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Rates of Reaction of Atomic Oxygen III. Spiropentane, Cyclopentane, Cyclohexane, and Cycloheptane

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Rate constants have been measured from 307 to 652 K for the reactions of atomic oxygen (O^3P) with spiropentane, cyclopentane, cyclohexane, and cycloheptane. The derived Arrhenius parameters are $k(\mathrm{sp}-C_5H_8)=10^{13.60\pm0.10}$ $\exp[(-2890\pm100)/T]$, $k(\mathrm{cy}-C_5H_{10})=10^{14.10\pm0.09}$ $\exp[(-2210\pm100)/T]$, $k(\mathrm{cy}-C_6H_{12})=10^{14.35\pm0.09}$ $\exp[(-2350\pm100)/T]$, and $(\mathrm{cy}-C_7H_{14})=10^{14.46\pm0.13}$ $\exp[(-2230\pm100)/T]$ all in units of $\mathrm{cm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$.

Key words: Cycloheptane; cyclohexane; cyclopentane; oxygen; rate constants; spiropentane.

1. Introduction

In the previous papers in this series [1, 2] [1] Arrhenius parameters for the reactions of atomic oxygen (O^3P) with some alkanes and haloalkanes were reported. The results were interpreted in terms of a hydrogen atom abstraction mechanism, and the reaction rates were found to be directly related to the number and types of C–H bonds. In the present paper this work is extended to the reactions of atomic oxygen with some cycloalkanes.

2. Experimental Section

The apparatus, which has been described previously [1], consists of a discharge-flow system coupled to a mass spectrometer. Atomic oxygen was produced by passing a flow of argon containing a few percent molecular oxygen through a microwave discharge. Reactant gas was added through a movable inlet downstream from the discharge. The distance between the discharge and the reactant inlet was sufficient to allow for the quenching of any oxygen atoms in higher electronic states. The reactor was a 20 mm in diam borosilicate glass tube which could be heated by means of a four-section resistance heater or by circulating fluid through a jacket surrounding the reactor. Temperature was measured with a Pt-Pt-10 percent Rd thermocouple. The uncertainty due to thermal gradients and the measurement of emf was about 3°.

The contents of the reactor were continuously sampled through an orifice at the base of the reactor, located directly over the ionization chamber of the mass spectrometer.

In these experiments the ratio of the partial pressures of the cycloalkane at times zero and t (i.e., the time required for the gas stream to flow from the reactant inlet to the sampling orifice) was determined as the ratio of the ion currents at the appropriate mass with the discharge turned off and on. The atomic oxygen partial pressure was followed at m/e 16 at about 20 eV ionizing energy (below the appearance potential of O^+ ions from O_2), and the absolute value of its partial pressure determined by titration with nitrogen dioxide.

Rate measurements were performed with atomic oxygen in considerable excess and the extent of reaction kept small. Under these conditions the decay of the cycloalkane would be due solely to reaction with atomic oxygen. Further since at most only 10 percent of the atomic oxygen is consumed, the measured rate is not dependent on the details of atomic oxygen loss.

For the bimolecular reaction

$$O+A\rightarrow \text{Products}$$

the integrated rate expression is $k=\{\ln[A]_0/[A]_t\}/\int_0^t[0]\,dt$ where $[A]_0$ and $[A]_t$ are the concentrations of cycloalkane at times zero and t respectively, and [0] is the concentration of atomic oxygen. For the case in which the loss of atomic oxygen is small, the integral may be replaced by the average value of the oxygen atom concentration times the overall reaction time.

The assumptions underlying this rate expression have been discussed more fully previously [1]. Principally they are that the reactant A is lost only by reaction with atomic oxygen, and is not reformed in

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[1] Figures in brackets indicate the literature references at the end of this paper.

subsequent reactions. These assumptions are satisfied by measuring the rate constants under conditions of excess atomic oxygen and low conversion of reactants.

However, this means that the value of the logarithm of the ratio $[A]_o/[A]_t$ is small and very sensitive to uncertainties in the measurement of ion currents. This is reflected in the scatter of the experimental data.

3. Results and Discussion

The experimental data and computed rate constants are given in tables 1–4. Velocity refers to linear flow velocity in the reactor and distance is that from the inlet to the mass spectrometer leak. Arrhenius parameters for the reactions studied were derived from plots of log k versus $1/T$ (figures 1 and 2) and are presented in table 5 along with derived rate constants at 298 and 1000 K. The reported uncertainties are standard errors based on a linear least squares treatment of the data.

In studying the reactions of atomic oxygen with the alkanes, we observed [2] that the Arrhenius plots were curved. This was interpreted as being due to the different rates of abstraction at different C–H bond sites. Consistent with this interpretation we find that the data on the cycloalkanes which have only one type of C–H bond are best fitted by a straight line.

Only a limited amount of data is available with which to compare our results. Stuckey and Heicklen [3] have studied the cyclopentane and cyclohexane reactions

TABLE 1. *Summary of rate measurements for the reaction* $O + sp-C_5H_8 \rightarrow OH + C_5H_7$

Temp. K	Total pressure Nm^{-2a}	Distance cm	Velocity cm s^{-1}	Reactant concentration mol cm^{-3}			10^{-10} k, cm^3 mol^{-1} s^{-1}
				$10^{11}(O)_{av}$	$10^{13}(A)_0$	$10^{13}(A)_t$	
337	282	14.4	730	10.9	11.2	9.81	0.623
339	299	14.2	750	40.8	18.1	16.7	1.01
339	299	14.2	750	45.2	18.0	16.4	1.01
339	288	14.2	740	52.2	16.3	15.1	0.792
339	304	14.0	470	46.5	18.7	15.2	0.987
339	304	14.0	470	28.9	59.8	52.3	0.614
416	318	14.3	930	50.1	10.9	8.14	3.77
417	206	13.1	1650	23.6	13.8	12.7	4.47
418	265	13.8	900	19.3	41.0	37.9	2.66
473	206	14.0	1920	9.99	10.9	9.99	11.8
480	179	14.3	1860	12.3	13.4	12.4	8.00
548	215	13.1	2235	17.9	73.8	59.8	20.3
553	272	14.7	2420	8.30	9.97	8.98	20.7
564	300	14.0	1270	4.31	11.7	10.8	16.1
647	187	15.0	3250	5.98	6.74	5.78	54.4
651	288	13.6	2850	7.26	6.97	5.76	54.8
652	182	15.0	3150	3.23	8.23	7.58	53.5

[a] 1 Torr = 133.32 Nm^{-2}.

TABLE 2. *Summary of rate measurements for the reaction* $O + cy-C_5H_{10} \rightarrow OH + C_5H_9$

Temp. K	Total pressure Nm^{-2}	Distance cm	Velocity cm s^{-1}	Reactant concentration mol cm^{-3}			10^{-10} k, cm^3 mol^{-1} s^{-1}
				$10^{11}(O)_{av}$	$10^{13}(A)_0$	$10^{13}(A)_t$	
307	182	16.0	1060	8.48	5.01	4.33	12.2
307	170	16.0	1050	10.9	5.10	4.41	9.87
331	203	13.6	1370	8.40	11.2	9.67	17.8
339	223	14.0	1440	9.29	12.4	10.7	14.9
339	410	13.9	770	4.96	12.7	11.1	15.0
415	345	13.3	940	5.70	11.4	8.96	57.0
418	198	13.6	1675	2.29	13.5	12.1	66.4
419	264	13.8	890	1.53	19.0	16.9	50.1
479	179	14.3	1860	5.06	4.82	3.13	106
493	264	14.0	2160	4.61	3.61	2.25	159
548	215	13.0	2235	2.05	10.4	7.77	240
557	205	15.0	2210	0.931	3.94	3.20	336
564	217	14.0	1680	2.22	5.16	3.47	213
631	218	13.1	3410	0.781	10.2	9.36	275
647	187	15.0	3270	0.793	4.93	4.04	541
652	182	15.0	3150	2.91	4.25	2.42	407

TABLE 3. *Summary of rate measurements for the reaction* $O + cy-C_6H_{12} \rightarrow OH + C_6H_{11}$

Temp. K	Total pressure Nm^{-2}	Distance cm	Velocity $cm\ s^{-1}$	Reactant concentration $mol\ cm^{-3}$			$10^{-10}\ k$, $cm^3\ mol^{-1}\ s^{-1}$
				$10^{11}(O)_{av}$	$10^{13}(A)_0$	$10^{13}(A)_t$	
307	210	16.0	590	20.5	5.38	2.74	14.2
307	225	16.0	610	14.0	9.55	6.11	13.7
307	170	16.0	1050	8.87	2.29	2.03	10.0
331	203	13.6	1370	7.50	9.91	8.47	21.2
339	410	13.9	770	4.54	11.0	9.59	17.1
339	223	14.0	1440	8.24	7.28	6.29	18.7
415	345	13.3	940	6.14	5.94	4.45	61.4
418	198	13.6	1675	1.90	10.4	9.25	75.3
419	264	13.8	890	1.73	7.19	6.16	57.7
474	179	14.3	1860	4.90	2.51	1.47	134
493	264	14.0	2160	4.32	3.19	1.95	174
557	205	15.0	2210	0.781	2.58	2.66	428
564	217	14.0	1680	2.07	1.52	0.83	352
631	218	13.1	3410	0.597	4.71	4.08	623
647	187	15.0	3270	0.678	3.47	2.71	774
652	182	15.0	3150	2.82	1.42	0.70	533

TABLE 4. *Summary of rate measurements for the reaction* $O + cy-C_7H_{14} \rightarrow OH + C_7H_{13}$

Temp. K	Total pressure Nm^{-2}	Distance cm	Velocity $cm\ s^{-1}$	Reactant concentration $mol\ cm^{-3}$			$10^{-10}\ k$, $cm^3\ mol^{-1}\ s^{-1}$
				$10^{11}(O)_{av}$	$10^{13}(A)_0$	$10^{13}(A)_t$	
331	203	13.6	1370	6.96	8.54	6.03	48.8
339	410	14.0	770	4.13	12.8	9.73	36.8
339	223	13.9	1440	7.78	20.7	15.3	38.3
418	198	13.6	1675	1.68	13.8	11.6	137
419	264	13.8	890	1.62	15.3	11.2	127
474	175	14.3	1860	4.70	6.85	3.52	180
493	264	14.0	2160	4.01	10.0	5.40	235
548	215	13.0	2235	1.82	7.84	4.62	486
557	205	15.0	2210	0.674	3.43	2.36	805
564	217	14.0	1680	1.90	5.95	3.11	411
631	218	13.1	3140	0.434	6.24	5.23	1010
647	187	15.0	3270	0.624	6.47	4.52	1240
652	182	15.0	3150	2.54	4.54	1.68	829

using the mercury photosensitized decomposition of nitrous oxide as their oxygen atom source. The rate constants were measured relative to that of hexafluoropropene which in turn was measured relative to 1-butene for which absolute values exist in the literature. Considering the limited precision of the data, and the amount of manipulation required to obtain the rate constants, the agreement between their rate constants and ours is reasonably good particularly near room temperature. The Arrhenius parameters differ considerably more. Because of the absolute nature of our measurements and the much greater temperature range employed we believe the results given here are to be preferred.

The only other data available is that of Avramenko et al. [4] who studied the cyclohexane reaction using a method based on the analysis of the final products of the reaction in a discharge-flow experiment and the imposition of an arbitrary and in our opinion incorrect reaction mechanism. This work is discussed more fully by Kaufman [5], and will not be considered further here.

The pre-exponential factors per C–H bond reported here for the C_5 to C_7 alkanes, i.e., $(1–2) \times 10^{13}$ cm^3 mol^{-1} s^{-1} are essentially the same as those found previously for the secondary C–H bonds in the normal alkanes [2]. Furthermore the activation energies for the cycloalkanes fit the same Evans-Polanyi expression

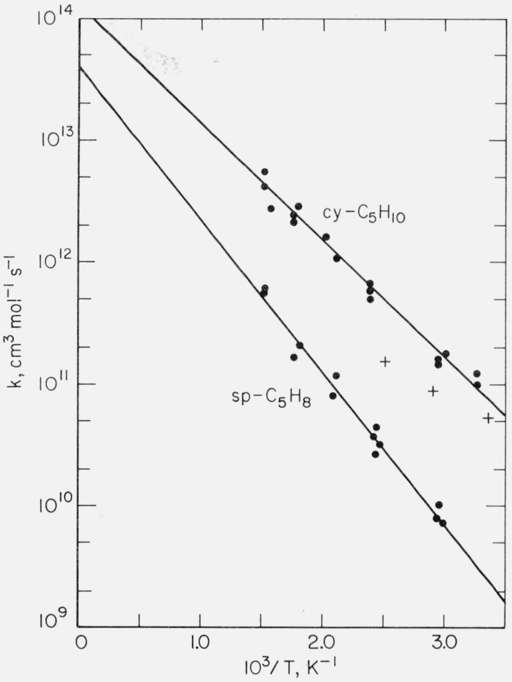

FIGURE 1. *Arrhenius plots for the reactions of atomic oxygen with spiropentane and cyclopentane.*

● This work; + Stuckey and Heicklen, Ref. [3].

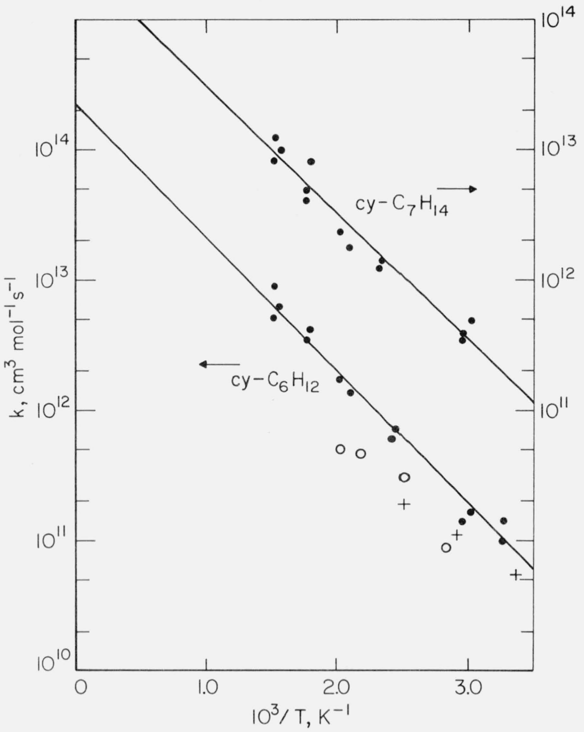

FIGURE 2. *Arrhenius plots for the reactions of atomic oxygen with cyclohexane and cycloheptane.*

● This work; + Stuckey and Heicklen, Ref. [3]; ○ Avramenko, et al., Ref. [4].

TABLE 5. *Arrhenius parameters and rate constants at 298 and 1000 K for the reactions of atomic oxygen with some cycloalkanes* [a]

Reactant	Log *A*	10^{-13} A (per C–H bond)	*E/R*	10^{-10} k(298 K)	10^{-12} *k*(1000 K)
Cy – C_3H_6 [b]	11.49		1900		
Cy – C_4H_8 [b]	12.79		2000		
Sp – C_5H_8	13.60 ± 0.10	0.50	2890 ± 100	0.25	2.2
Cy – C_5H_{10} [b]	12.68		1300		
Cy – C_5H_{10}	14.10 ± 0.09	1.25	2210 ± 100	7.5	14
Cy – C_6H_{12} [b]	12.88		1400		
Cy – C_6H_{12} [c]	13.73		2260		
Cy – C_6H_{12}	14.35 ± 0.09	1.87	2350 ± 100	8.3	21
Cy – C_7H_{14}	14.46 ± 0.13	2.06	2230 ± 140	16	31

[a] This work except as noted. Units of *A* and *k* are cm^3 mol^{-1} s^{-1}. Uncertainties are standard errors of the reported values based on a least-squares treatment.
[b] See Ref. 3.
[c] See Ref. 4.

derived earlier for the alkanes. Thus, the present results are consistent with and support the hydrogen atom abstraction mechanism proposed previously [1, 2].

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4. References

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