Rates of Reaction of Atomic Oxygen: II. Some C2 to C8 Alkanes

Rates of Reaction of Atomic Oxygen. II. Some C_2 to C_8 Alkanes[1]

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Rate constants have been measured for the reactions of atomic oxygen (O^3P) with eight straight and branched chain alkanes from 250 to 600°K, and for six other branched chain alkanes at 307°K. The reactions are interpreted on the basis of a hydrogen atom abstraction mechanism, and Arrhenius parameters are derived for abstraction of primary, secondary, and tertiary hydrogen atoms. The activation energies are found to be in the order primary > secondary > tertiary. For abstraction at secondary C–H bonds, the activation energy is observed to decrease with increasing molecular complexity of the alkane. A method for estimating the rate constants of other atomic oxygen–alkane reactions is given.

Introduction

In part I of this series[2] we reported rate data for the reactions of atomic oxygen with some chloro- and bromoalkanes from 336 to 622°K. These reactions were interpreted in terms of a hydrogen atom abstraction mechanism. It was suggested that the observed curvature in the Arrhenius plots for some of these reactions was due to the presence of different kinds of C–H bonds. However, the degree of curvature was not sufficiently great to lead to any firm conclusions.

In the case of the ordinary alkanes, the curvature is more apparent, and it is possible to interpret the Arrhenius plots in terms of abstraction at different C–H bond sites.

Experimental Section

The experimental method has been fully described,[2] and only a brief outline is given here.

The apparatus consists of a flow system coupled to a mass spectrometer. Atoms are generated by passing a mixture of several per cent oxygen in an argon carrier through a 2450-MHz electrodeless discharge. Alternately, atomic oxygen was generated by passing pure nitrogen through the discharge and titrating with nitric oxide to yield atomic oxygen *via* the very fast reaction $N + NO \rightarrow N_2 + O$.

The partial pressures of the reactants were monitored by means of the mass spectrometer. The atomic oxygen measurements were based on the m/e 16 peak at a nominal ionizing energy of 20eV. This was put on an absolute basis by titration with nitrogen dioxide or ethylene.

The ethylene titration was not used previously by us, but is necessary in the present case because of the breakdown in the nitrogen dioxide titration method at temperatures below about 273°K, as noted elsewhere[3] and confirmed here.

The use of ethylene as a titrating agent is based on the observation that with an excess of ethylene, the ratio of atomic oxygen consumed to ethylene consumed, $\Delta[O]/\Delta[C_2H_4]$, has a value of 2.0[4,5] (with an estimated uncertainty of ±0.2) independent of temperature over a wide range.[5] We have repeated the measurement of $\Delta[O]/\Delta[C_2H_4]$ at about 300°K and confirmed this value using the NO_2 titration to measure the oxygen atom concentration. At lower temperatures we find no evidence for a change in this ratio.

Rate constants are derived using the expression

$$k = \ln\left\{[A]_0/[A]_t\right\}/[O]_{0.5}t$$

where $[A]_0$ and $[A]_t$ are the concentrations of reactants at times zero and t, respectively, and $[O]_{0.5}$ is the oxygen atom concentration at the midpoint of the reactor (*i.e.*, at $0.5t$).

The basic assumptions involved in the rate measurements are: reactant is lost only through reaction with atomic oxygen, reactant is not reformed, and the oxygen atom concentration is unaltered by addition of reactant. The latter condition is met by keeping the oxygen atom concentration much larger than that of the second reactant. The atom concentration is determined by titrating the oxygen atoms along the length of the reactor and from a linear plot of concentration *vs.* reaction time reading off the value $[O]_{0.5}$.

To avoid problems associated with "background" in the mass spectrometer we have used ethane-1-d_1 for the ethane experiments and *n*-butane-1-d_1 for the high-temperature *n*-butane experiments.

For some of the low-temperature experiments the reactor was lined with a snug-fitting sheet of polytetrafluoroethylene. This is so indicated in the data tabulations.

Results

The data are given in Tables I–VIII and Figures 1–8.

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(2) J. T. Herron and R. E. Huie, *J. Phys. Chem.*, **73**, 1326 (1969).

(3) F. S. Klein and J. T. Herron, *J. Chem. Phys.*, **41**, 1285 (1964).

(4) J. T. Herron and R. D. Penzhorn, *J. Phys. Chem.*, **73**, 191 (1969).

(5) A. A. Westenberg and N. deHaas, Twelfth Symposium (International) on Combustion, The Combustion Institute, 1969, to appear.

Table I: Summary of Rate Measurements for the Reaction $O + n\text{-}C_4H_{10} \rightarrow OH + C_4H_9$

Temp, °K	Total pressure N m^{-2a} (1 Torr = 133.32 N m^{-2})	Velocity, cm sec^{-1}	Reactant concentration, mol cm^{-3}			$10^{-10} k$, cm^3 mol^{-1} sec^{-1}
			$10^{-11}(O)_{av}$	$10^{-13}(A)_0$	$10^{-13}(A)_t$	
255	219	528	12.1	432	413	0.414 (E)
276	329	631	10.1	583	492	0.635 (E)
276	252	594	19.1	935	891	1.18 (E)
276	303	620	22.4	886	825	1.25 (E)
307	252	679	21.6	969	874	2.21 (NE)
307	276	693	58.9	560	468	1.44 (NE)
307	229	654	34.9	627	535	1.59 (NE)
357	275	797	13.7	525	464	4.44 (NE)
357	284	791	12.1	886	574	6.31 (NE)
357	275	787	77.1	1190	1080	4.83 (NE)
386	295	1530	15.3	93.0	78.5	10.1
441	290	1720	16.4	47.0	32.5	24.2
513	291	2060	38.7	107.0	26.0	48.2
532	283	2180	36.0	628	114	63.6
595	307	3500	34.8	681	132	124
603	299	3530	36.6	405	81.9	112
607	293	3530	37.0	678	121	100

^{a} N m^{-2} = newtons per square meter.

Table II: Summary of Rate Measurements for the Reaction $O + n\text{-}C_5H_{12} \rightarrow OH + C_5H_{11}$

Temp, °K	Total pressure, N m^{-2} (1 Torr = 133.32 N m^{-2})	Velocity, cm sec^{-1}	Reactant concentration, mol cm^{-3}			$10^{-10} k$, cm^3 mol^{-1} sec^{-1}
			$10^{-11}(O)_{av}$	$10^{-13}(A)_0$	$10^{-13}(A)_t$	
255	219	528	31.8	66.3	57.0	1.53 (E)
255	228	513	30.8	82.0	73.3	1.22 (E)
258	216	533	37.0	78.2	63.4	1.32 (E)
276	263	589	14.7	56.1	50.8	2.38 (E)
276	272	584	19.0	56.8	50.4	2.43 (E)
276	227	684	28.1	55.3	48.3	2.06 (NET)
276	310	685	16.6	40.9	36.6	2.86 (ET)
307	248	646	21.1	43.9	35.1	4.72 (E)
307	223	633	13.7	79.4	69.9	4.02 (E)
307	254	727	21.5	64.6	51.6	4.57 (ET)
321	237	683	7.73	52.6	46.1	6.90 (E)
336	323	786	30.5	30.1	20.2	11.3
338	289	1350	14.9	60.0	50.4	9.46
357	250	742	9.19	40.3	33.3	11.1 (E)
386	295	1530	15.2	17.0	12.2	21.1
437	288	2520	9.74	20.0	15.4	43.0
437	283	2530	10.0	6.78	4.97	37.8
441	291	1720	14.7	11.2	6.42	43.2
508	291	2880	9.17	15.1	10.3	72.3
508	289	2870	7.15	8.53	5.32	116
593	289	3420	3.97	8.84	5.94	217
597	281	3540	4.90	9.17	5.79	197

In the tables, the symbols N, E, and T have the following meanings: N, oxygen atoms produced by means of the $N + NO \rightarrow N_2 + O$ reaction; E, oxygen atoms calibrated by titration with ethylene; T, reactor lined with polytetrafluoroethylene.

For most of the compounds we have examined, the Arrhenius plots are distinctly curved, although the degree of curvature is quite variable. At a given temperature the rate of reaction can be related to the numbers and kinds of C–H bonds in each compound. These general observations strongly favor a hydrogen atom abstraction mechanism for these reactions. If the abstraction mechanism is correct, then it should be possible to resolve the data into contributions due to reaction at primary, secondary, and tertiary C–H bonds and derive the relevant Arrhenius parameters.

The starting point for this procedure is the choice of a rate expression for abstraction at any primary C–H

Table III: Summary of Rate Measurements for the Reaction $O + neo\text{-}C_5H_{12} \rightarrow OH + C_5H_{11}$

Temp, °K	Total pressure, N m^{-2} (1 Torr = 133.32 N m^{-2})	Velocity, cm sec^{-1}	Reactant concentration, mol cm^{-3}			10^{-10} k, cm^3 mol^{-1} sec^{-1}
			$10^{-11}(O)_{av}$	$10^{-13}(A)_0$	$10^{-13}(A)_t$	
276	329	631	128	36.6	33.7	0.250 (E)
276	252	594	89.9	36.5	34.3	0.255 (E)
276	303	620	112	44.8	42.1	0.218 (E)
307	276	693	66.5	28.0	26.7	0.378 (NE)
307	385	719	40.7	11.9	11.6	0.294 (NE)
307	221	659	78.7	39.7	36.8	0.342 (NE)
307	229	654	95.9	34.1	31.5	0.322 (NE)
338	289	1350	16.1	152	148	1.48
357	275	797	15.4	92.4	89.3	1.09 (NE)
357	371	826	33.6	110	104	0.805 (NE)
357	284	791	60.5	25.9	22.4	1.14 (NE)
357	275	787	65.4	92.0	77.6	1.25 (NE)
386	295	1530	16.3	26.3	24.1	5.30
437	288	2520	10.5	89.7	84.9	8.29
437	283	2530	8.37	68.0	64.4	7.73
441	290	1720	2.25	27.5	23.8	9.03
508	291	2880	9.29	6.97	6.45	15.5
508	289	2870	7.31	59.9	55.3	19.5
593	289	3420	4.10	22.2	19.8	59.7
597	281	3540	4.93	29.5	26.2	52.6

Table IV: Summary of Rate Measurements for the Reaction $O + n\text{-}C_6H_{14} \rightarrow OH + C_6H_{13}$

Temp, °K	Total pressure, N m^{-2} (1 Torr = 133.32 N m^{-2})	Velocity, cm sec^{-1}	Reactant concentration, mol cm^{-3}			10^{-10} k, cm^3 mol^{-1} sec^{-1}
			$10^{-11}(O)_{av}$	$10^{-13}(A)_0$	$10^{-13}(A)_t$	
247	224	583	17.8	57.2	52.0	1.95 (ET)
255	219	528	30.6	47.5	37.9	2.36 (E)
255	228	522	27.9	57.5	47.4	2.37 (E)
258	216	533	33.6	36.3	24.5	2.47 (E)
276	263	589	13.3	48.6	42.7	3.86 (E)
276	272	584	18.2	40.3	34.2	3.53 (E)
276	227	684	23.6	42.9	35.9	3.16 (NET)
276	221	639	20.2	44.2	37.7	3.17 (ET)
276	310	685	16.2	49.0	41.9	4.15 (ET)
307	248	646	19.8	36.8	26.7	6.87 (E)
307	223	633	13.2	34.3	28.2	6.19 (E)
307	215	702	7.61	49.6	44.2	6.55 (ET)
307	254	727	21.5	22.4	15.7	7.50 (ET)
321	237	683	7.63	38.4	32.5	9.17 (E)
335	259	1490	39.6	31.5	20.8	14.6
336	323	786	31.7	11.7	6.07	17.5
338	289	1350	15.1	26.2	20.3	14.0
357	250	742	7.98	27.1	21.2	28.0 (E)
386	295	1530	15.2	13.3	8.05	31.8
437	288	2520	9.81	14.1	9.31	65.7
437	283	2530	9.78	8.44	5.69	64.5
441	291	1720	14.7	8.03	3.52	60.7
508	291	2880	9.10	11.8	6.80	107
508	289	2870	6.99	7.18	4.46	118
593	289	3420	4.07	3.57	1.98	317
597	281	3540	4.90	7.11	3.53	299

bond. For this quantity we have used the results for neopentane. The neopentane data, although having more scatter than we would wish (Figure 1), can be fitted to a straight line, leading to the Arrhenius parameters given in Table IX. The rate expression

for a single primary C–H bond is then given as $k_p = 0.49 \times 10^{12} \exp(-2920/T)$ cm^3 mol^{-1} sec^{-1}.

We now consider the data for the C_4 to C_8 normal alkanes which contain only primary and secondary C–H bonds. For each measured rate constant we have

Table V: Summary of Rate Measurements for the Reaction $O + C_6H_{14}$ (2,3-Dimethylbutane) $\rightarrow OH + C_6H_{13}$

Temp, °K	Total pressure, N m^{-2} (1 Torr = 133.32 N m^{-2})	Velocity, cm sec^{-1}	Reactant concentration, mol cm^{-3}			10^{-10} k, cm^3 mol^{-1} sec^{-1}
			10^{-11}(O)$_{av}$	$10^{-13}(A)_0$	$10^{-13}(A)_t$	
247	224	583	20.5	28.2	19.2	6.80 (E)
249	241	600	27.2	34.5	20.3	7.14 (ET)
249	237	590	21.8	29.6	21.3	5.48 (ET)
254	200	512	45.2	24.9	7.66	9.00 (E)
255	217	527	21.5	16.6	9.54	8.40 (E)
255	228	522	29.7	27.1	14.3	7.23 (E)
276	207	565	16.6	34.9	21.7	11.2 (E)
276	260	581	15.2	36.0	24.7	9.49 (E)
276	241	652	25.8	13.7	7.13	10.2 (E)
276	221	639	19.1	30.2	20.2	8.47 (ET)
276	310	685	18.8	14.4	9.22	10.0 (ET)
307	215	618	11.3	34.0	21.3	18.1 (E)
307	223	633	14.7	41.2	25.1	15.0 (E)
307	257	731	10.9	25.0	17.0	16.1 (ET)
307	215	702	11.0	18.5	13.7	12.0 (ET)
321	237	683	5.43	43.6	35.9	16.0 (E)
335	259	1490	38.9	26.0	13.1	24.7
336	323	786	30.9	18.3	5.76	32.1
338	289	1350	14.7	29.6	19.1	25.1
357	243	743	5.42	42.1	30.2	28.0 (E)
386	267	2450	49.8	5.97	1.86	47.0
386	295	1530	15.5	13.1	6.09	35.8
437	288	2520	9.78	13.2	8.54	71.9
437	283	2530	9.52	10.6	6.06	88.4
441	291	1720	14.8	11.0	4.11	73.5
508	291	2880	9.17	20.7	11.8	109
508	289	2870	7.15	8.09	4.14	165
593	289	3420	3.83	13.5	7.86	295
597	281	3540	4.85	17.2	10.3	230

Table VI: Summary of Rate Measurements for the Reaction $O + n\text{-}C_7H_{16} \rightarrow OH + C_7H_{15}$

Temp, °K	Total pressure, N m^{-2} (1 Torr = 133.32 N m^{-2})	Velocity, cm sec^{-1}	Reactant concentration, mol cm^{-3}			10^{-10} k, cm^3 mol^{-1} sec^{-1}
			10^{-11}(O)$_{av}$	$10^{-13}(A)_0$	$10^{-13}(A)_t$	
247	224	583	17.1	70.5	62.4	2.52 (ET)
249	241	600	26.3	16.3	12.9	3.23 (ET)
249	237	590	22.0	34.1	28.9	2.71 (ET)
255	219	528	26.5	33.5	22.4	5.25 (E)
255	217	527	20.4	39.2	30.8	3.85 (E)
255	228	522	27.2	22.6	14.9	5.01 (E)
276	263	589	12.8	28.1	23.6	5.26 (E)
276	272	584	17.4	25.5	19.7	5.80 (E)
276	227	684	25.3	25.6	19.9	4.30 (NET)
276	241	652	19.6	25.6	20.4	4.75 (ET)
276	221	639	16.8	53.2	43.8	4.60 (ET)
276	310	685	15.8	16.5	12.7	6.47 (ET)
307	248	646	19.9	10.0	5.95	11.2 (E)
307	223	633	11.8	35.4	27.9	8.97 (E)
307	215	702	7.35	34.6	29.1	10.4 (ET)
307	254	727	11.4	25.3	19.5	10.3 (ET)
321	237	683	7.43	18.1	14.3	12.7 (E)
335	259	1490	39.4	18.7	10.6	20.3
336	323	786	31.2	9.44	4.11	22.5
338	289	1350	14.9	26.6	19.8	16.6
357	250	742	8.52	14.6	10.1	21.6 (E)
386	295	1530	15.2	7.87	3.82	44.8
437	288	2520	9.52	10.3	6.56	79.6
437	283	2530	9.67	7.39	4.42	83.3
441	291	1720	14.8	4.06	1.57	69.6
508	291	2880	9.01	9.10	4.52	136
508	289	2870	6.99	5.75	2.85	181
593	289	3420	3.94	4.31	2.00	400
597	281	3540	4.93	4.85	2.06	363

Table VII: Summary of Rate Measurements for the Reaction $O + n\text{-}C_8H_{18} \rightarrow OH + C_8H_{17}$

Temp, °K	Total pressure, N m^{-2} (1 Torr = 133.32 N m^{-2})	Velocity, cm sec^{-1}	Reactant concentration, mol cm^{-3}			10^{-10} k, cm^3 mol^{-1} sec^{-1}
			$10^{-11}(O)_{av}$	$10^{-13}(A)_0$	$10^{-13}(A)_t$	
247	224	283	16.2	43.4	34.8	4.80 (ET)
254	200	512	40.2	25.2	7.66	10.2 (E)
255	219	528	25.9	29.5	13.7	9.37 (E)
255	217	527	17.4	29.1	13.5	6.29 (E)
255	228	522	22.7	69.1	42.6	6.70 (E)
276	207	565	16.0	33.9	19.8	12.6 (E)
276	263	589	11.8	47.3	38.5	6.52 (E)
276	260	581	15.8	29.9	21.1	8.52 (E)
276	272	584	17.7	14.5	9.6	8.96 (E)
276	238	682	21.6	78.1	69.9	2.13 (NET)
276	227	684	24.0	49.9	35.2	5.74 (NET)
276	241	652	19.4	29.9	22.4	5.05 (ET)
276	221	639	18.9	40.5	30.8	5.77 (ET)
276	310	685	16.2	43.4	34.8	8.12 (ET)
307	215	618	10.5	59.6	42.3	13.6 (E)
307	223	633	10.7	44.8	31.7	13.9 (E)
307	257	731	10.0	28.9	21.8	12.9 (ET)
307	215	702	6.88	49.9	42.0	10.9 (ET)
307	254	727	11.4	24.5	18.8	10.7 (ET)
321	257	680	7.08	26.8	19.9	17.1 (E)
336	323	786	29.8	17.1	6.71	27.3
338	289	1350	14.9	18.0	11.9	23.0
357	250	742	9.05	20.7	11.7	31.1 (E)
386	295	1530	14.7	14.3	6.78	50.2
437	288	2520	9.34	12.5	7.49	88.0
437	283	2530	9.37	9.55	5.71	88.2
441	291	1720	16.6	4.33	1.03	92.2
508	291	2880	8.47	14.7	6.88	159
508	289	2870	6.45	11.3	5.04	216
593	289	3420	3.62	7.97	4.50	328
597	281	3540	4.61	8.56	4.32	326

subtracted the contribution due to reaction at the six primary C–H bonds. These corrected rate constants were then fitted to a straight line which is represented in Figures 2 to 6 by the solid line. The derived Arrhenius parameters are given in Table IX and correspond to abstraction at secondary C–H bonds. In a similar manner, by considering the data for 2,3-dimethylbutane (Figure 7), we can arrive at the Arrhenius parameters characteristic of abstraction at tertiary C–H bonds. These are given in Table IX.

The broken lines in Figures 2 to 7 represent total rate constants, which are derived by summing the contributions due to the number of primary C–H bonds to those for the secondary or tertiary bonds. The rate constant for a primary C–H bond is that derived from neopentane and given above, while that for a secondary or tertiary is taken from Table IX. For example, the total rate constant for the n-pentane reaction is equal to $6[0.49 \times 10^{13} \exp(-2920/T)] + 6[1.34 \times 10^{13} \exp(-2320/T)]$ cm^3 mol^{-1} sec^{-1}.

In our treatment of the data we have excluded all data taken at temperatures less than 307°K. At these lower temperatures the data show a marked deviation from the predicted line. The most likely explanation

for this behavior, aside from "tunneling," is the occurrence of reactions on the walls of the reactor. There is some qualitative evidence to support this argument.

A limited number of experiments were carried out using a reactor of internal diameter of 1.5 cm rather than of 2.0 cm which was that used in obtaining the data reported in Tables I–VIII. The measured rate constants were found to coincide with those measured using the larger reactor at temperatures greater than about 300°K but were somewhat higher below 300°K.

We also note that the rate constants measured using a polytetrafluoroethylene-lined reactor were somewhat lower than those measured in an ordinary glass reactor. These effects are most noticeable for n-octane. In the case of n-octane we also observe a great increase in the scatter of the measured rate constants at the lowest temperatures used.

Table IX summarizes the results of our work along with results for CH_4 and C_2H_6 based on the data of Westenberg and deHaas.[6] The uncertainties attached to our measurements are the standard errors of the

(6) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, **46**, 490 (1967).

Table VIII: Summary of Rate Measurements for the Reactions of Atomic Oxygen with Ethane and Some Miscellaneous Alkanes

Temp, °K	Total pressure N m⁻² (1 Torr = 133.32 N m⁻²)	Velocity, cm sec⁻¹	$10^{-11}(O)_{av}$	$10^{-13}(A)_0$	$10^{-13}(A)_t$	$10^{-10} k$, cm³ mol⁻¹ sec⁻¹
				Reactant concentration, mol cm⁻³		
		$O + C_2H_5D \rightarrow OH + C_2H_4D$				
336	331	762	91.4	172	167	0.164
336	323	786	38.8	86.7	84.2	0.216
429	317	984	42.9	36.5	33.4	1.41
508	291	2880	9.70	99.1	96.3	5.05
595	307	3500	37.6	17.6	13.2	19.9
		$O + C_5H_{12}$ (Isopentane) $\rightarrow OH + C_5H_{11}$				
307	241	664	11.8	917	756	7.75
307	280	697	15.2	1214	886	8.53
307	193	605	14.8	1245	948	7.75
		$O + C_7H_{16}$ (2,2-Dimethylpentane) $\rightarrow OH + C_7H_{15}$				
307	241	664	10.5	12.7	11.1	6.71
307	280	697	15.8	21.4	17.6	5.96
307	198	605	14.8	17.7	14.0	6.69
		$O + C_7H_{16}$ (2,4-Dimethylpentane) $\rightarrow OH + C_7H_{15}$				
307	250	661	7.27	56.1	47.9	9.10
307	213	659	11.2	44.7	34.8	11.5
		$O + C_8H_{18}$ (2,2,4-Trimethylpentane) $\rightarrow OH + C_8H_{17}$				
307	250	661	5.78	110.0	98.7	6.05
307	213	659	9.9	38.4	32.9	8.08
		$O + C_8H_{18}$ (2,3,4-Trimethylpentane) $\rightarrow OH + C_8H_{17}$				
307	215	618	11.9	17.5	7.01	3.32 (E)
307	257	731	10.2	22.1	12.2	2.62 (ET)
		$O + C_8H_{18}$ (2,2,3,3-Tetramethylbutane) $\rightarrow OH + C_8H_{17}$				
307	276	693	60.3	10.7	9.43	0.964 (E)
307	385	719	40.7	33.0	30.9	0.708 (E)

Table IX: Arrhenius Parameters for Abstraction Reactions of Atomic Oxygen at Primary, Secondary, and Tertiary C–H Bonds and Total Rate Constants at 298 and 1000°K[a]

Reactant	Log A	$10^{-13} A$ (per C–H bond)	E/R	$10^{-10}k$ (298°K)	$10^{-12}k$ (1000°K)
				Total rate constant[c]	
		Primary			
CH_4[b]	13.34	0.55	4460	0.0007	0.25
C_2H_6[b]	13.60	0.68	3300	0.056	1.4
Neo-C_5H_{12}	13.77 ± 0.17	0.49	2920 ± 140	0.33	3.2
		Secondary			
n-C_4H_{10}	13.798 ± 0.089	1.57	2570 ± 80	1.3	6.4
n-C_5H_{12}	13.905 ± 0.090	1.34	2320 ± 80	3.5	9.6
n-C_6H_{14}	14.031 ± 0.083	1.34	2250 ± 70	5.6	13
n-C_7H_{16}	14.077 ± 0.079	1.20	2190 ± 70	7.7	15
n-C_8H_{18}	13.967 ± 0.053	0.77	2030 ± 50	10.1	13
		Tertiary			
2,3-Dimethyl-butane	13.494 ± 0.095	1.57	1650 ± 80	12	9.1

[a] This work except as noted. Units of A and k are cm³ mol⁻¹ sec⁻¹. Uncertainties for this work are standard errors of the reported values based on a least-squares treatment. [b] See ref 6. The Arrhenius parameters were recomputed by us using all the experimental data. They differ somewhat from those given in the original paper, $k(CH_4) = 1.7 \pm 0.2 \times 10^{13} \exp(-8700/RT)$ cm³ mol⁻¹ sec⁻¹ and $k(C_2H_6) = 1.8 \pm 0.2 \times 10^{13} \exp(-6100/RT)$ cm³ mol⁻¹ sec⁻¹. [c] See text.
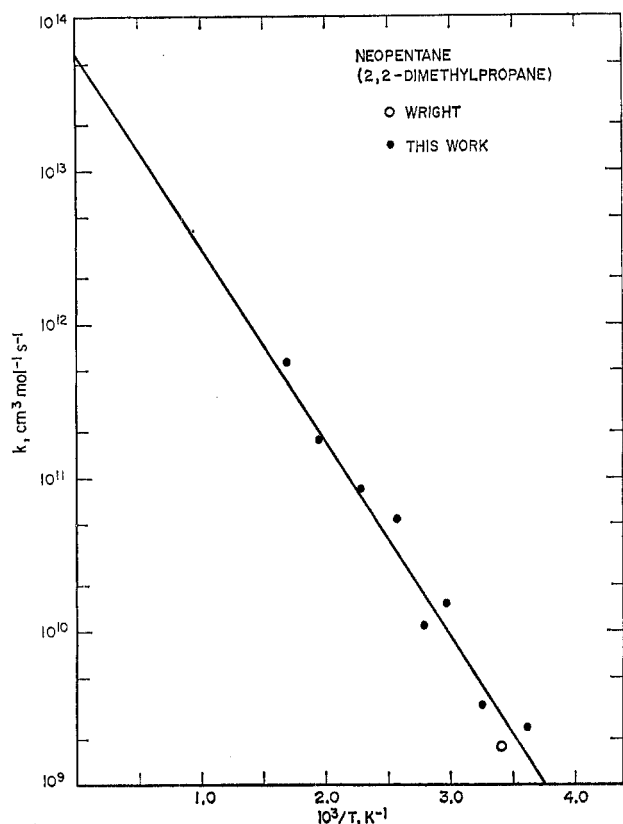
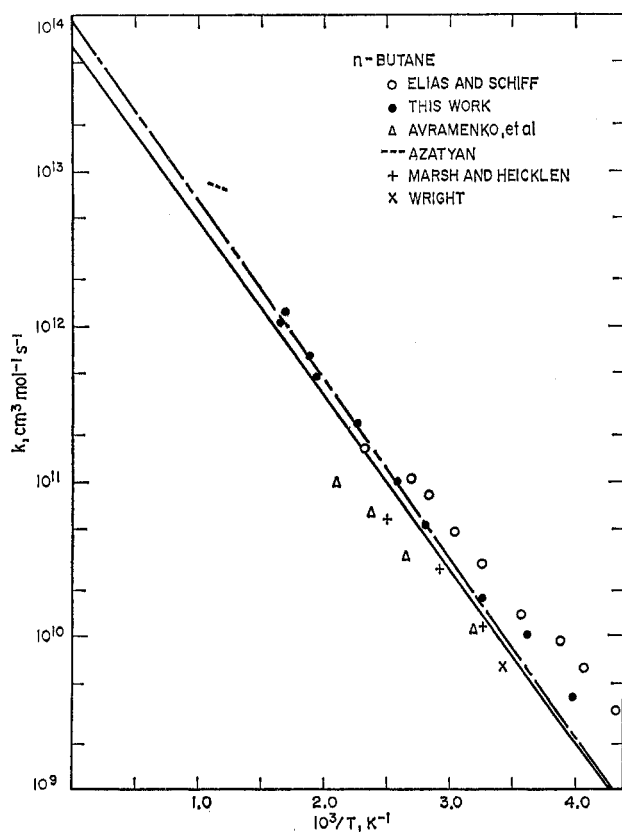Figure 1.   Arrhenius plot for the reaction of atomic oxygen with neopentane.

Figure 2. Arrhenius plots for the reaction of atomic oxygen with n-butane.   The solid line is the rate constant for abstraction at secondary C–H bonds; the dashed line is the total rate constant.
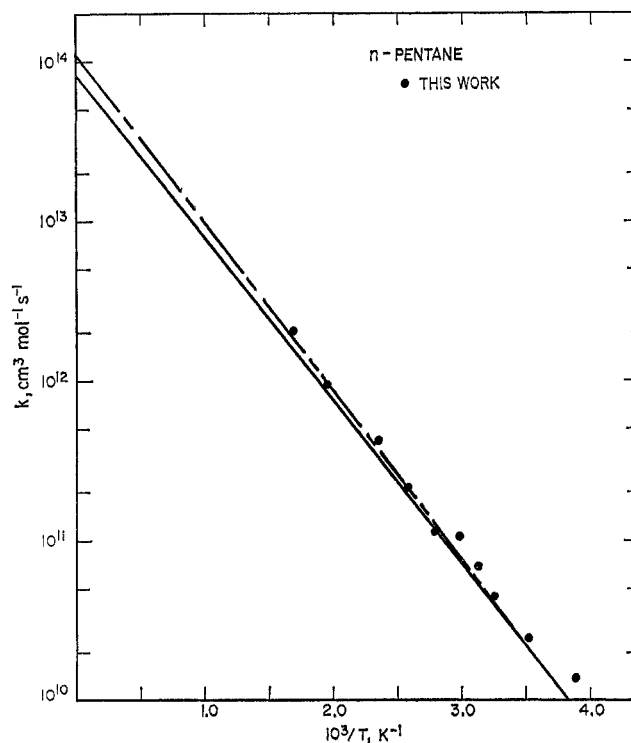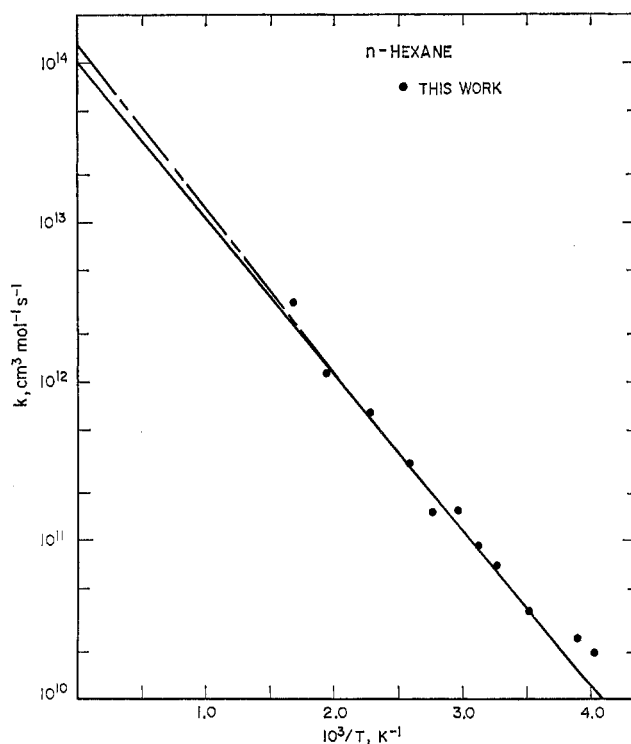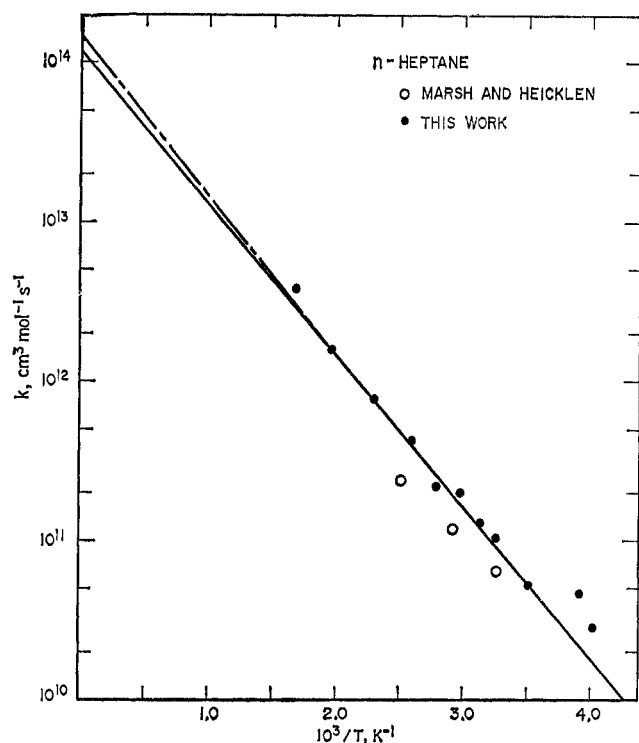

Figure 3.   Arrhenius plots for the reaction of atomic oxygen with n-pentane.   The solid line is the rate constant for abstraction at secondary C–H bonds; the dashed line is the total rate constant.

Figure 4. Arrhenius plots for the reaction of atomic oxygen with n-hexane.   The solid line is the rate constant for abstraction at secondary C–H bonds; the dashed line is the total rate constant.

Figure 5. Arrhenius plots for the reaction of atomic oxygen with n-heptane. The solid line is the rate constant for abstraction at secondary C–H bonds; the dashed line is the total rate constant.
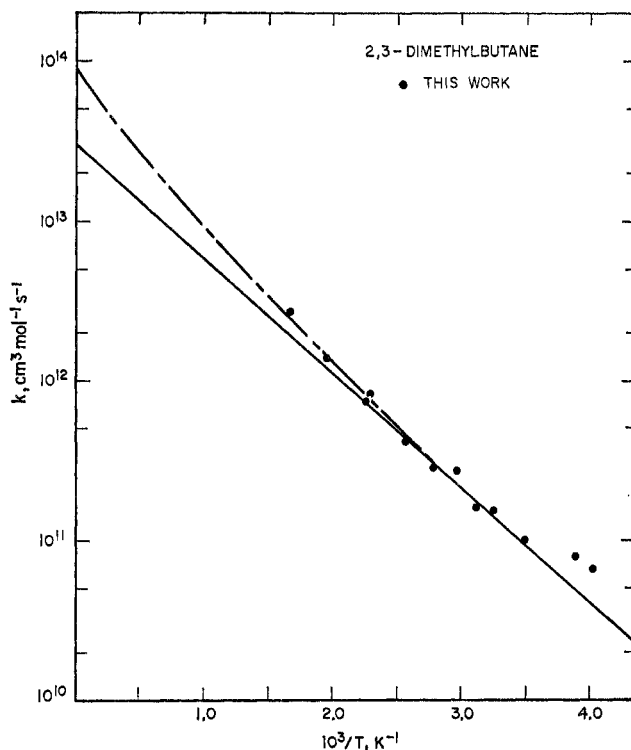

Figure 7. Arrhenius plots for the reaction of atomic oxygen with 2,3-dimethylbutane. The solid line is the rate constant for abstraction at tertiary C–H bonds; the dashed line is the total rate constant.
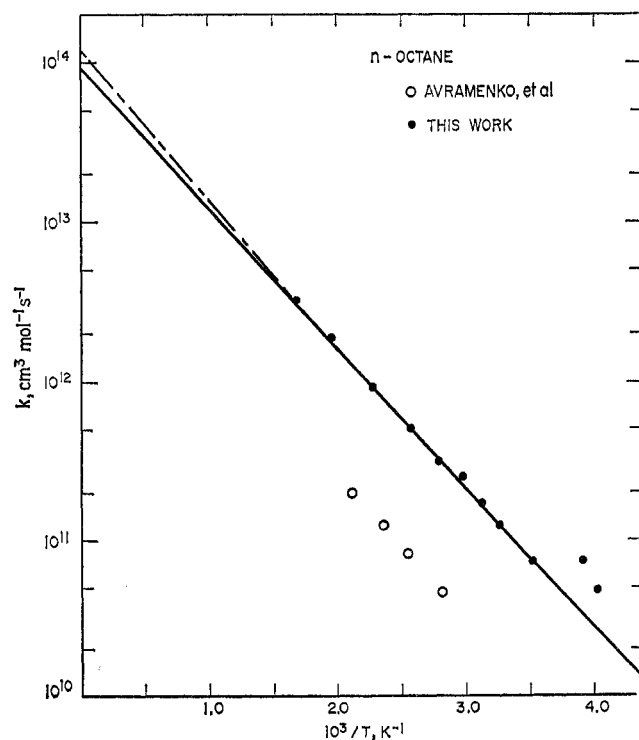

Figure 6. Arrhenius plots for the reaction of atomic oxygen with n-octane. The solid line is the rate constant for abstraction at secondary C–H bonds; the dashed line is the total rate constant.
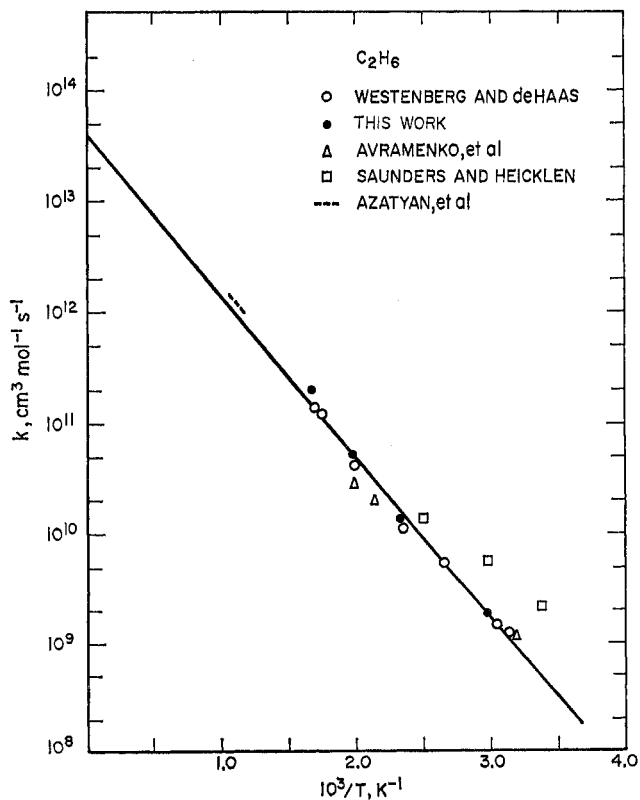

Figure 8. Arrhenius plot for the reaction of atomic oxygen with ethane.

reported values based on a least-squares treatment. The data will possess a higher degree of internal consistency than absolute accuracy, since unknown sources of error and bias will probably cancel out when making internal comparisons.

As we have noted previously,[2] the errors associated with the measurement of pressure, flow, temperature, and reactor geometry are small in comparison with the reported uncertainties.

The principal source of uncertainty, aside from spurious effects such as those arising as a result of heterogeneous reactions, is in the determination of ln $[A_0/A_t]$. When $[A_0/A_t]$ becomes very small (e.g., <1.10), the imprecision due to ln $[A_0/A_t]$ becomes large. This source of uncertainty is greatest for the slower reacting molecules such as neopentane.

An additional factor contributing to error in the $[A_0/A_t]$ measurement in the case of the n-butane measurements was the necessity of correcting the measured ion currents for background. Because of the size of this background signal it was also necessary to use much larger amounts of reactants than was desirable. This meant that the oxygen atom concentration was in fact reduced by reaction. Although we adjusted the quantity $[O]_{0.5}$ proportionately, the data on n-butane are probably the least reliable of our data on the normal alkanes.

Rate constants have been reported by other workers for ethane, n-butane, n-heptane, n-octane, and neopentane, with which we can compare our results.

In case of the ethane reaction only a limited number of measurements were made by us in view of the existence of the very precise and extensive data of Westenberg and deHaas.[6] The data are summarized in Figure 8. The line has been drawn to fit the data of Westenberg and deHaas. Our data all fall on this line. The significance of the agreement between our results and those of Westenberg and deHaas is that the experimental conditions of the latter are such that reactant is in excess of atomic oxygen whereas our conditions are just the opposite; i.e., atomic oxygen is in excess of the other reactant. Agreement over such a range of reactant concentrations is thus of considerable value in conforming the validity of the two methods. No account of the isotope effect has been made in this comparison.

The high-temperature measurements of Azatyan, et al.,[7] are derived from studies of flame inhibition and are of uncertain accuracy. However, they are compatible with the lower temperature results. Other data in Figure 8 are based on relative rate measurements[8] and on the analysis of final products.[9] The latter method is based on an arbitrary, and in our opinion, incorrect general reaction mechanism. The agreement in the case of ethane is probably fortuitous. For n-butane[10] and n-octane,[11] respectively, this method leads to values a factor of 3 to 10 lower than the

absolute values reported here (see Figures 2 and 6)

The only other reaction for which extensive data exist is n-butane (Figure 2), for which Elias and Schiff[12] have reported absolute rate measurements. We note that their data show the same low-temperature deviation as ours, but are displaced from our results by a factor of about 1.5. The differences are thus contained mostly in the preexponential factor rather than the activation energy. Because the two sets of data do not cover the same range of temperature, it is not possible to combine them to arrive at a "best" set of rate coefficients. However, in view of the suspect nature of all the low-temperature data we believe that our data, which extend to considerably higher temperatures, are the more reliable.

The high-temperature data of Azatyan, et al.,[13] are again compatable with the lower temperature work. The other sources of data for n-butane are relative rate measurements[14] and rates based on final product analysis.[10,15]

Wright[15] has reported a rate constant for the neopentane reaction at 293°K based on final product analysis which is compatable with our reported values (see Figure 1).

Discussion

Two general conclusions can be drawn from the data of Table IX. First, the activation energies are in the order primary > secondary > tertiary; second, for a particular bond type, the activation energy decreases as the molecule become more complex.

The order of activation energies primary > secondary > tertiary is the same as the order of the corresponding bond energies and is that normally observed for the abstraction of hydrogen atoms by other atomic and free-radical reactants.[16,17] However, the selectivity of attack at different bond sites is quite variable, ranging from fluorine atoms which are only slightly selective to bromine atoms which are strongly selective. Atomic oxygen is intermediate in selectivity, having approximate primary:secondary:tertiary relative rates at 307°K of 1.0:21:185.

(7) V. V. Azatyan, A. B. Nalbandyan, and Ts'ui Meng-Yuan, *Dokl. Akad. Nauk, SSSR*, **147**, 361 (1962).

(8) D. Saunders and J. Heicklen, *J. Phys. Chem.*, **70**, 1950 (1966).

(9) L. I. Avramenko, R. V. Kolesnikova, and N. L. Kuznetsova, *Izv. Akad. Nauk, SSSR, Otd. Khim. Nauk*, 620 (1963).

(10) L. I. Avramenko, R. V. Kolesnikova, and G. I. Savinova, *ibid.*, 976 (1963).

(11) L. I. Avramenko, R. V. Kolesnikova, and G. I. Savinova, *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 253 (1967).

(12) L. Elias and H. I. Schiff, *Can. J. Chem.*, **38**, 1657 (1960).

(13) V. V. Azatyan, *Arm. Khim. Zh.*, **20**, 577 (1967).

(14) G. Marsh and J. Heicklen, *J. Phys. Chem.*, **71**, 250 (1967).

(15) F. J. Wright, Tenth Symposium (International) on Combustion, The Combustion Institute, 1965, p 387.

(16) J. M. Tedder, *Quart. Rev.*, **14**, 336 (1960).

(17) A. F. Trotman-Dickenson, *Advan. Free Radical Chem.*, **1**, 1 (1965).

The second conclusion, that the activation energies vary with molecular complexity, has been shown by Knox and Nelson[18] to also hold for the abstraction of hydrogen atoms by chlorine atoms. Their data, given in Table X for comparison, indicate that the general

Table X: Data of Knox and Nelson on the Reactions RH + Cl → R + HCl[a]

Reactant	$10^{-13} A$ (per C–H bond)	E/R^b
	Primary	
CH_4	0.6 ± 0.1	1938 ± 30
C_2H_6	1.5 ± 0.2	523 ± 38
C_3H_8	1.7 ± 0.2	503 ± 38
$n\text{-}C_4H_{10}$	1.4 ± 0.2	398 ± 40
$i\text{-}C_4H_{10}$	1.3 ± 0.2	413 ± 40
Neo-C_4H_{10}	1.4 ± 0.2	463 ± 40
	Secondary	
C_3H_8	3.6 ± 0.5	342 ± 38
$n\text{-}C_4H_{10}$	2.2 ± 0.3	136 ± 40
$c\text{-}C_3H_6$	0.9 ± 0.1	2084 ± 40
$c\text{-}C_4H_8$	3.2 ± 0.4	4152 ± 43
	Tertiary	
$i\text{-}C_4H_{10}$	1.7 ± 0.3	10 ± 45

[a] See ref 18. Uncertainties are those given in the original paper, suitably converted as noted below. [b] Original data given in terms of E. To convert we have used $R = 1.987$ cal °K^{-1} mol^{-1}.

rate expression used by us for reaction at a primary bond based on the results for neopentane will probably be slightly in error when applied to the other alkanes. Fortunately, the degree of correction for a primary is small, so that an error in this quantity is not very significant.

The general trends in the activation energies of Table IX are better illustrated by fitting the data to an Evans–Polanyi expression of the form $E = \alpha[D(\text{C–H}) - C_1]$, where E is the activation energy, $D(\text{C–H})$ is the strength of the bond broken, and α and C_1 are empirical constants.[17]

In Figure 9 we plot E vs. $D(\text{C–H})$ for the alkanes, cycloalkanes, and acetaldehyde. Considering only the data on the noncyclic alkanes (i.e., that from Table IX) we derive values of the Evans–Polanyi coefficients

Table XI: Values α and C_1 for the Evans–Polanyi Expression $E = \alpha[D(\text{C–H}) - C_1]^a$

Radical	α	C_1
I	0.97	69.0
NF_2	1.1	76.1
Br	0.86	82.5
CH_3	0.49	74.3
O	0.36	82.0

[a] Data on atomic oxygen from this work. α and C_1 for other reactants from J. A. Kerr, Chem. Rev., **66**, 465 (1966).
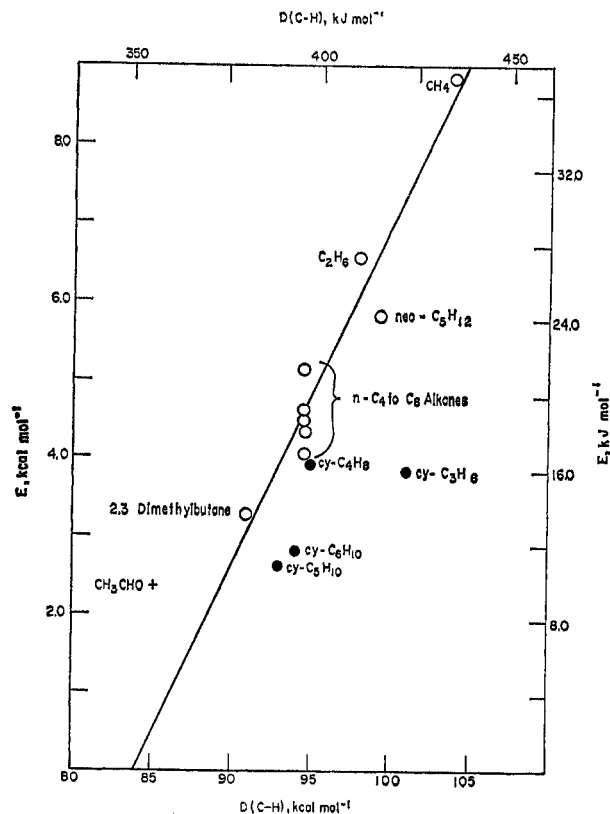

Figure 9. Activation energy as a function of the strength of the C–H bond broken. Activation energies for the alkanes from Table IX, for the cycloalkanes from W. K. Stuckey and J. Heicklen, J. Chem. Phys., **46**, 4843 (1967), and for acetaldehyde from R. D. Cadle and J. W. Powers, J. Phys. Chem, **71**, 1702 (1967). Bond dissociation energies from J. A. Kerr, Chem. Rev., **66**, 465 (1966).

α and C_1 given in Table XI. Values of these coefficients for other radicals are given for comparison.

The atomic oxygen reaction cannot be as well fitted by an Evans–Polanyi expression as can the other reactant species listed in Table XI. This is not only a consequence of the generally lower precision of flow-type experiments as compared with static-type experiments on which the other data of Table XI are based, but also to the fact that the range of activation energies found for abstraction of secondary hydrogens from the normal alkanes precludes an exact fit, assuming it is valid to use a common value for the secondary C–H bond energy.

A further consequence of the inconstancy of activation energy within bond type is that it is not possible to derive a set of exact rate parameters for individual primary, secondary, or tertiary bonds which could be used for estimating rate constants for other alkanes. Fortunately, the spread of values of rate coefficients is not so great that we cannot at least set up some approximate rate expressions.

(18) J. H. Knox and R. L. Nelson, Trans. Faraday Soc., **55**, 937 (1959).

On the basis of Table IX we suggest the following rate expressions (per C–H bond) for reaction at primary (p), secondary (s), and tertiary (t) bonds

$$k_p = 0.5 \times 10^{13} \exp(-2900/T)\text{cm}^3\ \text{mol}^{-1}\ \text{sec}^{-1}$$

$$k_s = 1.3 \times 10^{13} \exp(-2250/T)\text{cm}^3\ \text{mol}^{-1}\ \text{sec}^{-1}$$

$$k_t = 1.6 \times 10^{13} \exp(-1650/T)\text{cm}^3\ \text{mol}^{-1}\ \text{sec}^{-1}$$

Using these rate expressions, we have computed the rate constants given in Table XII for some miscellaneous alkanes and compared them with measured values taken from various sources.

In general, we find the predicted values to be within a factor of 2 or 3 of the measured values. The most striking exception is methane for which the ratio of predicted to measured values is 150. This is simply a consequence of the usual "uncharacteristic" behavior of the first member of a series and the manner in which the value of k_p was chosen. The other notable exception is isobutane, for which the difference between predicted and measured values is so great that it casts considerable doubt on the accuracy of the measured value. A more reasonable value would be about 3×10^{10} cm^3 mol^{-1} sec^{-1} at about 300°K.[19]

This method of estimating rate constants can be used at present only for the alkanes. In the case of the chloro- and bromoalkanes, although it is known that a halogen substituent has a strong inductive effect,[2] there is no detailed knowledge as to the relative importance of different reaction sites; therefore, it is not possible as yet to derive general rate parameters.

Table XII: Comparison of Predicted and Measured Rate Constants for the Reactions of Atomic Oxygen with Some Alkanes[a]

Reactant	Temp, °K	$10^{-10}k$, cm^3 mol^{-1} sec^{-1} Predicted	Measured	k (predicted) k (measured)
Methane	307	0.16	0.0011[b]	150
Ethane	307	0.24	0.085[b]	2.8
Propane	307	2.0	1.0[c]	2.0
n-Butane	307	3.7	1.6	2.3
Isobutane	293	6.0	0.36[d]	17
Isopentane	307	9.4	8.0	1.2
2,2-Dimethylpentane	307	3.9	6.5	0.60
2,4-Dimethylpentane	307	17.	10	1.7
2,2,4-Trimethylpentane	307	9.9	7.1[e]	1.4
2,3,4-Trimethylpentane	307	23.	30	0.77
3-Methylheptane	300	13.	6.5[f]	2.0
2,2,3,3-Tetramethylbutane	307	0.70	0.84	0.83
n-Octane	307	10.	12	0.83

[a] This work except as noted (experimental data from Tables I, VII, and VIII). [b] Computed from rate coefficients given in Table IX. [c] D. Saunders and J. Heicklen, *J. Phys. Chem.*, **70**, 1959 (1966). [d] Reference 15. [e] The data of Marsh and Heicklen[14] lead to a value of 4.6×10^{10} cm^3 mol^{-1} sec^{-1}, in fair agreement with out measurements. [f] H. W. Ford and N. Endow, *J. Chem. Phys.*, **27**, 1277 (1957).

(19) The principal peaks in the mass spectrum of isobutane correspond to major background peaks, so that we were unable to make a direct check on this rate constant.