4 and 5) is in agreement with our findings. Both attack at the halogen and subsequent X^+ transfer will increase when going from fluoro- to chloro- to bromobenzene; thus replacement of the halogen substituent and of the ortho hydrogen will also increase in the same direction.

Acknowledgment. The authors wish to thank Mr. H. Riesel for valuable experimental assistance.

Reaction of Oxygen Atoms, O(^{3}P), with Olefins in Liquid Nitrogen Solution at 77°K[1]

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Abstract: The reaction of ground state oxygen atoms, O(^{3}P), with propylene, 1-butene, and isobutene in liquid nitrogen solution at 77°K has been studied. The major and perhaps the exclusive addition products are: propylene oxide, propanal, and acetone for propylene; α-butene oxide, *n*-butanal, and methyl ethyl ketone for 1-butene; and isobutene oxide, isobutanal, and methyl ethyl ketone for isobutene. The ratios of the yields of these products have been determined. The type of products formed is discussed in terms of the general mechanism of addition of O(^{3}P) atoms to olefins. The effect of concentration of propylene and 1-butene on the quantum yield of addition products was measured. The quantum yield of oxygen atoms scavenged by propylene and 1-butene to form the addition products was 0.29 and 0.27, respectively. The quantum yields lower than unity suggest an appreciable cage recombination and scavenging of the ground state oxygen atoms with the trace amounts of molecular oxygen formed in the reaction and present as an impurity. Relative rates of addition of O(^{3}P) atoms to ethylene, propylene, 1-butene, and isobutene in liquid nitrogen solution at 77°K have been determined. The effect of the concentration of added oxygen on the product yields and the relative rate constants for addition of O(^{3}P) to molecular oxygen, to propylene, and to 1-butene have been investigated. The rates of addition of O(^{3}P) atoms to propylene, 1-butene, isobutene, and molecular oxygen in liquid nitrogen solution at 77°K are approximately the same, suggesting that these reactions are probably diffusion controlled.

In a previous publication the results of a detailed study of the reaction of oxygen atoms, O(^{3}P), with ethylene in liquid nitrogen solution have been reported.[2] The present work is an extension of this study to the reactions of oxygen atoms with three other olefins dissolved in liquid nitrogen at 77°K. This investigation has two distinct objectives: (1) to establish the reaction mechanism and the type of products formed and (2) to obtain information on the relative rates of these reactions in liquid nitrogen solution at 77°K.

The reaction of oxygen atoms, O(^{3}P), with simple olefins in the gas phase was studied extensively in this laboratory using several different sources of O(^{3}P) atoms, such as the mercury-photosensitized decomposition of N_2O and the photolysis of NO_2, and a general reaction mechanism has been established.[3-5]

Studies of the liquid phase O(^{3}P) atom reactions with olefins at low temperature should provide interesting additional information about the type of products formed because energy-rich intermediates may be expected to be rapidly stabilized by transfer of excess energy to the solvent molecules. Relative rate measurements for the O(^{3}P) addition to olefins in liquid nitrogen solution at 77°K may also complement the observations made in gas phase investigations because at low temperatures the competing reactions of higher activation energy tend to be suppressed and the reaction rate is very sensitive to small activation energy differences.[2,3c,6,7]

Reaction of O(^{3}P) atoms with simple olefins in liquid argon solution at 87.5°K has been recently studied by DeMore.[8]

Experimental Section

Oxygen atoms were generated by photolyzing ozone, using the 253.7-nm line from a low-pressure mercury lamp. The initially formed excited oxygen atoms, O(^{1}D$_2$), are rapidly deactivated to the ground state, O(^{3}P), by collisions with the excess nitrogen molecules present.

Matheson research grade nitrogen was used after it was passed through two spiral traps cooled with liquid oxygen. Matheson research grade ethylene, propylene, 1-butene, and isobutene were used after thorough degassing and distillation. The samples of the dissolved reactants were prepared and irradiated in the same manner as previously described.[2]

The products were analyzed at room temperature on a 3.6-m cyanosilicone-packed column with a thermistor detector and a 3.4 m long 20% w/w β,β'-thiodipropionitrile column in series with a 25-cm column of 20% w/w dinonyl phthalate, provided with flame ionization detector.

The following flame ionization detector molar responses relative to benzene taken as unity were used: ethylene oxide 0.159; acetaldehyde 0.161; propylene oxide 0.326; propanal 0.321; acetone 0.322; α-butene oxide 0.533; *n*-butanal 0.489; isobutene oxide 0.466; isobutanal 0.463; methyl ethyl ketone 0.500. The molar responses for ozonides were approximately obtained by extrap-

(1) Issued as N.R.C.C. No. 14026.
(2) S. Hirokami and R. J. Cvetanović, *Can. J. Chem.*, **51**, 373 (1973).
(3) (a) R. J. Cvetanović, *J. Chem. Phys.*, **23**, 1375 (1955); (b) *ibid.*, **25**, 376 (1956); (c) *Can. J. Chem.*, **36**, 623 (1958); (d) *ibid.*, **38**, 1678 (1960); (e) *Advan. Photochem.*, **1**, 115 (1963).
(4) S. Sato and R. J. Cvetanović, *Can. J. Chem.*, **36**, 970 (1958).
(5) K. F. Preston and R. J. Cvetanović, *Ber. Bunsenges. Phys. Chem.*, **72**, 177 (1968).
(6) R. J. Cvetanović, *J. Chem. Phys.*, **30**, 19 (1959).
(7) R. J. Cvetanović, *Can. J. Chem.*, **38**, 1678 (1960).
(8) W. B. DeMore, *Chem. Phys. Lett.*, **16**, 608 (1972); W. DeMore and O. F. Raper, *J. Chem. Phys.*, **37**, 2048 (1962).

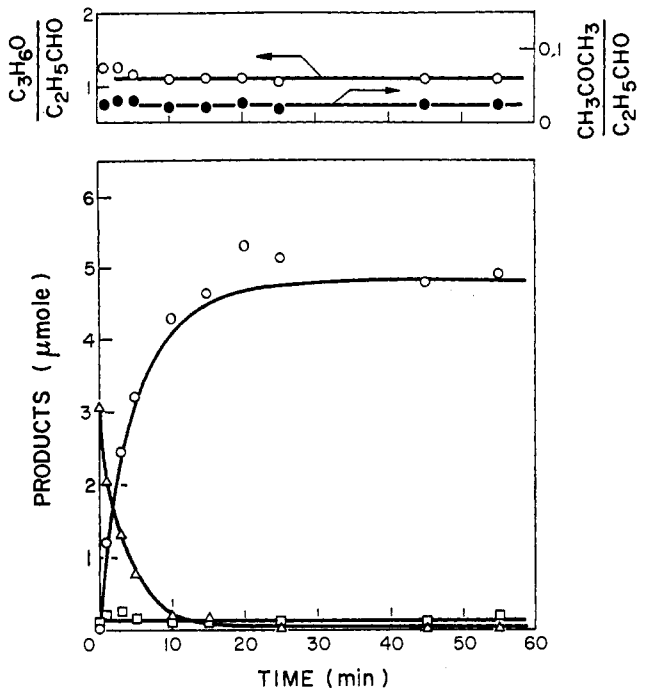

Figure 1. Effect of irradiation time on product yields and on the ratios of propylene oxide to propanal and of acetone to propanal formed in the reaction of $O(^3P)$ with propylene: ozone concentration is 1.62×10^{-4} mol/l.; propylene concentration is 1.43×10^{-3} mol/l.; (○) total addition products, *i.e.*, propylene oxide + propanal + acetone; (△) propylene ozonide; (□) acetaldehyde.

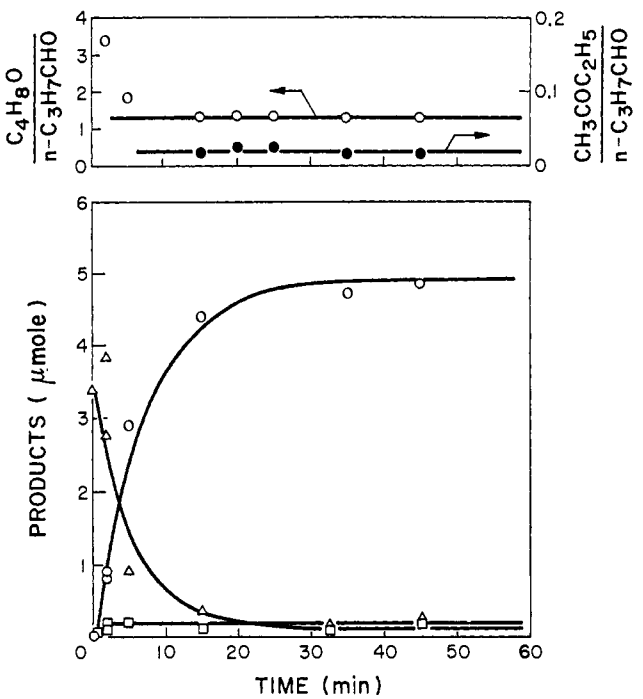

Figure 2. Effect of irradiation time on product yields and on the ratios of α-butene oxide to *n*-butanal and of methyl ethyl ketone to *n*-butanal formed in the reaction of $O(^3P)$ with 1-butene: ozone concentration is 1.62×10^{-4} mol/l.; 1-butene concentration is 1.54×10^{-3} mol/l.; (○) total addition products, *i.e.*, α-butene oxide + *n*-butanal + methyl ethyl ketone; (△) α-butene ozonide; (□) propanal.

olating a linear plot of the peak area responses against the molecular weight.[9]

The solubilities of ethylene and propylene in liquid nitrogen have been reported in the literature.[10] The solubilities of 1-butene and isobutene on the other hand could not be found in the literature and were therefore measured using an apparatus similar to that described by Din and Goldman.[11] An excess amount of the hydrocarbon was transferred into a sample tube and then nitrogen was introduced to obtain up to 10 ml of liquid nitrogen solution. After the solution containing the precipitate was mixed and was maintained for 0.5 to 2 hr at liquid nitrogen temperature, 77°K, the saturated solution was filtered out and was sucked up a capillary into three connected evacuated bulbs of total volume of about 15 l. The solution was then allowed to evaporate completely and was pumped out slowly through traps cooled in liquid nitrogen. The amount of the hydrocarbon recovered from the traps was measured at room temperature on a 12-m dimethylsulfolane column, provided with flame ionization detector. The solubility of ethylene was measured in the same manner for comparison with the literature data.[10] The solubilities of ethylene, 1-butene, and isobutene obtained in this work are shown in Table I. The solubilities of ethylene and propylene measured by Tsin[10] are given for comparison.

Table I. Solubility of Olefins in Liquid Nitrogen Solution at 77°K

Olefin	Solubility, mol/l. This work (77°K)	Solubility, mol/l. Tsin[a]
Ethylene	$8.69 \pm 0.45 \times 10^{-2}$	6.46×10^{-2} (77.7°K)
Propylene		2.02×10^{-1} (75°K)
1-Butene	$1.95 \pm 0.07 \times 10^{-3}$	
Isobutene	$1.30 \pm 0.11 \times 10^{-4}$	

[a] Reference 10.

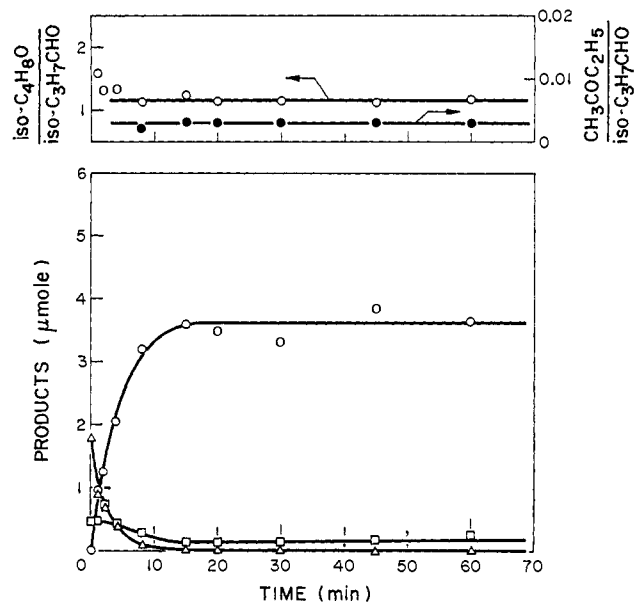

Figure 3. Effect of irradiation time on product yields and on the ratios of isobutene oxide to isobutanal and of methyl ethyl ketone to isobutanal formed in the reaction of $O(^3P)$ with isobutene: ozone concentration is 1.10×10^{-4} mol/l. and the total added amount of isobutene is 22.3 μmol; (○) total addition products, *i.e.*, isobutene oxide + isobutanal + methyl ethyl ketone; (△) isobutene ozonide; (□) acetone.

Results

The observed products are propylene oxide, propanal, acetone, formaldehyde, acetaldehyde, and propylene ozonide for propylene; α-butene oxide, *n*-butanal, methyl ethyl ketone, formaldehyde, propanal,

(9) W. A. Dietz, *J. Gas Chromatogr.*, **5**, 68 (1967).
(10) N. M. Tsin, *Zh. Fiz. Khim.*, **14**, 418 (1940).
(11) F. Din and K. Goldman, *Trans. Faraday Soc.*, **55**, 239 (1959).

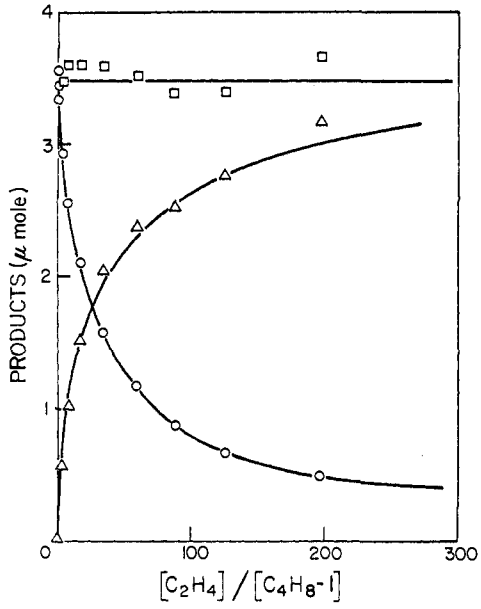

Figure 4. Dependence of the addition product yields of ethylene and of 1-butene on the $[C_2H_4]/[1\text{-}C_4H_8]$ ratio at longer irradiation time: ozone concentration is 1.10×10^{-4} mol/l.; 1-butene concentration is 1.81×10^{-4} mol/l.; irradiation time is 50–60 min; (○) total addition product of 1-butene, *i.e.*, α-butene oxide + *n*-butanal + methyl ethyl ketone; (△) total addition product of ethylene, *i.e.*, ethylene oxide + acetaldehyde; (□) total amounts of addition products from both reactions.

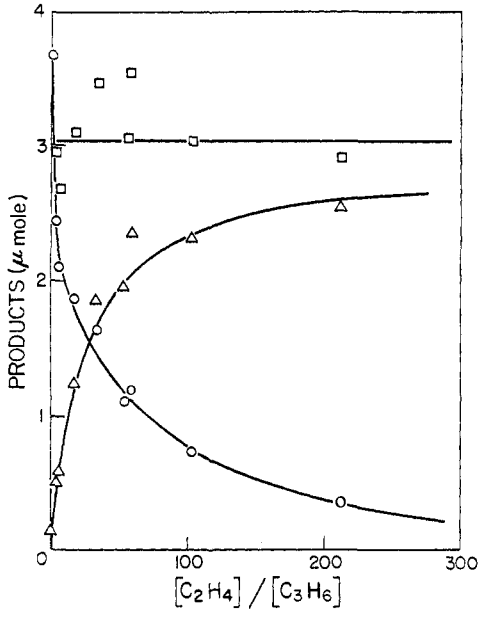

Figure 5. Dependence of the addition product yields of ethylene and of propylene on the $[C_2H_4]/[C_3H_6]$ ratio at longer irradiation time: ozone concentration is 1.10×10^{-4} mol/l.; propylene concentration is 1.81×10^{-4} mol/l.; irradiation time is 50–60 min; (○) total addition product of propylene, *i.e.*, propylene oxide + propanal + acetone; (△) total addition product of ethylene, *i.e.*, ethylene oxide + acetaldehyde; (□) total amounts of addition products from both reactions.

and α-butene ozonide for 1-butene; isobutene oxide, isobutanal, methyl ethyl ketone, acetone, and isobutene ozonide for isobutene.

The effect of irradiation time on product yields (except for formaldehyde) is shown in Figures 1–3. The concentrations of the reactants in these experiments

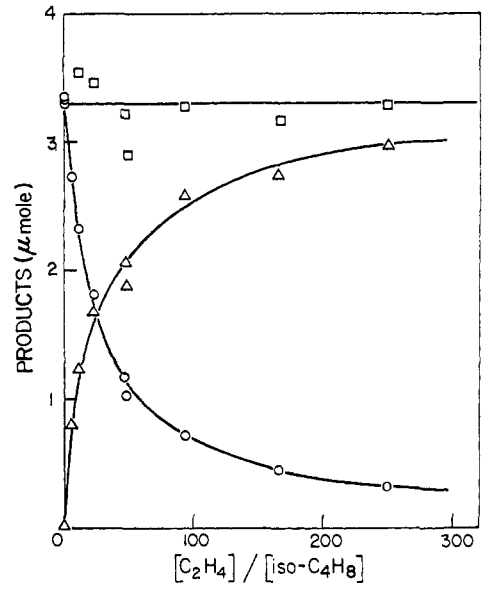

Figure 6. Dependence of addition product yields of ethylene and of isobutene on the $[C_2H_4]/[\text{isobutene}]$ ratio at longer irradiation time: ozone concentration is 1.10×10^{-4} mol/l.; isobutene concentration is 1.30×10^{-4} mol/l.; total added amount of isobutene is 9.03 μmol; irradiation time is 55–70 min; (○) total addition product of isobutene, *i.e.*, isobutene oxide + isobutanal + methyl ethyl ketone; (△) total addition product of ethylene, *i.e.*, ethylene oxide + acetaldehyde; (□) total amounts of addition products from both reactions.

have been: 1.62×10^{-4} mol/l. of ozone and 1.43×10^{-3} mol/l. of propylene dissolved in liquid N_2 for propylene; 1.62×10^{-4} mol/l. of ozone and 1.54×10^{-3} mol/l. of 1-butene solution for 1-butene; and 1.10×10^{-4} mol/l. of ozone and 1.30×10^{-4} mol/l. of isobutene solution for isobutene. In this last case a solution saturated with isobutene was used (an excess of 22.3 μmol of isobutene was added to 50 ml of liquid nitrogen). The yield of formaldehyde was not measured because the separation of formaldehyde from olefins by distillation is very difficult.

In the propylene reaction (Figure 1) the yields of propylene oxide, propanal, and acetone increased with increasing irradiation time up to constant values. The ratios of propylene oxide to propanal and acetone to propanal remained constant except at shorter irradiation times (1 to 5 min). The yield of propylene ozonide decreased to zero with increasing irradiation time. The yield of acetaldehyde remained at a small constant value independent of irradiation time.

In the 1-butene reaction (Figure 2), the yields of α-butene oxide, *n*-butanal, and methyl ethyl ketone increased with increasing irradiation time up to constant values. The ratios of α-butene oxide and methyl ethyl ketone to *n*-butanal remained constant except at shorter irradiation times (1 to 5 min). The yield of α-butene ozonide decreased to a small constant value with increasing irradiation time. The yield of propanal remained at a small constant value independent of irradiation time.

In the isobutene reaction (Figure 3), the yields of isobutene oxide, isobutanal, and methyl ethyl ketone increased with increasing irradiation time up to constant values. The ratios of isobutene oxide and methyl ethyl ketone to isobutanal remained constant except at shorter irradiation times (1–4 min). The yield of isobutene

ozonide decreased with increasing irradiation time to zero. The yield of acetone remained at a small constant value independent of irradiation time.

These results show that the products propylene oxide, propanal, and acetone for propylene, α-butene oxide, n-butanal, and methyl ethyl ketone for 1-butene, and isobutene oxide, isobutanal, and methyl ethyl ketone for isobutene are formed by direct addition of oxygen atoms to propylene, 1-butene, and isobutene, respectively. The products propylene ozonide and acetaldehyde for propylene, α-butene ozonide and propanal for 1-butene, and isobutene ozonide and acetone for isobutene are not photochemical products but are formed by thermal reactions of O_3 with propylene, 1-butene, and isobutene, respectively. The lower ratios of the aldehydes to epoxides at shorter irradiation times in Figures 1–3 may be explained by their secondary reactions (probably during the warming up of the products prior to their analysis) with the zwitterions formed from the thermal reactions of the unreacted ozone with residual olefins.[12,13]

Further support for direct addition of $O(^3P)$ atoms to olefins to form epoxides and isomeric carbonyl compounds was obtained from experiments in which two olefins were used simultaneously and the mixed solution was irradiated for a longer period of time (40–70 min). In these experiments no new products were found but only those observed with the same two olefins when used singly. These results showed that the products are formed by direct addition of the oxygen atoms to the olefinic double bonds and subsequent molecular rearrangement and not by combination of free radicals.

The effects of varying ethylene concentration on product yields at a constant concentration of ozone (1.10×10^{-4} mol/l.) and of another olefin (1.81×10^{-4} mol/l. of 1-butene, 1.81×10^{-4} mol/l. of propylene, or 1.30×10^{-4} mol/l. of isobutene) are shown in Figures 4–6. In these experiments the yields of the addition products of 1-butene, propylene, and isobutene decrease, and the yield of the addition products of ethylene increases with increasing ethylene concentration. The effect of varying concentration of propylene on product yields at constant concentrations of ozone (1.10×10^{-4} mol/l.) and 1-butene (1.81×10^{-4} mol/l.) is shown in Figure 7. The yield of the 1-butene addition products is seen to decrease and the yield of the propylene addition products increases with increasing propylene concentration. The total sum of the addition products, on the other hand, remains constant within the experimental error.

The types of addition products observed and their fractional yields are shown in Table II. The fractions of addition products in the gas phase at 298°K[3] and in solid phase at cryogenic temperatures[14,15] are also shown, for comparison.

The effects of 1-butene and propylene concentrations on product yields at constant concentration of ozone (1.62×10^{-4} mol/l.) and at constant irradiation time (2 min except where otherwise stated) are shown in Tables III and IV, respectively. The yields of the epoxides in Tables III and IV are constant within the experimental error, but the yields of aldehydes are not and, moreover, the ratios of the aldehydes to the epoxides are much lower than shown in Table II. This is explained by incomplete photodecomposition of ozone at these short irradiation times and secondary consumption of the aldehydes in the reactions with the zwitterions formed (during the warming up of the products prior to analysis) by the attack of the residual ozone on the olefins.[12,13] This explanation was confirmed by the observation that, as shown in the lower part of Table III, prior addition of a small amount of acetaldehyde to the solution containing ozone (1.62×10^{-4} mol/l.) and 1-C_4H_8 (1.54×10^{-3} mol/l.) increases the yields of n-butanal after 2 min of irradiation but does not affect the yields of α-butene oxide. These results show also that, under the present experimental conditions, the epoxides react quite slowly or not at all with the zwitterions. The quantum yields of the sums of all addition

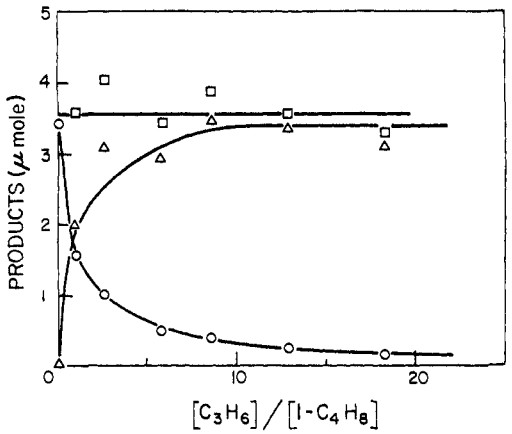

Figure 7. Dependence of addition product yields of propylene and of 1-butene on the $[C_3H_6]/[1\text{-}C_4H_8]$ ratio at longer irradiation time: ozone concentration is 1.10×10^{-4} mol/l.; 1-butene concentration is 1.81×10^{-4} mol/l.; irradiation time is 50–63 min; (○) total addition product of 1-butene, *i.e.*, α-butene oxide + n-butanal + methyl ethyl ketone; (△) total addition product of propylene, *i.e.*, propylene oxide + propanal + acetone; (□) total amounts of addition products from both reactions.

Table II. Fractional Yields of the Addition Products Formed in the Reaction of Ground State Oxygen Atoms $O(^3P)$ with Olefins

Olefin	Products	Gas phase[a]	Liquid phase (this work)	Solid phase
Ethylene	Ethylene oxide		0.45	0.46[b]
	Acetaldehyde		0.55	0.54[b]
Ethylene-d_4	Ethylene oxide		0.52	
	Acetaldehyde		0.48	
Propylene	Propylene oxide	0.50	0.53	0.56[c] 0.55[b]
	Propanal	0.45	0.46	0.38[c] 0.42[b]
	Acetone	0.05	0.01	0.06[c] 0.03[b]
1-Butene	α-Butene oxide	0.53	0.58	0.53[c]
	n-Butanal	0.43	0.41	0.47[c]
	Methyl ethyl ketone	0.04	0.01	
Isobutene	Isobutene oxide	0.54	0.55	
	Isobutanal	0.43	0.45	
	Methyl ethyl ketone	0.03	0.001	

[a] Cvetanović, ref 3. [b] Ponomarev, ref 15. [c] Hughes, Scheer, and Klein, ref 14.

(12) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).
(13) R. Criegee, "Ozone Chemistry and Technology," *Advan. Chem. Ser.*, **No. 21**, 133 (1959).
(14) A. N. Hughes, M. D. Scheer, and R. Klein, *J. Phys. Chem.*, **70**, 798 (1966); R. Klein and M. D. Scheer, *ibid.*, **72**, 616 (1968).
(15) A. N. Ponomarev, *Kinet. Katal.*, 7, 237 (1966); V. M. Orlov and A. N. Ponomarev, *ibid.*, 7, 419 (1966).

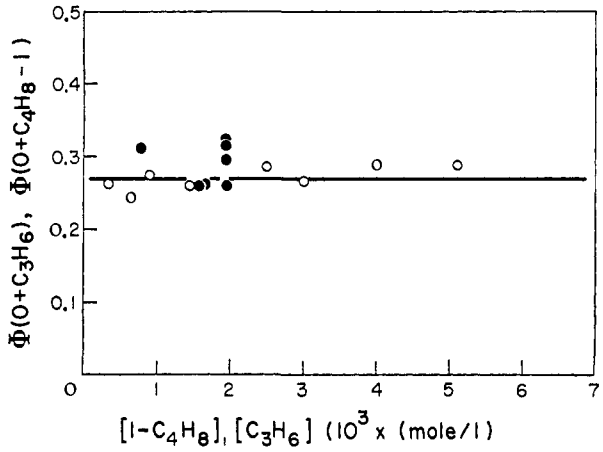

Figure 8. Dependence of $\Phi(O + C_3H_6)$ and $\Phi(O + 1\text{-}C_4H_8)$ on $[C_3H_6]$ and $[1\text{-}C_4H_8]$, respectively: ozone concentration is 1.62×10^{-4} mol/l.; (○) the quantum yield of total addition products of propylene, *i.e.*, propylene oxide + propanol + acetone; (●) the quantum yield of total addition products of 1-butene, *i.e.*, α-butene oxide + *n*-butanal + methyl ethyl ketone.

Table III. Effect of 1-Butene Concentration and of CH_3CHO Addition on Product Yields in the Reaction of $O(^3P)$ with 1-Butene ($[O_3] = 1.62 \times 10^{-4}$ mol/l.; Irradiation Time 2 min)

Amount of 1-butene μmol	mol/l. × 10^4	PA,[a] μmol	α-BO,[a] μmol	*n*-BA,[a] μmol	Φ(α-BO + *n*-BA + MEK)[a]
39.3	7.86	0.124	0.497	0.0406	0.312
77.0	15.4	0.166	0.417	0.0638	0.262
78.5	15.7	0.137	0.426	0.0182	0.267
125	19.5	0.115	0.503	0.0351	0.315
150	19.5	0.0556	0.505	0.0882	0.317
187	19.5	0.139	0.466	0.0207	0.293
242	19.5	0.0543	0.411	0.0185	0.258
					Av 0.289

Amount of CH_3CHO added, μmol	1-Butene, mol/l. × 10^4	PA,[a] μmol	α-BO,[a] μmol	*n*-BA,[a] μmol	α-Butene ozonide, μmol
0[b]	15.4	0.0591	0	0	3.39
0	15.4	0.0827	0.729	0.0827	2.74
19.4	15.4	0.152	0.731	0.217	3.84

[a] PA, α-BO, *n*-BA, and MEK stand for propanal, α-butene oxide, *n*-butanal, and methyl ethyl ketone, respectively. [b] Not irradiated.

Table IV. Effect of Propylene Concentration on Product Yields in the Reaction of $O(^3P)$ with Propylene ($[O_3] = 1.62 \times 10^{-4}$ mol/l.; Irradiation Time 2 min)

Propylene, mol/l. × 10^4	CH_3CHO, μmol	PO,[a] μmol	PA,[a] μmol	Φ(PO + PA + AC)[a]
4.31	0.242	0.384	0.0824	0.264
6.45	Nd[b]	0.353	0.130	0.243
9.13	0.188	0.401	0.140	0.275
14.6	0.350	0.377	0.194	0.260
24.9	0.325	0.427	0.122	0.285
29.9	0.323	0.389	0.109	0.266
40.0	0.308	0.420	0.132	0.288
51.0	0.132	0.419	0.146	0.288
				Av 0.271

[a] PO, PA, and AC stand for propylene oxide, propanal, and acetone, respectively. [b] Not determined.

products shown in Tables III and IV were calculated using the yields and the relative fractions of the epoxide given in Table II. They are presented graphically in Figure 8. The total quantum yields of addition products smaller than unity can be explained[2] by a partial cage recombination of oxygen atoms with the O_2 formed in the reaction and their scavenging by the traces of O_2 present as impurity in the liquid nitrogen solvent.

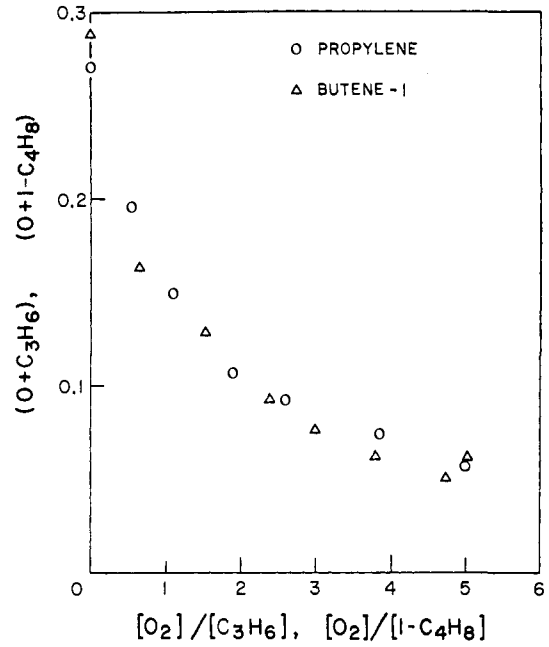

Figure 9. Dependence of $\Phi(O + C_3H_6)$ and $\Phi(O + 1\text{-}C_4H_8)$ on $[O_2]/[C_3H_6]$ and $[O_2]/[1\text{-}C_4H_8]$ ratios, respectively: ozone concentration is 1.62×10^{-4} mol/l.; propylene concentration is 1.54×10^{-3} mol/l.; 1-butene concentration is 1.54×10^{-3} mol/l.; (○) the quantum yield of total addition products of propylene, *i.e.*, propylene oxide + propanal + acetone; (△) the quantum yield of total addition products of 1-butene, *i.e.*, α-butene oxide + *n*-butanal + methyl ethyl ketone.

The effect of O_2 concentration on product yields at constant concentration of ozone (1.62×10^{-4} mol/l.) and of 1-butene and propylene (1.54×10^{-3} mol/l. for both olefins) is shown in Tables V and VI. The quantum yields of the sums of addition products shown in Tables V and VI, calculated from the yields and the relative fractions of the epoxides, are presented graphically in Figure 9. The quantum yield of total addition products decreases monotonically with increasing O_2 concentration.

Table V. Effect of Oxygen Concentration on Product Yields in the Reaction of $O(^3P)$ with 1-Butene ($[O_3] = 1.62 \times 10^{-4}$ mol/l.; $[1\text{-}C_4H_8] = 1.54 \times 10^{-3}$ mol/l.; Irradiation Time 2 min)

[Oxygen]/[1-butene]	PA,[a] μmol	α-BO,[a] μmol	*n*-BA,[a] μmol	Φ(α-BO + *n*-BA + MEK)[a]
0.638	0.113	0.259	0.00789	0.163
1.53	0.104	0.204	0.00572	0.128
2.40	0.0776	0.147	0.00322	0.0924
2.99	0.113	0.121	0.00473	0.0759
3.81	0.127	0.0990	0.00884	0.0622
4.74	0.0758	0.0798	0.00323	0.0501
5.02	0.105	0.0970	0.00727	0.0608

[a] PA, α-BO, *n*-BA, and MEK stand for propanal, α-butene oxide, *n*-butanal, and methyl ethyl ketone, respectively.

Table VI. Effect of Oxygen Concentration on Product Yields in the Reaction of $O(^3P)$ with Propylene ($[O_3] = 1.62 \times 10^{-4}$ mol/l.; $[C_3H_6] = 1.54 \times 10^{-3}$ mol/l.; Irradiation Time 2 min)

[Oxygen]/ [propylene]	CH_3CHO, μmol	PO,[a] μmol	PA,[a] μmol	Φ(PO + PA + AC)[a]
0.562	0.266	0.283	0.0804	0.195
1.01	0.266	0.217	0.0470	0.149
1.90	0.311	0.155	0.0621	0.107
2.61	0.202	0.134	0.0307	0.0922
3.83	0.257	0.108	0.0212	0.0742
4.97	0.258	0.0824	0.0243	0.0567

[a] PO, PA, and AC stand for propylene oxide, propanal, and acetone, respectively.

Discussion

Mechanism of $O(^3P)$ Addition to Olefins. It has been established previously in this laboratory[3] that addition of $O(^3P)$ atoms to simple alkene molecules can always be explained and the products predicted on the basis of a relatively simple reaction mechanism. This mechanism postulates that (1) $O(^3P)$ atom adds predominantly to the less substituted of the two doubly bonded carbon atoms and (2) the initial adduct (assumed to be a "triplet biradical") rearranges to the final products by ring closure (to form epoxide) and by migration of an H atom or an alkyl group from the C atom to which $O(^3P)$ becomes attached to the other C atom of the original double bond (to form carbonyl compounds). Thus, in agreement with this mechanism, the addition products formed in the case of ethylene are ethylene oxide and acetaldehyde.[2,15] The products observed in the present study are also in agreement with the general mechanism. In the case of propylene, the main addition products are propylene oxide and propanal. Addition to the "more-substituted" carbon atom of the double bond would require the formation of acetone; acetone is indeed formed but its amount is very small. In the case of 1-butene, small amounts of methyl ethyl ketone besides the main addition products, α-butene oxide and *n*-butanal, indicate that minor addition to the more-substituted carbon atom of the double bond might be also taking place. The same is true for isobutene where very small amounts of methyl ethyl ketone appear to be formed besides the expected main addition products, isobutene oxide and isobutanal.

The fractional yields of the main addition products, propylene oxide and propanal, α-butene oxide and *n*-butanal, and isobutene oxide and isobutanal, observed in the present work in liquid nitrogen solution at 77°K, are very much the same as found by Cvetanović for the addition of $O(^3P)$ atoms to propylene, 1-butene, and isobutene in the gas phase at room temperature.[3] The fractional yields of the minor addition products, acetone and methyl ethyl ketone, in liquid nitrogen solution at 77°K are appreciably lower than observed in the gas phase.[3] The lower fraction of acetone and methyl ethyl ketone in liquid nitrogen solution at 77°K is explainable by assuming a small activation energy difference (about 0.3 kcal/mol for propylene and 1-butene and about 0.7 kcal/mol for isobutene) for the addition of $O(^3P)$ atoms to the less-substituted and the more-substituted carbon atom of the double bond. The fractional yields of the main addition products in liquid nitrogen solution at 77°K are also very much the same as found by Ponomarev for the addition of $O(^3P)$ atoms to solid propylene at 65–77°K and by Hughes, Scheer, and Klein for the addition of $O(^3P)$ atoms to propylene and 1-butene in the condensed phase at 90°K.[14,15] The fractional yields of the minor product, acetone, in liquid nitrogen solution at 77°K are lower than found by Ponomarev and by Hughes, Scheer, and Klein in the solid phase. The reason for this difference is not clear.

It is evident from present results and their comparison with earlier work that the general reaction mechanism postulated previously[3] applies equally well to the $O(^3P)$ addition to olefins in the gas, liquid, and solid phase.

Reaction Scheme and Values of the Relative Rate Constants. The following reaction scheme, incorporating solvent cage effects, was discussed in the previous paper[2]

$$O_3 + h\nu \longrightarrow (O^* + O_2) \quad (1a)$$

$$(O^* + O_2) + N_2 \longrightarrow N_2O + O_2 \quad (1b)$$

$$\longrightarrow (O + O_2) + N_2 \quad (1c)$$

$$(O + O_2) \longrightarrow O_3 \quad (2)$$

$$\longrightarrow O + O_2 \quad (3)$$

$$O + \text{olefin} \longrightarrow \text{products} \quad (4)$$

$$O + O_2 \longrightarrow O_3 \quad (5)$$

O^* and O stand for $O(^1D_2)$ and $O(^3P)$ atoms, respectively, and the parentheses indicate solvent cages. The steady state treatment gives[2] the following expressions for the initial quantum yields of N_2O (Φ_{N_2O}) and the products (Φ_P) of reaction 4

$$\Phi_{N_2O} = k_{1b}/(k_{1b} + k_{1c}) \quad (6)$$

$$\Phi_P^{-1} = \alpha\{1 + (k_5[O_2^*] + k_5[O_2])/k_4[\text{olefin}]\} \quad (7)$$

where O_2^* is the initially present oxygen impurity in the liquid nitrogen solvent and[16] $\alpha = (1 + (k_{1b}/k_{1c}))(1 + (k_2/k_3))$.

The quantum yield of N_2O in liquid nitrogen solution, determined by DeMore and Raper,[8,17] is 0.014–0.018, with an "approximate" error[8] of 0.004. These values and the measured yields of N_2O have been used to calculate the amount of light absorbed and thus also the quantum yields of the reaction products. Solvent cage effects were invoked[2] to explain the limiting Φ_P values (for $[O_2] = 0$ and $k_5[O_2^*]/k_4[\text{olefin}] \rightarrow 0$) considerably smaller than unity.

In the present work, the relative rate constants (k_A/k_B) for two olefins (A and B) reacting with $O(^3P)$ atoms have been determined from the ratios of the yields of the respective products (P_A and P_B) in competitive experiments. The only reactions which have to be considered in this case are

$$O + A \longrightarrow P_A \quad (4A)$$

$$O + B \longrightarrow P_B \quad (4B)$$

If the initial concentrations of the two olefins ($[A_i]$ and $[B_i]$) are sufficiently high so that they remain es-

(16) Reference 2 gives the correct form of eq 7 with α expressed explicitly as $(1 + (k_{1b}/k_{1c}))(1 + (k_2/k_3))$. However, in subsequent discussion this quantity was in two places incorrectly transcribed as $\alpha = (1 + (k_{1c}/k_{1b}))(1 + (k_2/k_3))$. The discussion and the derived quantities were not in any way affected by these two misprints.

(17) O. F. Raper and W. B. DeMore, *J. Chem. Phys.*, 40, 1053 (1964).

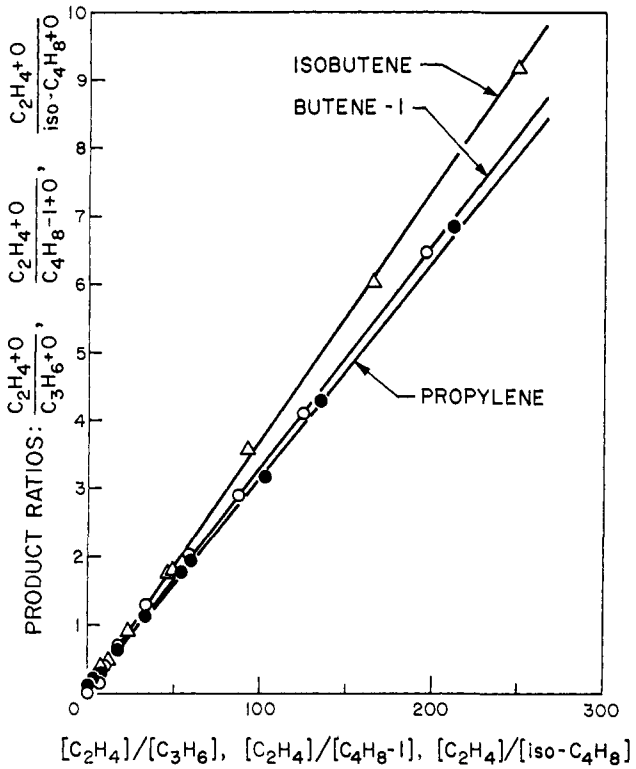

Figure 10. Dependence of product ratios $(C_2H_4 + O)/(C_3H_6 + O)$, $(C_2H_4 + O)/(1\text{-}C_4H_8 + O)$, and $(C_2H_4 + O)/(i\text{-}C_4H_8 + O)$ on $[C_2H_4]/[C_3H_6]$, $[C_2H_4]/[1\text{-}C_4H_8]$, and $[C_2H_4]/[i\text{-}C_4H_8]$, respectively. Conditions are the same as stated in the caption to Figures 4, 5, and 6.

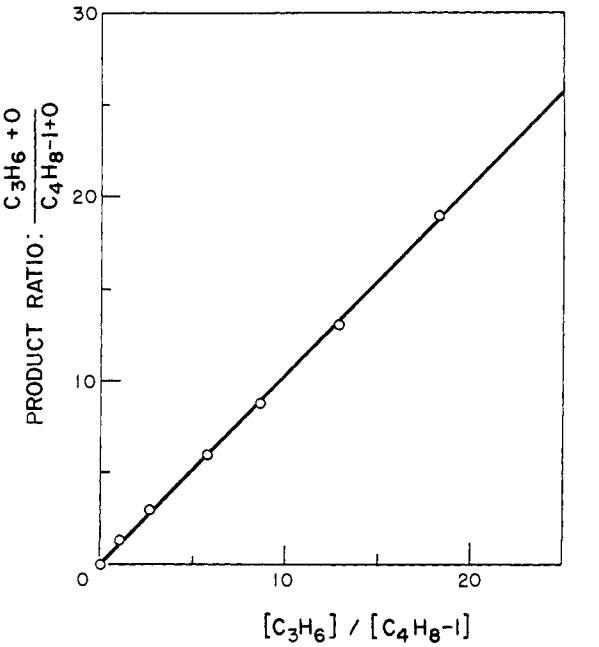

Figure 11. Dependence of the reaction product ratio $(C_3H_6 + O)/(1\text{-}C_4H_8 + O)$ on $[C_3H_6]/[1\text{-}C_4H_8]$. Conditions are the same as stated in the caption to Figure 7.

sentially unaltered in the course of the reaction, the ratio of the products formed is given by

$$\frac{[P_A]}{[P_B]} = \frac{k_A[A_i]}{k_B[B_i]} \tag{8}$$

When the concentrations of the olefins change appreciably in the course of the reaction, the ratio of the rate constants is given by the expression

$$k_A/k_B = \ln [1 - \{[P_A]/[A_i]\}]/\ln [1 - \{[P_B]/[B_i]\}] \tag{9}$$

where olefins A and B are consumed only in reactions with oxygen atoms (reaction 4) and form the products P_A and P_B.[6]

Equations 8 and 9 were used for the determinations of k_A/k_B. The plots of eq 8 for ethylene and 1-butene, ethylene and propylene, ethylene and isobutene, and propylene and 1-butene are shown in Figures 10 and 11. The experimental points give reasonably good linear plots in agreement with eq 8, and the least squares values and standard deviations of the relative rate constants obtained are

$$k_{Pr}/k_E = 31.1 \pm 0.3 \qquad k_{1-B}/k_E = 30.2 \pm 0.3$$

$$k_{i-B}/k_E = 27.1 \pm 0.2 \qquad k_{Pr}/k_{1-B} = 1.02 \pm 0.01$$

where k_E, k_{Pr}, k_{1-B}, and k_{i-B} are the k_4 values for ethylene, propylene, 1-butene, and isobutene. Since eq 8 is based on the simplifying assumption that the initial concentrations of the olefins are essentially unaltered in the course of reaction, the relative rate constants were also calculated using eq 9. The values obtained are in good agreement with those obtained from eq 8.

The effect of additions of molecular oxygen on the reactions of $O(^3P)$ atoms with an olefin (A) may be explained by the following simple reaction scheme

$$O + A \longrightarrow P \tag{4A}$$

$$O + O_2 \longrightarrow O_3 \tag{5}$$

The initial quantum yield (Φ_P) of the addition products (P) in the presence of molecular oxygen at constant concentrations of O_3 and olefin can be expressed by the following relation (which is a special case of eq 7, valid only when $k_5[O_2^*]/k_4[\text{olefin}] \ll 1$, in which case also $\Phi_P^0 = 1/\alpha$)

$$\Phi_P = \Phi_P^0 \frac{k_A[A]}{k_A[A] + k_5[O_2]} \tag{10}$$

or

$$(\Phi_P^0/\Phi_P) - 1 = \frac{k_5[O_2]}{k_A[A]} \tag{11}$$

Φ_P^0 is the initial quantum yield of addition products in the absence of added O_2. These expressions are applicable to propylene and 1-butene, for which the effect of molecular oxygen contained initially in the liquid nitrogen solvent as an impurity (O_2^*) appears to be negligible. This is evident from Figure 8, which shows that the initial quantum yields of addition products are approximately constant for the concentration ranges of the two olefins of 4×10^{-4} to 5×10^{-3} mol/l. and 4×10^{-4} to 2×10^{-3} mol/l., respectively.

The plot of $[\{\Phi_P^0(C_3H_6 + O)/\Phi_P(C_3H_6 + O)\} - 1]$ *vs.* $[O_2]/[C_3H_6]$ and $[\{\Phi_P^0(1\text{-}C_4H_8 + O)/\Phi_P(1\text{-}C_4H_8 + O)\} - 1]$ *vs.* $[O_2]/[1\text{-}C_4H_8]$ is linear, as shown in Figure 12. The least-squares values and standard deviations of the slopes of the plots in Figure 12 are

$$k_5/k_{Pr} = 0.742 \pm 0.015$$

$$k_5/k_{1-B} = 0.895 \pm 0.042$$

where, as before, k_{Pr} and k_{1-B} are the k_4 values for propylene and 1-butene.

The relative rate constants of oxygen atom reactions with olefins and with O_2 obtained here are given in Table VII. Several relative rate constants of oxygen atom reactions in liquid argon solution at 87.5°K measured by DeMore[8] and in the gas phase at 298°K measured by Cvetanović[3c] are given for comparison.[18]

Table VII. Relative Rate Constants of the Reaction of Oxygen Atoms with Olefins and Oxygen

Rate constant ratios	Relative rate constants: This work (77°K)	DeMore[a] (87.5°K)	Gas phase[b] (298°K)
$k_{C_3H_6}/k_{C_2H_4}$	31	20	5.8
$k_{1\text{-}C_4H_8}/k_{C_2H_4}$	30	20	5.8
$k_{i\text{-}C_4H_8}/k_{C_2H_4}$	27		25
$k_{C_3H_6}/k_{1\text{-}C_4H_8}$	1.0		1.0
$k_{O_2}/k_{C_3H_6}$	0.74		
$k_{O_2}/k_{1\text{-}C_4H_8}$	0.90		
$k_{O_2}/k_{C_2H_4}$	25[c]	≤ 40[d]	

[a] DeMore, ref 8. [b] Cvetanović, ref 3c. [c] Mean value derived indirectly from the results obtained in the present work. [d] Derived assuming $\alpha \geq 1$, as explained in the text.

The relative rate constant of propylene to 1-butene is approximately unity in liquid nitrogen solution at 77°K, in liquid argon solution at 87.5°K,[8] and in the gas phase at 298°K.[3c] However, isobutene in the gas phase at 298°K reacts with O(^{3}P) atoms about four times as rapidly as propylene and 1-butene, but in liquid nitrogen solution at 77°K it reacts with O(^{3}P) atoms at approximately the same rate as do propylene and 1-butene. The relative rates of molecular oxygen to propylene and to 1-butene are within the experimental error also approximately unity. From these relative rate constants, it appears therefore that propylene, 1-butene, isobutene, and molecular oxygen react with O(^{3}P) atoms in liquid nitrogen solution at 77°K at approximately the same rates. The reaction of molecular oxygen with O(^{3}P) atoms is probably a second-order diffusion-controlled reaction in liquid nitrogen solution at 77°K, and the activation energy of this reaction is probably negligibly small because a negative Arrhenius activation energy is reported for the reaction of molecular oxygen with O(^{3}P) atoms in the gas phase.[19] If it can be postulated that the reaction of molecular oxygen with O(^{3}P) atoms in liquid nitrogen solution at 77°K is diffusion controlled, the reactions of O(^{3}P) with propylene, 1-butene, and isobutene would also have to be assumed to be diffusion controlled.

From the k_5/k_{Pr} and k_{Pr}/k_E values obtained it is indirectly calculated that $k_5/k_E = 23.1$. Similarly, the corresponding values for 1-butene give $k_5/k_E = 27.0$. These two values are in reasonable mutual agreement but an O_2 to ethylene relative rate constant $k_5/k_E = 6 \pm 1$ was evaluated in the previous work[2] after allowance for the low value of $\Phi_P(C_2H_4)$, *i.e.*, for the postulated cage recombination of O(^{3}P) with O_2. Thus, there is an apparent large difference between the mean value of about 25 estimated here for the relative rate of O_2 to ethylene and the value of 6 obtained in the previous work.

(18) Table VII does not show any of the considerable number of the absolute rate constants of O-atom reactions now available in the literature since they are fully consistent with the relative rates given in the table. The gas phase combination of O with O_2 is a third-order reaction and while the third-order rate constant is known[19] a meaningful comparison with the corresponding rates in the liquid nitrogen solution at 77°K would be difficult.

(19) R. E. Huie, J. T. Herron, and D. D. Davis, *J. Phys. Chem.*, **76**, 2653 (1972).

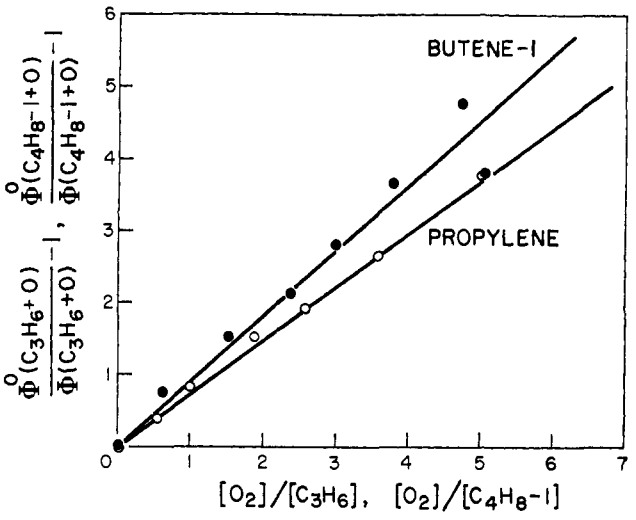

Figure 12. Dependence of $[\Phi^0(C_3H_6 + O)/\Phi(C_3H_6 + O)] - 1$ and $[\Phi^0(1\text{-}C_4H_8 + O)/\Phi(1\text{-}C_4H_8 + O)] - 1$ on $[O_2]/[C_3H_6]$ and $[O_2]/[1\text{-}C_4H_8]$, respectively. Conditions are the same as stated in the caption to Figure 9.

This difference is probably mainly due to quantitative uncertainties and possibly also to some mechanistic complexities inherent in the earlier[2] evaluation of k_5/k_E. At 77°K ethylene reacts with O(^{3}P) atoms much slower than other simple alkenes and the initial quantum yield of its addition products, Φ_P, was found to decrease with decreasing ethylene concentration even when no O_2 was added.[2] The low values of Φ_P were presumably due to appreciable scavenging of O(^{3}P) atoms by the O_2 impurity in the N_2 solvent and by the O_2 formed in the reaction. A value of α, required to calculate k_5/k_E from the slope of a plot[2] of the analog of eq 7, was therefore obtained from the least-squares value of the small intercept at $[C_2H_4]^{-1} = 0$ of the plot[2] of Φ_P^{-1} *vs.* $[C_2H_4]^{-1}$ in the absence of added O_2. The evaluations of this small intercept and of the amount of light absorbed (I_a, required to calculate the absolute values of Φ_P) are both subject to large potential errors, especially since I_a was calculated indirectly from the literature value of Φ_{N_2O} and the small amount of N_2O recovered from a huge excess of the N_2 solvent. It may also be possible that in the case of ethylene[2] there were additional sinks for O(^{3}P) atoms and that the value of α was therefore exaggerated, giving low k_5/k_E. The minimum value of α is close to 1 (*ca.* 1.01 to 1.02 for liquid N_2 solvent, as a result of some N_2O formation) corresponding to $\Phi_P \approx 1$, *i.e.*, to no O(^{3}P) scavenging and loss by recombination in solvent cages. If it is then taken that $\alpha \geq 1$, earlier data give *upper limits* for k_5/k_E of 52 in liquid N_2 at 77°K[2] and of 40 in liquid Ar at 87.5°K.[8] These upper limits are consistent with the present mean value for k_5/k_E of about 25 given in Table VII.

In contrast to the earlier results for ethylene,[2] the Φ_P values for propylene and 1-butene in the absence of added O_2 have been found in the present work to be independent of olefin concentrations (Figure 8) so that k_5/k_{Pr} and $k_5/k_{1\text{-}B}$ could be determined directly from plots of eq 11 without an explicit value of α. Moreover,

absolute values of the quantum yields are not required since eq 11 contains the ratio Φ_P^0/Φ_P. It is therefore felt that the present mean k_5/k_E value of about 25 is more reliable than the previous[2] estimate. For this reason the earlier value[2] is not listed in Table VII.

The activation energy for addition of O(^{3}P) atoms to ethylene has been discussed by DeMore in a very recent paper.[8] Using DeMore's method of calculation, we also obtain about 0.5 kcal/mol as an activation energy difference (ΔE) between the O + C_2H_4 reaction and O + C_3H_6 or O + 1-C_4H_8 reaction. Similar ΔE values can be also obtained by comparing the ratios of rate constants at 77 and 87.5°K listed in Table VII. On the other hand, comparison of the relative rates at cryogenic temperatures with the gas phase values at 298°K gives ΔE of about 0.3 to 0.35 kcal/mol for the above reactions and it also gives for isobutene an activation energy approximately equal to that of ethylene but a 25 times larger A factor. This last result would be particularly difficult to accept but would be readily understandable assuming, as discussed earlier, that O(^{3}P) reactions with C_3H_6, 1-C_4H_8, i-C_4H_8, and O_2 are diffusion controlled in liquid nitrogen solution at 77°K (and perhaps also in liquid argon at 87.5°K). Under these conditions the above calculations give only the *lower limits* for ΔE. At the same time, the fact that the reactions studied here occur readily at cryogenic temperatures and that some of them are fast enough to be diffusion controlled in liquid nitrogen solution at 77°K places some constraints on the upper limits of the ΔE values and of the individual activation energies. It may therefore be concluded that the latter must be relatively small, as has been known for some time,[3c,20,21] although this conclusion retains here a largely qualitative character. The quantitative aspect of the competitive cryogenic results may be influenced by such factors as the finer details of the diffusion-controlled processes in liquid nitrogen solution at 77°K and the possibility[3c,21] that π-complex formation between O(^{3}P) and olefins may precede the addition reaction under the experimental conditions employed in this study and thus effectively prolong the duration of the "encounters" and speed up the slower of these reactions.

Formation of Minor Products. As mentioned earlier, formation of certain minor products (acetaldehyde and formaldehyde in the case of propylene, propanal and formaldehyde in the case of 1-butene, and acetone in the case of isobutene) was observed in the course of the reactions studied. Formaldehyde was also observed as a minor product in the previous study of the O(^{3}P) reaction with ethylene in liquid N_2 solution.[2] These minor products are perhaps due to an unavoidable minor thermal attack of ozone on these olefins under the experimental conditions employed, since these products are the major products in the thermal reaction of ozone with the same olefins in the gas phase.[22]

(20) D. D. Davis, R. E. Huie, J. T. Herron, M. J. Kurylo, and W. Braun, *J. Chem. Phys.*, **56**, 4868 (1972).
(21) R. Atkinson and R. J. Cvetanović, *J. Chem. Phys.*, **56**, 432 (1972).
(22) T. Vrbaski and R. J. Cvetanović, *Can. J. Chem.*, **38**, 1063 (1960).

Stabilization of the Local Water Structure due to Oxygen or Nitrogen Molecules

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Abstract: A CNDO study of the influence of oxygen, nitrogen, and water molecules on a model for the local water structure indicates that it is quite possible that air in water would have a stabilizing effect on the water structure. The calculated effect is about 0.5 kcal/mol per hydrogen bond in the particular water model chosen, which should be compared with an experimental value of 0.1 kcal/mol per hydrogen bond for such a stabilizing effect due to air obtained in surface tension experiments.

During the past years a great number of qualitative and quantitative theories[1-7] have been proposed to explain the properties of water and water solutions and to elucidate their structures. Most of these theories include considerations of water polymers with long lifetimes compared to the dielectric relaxation time, around 10^{-11} seconds at room temperature. Among the configurations which have been considered for these hydrogen-bonded water polymers, ice-like cage structures have always played a central role in the description of the local geometry of water in the bulk of the liquid and in the surface or the interface. This is just natural if the hydrogen bonds in water are thought to be similar to those in ice in any of its many polytypes. In an early study of the X-ray diffraction pattern of water, Bernal and Fowler[2] suggested that liquid water had an extensive four-coordinated struc-

(1) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford University Press, 1969, general survey of experimental and theoretical work on water.
(2) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1, 515 (1933).
(3) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).
(4) O. Ya. Samoilov, "Structure of Aqueous Electrolyte Solutions and the Hydration of Ions," Consultants Bureau, New York, N. Y., 1965.
(5) J. A. Pople, *Proc. Roy. Soc., Ser. A*, **205**, 163 (1951).
(6) J. D. Bernal, *Proc. Roy. Soc., Ser. A*, **280**, 299 (1964).
(7) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.