced D atoms by the photolysis of D_2S , and determined the ratio $k(D + RH)/k(D + D_2S)$ over the temperature range 300–750 K. In earlier papers,^{49, 50} k_{22} was evaluated from their ratios using their ratio of $k(D + H_2)/k(D + D_2S)$ and Shavitt's⁵¹ evaluation of $k(D + H_2)$; it was assumed that $k(D + RH) = k(H + RH)$. If the reliability of the recent figure for $H + C_2H_6$ is accepted, a more direct evaluation from Darwent and Roberts' data may be made using their ratios for $k(D + C_2H_6)/k(D + D_2S)$ to eliminate $D + D_2S$, the only assumption being that $k(D + RH)/k(D + C_2H_6) = k(H + RH)/k(H + C_2H_6)$.

Fig. 4 shows the values for $H + C_3H_8$ obtained in this way from Darwent and Roberts' data, and from the revised treatment of Kazmi, Diefendorf and Le Roy.⁴⁷ The plot gives $A_{22p} = 1.93 \times 10^{11}$ and an overall activation energy $E_{22p} = 34.9$ kJ mol⁻¹, identical with the previously published value. The plot also shows the data for the secondary CH_2 group, obtained by subtracting the rate constant for C_2H_6 from that for C_3H_8 , on the assumption of bond additivity. The corresponding parameters are $E_{22p}^s = 33.4$ kJ mol⁻¹, $A_{22p}^s = 4.80 \times 10^{10}$ dm³ mol⁻¹ s⁻¹ per secondary C—H bond.

Combinations of Darwent and Roberts' data⁴⁸ for $n\text{-C}_4\text{H}_{10}$, treated as for C_3H_8 , with the present value at 480°C give $E_{22\text{nb}} = 34.1 \text{ kJ mol}^{-1}$, $A_{22\text{nb}} = 2.85 \times 10^{11}$ and $A_{22\text{nb}}^s = 2.00 \times 10^{11}$, or 5.0×10^{10} per secondary C—H bond, $E_{22\text{nb}}^s = 33.2 \text{ kJ mol}^{-1}$. Corresponding treatment for $i\text{-C}_4\text{H}_{10}$ gives $E_{22\text{ib}} = 27.1 \text{ kJ mol}^{-1}$, $E_{22\text{ib}}^t = 25.2 \text{ kJ mol}^{-1}$.

Unfortunately, the difference $(E_{22\text{e}} - E_{22\text{p}}^s) = 5.9 \text{ kJ mol}^{-1}$ is not consistent with the estimate of $E_{22\text{p}}^p - E_{22\text{p}}^s = 8.4 \pm 0.8 \text{ kJ mol}^{-1}$ obtained by Campbell, Strauss and

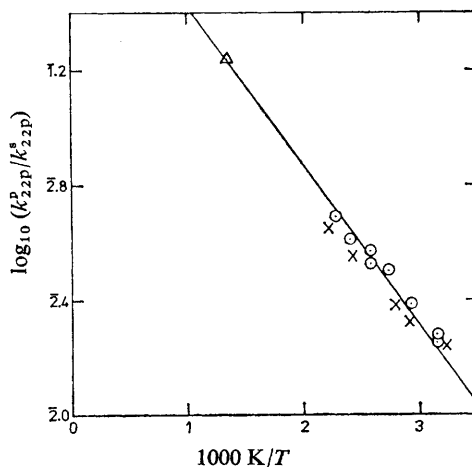


FIG. 5.—Plot of $\log(k_{22\text{p}}^p/k_{22\text{p}}^s)$ against $1/T$ for C_3H_8 . Δ Present work; \circ , Campbell *et al.*,⁵² low intensity static system; \times , Campbell *et al.*,⁵² high intensity circulating system.

Gunning⁵² by measurement of the yield of isomeric hexanes obtained by the attack of H atoms, produced by Hg-photosensitisation of H_2 , on C_3H_8 over the temperature range 300–450 K. If a value at 480°C is obtained by assuming that attack on the primary C—H bonds in C_3H_8 has the same value as for C_2H_6 , the activation energy difference (fig. 5) increases to 10.8 kJ mol^{-1} . If the data of Campbell, Strauss and Gunning are extrapolated to 480°C to obtain $k_{22\text{p}}^p/k_{22\text{p}}^s$, the resultant value of $k_{22\text{p}}^s$ reduces slightly the value of $E_{22\text{p}}^s$ obtained from fig. 3, so that the discrepancy remains.

TABLE 6.—ARRHENIUS PARAMETERS FOR $\text{H} + \text{RH}$

type of bond	using results of			
	Campbell <i>et al.</i> ⁵²		recommended	
	$E/\text{kJ mol}^{-1}$	A per C—H bond	$E/\text{kJ mol}^{-1}$	A per C—H bond
primary	39.2	2.2×10^{10}	39.2	2.2×10^{10}
secondary	29.6	2.7×10^{10}	33.3	4.9×10^{10}
tertiary	21.4	2.75×10^{10}	25.2	5.1×10^{10}

None of the estimates are free from criticism. Kazmi, Diefendorf and Le Roy⁴⁷ give the ratio $k_{22\text{nb}}/k_{22\text{p}}$, which decreases from 2.3 at 340 K to 1.6 at 450 K corresponding to $E_{22\text{p}} - E_{22\text{nb}} = 4.5 \text{ kJ mol}^{-1}$. In contrast, our measurements at 480°C give $k_{22\text{nb}}/k_{22\text{p}} = 1.74$ suggesting negligible variation with temperature over the range 340–753 K, as would be expected since secondary C—H abstraction dominates even at 753 K. Darwent⁵³ suggests that photolysis of H_2S gives “hot” H atoms, and there is also the assumption that the relative rates of abstraction by D and by H are the same for different hydrocarbons. The existence of “hot” atoms might

reduce the higher activation energy E_{22e} more than E_{22p}^s , so that the difference ($E_{22e} - E_{22p}^s$) is reduced.

Use of the results of Campbell, Gunning and Strauss⁵² gives a mean value of $(E_{22p}^p - E_{22p}^s) = 9.6 \pm 1.2 \text{ kJ mol}^{-1}$. Acceptance of this value implies that use of the Darwent and Roberts'⁴⁸ points gives E_{22}^s (for the CH_2 group both in C_3H_8 and $n\text{-C}_4\text{H}_{10}$) about 3.8 kJ mol^{-1} too high, and would suggest a reasonable estimate of $E_{22}^t = 25.2 - 3.8 = 21.4 \text{ kJ mol}^{-1}$. Use of the values of k_{22}^s, k_{22}^t at 480°C then gives the Arrhenius parameters shown in table 6. However, although it is difficult to suggest any reason why the value obtained by Campbell, Gunning and Strauss⁵² should be in error, the activation energy differences in table 6 are rather higher than would be expected from the differences in bond strength, and the earlier values for E_{22s}^s, E_{22}^t are thus preferred, with the corresponding A factor obtained from k_{22}^s, k_{22}^t at 480°C .

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