The Photolysis of Carbon Suboxide at 3000 A in the Presence of Olefins[1]

Clive Willis and Kyle D. Bayes

Contribution No. 1916 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received March 11, 1966*

Abstract: Carbon suboxide has been photolyzed at 3000 A in the gas phase. With pure ethylene, propylene, *cis*-2-butene, *trans*-2-butene, and isobutene, the corresponding allenes are produced. The reactivity of the primary intermediate toward the various olefins was measured by comparing the efficiencies of oxygen quenching of the allene yields. The relative reactivities thus measured are in complete disagreement with recently published values. Increasing the pressure of olefin or of inert gases decreases the yield of the allene. Experiments involving the direct competition between ethylene and *cis*-2-butene require a mechanism involving at least two reactive intermediates. The probable nature of these intermediates is discussed.

Earlier experiments on the photolysis of carbon suboxide in the presence of ethylene revealed a simple carbon atom insertion reaction.[2-4] The major products are propadiene and carbon monoxide. Smaller amounts of the isomer, propyne, are also formed.

$$C_3O_2 + C_2H_4 + h\nu \longrightarrow C_3H_4 + 2CO$$

The newly inserted carbon atom derives from the center position of the C_3O_2 molecule and is found predominantly in the 2 position of the propadiene.[3]

Although the above carbon insertion reaction occurs for all exciting wavelengths between 2400 and 3200 A, the sensitivity of the reaction toward molecular oxygen and nitric oxide is a strong function of the wavelength.[4] At wavelengths longer than 2900 A, a few per cent O_2 strongly inhibit the formation of propadiene from ethylene. However, at about 2500 A large amounts of oxygen have little effect on the photochemical formation of propadiene. It has been shown that there are two distinct intermediates involved, rather than a gradual change in reactivity.[4] The present paper is concerned with photolysis at 3000 A where only the long wavelength intermediate is significant.

Experimental Section

The photolysis experiments were carried out in matched pairs of quartz cells. Initially, two adjacent rectangular cells, 10 × 10 × 50 mm, were used. Later experiments were performed in a cylindrical cell, 30 mm in diameter and 50 mm in length, with a gas-tight partition along its axis.[5] In all experiments, the pair of cells contained identical pressures of carbon suboxide. One cell (hereafter called cell 1) contained some standard pressure of olefin. The second cell (cell 2) contained a different pressure of the olefin, or the same pressure of olefin together with an additional quenching gas. The two cells were placed in a fixed geometry relative to the light source. By measuring the amount of product formed in cell 1, the integrated amount of light absorbed during an experiment could be monitored, thus eliminating errors due to the variation of intensity of the light source. Good reproducibility was achieved in this manner.

The light source used was a 1-kw, high-pressure, capillary, mercury arc (General Electric BH6) which served as the effective entrance slit for a 0.5-m grating monochromator. The cells were positioned at the exit slit of the monochromator so as to receive approximately equal intensities. All experiments reported here used light of 3000 A with an effective band pass of 30 A. The grating, blazed at 7500 A, was used in the second order, so the reaction cells were also illuminated with first-order light at 6000 A. Shorter wavelength light in higher orders was eliminated with a Vycor filter.

A vacuum system, capable of 10^{-5} torr, was used. Pressures were measured with a quartz spiral manometer to 0.01 torr. All experiments were performed at 23 ± 6°. Less than 7% of the suboxide was photolyzed in any one experiment, and no effect of per cent decomposition on product behavior was observed. Thermal decomposition of the carbon suboxide was negligible for the photolysis times used.

Samples of the photolyzed gas mixture were introduced directly into a gas chromatograph equipped with a hydrogen flame ionization detector. For most of the experiments one of two columns was used: a 2.0-m dimethylsulfolane (20% on Chromosorb W) with a terminal section of 0.7-m silicone oil (8% on firebrick), or a 1.5-m dioctyl phthalate (25% on firebrick). Products were identified by their retention times and their mass spectra.

Carbon suboxide was prepared from malonic acid and phosphorus pentoxide by a method similar to that of Long, Murfin, and Williams.[6] Improved yields were achieved by intimate mixing of the reactants. Also, it was found that warming the mixture to only 50–60° was sufficient to initiate the reaction. After several distillations, the suboxide contained a fraction of a per cent of carbon dioxide, which did not interfere with the photolysis experiments.

The hydrocarbons (Phillips Petroleum research grade) were condensed at 77°K and any permanent gases pumped away. Oxygen (Gordon Duff medical grade 99.8%), nitrogen (Matheson prepurified grade, 99.997%), and argon (General Dynamics CP grade 99.99%) were used without further purification.

Results

For the olefins studied, the major carbon insertion product was the corresponding allene (*e.g.*, 2,3-pentadiene from *cis*-2-butene). Smaller amounts of the acetylene isomers were also formed.[7] When significant, the chromatogram area corresponding to the acetylene product was added directly to that of the allene, and the total reported as "yield." The yield values reported in the tables give the approximate partial pressure of the allene (plus isomers) in the cell at the end of a run. In calculating these partial pressures from chromatogram areas, it was assumed that the flame ionization detector response was directly proportional to the partial pressure and also to the number of carbon atoms of the product.[8] This assumption was

---

[1] Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] K. D. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).

[3] R. T. Mullen and A. P. Wolf, *ibid.*, **84**, 3214 (1962).

[4] K. D. Bayes, *ibid.*, **84**, 4077 (1962).

[5] G. B. Kistiakowsky and K. Sauer, *ibid.*, **80**, 1066 (1958).

[6] D. A. Long, F. S. Murfin, and R. L. Williams, *Proc. Roy. Soc.* (London), **A223**, 251 (1954).

[7] The amount and behavior of the various isomers of the allenes will be presented in a separate publication.

[8] J. C. Sternberg, W. S. Gallaway, and D. T. L. Jones in "Gas Chromatography," N. Brenner, J. E. Callen, and M. D. Weiss, Ed., Academic Press Inc., New York, N. Y., 1962, p 231.

valid for the allenes tested. However, since not all of the allenes and their isomers were standardized, the reported partial pressures should be used only as a guide to the amount of product formed. The reported yields have been corrected for the slightly different light intensities in the two cells.

Table I records the results of photolyzing carbon suboxide in various oxygen–olefin mixtures. Both cells contained identical pressures of olefins and carbon suboxide, with oxygen added to cell 2 only.

Table I. Quenching of Photochemical Yields by Molecular Oxygen

	Pressure, torr			Yield	
Olefin	Olefin	C_3O_2	O_2	Cell 1	Cell 2
Ethylene	54.2	4.32	0.92	0.0429	0.0154
	74.0	10.67	2.31	0.0258	0.0070
	565.0	11.08	18.02	0.1151	0.0319
	59.8	5.53	3.40	0.1105	0.0190
	155.7	4.84	9.83	0.0267	0.0038
	152.2	5.10	18.08	0.1524	0.0120
Propylene	22.0	3.17	2.60	0.0246	0.0076
	17.81	2.89	5.25	0.0251	0.0041
	20.94	3.00	8.90	0.0525	0.0060
cis-2-Butene	7.44	2.94	0.67	0.0120	0.0059
	8.05	4.00	1.91	0.0098	0.0028
	48.3	4.28	16.8	0.0241	0.0045
	65.9	4.14	26.0	0.0348	0.0066
	6.00	3.97	3.02	0.0331	0.0047
	7.44	2.93	7.88	0.0117	0.0008
trans-2-Butene	10.73	3.08	1.14	0.0239	0.0116
	10.37	2.91	5.45	0.0176	0.0026
	10.56	2.76	13.90	0.0196	0.0014
Isobutene	11.31	2.67	1.62	0.0243	0.0169
	10.84	3.16	5.02	0.0136	0.0065
	11.25	3.14	7.50	0.0189	0.0074
	10.12	2.89	14.35	0.0200	0.0049

It was observed that the yields depended upon the partial pressure of the olefin. An increase in olefin pressure resulted in a decrease in yield. The results of such self-quenching experiments are collected in Table II. The olefin pressure in cell 1 was approximately constant while that in cell 2 was varied. The pressure of carbon suboxide was identical in both cells and was held approximately constant within a series of runs.

Table II. Self-Quenching of Photochemical Yields

	Olefin pressure, torr		C_3O_2 pressure, torr	Yield	
Olefin	Cell 1	Cell 2		Cell 1	Cell 2
Ethylene	14.6	187	5.04	0.0631	0.0558
	14.6	450	5.36	0.0593	0.0476
	14.7	595	5.16	0.0577	0.0435
Propylene	16.85	94.7	3.19	0.0168	0.0157
	17.50	336	3.21	0.0379	0.0174
	17.62	733	2.94	0.0648	0.0161
cis-2-Butene	6.8	2.3	3.08	0.0088	0.0094
	7.6	7.6	2.42	0.0071	0.0071
	7.9	12.7	2.12	0.0062	0.0054
	7.7	17.0	2.33	0.0064	0.0051
	7.6	24.8	2.38	0.0071	0.0048
	7.7	57.0	2.34	0.0063	0.0022
	7.7	95.5	2.28	0.0042	0.0010
	5.1	672	5.07	0.0663	0.0021
trans-2-Butene	7.26	39.9	3.02	0.0216	0.0111
	7.66	75.3	2.73	0.0223	0.0067
	7.72	106	2.79	0.0137	0.0035
Isobutene	6.82	33.0	3.36	0.0086	0.0049
	7.15	67.2	2.77	0.0214	0.0076
	7.34	103	2.89	0.0157	0.0041

Inhibition of allene formation was not restricted to self-quenching by olefins. Other gases, which appear to be inert in the photolysis of carbon suboxide, were also found to reduce yields. Results for this inert gas quenching are shown in Table III. Both cells contained identical suboxide and olefin pressures, and the inert gas was added only to cell 2.

Table III. Inert Gas Quenching of Photochemical Yields

		Pressure, torr			Yield	
Olefin	Inert gas	Olefin	Inert gas	C_3O_2	Cell 1	Cell 2
cis-2-Butene	Nitrogen	7.02	46.6	2.97	0.0041	0.0028
		7.00	87.0	3.00	0.0043	0.0021
		7.20	127	2.81	0.0059	0.0026
		6.80	150	3.21	0.0030	0.0011
		6.79	185	3.20	0.0064	0.0020
		16.1	75.1	3.41	0.0048	0.0031
		15.6	279	4.94	0.0210	0.0066
		36.7	229	4.77	0.0292	0.0129
		35.7	709	5.08	0.0249	0.0051
		92.7	109	5.14	0.0123	0.0107
		95.5	659	5.01	0.0123	0.0044
		5.82	20.1	4.22	0.0117	0.0082
		6.04	40.0	3.98	0.0104	0.0071
		5.91	60.0	4.05	0.0263	0.0179
		6.11	72.8	3.79	0.0093	0.0051
		6.05	108	4.01	0.0214	0.0089
trans-2-Butene	Argon	6.89	73.2	3.17	0.0104	0.0075
		7.33	158	2.95	0.0297	0.0127
		6.89	284	3.17	0.0149	0.0046
trans-2-Butene	Isobutane	7.28	34.6	2.83	0.0171	0.0088
		7.21	67.4	2.84	0.0220	0.0071
		7.44	93.6	3.05	0.0120	0.0031

Direct competition between two olefins was studied in a series of experiments using mixtures of ethylene and *cis*-2-butene. Although it is possible to study such a competition with a single cell, in most experiments matched cells were used, thus enabling the relative quantum yields to be followed. The cells contained identical suboxide and *cis*-2-butene pressures, and ethylene was added to cell 2 only. The results are in Table IV.

Table IV. Competition between Ethylene and *cis*-2-Butene

Pressure, torr			C_5 yield		C_3 yield in cell 2	θ
cis-2-Butene	Ethylene	C_3O_2	Cell 1	Cell 2		
19.9	28.0	4.50	0.0643	0.0337	0.0095	0.200
14.1	37.8	4.06	0.0517	0.0203	0.0126	0.231
14.4	72.8	4.46	0.0706	0.0177	0.0287	0.321
13.8	145	4.26	0.0657	0.0069	0.0269	0.374
11.1	185	5.05	0.136	0.0066	0.0785	0.716
14.2	194	5.44	0.222	0.0092	0.0758	0.604
19.8	279	5.19	...	0.0051	0.0603	0.832
19.8	473	5.19	...	0.0027	0.0837	1.292
14.4	564	5.34	0.307	0.0047	0.271	1.466
53.4	49.6	5.19	...	0.0496	0.0170	0.396
53.4	120	5.19	...	0.0200	0.0296	0.656
53.7	268	5.05	0.126	0.0171	0.0948	1.107
56.9	414	5.10	0.126	0.0096	0.0961	1.381
53.0	625	5.11	0.118	0.0064	0.1436	1.894
207	108	5.19	...	0.0276	0.0199	1.376
215	124	5.17	0.0343	0.0163	0.0141	1.498
207	256	5.19	...	0.0214	0.0446	1.690
216	410	5.55	0.0589	0.0166	0.0641	1.995
219	462	5.30	0.0634	0.0171	0.0784	2.169

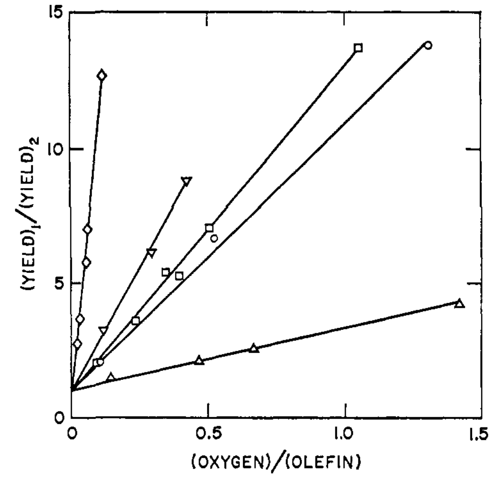


Figure 1. The ratio of yield in cell 1 to yield in cell 2 as a function of the oxygen to olefin ratio in cell 2: ◇, ethylene; ▽, propylene; □, *cis*-2-butene; ○, *trans*-2-butene; △, isobutene. The straight lines were determined by the method of least squares.

Mechanism

The results of the experiments described above cannot be explained by a mechanism that involves a single reactive intermediate. A general reaction scheme involving two reactive intermediates is proposed below.

Photoinitiation: $C_3O_2 + h\nu \longrightarrow S$ (1)
Primary reaction: $S + \text{olefin} \longrightarrow I^*$ (2)
Yield formation: $I^* \longrightarrow \text{allene} + \text{isomers}$ (3)
Yield quenching: $I^* + M \longrightarrow \text{nonallene products}$ (4)

Initially carbon suboxide absorbs the radiation to form the first intermediate, S. This intermediate can react with an olefin to form the second intermediate, I*, or it can be quenched by oxygen[9] (step 5). The

$$S + O_2 \longrightarrow CO \text{ and } CO_2 \tag{5}$$

second intermediate eventually forms the allene (step 3) unless a collision with another molecule, M, takes place, in which case allene formation is somehow prevented (step 4). Later it will be suggested that S is the C_2O molecule, and that I* may be a cyclopropylidene ketene, probably with excess vibrational energy.

If it is assumed that oxygen reacts with S only, the above reaction scheme predicts that the data in Table I should follow equations of the form

$$\frac{(\text{yield})_1}{(\text{yield})_2} = 1 + \frac{k_5(O_2)}{k_2(\text{olefin})} \tag{I}$$

As can be seen in Figure 1, good linearity is observed for all the olefins studied. It is clearly the oxygen/olefin ratio in these experiments, and not the absolute pressure of oxygen, that determines the yield. The slopes of the least-squares lines give the relative ratio of rate constants, k_5/k_2, and these are collected in Table V. Since k_5 should be the same for all these competitions, the reciprocals of the slopes are a measure of the reactivities of the olefins toward the intermediate S.[10]

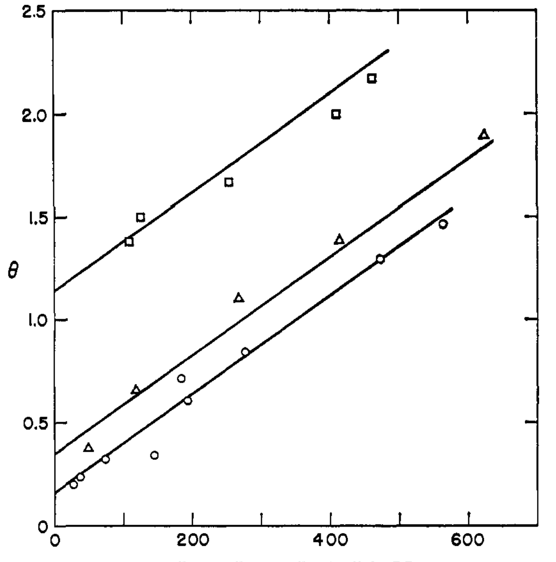


Figure 2. The value of θ, as defined in eq II, as a function of the ethylene pressure for three different average *cis*-2-butene pressures: ○, 15 torr; △, 56 torr; □, 213 torr. The straight lines represent eq II.

If only one intermediate were involved, the relative reactivities of the olefins toward S also could be determined by photolyzing carbon suboxide in mixtures of two olefins. Thus, if the reaction scheme is simplified by neglecting step 4 and assuming that step 3 always results in allene formation, the factor θ

$$\theta = \frac{(\text{yield})_a(\text{olefin})_b}{(\text{olefin})_a(\text{yield})_b}$$

should be a constant. Here $(\text{yield})_a$ represents the carbon insertion products derived from the olefin whose pressure is $(\text{olefin})_a$, etc. As can be seen in Table IV, the factor θ is not a constant for mixtures of ethylene and *cis*-2-butene. It is this strong variation of θ that requires the postulation of a second intermediate, I*. The factor θ is plotted against the ethylene pressure for three different *cis*-2-butene pressures in Figure 2. A least-squares analysis of the data for each butene pressure yielded three straight lines which were parallel within their experimental errors. In addition, the intercepts of the straight lines were approximately proportional to the *cis*-2-butene pressure. All of the *cis*-2-butene–ethylene competition results can be represented by the empirical equation

$$\theta = \frac{(C_3 \text{ yield})(B)}{(C_5 \text{ yield})(E)} = 8.53 \times 10^{-2} + 4.77 \times 10^{-3}(B) + 2.39 \times 10^{-3}(E) \tag{II}$$

Table V. Rate Constants Determined from the Least-Squares Lines of Figures 1 and 3

Olefin	k_5/k_2	k_4/k_3, torr^{-1}
Ethylene	95	5.80×10^{-4}
Propylene	18.0	4.43×10^{-3}
cis-2-Butene	11.9	5.05×10^{-2}
trans-2-Butene	9.8	4.06×10^{-2}
Isobutene	2.24	3.83×10^{-2}

---

[9] D. G. Williamson, private communication.

[10] For simplicity, the small additional effect of the added oxygen in step 4 has been neglected in eq I. If it is included, and O_2 is assumed to be as efficient as N_2 in step 4 (see Table VII), corrections to $(\text{yield})_1/(\text{yield})_2$ ratios up to 14% are necessary. The resulting changes in slopes, amounting to decreases of k_5/k_2 of 10% or less, are comparable to the experimental errors.

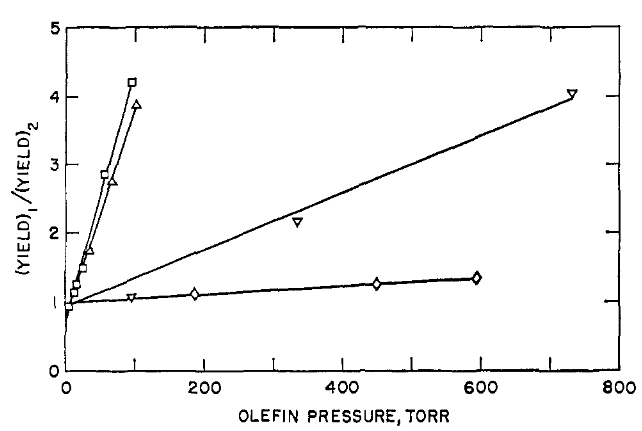


Figure 3. The ratio of yield in cell 1 to yield in cell 2 as a function of the olefin pressure in cell 2: ◊, ethylene; ▽, propylene; △, isobutene; □, *cis*-2-butene.

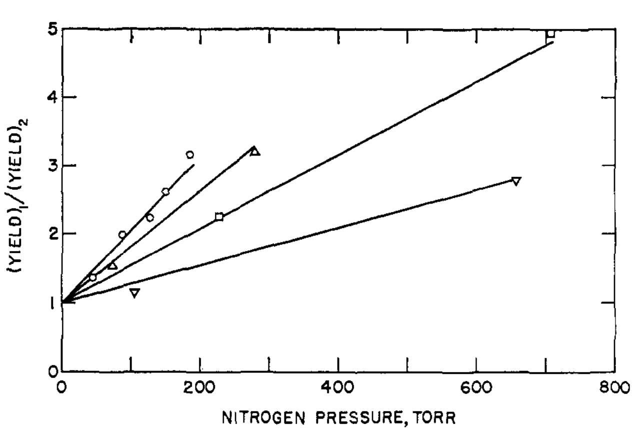


Figure 4. The effect of nitrogen pressure in cell 2 on the ratio of yields for four different *cis*-2-butene pressures: ▽, 94 torr; □, 36 torr; △, 16 torr; ○, 7 torr. The straight lines represent a least-squares fit of all of the data to eq VII.

where (B) and (E) are the pressures in torr of *cis*-2-butene and ethylene, respectively, and the coefficients have been taken from a least-squares fit of all of the cell 2 data in Table IV. Using the proposed reaction scheme, however, a more complex expression for θ results. In this equation, the number suffix, as previously, refers to the step in the reaction mechanism; the letter subscripts, B or E, identify the collision partner in steps 2 and 4 as *cis*-2-butene or ethylene, respectively; and the letter superscripts refer to the origin of the intermediate I*, b to that derived from *cis*-2-butene and e to that from ethylene. For example, $k_{4E}{}^{b}$ represents the rate constant for step 4 in which an ethylene molecule collides with an intermediate I* that was originally formed from S and *cis*-2-butene.

$$\theta = \frac{k_{2E}}{k_{2B}}\left[\frac{1 + \frac{k_{4B}{}^{b}}{k_3{}^{b}}(B) + \frac{k_{4E}{}^{b}}{k_3{}^{b}}(E)}{1 + \frac{k_{4B}{}^{e}}{k_3{}^{e}}(B) + \frac{k_{4E}{}^{e}}{k_3{}^{e}}(E)}\right] \tag{III}$$

Equation III is equivalent to eq II only if $k_{4B}{}^{e}$(B) and $k_{4E}{}^{e}$(E) are much less than $k_3{}^{e}$. In terms of the mechanism, this means that the intermediate formed from ethylene always forms propadiene or propyne in the pressure range studied. Equation III then reduces to

$$\theta = \frac{k_{2E}}{k_{2B}}\left[1 + \frac{k_{4B}{}^{b}}{k_3{}^{b}}(B) + \frac{k_{4E}{}^{b}}{k_3{}^{b}}(E)\right] \tag{IV}$$

which has the same form as the empirical eq II.

The relative quantum yields of 2,3-pentadiene also agree with the proposed reaction scheme. For the *cis*-2-butene–ethylene competition experiments recorded in Table IV, the mechanism predicts for the ratio of 2,3-pentadiene formed in cell 1 to that formed in cell 2

$$\frac{(\text{2,3-pentadiene})_1}{(\text{2,3-pentadiene})_2} = \left[1 + \frac{k_{2E}(E)}{k_{2B}(B)}\right]\left[1 + \frac{k_{4E}{}^{b}(E)}{k_3{}^{b} + k_{4B}{}^{b}(B)}\right] \tag{V}$$

Since the measurements of 2,3-pentadiene in both cells are less extensive than the measurements of θ, an evaluation of all of the constants in eq V is not possible. In order to evaluate some of the constants, the relative quantum yields, (2,3-pentadiene)$_1$/(2,3-pentadiene)$_2$, were divided by the factor $(1 + k_{2E}(E)/k_{2B}(B))$ using the rate constant ratios found in the oxygen–olefin competition experiments. The resulting quantities were then plotted against the ethylene pressures. Approximate straight lines were obtained, and the slopes at different *cis*-2-butene pressures were used to obtain the rate constant ratios, $k_{4E}{}^{b}/k_3{}^{b}$ and $k_{4B}{}^{b}/k_3{}^{b}$.

The self-quenching behavior of the olefins is explained by deactivation of the intermediate, I*. The ratio of yields when different olefin pressures are used in cells 1 and 2 can be expressed as

$$\frac{(\text{yield})_1}{(\text{yield})_2} = \frac{k_3 + k_4(\text{olefin})_2}{k_3 + k_4(\text{olefin})_1} \tag{VI}$$

The self-quenching data reported in Table II obey such equations, as shown in Figure 3. The ratio of the slopes to the intercepts of the lines gives the relative rate constants, k_4/k_3, for the olefins studied. These ratios of rate constants, taken from least-squares lines, are collected in Table V.

The quenching effect of an inert gas can also be explained in terms of deactivation of the intermediate, I*. For example, quenching of the allene yield from *cis*-2-butene by the inert gas M, would obey the equation

$$\frac{(\text{yield})_1}{(\text{yield})_2} = 1 + \frac{k_{4M}{}^{b}(M)}{k_3{}^{b} + k_{4B}{}^{b}(B)} \tag{VII}$$

The term $k_{4M}{}^{b}$(M) represents quenching of the intermediate I* by M, a process which occurs only in cell 2. The data obtained from nitrogen quenching in *cis*-2-butene are plotted in Figure 4. A series of straight lines is obtained, the smaller slopes occurring for higher olefin pressures, as predicted by eq VII. Using the slopes of the lines both $k_{4B}{}^{b}/k_3{}^{b}$ and $k_{4N}{}^{b}/k_3{}^{b}$ can be obtained. Argon and isobutane quenching in *trans*-2-butene obey similar equations, and the values of k_{4M}/k_3 for these gases have been evaluated from the data in Table III, together with the value of k_4/k_3 for *trans*-2-butene from Table V.

Thus the proposed reaction mechanism, steps 1 through 5, is compatible with the observed kinetic behavior. Only one additional assumption, the simplification of eq III to IV, is required. Several independent determinations of the same rate constant ratios have been made in the course of fitting the experimental data to the proposed mechanism. The agreement between these independently determined numbers, as shown in Table VI, is given in justification of the proposed mechanism. The value of k_{2B}/k_{2E} obtained in the *cis*-2-butene–ethylene competition experiments is an extrapolated value and has a rather large probable error that easily encompasses the more accurate determination from the oxygen–olefin competition experiments. The discrepancies among the four independent values of $k_{4B}{}^b/k_3{}^b$ ($\pm 30\%$ about the mean) may be due to experimental error, or to an over-simplification of the reaction mechanism.

Table VI. A Comparison of Independently Determined Rate Constant Ratios Involving Ethylene (E) and *cis*-2-Butene (B)

Rate constant ratios	Experimentally observed ratios	Method of determination
k_{2B}/k_{2E}	8.0	Oxygen–olefin competitions
	11.7	Butene–ethylene competition
$k_{4B}{}^b/k_3{}^b$	5.6×10^{-2} torr^{-1}	Butene–ethylene competition
	5.1×10^{-2}	Butene self-quenching
	4.2×10^{-2}	Nitrogen quenching in *cis*-2-butene
	3.1×10^{-2}	Butene–ethylene relative quantum yields
$k_{4E}{}^b/k_3{}^b$	2.8×10^{-2} torr^{-1}	Butene–ethylene competition
	3.4×10^{-2}	Butene–ethylene relative quantum yields

Discussion

The available experimental evidence favors identifying the intermediate S with the C_2O molecule. The infrared spectrum of C_2O has been observed recently at low temperature.[11] It is formed when matrix isolated C_3O_2 is photolyzed, although this is not the most abundant source of the radical. However, the matrix photolysis employed the xenon resonance line at 1470 A, while the current experiments used only light of 3000-A wavelength. Therefore, identifying S with the C_2O radical is not a certainty, although it seems probable.

The recently determined heat of formation of C_3O_2 eliminates the possibility that the initial reactive intermediate could be a carbon atom.[12] The one-step photochemical decomposition

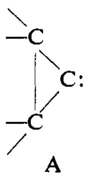
$$C_3O_2 \longrightarrow C(^3P) + 2CO \qquad \Delta H = 141.5 \text{ kcal/mole}$$

would require light of wavelength 2021 A or shorter. Photolysis experiments in the wavelength range 2400 to 3300 A are not capable of producing a carbon atom directly.

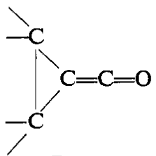
The sum of the bond energies, D(OC–CCO) and D(C–CO), must equal the above ΔH, 141.5 kcal/mole. The matrix isolated C_2O has a broad absorption near 5000 A, and apparently photodissociates to C and CO.[11] This places an upper limit on D(C–CO) of 57 kcal/mole, which requires the D(OC–CCO) be equal to or greater than about 84 kcal/mole. The onset of photochemical reactivity of C_3O_2 occurs at about 3200 A, corresponding to an energy of 89 kcal/mole. The agreement between these two energies supports the formation of C_2O in the primary photoreaction. An alternate value of D(OC–CCO) of 54 kcal/mole has been suggested from the thermal decomposition of C_3O_2 at high temperatures.[13] Regardless of which bond energy is correct, it appears that photolysis at 3000 A is sufficiently energetic to form C_2O from C_3O_2.

Simple molecular orbital theory predicts that the molecule C_2O will have a $^3\Sigma$ ground state and low-lying $^1\Delta$ and $^1\Sigma$ states.[4] The rapid reaction of S with oxygen and nitric oxide as well as the range of its reactivity with the olefins favor identifying S with the $^3\Sigma$ state of C_2O. The formation of triplet C_2O by the photolysis of singlet C_3O_2 is forbidden by the spin-conservation rule, since there is insufficient energy to simultaneously excite the triplet state of carbon monoxide. The intensity of the first electronic transition of C_3O_2 (oscillator strength = 0.002) is too large to be a singlet-to-triplet transition. However, the absence of both fluorescence and phosphorescence suggests photodissociation.[14] Both of these observations are consistent with excitation of the C_3O_2 initially to a singlet state which crosses over to a dissociative triplet state before reemission can occur. It is known that such spin-forbidden predissociations can dominate a fully allowed emission.[15]

The identification of I* is not certain. If the intermediate S is the C_2O molecule, then I*, which results from the reaction of S with an olefin, would probably be a cyclopropylidene, A, or the cyclopropylidene ketene, B. Identification of the intermediate I* with



A



B

A is attractive, since it is known that cyclopropylidenes can collapse to form allenes.[16] Also, being very reactive, A could add to another molecule of olefin or C_3O_2, and thereby prevent the formation of allene. Even if A is formed, it must at some stage pass through a structure similar to B. The kinetic behavior of I* does not permit choosing between these two alternatives.

It is certain that the loss of yield at higher pressures, represented by step 4 in the mechanism, is not a direct reaction of I* with another olefin. The effectiveness of various gases in causing loss of yield are shown in Table VII. Step 4 cannot be a chemical reaction, since argon and nitrogen are within a factor of 4 as effective as the butenes. Instead, step 4 is probably a removal of excess energy that inhibits the collapse of I* to the allene. Once stabilized, the intermediate may make many collisions and, for the conditions of these experiments, eventually forms another product.

Several attempts have been made to observe this alternate product or products. Runs in high pressures of *cis*-2-butene, or *cis*-2-butene pressurized with N_2, resulted in the formation of at least one additional prod-

---

[11] M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, *J. Chem. Phys.*, **43**, 3734 (1965).

[12] B. D. Kybett, G. K. Johnson, C. K. Barker, and J. L. Margrave, *J. Phys. Chem.*, **69**, 3603 (1965).

[13] H. B. Palmer and T. J. Hirt, *J. Am. Chem. Soc.*, **84**, 113 (1962).

[14] H. W. Thompson and N. Healey, *Proc. Roy. Soc.* (London), **A157**, 331 (1936).

[15] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p 419.

[16] W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963).

Table VII. The Efficiencies of Various Gases, Relative to the Parent Butene, of Quenching the Photochemical Yield

M	k_{4M}/k_{4B}	I* formed from
Isobutane	0.99	*trans*-2-Butene
Ethylene	0.61	*cis*-2-Butene
Nitrogen	0.39	*cis*-2-Butene
Argon	0.25	*trans*-2-Butene

uct having a molecular weight higher than C_5H_8. However, duplicate runs did not give consistent results, and sufficient material could not be accumulated for a proper purification and analysis. The mass spectrum of the photolyzed mixture contained peaks at least up to C_9, suggesting the addition of two butene molecules.

Experiments using 2,3-dimethyl-2-butene resulted in the formation of crystals on the walls of the cell. Earlier attempts to measure the reactivity of 2,3-dimethyl-2-butene by competition with oxygen showed that allene formation occurred only at low pressures. This is expected from the trend of k_4/k_3 values shown in Table V. When 6 torr of C_3O_2 was photolyzed with approximately 100 torr of 2,3-dimethyl-2-butene in a 5-l. Pyrex bulb, using a 300-w medium-pressure mercury arc, tiny crystals began forming after several hours. A high-resolution mass spectrum of the crystals determined their formula as $C_{16}H_{24}O_2$. Although the complete structure of this compound has not been determined, the infrared and nmr spectra are consistent with a symmetrical ketene dimer. The logical precursor to such a dimer, although not the only conceivable one, would be the cyclopropylidene ketene, **B**. If this is the case, then step 4 may involve the removal of excess energy from the ketene which prevents its decomposition.

The relative reactivities of the various olefins with the intermediate S are collected in Table VIII. The values in column 1 are taken as the reciprocal of the slopes of the oxygen quenching curves in Figure 1, normalized to ethylene. The numbers recently reported by Baker, Kerr, and Trotman-Dickenson,[17] supposedly for the relative reactivities of olefins with C_2O, are shown in the second column. For comparison, the relative reactivities of the various olefins toward ground-state atomic oxygen are shown in the last column.

Table VIII. Relative Reactivity of Olefins in the Photolysis of Carbon Suboxide and with Oxygen Atoms

Olefin	C_3O_2 photolysis[a]	C_3O_2 photolysis[b]	$O(^3P)$[c]
Ethylene	1.00	1.00	1.00
Propylene	5.3	0.313	5.8
cis-2-Butene	8.0	0.155	24
trans-2-Butene	9.7	0.091	28
Isobutene	42	0.096	25

[a] This work. [b] Ref 17. [c] R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

Columns 1 and 2 show a completely opposite trend in reactivities. The reason for this disagreement is not apparent, since it is not stated how the numbers in column 2 were measured. Baker, Kerr, and Trotman-Dickenson do state that their relative reactivities do not depend on pressure, so apparently they have not overlooked pressure effects of the type described above. A resolution of this disagreement must await the publication of more experimental details. It should be noted that any quantitative experiments in the photolysis of C_3O_2 must involve very good wavelength control, since the reactivities change significantly in going from the long to short wavelength region.[4]

If the reactivity of C_2O is characterized by the numbers in the first column, then it behaves as a typical electrophilic agent, similar to most of the other carbenes, and to atomic oxygen.

Acknowledgments. This work was supported by the National Science Foundation through Grants GP-2489 and GP-3672. We wish to thank M. E. Jacox and D. E. Milligan for a prepublication copy of their manuscript, C. S. Foote for useful discussions, and M. J. Haugh for technical assistance.

(17) R. T. K. Baker, J. A. Kerr, and A. F. Trotman-Dickenson, *Chem. Commun.*, 358 (1965).