Atomic Oxygen. I. The Reactions of Allenes with Oxygen (^{3}P) Atoms

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Abstract: Ground state (^{3}P) oxygen atoms, generated by the mercury photosensitized decomposition of nitrous oxide, react in the gas phase with allenes to produce carbon monoxide, olefins, and α,β-unsaturated carbonyl compounds. It is proposed that carbon monoxide and olefin are formed by decarbonylation of an excited cyclopropanone, while carbonyl compounds are produced by rearrangement, either of the excited cyclopropanones or of the initially formed biradicals. Small amounts of substituted cyclopropanones could be trapped by methanol as hemiketals. Relative rates of reaction of allenes and olefins with O(^{3}P) have been determined.

The gas phase reactions of atomic oxygen with organic compounds have been studied by Cvetanovic and coworkers.[1] Ground state (^{3}P) oxygen atoms react with olefins of formula C_nH_{2n} to produce epoxides, aldehydes, and ketones of formula $C_nH_{2n}O$.

The initial addition of O(^{3}P), a biradical, to a carbon-carbon double bond is similar to the addition of monoradicals. In the case of unsymmetrical olefins, addition to the less substituted olefinic carbon atom (producing the more stable radical) is favored. Epoxide formation by O(^{3}P) addition to *cis*- or *trans*-2-butene is nonstereospecific. The addition of O(^{3}P) to carbon-carbon double bonds is much faster than the abstraction of allylic hydrogens. Based on the above and other observations, Cvetanovic has proposed that O(^{3}P) atoms add to olefins to form short-lived 1,3-biradicals (Scheme I). The biradicals can either close

Scheme I

$$R_2C{=}CR_2' \ + \ O(^3P)$$
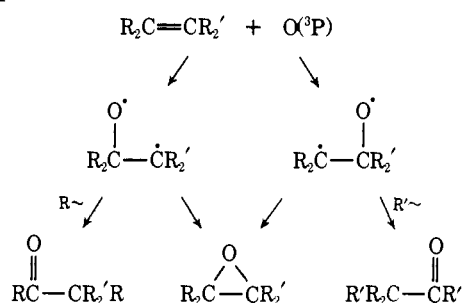
to epoxides or rearrange to aldehydes or ketones *via* a 1,2-hydrogen or -alkyl migration.

The reactions of alkyl-substituted allenes with peracids have been reported. Only in the cases of 1,3-di-*tert*-butylallene and 1,1,3-tri-*tert*-butylallene have stable allene oxides been isolated.[2,3] Allene oxides have not been isolated from the oxidation of more simply substituted allenes.[4] Instead, these allene oxides isomerize to cyclopropanones by an acid-catalyzed process.[5] Atomic oxygen is an epoxidizing reagent that can be generated in the absence of acids.

Results and Discussion

A. Production of Oxygen Atoms. Atomic oxygen was produced in the presence of an allene by the gas phase photolysis of a mixture of nitrous oxide, the allene, and mercury vapor. Ground state (^{3}P) oxygen atoms arise from the mercury photosensitized decomposition of nitrous oxide (eq 1 and 2).[6] The amount

$$Hg(^1S_0) + h\nu \longrightarrow Hg(^3P_1) \tag{1}$$

$$Hg(^3P_1) + N_2O \longrightarrow Hg(^1S_0) + N_2(^1\Sigma) + O(^3P) \tag{2}$$
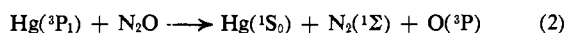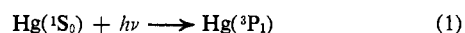
of nitrogen generated by nitrous oxide decomposition provides a basis for the determination of product yields from atomic oxygen reactions.

The interpretation of results obtained using the nitrous oxide technique was simplified by the use of two experimental conditions. First, a high ratio of nitrous oxide to allene (>25) was maintained, in order to minimize the mercury photosensitized decomposition of reactants or products.[7] Second, low conversions of allene (<20%) were used, in order to minimize reactions of primary products with atomic oxygen. Nitrous oxide does not react with allenes at room temperature.

B. Reactions with Allenes. 1. Allene. Since the orientation of addition of atomic oxygen to an unsymmetrical olefin is directed by the substituents of the olefin, it is pertinent to consider the direction of addition of monoradicals to allenes. The orientation of addition of several radical species to allene itself has been studied.[8] The position of addition varies greatly with the attacking radical. For example, the CF$_3\cdot$ radical adds exclusively to the terminal carbons. On the other hand, 52–100% of the attack of atomic bromine is at the central carbon atom.

The products of the reaction of atomic oxygen with allene are: carbon monoxide (57% yield), ethylene (38%), and acrolein (1.1%). Total recovery of oxygenated organic products is 58%.

Possible precursors to the observed products are shown in Scheme II. The isomerization of substituted allene oxides to cyclopropanones has been demonstrated.[4] Recent calculations by Liberles, Greenberg,

(1) R. J. Cvetanovic, *Advan. Photochem.*, 1, 115 (1963).
(2) R. L. Camp and F. D. Greene, *J. Amer. Chem. Soc.*, 90, 7349 (1968).
(3) J. K. Crandall and W. H. Machleder, *J. Heterocycl. Chem.*, 6, 777 (1969).
(4) J. K. Crandall, W. H. Machleder, and S. A. Sojka, *J. Org. Chem.*, 38, 1149 (1973), and references therein.
(5) J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, 90, 7347 (1968).
(6) R. J. Cvetanovic, *J. Chem. Phys.*, 23, 1203 (1955).
(7) R. J. Cvetanovic, *J. Chem. Phys.*, 23, 1208 (1955).
(8) For reviews, see (a) K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, 5, 933 (1966); (b) D. R. Taylor, *Chem. Rev.*, 67, 317 (1967).

Scheme II
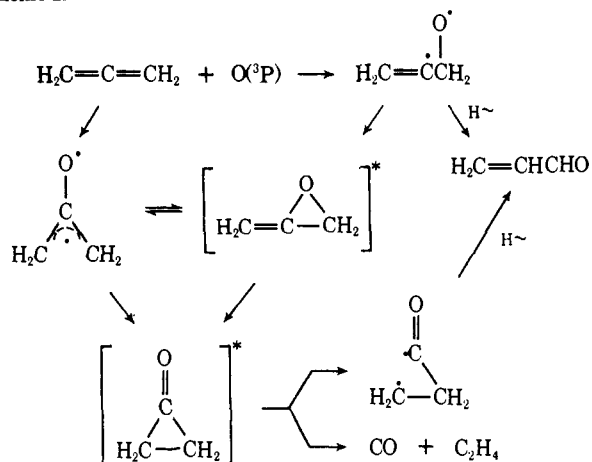
and Lesk[9] predict that allene oxide is 21 kcal/mol less stable than cyclopropanone. Cyclopropanone and its alkyl derivatives polymerize rapidly at room temperature.[10]

2-Oxo-1,3-alkanediyl biradicals (a resonance form of the biradical obtained by $O(^3P)$ addition to the central carbon atom of an allene) have been generated by the reaction of α,α'-dihalo ketones with potassium vapor.[11] Products isolated from the reaction of 1,3-dichloropropanone included ethylene and carbon monoxide, formed from the thermal decarbonylation of cyclopropanone. Acrolein or other carbonyl products would not have survived the conditions of the potassium vapor reaction.

2. 1,2-Butadiene. The volatile products of the reaction of 1,2-butadiene with atomic oxygen are carbon monoxide (64% yield), propene (43% yield), 3-buten-2-one (1.7), crotonaldehyde (1.1%), and methacrylaldehyde (0.3%). Propene and carbon monoxide are products of the decarbonylation of methylcyclopropanone (eq 3).

(3)
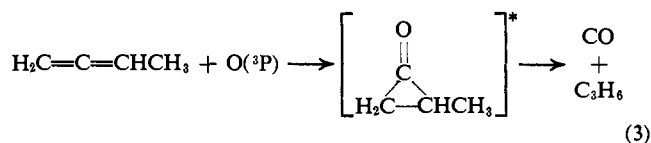
The carbonyl products may arise either by rearrangement of the biradicals initially formed by oxygen atom addition or by rearrangement of excited methylcyclopropanone. The distribution of carbonyl products corresponds to the orientation of addition of other radicals[12] to 1,2-butadiene (addition to C-2 > C-1 > C-3).

3. 3-Methyl-1,2-butadiene. The addition of $C_2H_5S\cdot$, $(CH_3)_3Sn\cdot$, and $CCl_3\cdot$ radicals to 3-methyl-1,2-butadiene has been studied.[12,13] In each case, attack occurs only at the central carbon atom of the allene linkage.

The reaction of atomic oxygen with 3-methyl-1,2-butadiene produces carbon monoxide (6% yield), 2-

(9) A. Liberles, A. Greenberg, and A. Lesk, *J. Amer. Chem. Soc.*, **94**, 8686 (1972).

(10) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(11) R. G. Doerr and P. S. Skell, *J. Amer. Chem. Soc.*, **89**, 4684 (1967).

(12) For additions of $C_2H_5S\cdot$, see T. J. Jacobs and G. E. Illingworth, *J. Org. Chem.*, **28**, 2692 (1963); for additions of $(CH_3)_3Sn\cdot$, see H. G. Kuivila, W. Rahman, and R. H. Fisk, *J. Amer. Chem. Soc.*, **87**, 2835 (1965).

(13) G. E. Illingworth, Ph.D. Thesis, University of California at Los Angeles, 1963.

methylpropene (45%), and 3-methyl-3-buten-2-one (8.6%). Total recovery of oxygenated organic products is 76%. No trace of 3-methylcrotonaldehyde could be detected by vpc or nmr analysis.

A reaction which bears on the above results is the thermolysis of 2,2-dimethylcyclopropanone.[10] The hot-tube pyrolysis of this compound at 250° produces 2-methylpropene and carbon monoxide. On the other hand, vpc pyrolysis produces 3-methyl-3-buten-2-one. The ring opening of 2,2-dimethylcyclopropanone can proceed by three modes (Scheme III). Two modes of

Scheme III
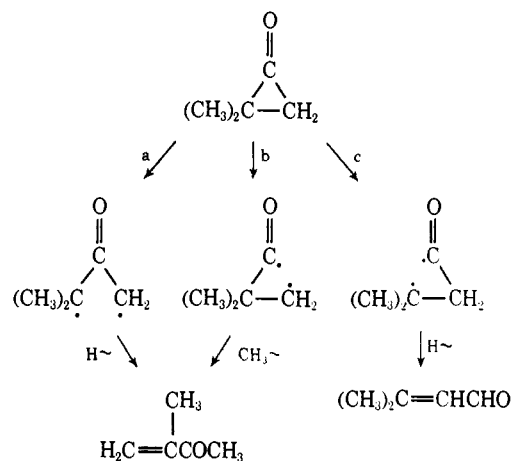
cleavage (a and b) lead to the observed ketone, while the third mode (c) leads to the unreported aldehydic product.

In comparing the relative rates of ring opening by paths b and c, one would expect path c (which produces a tertiary alkyl radical and an acyl radical) to be more prominent than path b (which leads to a primary alkyl radical and an acyl radical). Since the product of path c is not reported, cleavage of the C-2 to C-3 bond, path c, is an attractive explanation for 3-methyl-3-buten-2-one formation from 2,2-dimethylcyclopropanone pyrolysis.

A mechanism which explains the formation of the observed products of the reaction of atomic oxygen with 3-methyl-1,2-butadiene is shown in Scheme IV.

Scheme IV
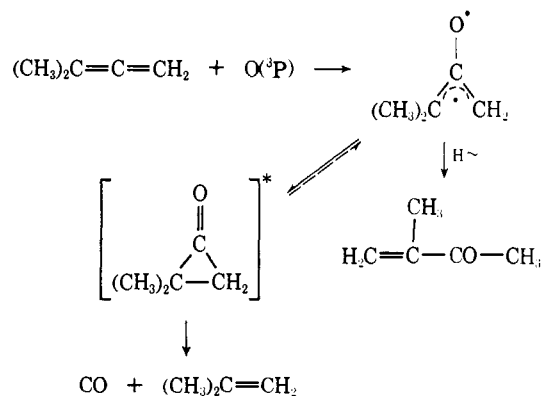
**4. 2-Methyl-2,3-pentadiene.** The only previous report of the addition of a radical to 2-methyl-2,3-pentadiene concerns the $(CH_3)_3Sn\cdot$ radical.[12] This species attacks only the central carbon atom of the allene linkage.

The products of the reaction of $O(^3P)$ with 2-methyl-

2,3-pentadiene are: carbon monoxide (65% yield), 2-methyl-2-butene (45%), 2-methyl-1-penten-3-one (8.3%), and 4-methyl-1-penten-3-one (1.9%). The total yield of oxygenated organic products is 75%.

Atomic oxygen adds to the central carbon of the allene. The resultant biradical either rearranges to the α,β-unsaturated ketones or cyclizes to an excited cyclopropanone (Scheme V). The excited cyclopro-

Scheme V

$(CH_3)_2C=C=CH(CH_3) + O(^3P) \longrightarrow$

$$CO + (CH_3)_2C=CH(CH_3)$$
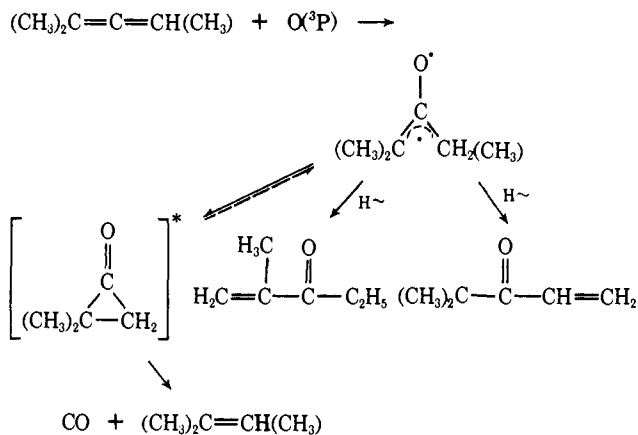
panone decomposes primarily to carbon monoxide and olefin.

C. Relative Rates of Reaction of $O(^3P)$ with Olefins and Allenes. Because olefins are produced by the reaction of $O(^3P)$ with allenes, it was necessary to establish the relative reactivity of allenes and olefins. These relative rates were determined by reactions of $O(^3P)$ with mixtures of unsaturated hydrocarbons (eq 4 and 5). Concentrations of reactants were determined before and after reaction ($\sim$30% total conversion). The expression used for the determination of relative rates is

$$O(^3P) + \text{allene} \xrightarrow{k_A} \text{products} \quad (4)$$

$$O(^3P) + \text{olefin} \xrightarrow{k_O} \text{products} \quad (5)$$
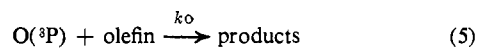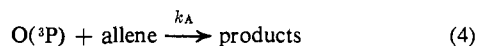
$$\frac{k_A}{k_O} = \frac{\log (\text{allene})_f/(\text{allene})_i}{\log (\text{olefin})_f/(\text{olefin})_i}$$

Relative rates of reaction of $O(^3P)$ are listed in Table I.

The rate of reaction of allenes with $O(^3P)$ increases

**Table I.** Relative Rates[a] of Reaction of $O(^3P)$ at 25°

Compd	Rel rate constant	Ref
Ethylene	0.040	b
Allene	0.197	c
Propene	0.23	b
1-Butene	0.23	c
1,2-Butadiene	0.43	b
cis-2-Butene	0.95	c
2-Methylpropene	1.00	
Cyclohexene	1.08	b
trans-2-Butene	1.13	b
3-Methyl-1,2-butadiene	2.40	d
2-Methyl-2-butene	3.17	b
2-Methyl-2,3-pentadiene	3.27	d
2,3-Dimethyl-2-butene	4.07	b

[a] The relative rate of 2-methylpropene is taken as 1.00. [b] Reference 1. [c] This work. [d] Calculated from the results of this work and R. J. Cvetanovic (ref 1).

with increased alkyl substitution. This trend has also been observed for the reaction of olefins with atomic oxygen.[1]

The relative rates of reaction of 1-butene with allene and 1,2-butadiene have been determined ($k_{\text{allene}}/k_{\text{1-butene}} = 0.66$ and $k_{1,2\text{-butadiene}}/k_{\text{1-butene}} = 1.39$). Using the value of Cvetanovic[1] for $k_{\text{1-butene}}/k_{2\text{-methylpropene}}$ (0.23), the calculated relative rates of reaction of allene and 1,2-butadiene are $k_{\text{allene}}/k_{2\text{-methylpropene}} = 0.152$ and $k_{1,2\text{-butadiene}}/k_{2\text{-methylpropene}} = 0.32$. These calculated reactivities are 23 and 25% lower than those observed by direct comparison with 2-methylpropene (Table I). However, the use of the value of Elias[14] for $k_{\text{1-butene}}/k_{2\text{-methylpropene}}$ (0.32) puts the calculated and observed values in close agreement.[15]

D. Trapping of a Substituted Cyclopropanone. Cyclopropanone and its methyl derivatives are known to polymerize very rapidly at room temperatures.[10] No cyclopropanones could be detected by nmr or ir spectroscopy from the reactions of atomic oxygen with allenes. Cyclopropanones react rapidly with alcohols to form stable hemiketals (eq 6).[16]
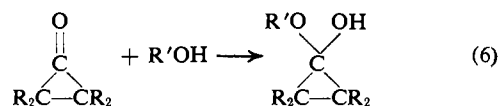
Methanol, ethanol, and 2-propanol react with $O(^3P)$ by abstraction of a hydrogen atom on the carbon adjacent to oxygen (eq 7).[17,18] The resultant "α-alcohol

$$R_2HCOH + O(^3P) \longrightarrow R_2\dot{C}OH + HO\cdot \quad (7)$$

radicals" either dimerize to glycols or disproportionate to a carbonyl compound and the parent alcohol. The rate of reaction of $O(^3P)$ with alcohols is slow compared to the addition of $O(^3P)$ to an olefin ($k_{\text{ethanol}}/k_{2\text{-methylpropene}} = 0.0072$ and $k_{2\text{-propanol}}/k_{2\text{-methylpropene}} = 0.011$ at 25°). The relative rate of reaction of $O(^3P)$ with methanol has not been reported; however, methanol should react more slowly than ethanol. The $O(^3P)$–allene reaction would be expected to be at least 27 times faster than the $O(^3P)$–methanol reaction (the calculated $k_{\text{allene}}/k_{\text{ethanol}}$ is 27.4). Thus, methanol is an ideal reagent for the trapping of cyclopropanones from the reaction of $O(^3P)$ with allenes.

When $O(^3P)$ reacted with a 1:1 mixture of allene and methanol, no 1-methoxycyclopropanol could be detected by nmr (methanol solvent). The reaction of a 1:1 mixture of 3-methyl-1,2-butadiene and methanol with oxygen atoms produced carbon monoxide (68% yield), isobutene (42%), 3-methyl-3-buten-2-one (6.7%), and 2,2-dimethyl-1-methoxycyclopropanol (1.3%). This last compound was detected and determined only by nmr spectroscopy[16] (in methanol, with benzene internal standard for quantitative analysis).

These results indicate that any cyclopropanone formed in the allene–$O(^3P)$ system polymerizes or de-

(14) L. Elias, J. Chem. Phys., 38, 989 (1963).

(15) A referee has commented that the use of reactant concentration for the determination of relative rate constants is valid only if the consumption of reactants by secondary radical reactions or by mercury photosensitized decomposition is negligible. Experiments conducted subsequent to the initial submission of this paper have shown that relative rates determined by product composition[1] differ from the values listed in Tables I and II by no more than 6%.

(16) N. J. Turro and W. B. Hammond, Tetrahedron, 24, 6017 (1968).

(17) A. Kato and R. J. Cvetanovic, Can. J. Chem., 45, 1845 (1967).

(18) A. Kato and R. J. Cvetanovic, Can. J. Chem., 46, 235 (1968).

composes before a detectable amount can be trapped. In the atomic oxygen reaction with 3-methyl-1,2-butadiene, a small amount of 2,2-dimethylcyclopropanone (which polymerizes less rapidly than cyclopropanone[10]) can be trapped by methanol. Even in the presence of alcohol, the major reaction of the excited cyclopropanone is still cleavage to carbon monoxide and olefin.

Experimental Section

Materials. Allene and nitrous oxide were obtained from Matheson Gas Products. 1,2-Butadiene was obtained from Chemical Samples Co. 3-Methyl-1,2-butadiene was prepared by the procedure of Jacobs, Teach, and Weiss.[19] 2-Methyl-2,3-pentadiene[20] was prepared by the method of Skattebol.[21] All reactants were degassed three times and purified by trap-to-trap distillation. Reaction products were identified by ir, nmr, and mass spectrometry, and, where possible, by comparative vpc retention times.

General Procedure for Atomic Oxygen Reactions. The reaction vessel consisted of a three-necked flask connected to a vacuum line and equipped with a magnetic stirrer, thermometer, condensation finger, manometer, and a PCQ9G-1 low-pressure mercury lamp (Ultraviolet Products, Inc.). The flask was charged with 1 ml of mercury and evacuated to below 2×10^{-3} Torr. The reactants (typically, 100 mmol of nitrous oxide and 4 mmol of the allene) were then cryogenically pumped into the flask. The reactants were vaporized, and the gaseous mixture (at a pressure of 610 Torr) was allowed to equilibrate with magnetic stirring for 2 hr at room temperature.

The mixture was then photolyzed for 30 min. If no precautions for the cooling of the reactor were taken, the temperature rose from 24 ± 1 to $28 \pm 1°$. Upon completion of the photolysis, condensable material was cryogenically pumped into the condensation finger. Noncondensable products (nitrogen and carbon monoxide) were expanded through two liquid nitrogen traps into a large bulb. Aliquots of this noncondensable material were analyzed by vpc (5A molecular sieves). Condensable products were separated by vacuum distillation through appropriate low-temperature traps[22] and analyzed by vpc.

Determination of Relative Rate Constants. Relative rate constants for the reactions of allenes and olefins with atomic oxygen were determined by photolysis of a gaseous mixture of the allene (2 mmol), olefin (2 mmol), nitrous oxide (100 mmol), and mercury vapor. The temperature of the reaction was maintained at $25 \pm 1°$ by the addition of ice to a stirred water bath surrounding the reaction vessel. Concentrations of hydrocarbon reactants were determined by vpc before and after reaction. Relative rate constants, as calculated by the formula given previously, are listed in Table II.

Table II. Relative Rates of Reaction of O(^{3}P) at 25°

Reactant A	Reactant O	k_A/k_O
Allene	2-Methylpropene	0.197
Allene	1-Butene	0.66
1,2-Butadiene	2-Methylpropene	0.43
1,2-Butadiene	1-Butene	1.39
3-Methyl-1,2-butadiene	2-Methyl-2-butene	0.76
2-Methyl-2,3-pentadiene	Cyclohexene	3.03

Trapping of a Substituted Cyclopropanone. 3-Methyl-1,2-butadiene (4 mmol), methanol (4 mmol), nitrous oxide (100 mmol), and mercury vapor were photolyzed for 30 min. Upon completion of the photolysis, noncondensable products were analyzed as above, and condensable products were vacuum distilled through traps at -63, -131, and $-196°$. The nmr spectrum of the $-63°$ trap material showed the presence of 3-methyl-3-buten-2-one and 2,2-dimethyl-1-methoxycyclopropanol[16] (1.3% yield) which were quantitatively analyzed by the addition of benzene and reintegration of the spectrum.

(19) T. L. Jacobs, E. G. Teach, and D. Weiss, *J. Amer. Chem. Soc.*, **77**, 6254 (1955).

(20) This compound was synthesized by Mr. William T. Chamberlain.

(21) L. Skattebol, *Acta Chem. Scand.*, **17**, 1683 (1963).

(22) R. E. Rondeau, *J. Chem. Eng. Data*, **11**, 124 (1966).