rates of positronium reactions with diamagnetic organic molecules in liquids was offered by Goldanskii et al.[22] on the basis of the "bubble" model. Tao et al.[37] suggest that Ps may not be fully thermalized when it reacts and thus causes the deviations from the $K \propto 1/T$ correlation.
(37) S. J. Tao, T. M. Kelly, S. Y. Chuang, and J. M. Wilkenfeld, *Appl. Phys.*, 3, 31 (1974).
(38) It should be noted that if the positron annihilation includes another step, e.g., the complete electron transfer in the Ps complex leading to $e^+ + M^-$, then E_A' would represent the energy of activation for this process and thus $\neq 0$.

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

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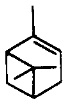
Abstract: Using a competitive technique, rate constants for the gas phase reaction of $O(^3P)$ atoms with selected monoterpenes, unsaturated aldehydes, and olefins have been determined relative to that for the reaction of $O(^3P)$ atoms with cyclopentene at 296 ± 2 K. The rate constants obtained, relative to cyclopentene as unity, were: propylene (0.181 ± 0.010), α-pinene (1.38 ± 0.05), β-pinene (1.30 ± 0.05), *d*-limonene (5.61 ± 0.45), 1-methylcyclohexene (4.21 ± 0.17), 1,3-cyclohexadiene (4.33 ± 0.20), ketene (0.024 ± 0.003), acrolein (0.020 ± 0.002), and crotonaldehyde (0.044 ± 0.005). These relative rate constants have been placed on an absolute basis using the recent literature room temperature rate constant for the reaction of $O(^3P)$ atoms with propylene, $k(\text{propylene}) = 2.10 \times 10^9$ l. mol^{-1} sec^{-1}, and those for ketene, acrolein, and crotonaldehyde are compared and discussed with existing literature values.

The reactions of ground state oxygen atoms with simple olefins, alkenes, and, to a lesser extent, aromatic hydrocarbons have been extensively investigated.[1-3] However, little work has been reported on the products and rate constants for the reaction of $O(^3P)$ atoms with unsaturated aldehydes and the naturally occurring monoterpene (C_{10}) hydrocarbons.[1,2]

Recently there has been considerable interest in these systems, not only from the fundamental grounds of structure and reactivity but also because of their possible significance in the chemistry of polluted atmospheres. Thus for example, the monoterpene hydrocarbons such as α-pinene (I), β-pinene (II), and *d*-limonene (III) have been shown to be emitted into the atmosphere by plant life,[4] and on a global basis have been proposed to be the major source of atmospheric hydrocarbon.[4] Accordingly, the role that these terpenes may play in air pollution chemistry has been studied by a number of investigators.[4-10] Terpenes have been shown to form large amounts of aerosol when photooxidized[5] or allowed to react with ozone in air,[6] and the aerosol from their reaction with ozone is thought to be the source of the blue haze phenomenon observed in forested areas.[7] Furthermore, peroxyacetyl nitrate and aldehydes have been found as products in the photooxidation of pinene.[8] Recently NO_x photooxidation[9] and ozonolysis rate studies[9,10] for a number of monoterpene reactions have been reported which show these compounds to be highly reactive.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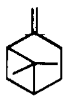
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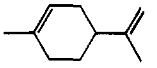
III

The oxidation of unsaturated aldehydes and ketene are also of particular interest both fundamentally and because of their role in photochemical smog. Thus ketene, acrolein, and crotonaldehyde are toxic and are powerful lachrymators. Indeed, acrolein has been detected in ambient air[11] and is considered to be one of the contributors to intense eye irritation accompanying photochemical smog because of its stability to photochemical oxidation and direct photolysis.[12] The possible presence of ketene in polluted urban atmospheres has been previously postulated,[13] and ketene has been shown to be produced from gas phase ozone-olefin reactions under a variety of conditions.[14-17]

Because of the considerations cited above, as part of a broader investigation into the rates and products of the reactions of $O(^3P)$ atoms with unsaturated organic compounds involved in the formation of photochemical air pollution, we have determined room temperature rate constants for the reactions of $O(^3P)$ atoms with ketene, acrolein, crotonaldehyde, α-pinene, β-pinene, *d*-limonene, 1-methylcyclohexene, and 1,3-cyclohexadiene relative to that for the reaction of $O(^3P)$ atoms with cyclopentene. The reaction of $O(^3P)$ atoms with cyclopentene has been thoroughly investigated[18] and has been extensively used to determine relative $O(^3P)$ atom reaction rate constants by Cvetanovic and coworkers.[1,19]

In order to test the experimental system and to place the relative rate constants on an absolute basis, propylene was included in the compounds studied, as its absolute room temperature rate constant is known to a high degree of accuracy.[3,20-23]

Experimental Section

Ground state $O(^3P)$ oxygen atoms were generated by the mercury photosensitization of nitrous oxide at 2537 Å:

$$Hg(6^1S_0) + h\nu \rightarrow Hg(6^3P_1) \qquad \text{(Ia)}$$

$$Hg(6^3P_1) + N_2O \rightarrow Hg(6^1S_0) + N_2 + O(^3P) \qquad \text{(1)}$$

In order to minimize short wavelength photolysis of the reactants and products, the 2537 Å resonance radiation from a low pressure mercury arc was passed through a Corning 7-54 filter to remove

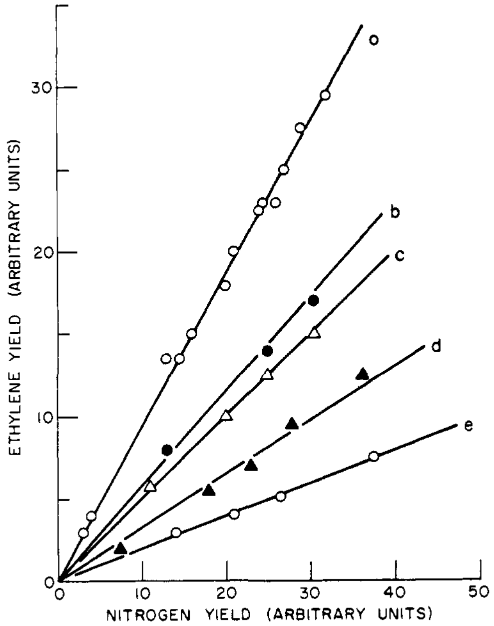

Figure 1. Plots of C_2H_4 yield against N_2 yield for cyclopentene in the absence and presence of limonene: (a) cyclopentene alone (four runs) (*P* cyclopentene 3-8 Torr; *P* total 260-450 Torr); (b) *P* cyclopentene 4.75 Torr, *P* limonene 0.55 Torr, *P* total 240 Torr; (c) *P* cyclopentene 5.89 Torr, *P* limonene 0.90 Torr, *P* total 400 Torr; (d) *P* cyclopentene 2.33 Torr, *P* limonene 0.72 Torr, *P* total 340 Torr; (e) *P* cyclopentene 1.39 Torr, *P* limonene 1.01 Torr, *P* total 400 Torr.

wavelengths ≤2350 Å. A conventional static high vacuum system was used, fitted with greaseless stopcocks to minimize absorption of reagents and products. The cylindrical quartz reaction cell, diameter 5.0 cm, length 20.0 cm, had a volume of 393 cm^3 and, in order to ensure homogeneity, the gas mixture was circulated in a total volume of 1043 cm^3 by means of a magnetically driven all-glass circulating fan. Reactant pressures were measured using either a 0-20 Torr Wallace and Tiernan FA160 absolute pressure gauge or a 0-800 Torr mercury manometer.

Reactant purities and purification procedures were as follows. Ketene was prepared by the pyrolysis of acetone[24] and degassed and vacuum distilled at 196 K. The resulting ketene purity level was ≥98% with acetone being the major impurity. All other reagents were ≥98% stated purity and were further purified by thorough degassing at 196 or 77 K and bulb-to-bulb distillation under vacuum. As a further check on the reactant purities, the reagents used were gas chromatographed on a 10 ft × ⅛ in. β,β'-oxydipropionitrile (9.7% on 80-100 mesh Firebrick) column using a flame ionization detector, and mass spectra were obtained on a Finnigan 3100D quadrapole mass spectrometer. In all cases purity levels consistent with the above were observed.

Photolysis times were typically 5-15 min during which 5-cm^3 samples were periodically removed for analysis by a Carle gas sampling valve. The sample was split into two streams and N_2 from the N_2O and C_2H_4 from cyclopentene were analyzed by gas chromatography. N_2 was measured on a 5 ft × 0.25 in. Linde Molecular Sieve 13X column at room temperature by a thermal conductivity detector, while C_2H_4 was analyzed on a 6 ft × ⅛ in. Poropak Q column at room temperature by a flame ionization detector; (18.9 ± 0.4)% C_2H_4 in N_2 was used to periodically check retention times and relative responses of the detectors. All experiments were carried out at room temperature (296 ± 2 K).

Results

Relative rate constants were determined using the same technique developed and used by Cvetanovic and coworkers.[1,19] From the reaction scheme:

$$O(^3P) + \text{cyclopentene} \rightarrow$$
$$\alpha(C_2H_4 + CH_2{=}CHCHO) + \text{other products}^{18} \qquad (2CP)$$
$$O(^3P) + \text{reactant A} \rightarrow \text{products} \qquad (2A)$$

Table I. Relative Rate Constants k_2^A/k_2^{CP} and Rate Constants k_2^A for the Reaction of $O(^3P)$ Atoms at 296 ± 2 K. The Error Limits are the Least-Square Standard Deviations

Reactant A	k_2^A/k_2^{CP}	$10^{-9}k_2^A$,[a] l. mol^{-1} sec^{-1}
Cyclopentene	1.00	11.6 ± 0.7
Propylene	0.181 ± 0.010	2.10
α-Pinene	1.38 ± 0.05	16.0 ± 0.6
β-Pinene	1.30 ± 0.05	15.1 ± 0.6
d-Limonene	5.61 ± 0.45	65.0 ± 5.2
1-Methylcyclohexene	4.21 ± 0.17	48.9 ± 2.0
1,3-Cyclohexadiene	4.33 ± 0.20	50.3 ± 2.3
Ketene	0.024 ± 0.003	0.278 ± 0.035
Acrolein	0.020 ± 0.002	0.232 ± 0.023
Crotonaldehyde	0.044 ± 0.005	0.510 ± 0.058

[a] Placed on an absolute basis using the value of k_2 (propylene) = 2.10 × 10^9 l. mol^{-1} sec^{-1}.[3,20-23]

with rate constants k_2^{CP} and k_2^A respectively, it can be shown that

$$\frac{(C_2H_4/N_2)^{A=0}}{(C_2H_4/N_2)^A} = 1 + \frac{k_2^A[A]}{k_2^{CP}[CP]} \qquad (I)$$

where $(C_2H_4/N_2)^{A=0}$ and $(C_2H_4/N_2)^A$ are the C_2H_4/N_2 yield ratios in the absence and presence of reactant A, respectively. In all cases runs were carried out in the absence of cyclopentene to check that ethylene was not produced from the reaction of $O(^3P)$ atoms with reactant A. Only for ketene and acrolein was any ethylene production observed. However, in both cases the C_2H_4 production from the reactant 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 $O(^3P)$ atoms with cyclopentene was determined before and after every rate determination and was observed to be constant to better than ±5%, providing that the reaction cell was heated to ≥373 K under vacuum between rate constant determinations for the pinenes, limonene, acrolein, and crotonaldehyde. The C_2H_4/N_2 ratio from the reaction of $O(^3P)$ atoms with cyclopentene alone was determined to be 0.23 ± 0.02 over the pressure range 200-500 Torr, in good agreement with the work of Cvetanovic, Ring, and Doyle.[18]

For each run, at a given reactant/cyclopentene ratio, several determinations of the ethylene and nitrogen yields were carried out as a function of time. Typical results are shown in Figure 1, which shows the C_2H_4 yield vs. N_2 yield for cyclopentene alone and for four runs with differing limonene/cyclopentene ratios.

Table I gives the values of k_2^A/k_2^{CP} determined from the slopes of the plots of C_2H_4 yield vs. N_2 yield such as those shown in Figure 1 for limonene. Also given in Table I are the rate constants k_2^A placed on an absolute basis by adopting k_2(propylene) = 2.10 × 10^9 l. mol^{-1} sec^{-1} (the mean of the literature values of k_2(propylene) = 2.16 × $10^{9,20}$ (2.21 ± 0.13) × $10^{9,21}$ (2.01 ± 0.22) × $10^{9,3,22}$ (2.02 ± 0.17) × 10^9 l. mol^{-1} sec^{-1}).[23]

Discussion

In all cases, experiments were carried out under conditions of low conversion where secondary reactions of $O(^3P)$ atoms with the products should be negligible. This is substantiated by the linearity of the plots of C_2H_4 yield vs. N_2 yield such as those shown in Figure 1. Similarly, the reaction of $O(^3P)$ atoms with impurities can be estimated to cause errors in the measured rate constants of ≤5%. Although 1,3-cyclohexadiene absorbs 2537 Å radiation strongly (ϵ 3360 l. mol^{-1} cm^{-1}),[25] a variation of a factor of two in the cyclohexadiene concentration had no observable effect on the rate constant. This seems reasonable because

Table II. Comparison of the Rate Constants k_2^A Determined in This Work for Ketene, Acrolein, and Crotonaldehyde with Selected Room Temperature Literature Values

Reactant A	$10^{-8}k_2^A$, l. mol^{-1} sec^{-1} This work	Lit.
Ketene	2.78 ± 0.35	1.7 ± 0.4[a] 3.4 ± 0.3[b] 5.3[c]
Acrolein	2.32 ± 0.23	1.6[d]
Crotonaldehyde	5.10 ± 0.58	5[e]

[a] Reference 29. [b] Reference 28. [c] Reference 30. [d] Reference 26. [e] Reference 27.

at the total pressures used in this work any excited cyclohexadiene molecules should be efficiently quenched to the ground state.[25]

The value of k_2(propylene)/k_2(cyclopentene) of 0.181 ± 0.010 determined in this work is in good agreement with the ratio of 0.192 determined by Cvetanovic at room temperature.[1] The rate constants for ketene, acrolein, and crotonaldehyde are compared with literature values in Table II. It can be seen that there is reasonable agreement with the values of Cadle and coworkers for acrolein[26] and crotonaldehyde[27] obtained using discharge flow techniques. For ketene, the present rate constant is in good agreement with that determined recently by Mack and Thrush,[28] but lies between those of Jones and Bayes[29] and of Glass et al.[30]

As has been previously noted,[1,19] the rate constants for the reaction of O(^{3}P) atoms with the olefins increases with the number of alkyl substituents on the double bond (Table I), which is expected because of the electrophilic nature of the O(^{3}P) atoms. Thus cyclopentene (relative rate constant = 1.0), cyclohexene (0.91),[1] isobutene (0.84),[1] *cis*-2-butene (0.80),[1] and β-pinene (1.30), which all have two alkyl substituents on the double bond, also have similar rate constants. Similarly, the trialkyl substituted olefins trimethylethylene (2.66),[1] *d*-limonene (5.61) and 1-methylcyclohexene (4.21) have higher rate constants than the dialkyl substituted olefins. A similar trend is observed in going from 1,3-butadiene (0.82)[1] to 1,3-cyclohexadiene (4.33). However, it can be seen that the precise structure of the olefin has a significant effect on the rate constants, especially for the bridged cyclic olefins such as α-pinene where the lower rate constant might be ascribed to ring strain.

It is thus evident (Table I) that the naturally occurring monoterpenes studied in this work are extremely reactive toward O(^{3}P) atoms, with rate constants approximately an order of magnitude higher than that for the reaction of O(^{3}P) atoms with propylene. Further work is in progress on the temperature dependence and products of these reactions.

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References and Notes

(1) R. J. Cvetanovic, *Adv. Photochem.*, **1**, 115 (1963).
(2) J. T. Herron and R. E. Hule, *J. Phys. Chem. Ref. Data*, **2**, 467 (1973), and references therein.
(3) R. Atkinson and J. N. Pitts, Jr., *J. Phys. Chem.*, **78**, 1780 (1974).
(4) R. A. Rasmussen, *J. Air Pollut. Control Assoc.*, **22**, 537 (1972).
(5) E. R. Stephens and M. A. Price, *Science*, **168**, 1584 (1970).
(6) L. A. Ripperton, H. E. Jeffries, and O. White, *Adv. Chem. Ser.*, **No. 113**, 219 (1971).
(7) F. W. Went, *Nature (London)*, **187**, 641 (1960).
(8) E. R. Stephens and W. E. Scott, *Proc. Air Pollut. Control Inst.*, **42III**, 665 (1962).
(9) E. P. Grimsrud, H. H. Westberg and R. A. Rasmussen, Symposium on Chemical Kinetics Data for the Lower and Upper Atmosphere, Warrenton, W.Va., Sept. 1974.
(10) S. M. Japar, C. H. Wu, and H. Niki, *Environ. Lett.*, **7**, 245 (1974).
(11) Kanagawa Prefecture (Japan). Working Group of Countermeasure for Photochemical Pollution. Interim Report of Survey and Investigation on Irritant Substance at the Time of Occurrence of Environmental Hazard Due to Photochemistry. Report APTIC 37723 (1971).
(12) A. D. Osborne, J. N. Pitts, Jr., and E. F. Darley, *Int. J. Air Water Pollut.*, **6**, 1 (1962).
(13) J. N. Pitts, Jr., and G. E. Grimstone, "Photochemical Smog" in Proceedings of the International Symposium on Air Pollution, Oct 17–19, 1972, Tokyo, Japan, pp 41–60.
(14) W. E. Scott, E. R. Stephens, P. L. Hanst, and R. C. Doerr, *Proc., Am. Pet. Inst.*, **3** (37), 171 (1957).
(15) P. L. Hanst, E. R. Stephens, W. E. Scott, and R. C. Doerr, "Atmospheric Ozone-Olefin Reactions", The Franklin Institute, 1958.
(16) R. Atkinson, B. J. Finlayson, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **95**, 7592 (1973).
(17) J. M. McAfee, A. M. Winer, and J. N. Pitts, Jr., ref 9.
(18) R. J. Cvetanovic, D. F. Ring, and L. C. Doyle, *J. Phys. Chem.*, **75**, 3056 (1971).
(19) R. J. Cvetanovic, *J. Chem. Phys.*, **30**, 19 (1959); **33**, 1063 (1960).
(20) F. Stuhl and H. Niki, *J. Chem. Phys.*, **55**, 3954 (1971).
(21) M. J. Kurylo, *Chem. Phys. Lett.*, **14**, 117 (1972).
(22) R. Atkinson and J. N. Pitts, Jr., *Chem. Phys. Lett.*, **27**, 467 (1974).
(23) S. Furuyama, R. Atkinson, A. J. Colussi, and R. J. Cvetanovic, *Int. J. Chem. Kinet.*, **6**, 741 (1974).
(24) J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).
(25) S. W. Orchard and B. A. Thrush, *Proc. R. Soc., London, Ser. A*, **337**, 243 (1974).
(26) R. D. Cadle and E. R. Allen, "Chemical Reactions in Urban Atmospheres", C. S. Tuesday, Ed., Elsevier, New York, N.Y., 1971, p 63.
(27) R. D. Cadle, H. H. Wickman, C. B. Hall, and K. M. Eberle, paper presented at 167th National Meeting of the American Chemical Society, Los Angeles, Calif., 1974.
(28) G. P. R. Mack and B. A. Thrush, *J. Chem. Soc., Faraday Trans. 1*, **70**, 187 (1974).
(29) I. T. N. Jones and K. D. Bayes, *Proc. R. Soc., London, Ser. A*, **335**, 567 (1973).
(30) R. W. Carr, Jr., I. D. Gay, G. P. Glass, and H. Niki, *J. Chem. Phys.*, **49**, 846 (1968).