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Temperature Dependence of the Relative Rate Constants for the Reaction of O(^{3}P) Atoms with Selected Olefins, Monoterpenes, and Unsaturated Aldehydes

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Abstract: Using a competitive technique, rate constants for the gas phase reactions of O(^{3}P) atoms with selected monoterpenes, unsaturated aldehydes, and olefins have been determined relative to that for the reaction of O(^{3}P) atoms with cyclopentene over the temperature range 296–423 K. The Arrhenius expressions obtained, relative to cyclopentene as unity, when placed on an absolute basis using k(propylene) = $2.4 \times 10^9 e^{-76/RT}$ l. mol^{-1} sec^{-1} derived from the literature, were (l. mol^{-1} sec^{-1}): cyclopentene, $5.6 \times 10^9 e^{(430\pm80)/RT}$; α-pinene, $7.5 \times 10^{10} e^{-(910\pm140)/RT}$; β-pinene, $6.0 \times 10^{10} e^{-(820\pm140)/RT}$; *d*-limonene, $1.1 \times 10^{11} e^{-(300\pm150)/RT}$; 1-methylcyclohexene, $5.3 \times 10^9 e^{(1330\pm220)/RT}$; 1,3-cyclohexadiene, $5.1 \times 10^9 e^{(1320\pm180)/RT}$; acrolein, $1.4 \times 10^{10} e^{-(2400\pm270)/RT}$; crotonaldehyde, $1.5 \times 10^{10} e^{-(1980\pm130)/RT}$. The rate constants for acrolein and crotonaldehyde are compared and discussed with existing literature values.

Although there has been a large amount of reliable rate constant and product data reported in the literature for the reaction of O(^{3}P) atoms with alkenes and alkanes, which have been reviewed by Cvetanovic[1] and by Herron and Huie,[2] there are little data available for the reaction of O(^{3}P) atoms with unsaturated aldehydes and the naturally occurring monoterpene hydrocarbons.

These compounds are not only of interest from the fundamental grounds of structure and reactivity, but also because of their possible significance in the chemistry of polluted atmospheres, as pointed out in our previous study,[3] which reported the room temperature rate constants for the reaction of O(^{3}P) atoms with several monoterpenes, unsaturated aldehydes, and alkenes using a competitive technique. In this work we have extended these measurements to elevated temperatures (296–423 K) in order to obtain the Arrhenius parameters. Propylene was again included in the compounds studied as its absolute rate constant is reliably known[4-8] over the temperature range used in this work.

Experimental Section

The experimental apparatus and technique used have been described previously,[3] and hence only a brief summary will be given here. Ground state oxygen O(^{3}P) atoms were generated by the mercury photosensitization of N_2O in a circulating system of 1043 cm^3 volume. The reaction cell and circulating system was enclosed by a furnace whose temperature could be held constant to better than ±1 K over the temperature range 296–423 K.

Samples (5 cm^3) were periodically removed for analysis using a Carle gas sampling valve and split into two fractions. N_2 from the N_2O photosensitization was measured on a 5 ft × 0.25 in. Linde Molecular Sieve 13X column at 296 ± 2 K by a thermal conductivity detector, while C_2H_4 from the reaction of O(^{3}P) atoms with cyclopentene was analyzed on a 6 ft × ⅛ in. Poropak Q column at 296 ± 2 K by a flame ionization detector. Retention times and relative responses were periodically monitored using a calibrated mixture of N_2 in C_2H_4. In all cases, the N_2 yield served as an internal actinometer for the amount of O(^{3}P) atoms produced during the reaction.

As reported previously,[3] in all cases, reactant purities were ≥98% and were further purified by thorough degassing at 196 or 77 K and bulb-to-bulb distillation in vacuum.

Results

Relative rate constants were determined using the technique developed and used by Cvetanovic and coworkers.[1,9,10] From the reaction scheme:

$$\mathrm{O}(^3\mathrm{P}) + \text{cyclopentene} \rightarrow \alpha(\mathrm{C_2H_4} + \mathrm{CH_2{=}CHCHO}) + \text{other products}^{11} \qquad \text{(1CP)}$$

$$\mathrm{O}(^3\mathrm{P}) + \text{reactant A} \rightarrow \text{products} \qquad \text{(1A)}$$

with rate constants k_1^{CP} and k_1^{A}, respectively, then

$$\frac{(\mathrm{C_2H_4/N_2})^{\mathrm{A}=0}}{(\mathrm{C_2H_4/N_2})^{\mathrm{A}}} = 1 + \frac{k_1^{\mathrm{A}}[\mathrm{A}]}{k_1^{\mathrm{CP}}[\mathrm{CP}]} \qquad \text{(I)}$$

where $(\mathrm{C_2H_4/N_2})^{\mathrm{A}=0}$, $(\mathrm{C_2H_4/N_2})^{\mathrm{A}}$ are the C_2H_4/N_2 yield ratios in the absence and presence of reactant A, respectively. In all cases, experiments were carried out in the absence of cyclopentene to check that ethylene was not pro-

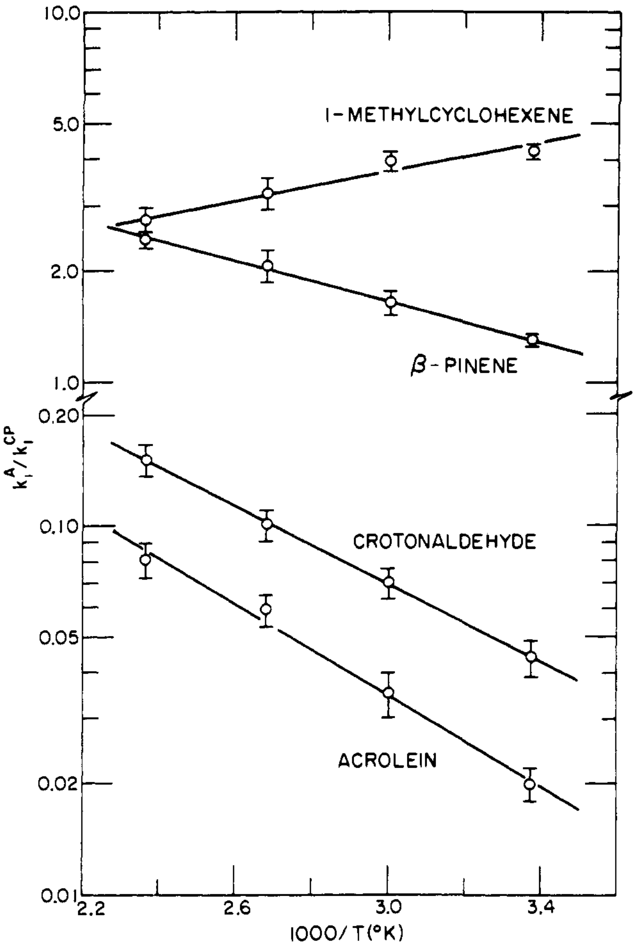

Figure 1. Arrhenius plots of k_1^A/k_1^{CP} against $1000/T$ for the reaction of O(^{3}P) atoms with acrolein, crotonaldehyde, β-pinene, and 1-methylcyclohexene.

duced from the reaction of O(^{3}P) atoms with reactant A. Only for acrolein was any ethylene production observed, but this was calculated to cause less than 2% error in the determination of the relative rate constants.

The C_2H_4/N_2 ratio for the reaction of O(^{3}P) atoms with cyclopentene was determined before and after every rate determination and was observed to be constant to better than ±5% at any given temperature. This ratio was determined to be 0.23 ± 0.03 over the pressure range 200-500 Torr at temperatures from 296 to 423 K, in good agreement with the work of Cvetanovic, Ring, and Doyle.[11]

Relative rate constants k_1^A/k_1^{CP} were determined as described previously[3] and are plotted in Arrhenius form in Figures 1 and 2 and given in Table I. The relative Arrhenius parameters

$$\frac{k_1^A}{k_1^{CP}} = \frac{A^A}{A^{CP}} e^{-(E^A - E^{CP})/RT}$$

obtained by least-squares analysis are given in Table II, along with the absolute Arrhenius parameters obtained by using $k_1(\text{propylene}) = 2.4 \times 10^9 e^{-76/RT}$ l. mol^{-1} sec^{-1}, ($k_1(\text{propylene}) = 2.10 \times 10^9$ l. mol^{-1} sec^{-1} at 298 K), derived from the recent literature rate constant data.[4-8]

Discussion

In all cases, experiments were carried out under conditions of low conversion where secondary reactions of O(^{3}P) atoms with the products should have been negligible.[3] Simi-

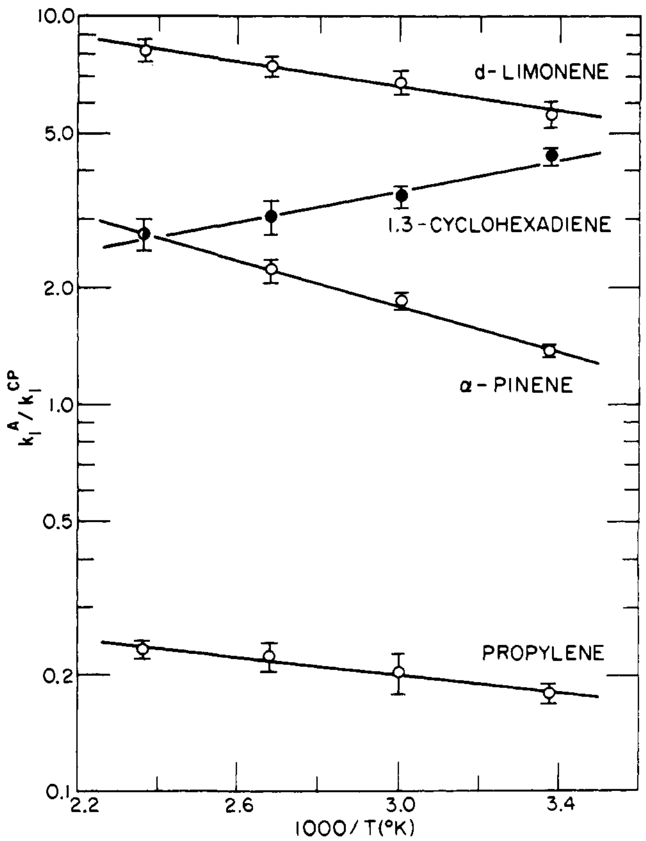

Figure 2. Arrhenius plots of k_1^A/k_1^{CP} against $1000/T$ for the reaction of O(^{3}P) atoms with propylene, α-pinene, 1,3-cyclohexadiene, and *d*-limonene.

Table I. Relative Rate Constants k_1^A/k_1^{CP} for the Reaction of O(^{3}P) Atoms[a]

Reactant A	T, K	k_1^A/k_1^{CP}
Propylene	296 ± 2	0.181 ± 0.010
	333 ± 1	0.203 ± 0.026
	373 ± 1	0.225 ± 0.019
	423 ± 1	0.231 ± 0.012
α-Pinene	296 ± 2	1.38 ± 0.05
	333 ± 1	1.84 ± 0.09
	373 ± 1	2.22 ± 0.15
	423 ± 1	2.73 ± 0.27
β-Pinene	296 ± 2	1.30 ± 0.05
	333 ± 1	1.64 ± 0.11
	373 ± 1	2.07 ± 0.20
	423 ± 1	2.41 ± 0.12
d-Limonene	296 ± 2	5.61 ± 0.45
	333 ± 1	6.74 ± 0.50
	373 ± 1	7.45 ± 0.45
	423 ± 1	8.16 ± 0.57
1-Methylcyclohexene	296 ± 2	4.21 ± 0.17
	333 ± 1	3.93 ± 0.25
	373 ± 1	3.22 ± 0.32
	423 ± 1	2.71 ± 0.27
1,3-Cyclohexadiene	296 ± 2	4.33 ± 0.20
	333 ± 1	3.43 ± 0.24
	373 ± 1	3.05 ± 0.31
	423 ± 1	2.74 ± 0.27
Acrolein	296 ± 2	0.020 ± 0.002
	333 ± 1	0.035 ± 0.005
	373 ± 1	0.059 ± 0.006
	423 ± 1	0.081 ± 0.009
Crotonaldehyde	296 ± 2	0.044 ± 0.005
	333 ± 1	0.070 ± 0.007
	373 ± 1	0.100 ± 0.010
	423 ± 1	0.150 ± 0.015
Toluene	423 ± 1	0.026 ± 0.003

[a] The error limits are the least-square standard deviations.

Table II. Arrhenius Parameters for the Reaction of O(^{3}P) Atoms[a]

Reactant A	$A^{\mathrm{A}}/A^{\mathrm{CP}}$	$(E^{\mathrm{A}} - E^{\mathrm{CP}})$ kcal mol^{-1}	A^{A} l. mol^{-1} sec^{-1} [b]	E^{A}, kcal mol^{-1} [b]
Propylene	0.43	0.50 ± 0.08	2.4×10^{9}	0.076
Cyclopentene	1.00	0.00	5.6×10^{9}	−0.43 ± 0.08
α-Pinene	13.46	1.34 ± 0.06	7.5×10^{10}	0.91 ± 0.14
β-Pinene	10.77	1.23 ± 0.06	6.0×10^{10}	0.82 ± 0.14
d-Limonene	19.63	0.72 ± 0.07	1.1×10^{11}	0.30 ± 0.15
1-Methylcyclohexene	0.95	−0.90 ± 0.14	5.3×10^{9}	−1.33 ± 0.22
1,3-Cyclohexadiene	0.92	−0.89 ± 0.11	5.1×10^{9}	−1.32 ± 0.18
Acrolein	2.46	2.82 ± 0.19	1.4×10^{10}	2.40 ± 0.27
Crotonaldehyde	2.62	2.41 ± 0.05	1.5×10^{10}	1.98 ± 0.13

[a] The indicated errors in the activation energies are the least-square standard deviations. [b] Placed on an absolute basis using k_1 (propylene) = $2.4 \times 10^{9} e^{-7.6/RT}$ l. mol^{-1} sec^{-1} [4-8]

Table III. Comparison of the Room Temperature Rate Constants (k) and Activation Energies (E) from the Present Work with Literature Values

Reactant	$k \times 10^{-8}$, l. mol^{-1} sec^{-1}		E, kcal mol^{-1}	
	Present work	Lit.	Present work	Lit.
Acrolein	2.32 ± 0.23	1.6[a]	2.40 ± 0.27	2.0[a]
Crotonaldehyde	5.10 ± 0.58	5[b]	1.98 ± 0.13	2.3[b]

[a] References 14 and 15. [b] Reference 16.

larly, the reaction of O(^{3}P) atoms with impurities was estimated to cause errors in the measured rate constants of ≤5%.

The value of k_1(propylene)/k_1(cyclopentene) of 0.181 ± 0.010 at 296 ± 2 K determined here is in good agreement with the ratio of 0.192 obtained by Cvetanovic.[1] Similarly, the present ratio of k_1(toluene)/k_1(cyclopentene) = 0.026 ± 0.003 at 423 ± 1 K agrees well with that of 0.023 interpolated from the data of Jones and Cvetanovic.[12] When placed on an absolute basis using the derived rate expression for O(^{3}P) + cyclopentene, the value of k_1(toluene) = $(2.4 \pm 0.3) \times 10^{8}$ l. mol^{-1} sec^{-1} at 423 ± 1 K agrees within experimental error with the absolute value of 2.05×10^{8} l. mol^{-1} sec^{-1} calculated from the Arrhenius parameters obtained recently in these laboratories[13] using a modulation technique. Furthermore, from the activation energy for cyclopentene ($E = -0.43 \pm 0.08$ kcal mol^{-1}) an activation energy for O(^{3}P) + toluene of $E = 2.8$ kcal mol^{-1} can be obtained from the data of Jones and Cvetanovic[12] in good agreement with $E = 3.10 \pm 0.3$ kcal mol^{-1} determined recently.[13]

Table III compares the room temperature rate constants and the activation energies determined in the present work for the reaction of O(^{3}P) atoms with acrolein and crotonaldehyde with the values determined by Cadle and coworkers[14-16] using discharge flow techniques. There is seen to be general agreement within the likely experimental error.

It can be seen from Table II that cyclopentene, 1,3-cyclohexadiene, and 1-methylcyclohexene have similar preexponential factors and negative activation energies. This behavior is similar to that observed for other simple olefins such as *cis*-2-butene and tetramethylethylene.[17] Negative activation energies have also been reported for the other group 6a atoms with olefins[18,19] and seem to be a general phenomena for the reaction of group 6a atoms with olefins of low ionization potential. Possible reasons for the observation of negative Arrhenius activation energies have been discussed by previous workers.[17-20] Two recently postulated reasons for the observation of negative Arrhenius activation energies are that either the preexponential factor is temperature dependent[17,18,20] or that there is a temperature dependent potential energy curve crossing probability.[19]

However, α-pinene, β-pinene, and *d*-limonene have preexponential factors which are a factor of ~10–20 higher than those for cyclopentene, 1-methylcyclohexene, and 1,3-cyclohexadiene and have low but positive activation energies. It may be that, for these more complex molecules, abstraction reactions are occurring together with addition of O(^{3}P) atoms to the double bond. Thus the preexponential factors for O(^{3}P) atoms abstraction from cyclopentane and cyclohexane are 1.3×10^{11} l. mol^{-1} sec^{-1} and 2.2×10^{11} l. mol^{-1} sec^{-1} respectively,[2,21] while the preexponential factors for O(^{3}P) atoms addition to simple olefins are in the region of 5×10^{9} l. mol^{-1} sec^{-1}.[2,5,7,17,22,23] Similar behavior is postulated to occur in the case of the reaction of O(^{3}P) atoms with 1-butene where the abstraction reaction may become important above ~260 K.[23]

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