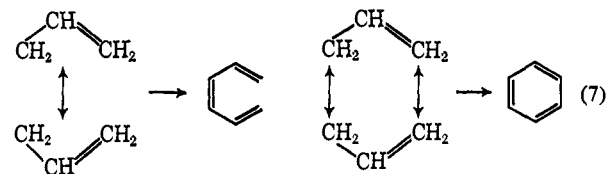


ference in steric strain between the hydrocarbon and the anion or to an abnormal solvation energy difference as a result of the peculiar shape of this molecule. Table IV also lists calculated ionization potentials.

Justification for the PMO Method

Fifteen years ago, one of us⁵ developed a general semiquantitative treatment of organic chemistry based on the application of perturbation theory to the Hückel MO (HMO) method. This perturbational MO (PMO) treatment has proved remarkably successful in practice; indeed, it often works better than the HMO method itself. A good example is provided by the phenomenon of aromaticity. The HMO method fails completely in this connection, regularly predicting large resonance energies for molecules (*e.g.*, pentalene and heptalene) which are not aromatic. The PMO method invariably predicts correctly¹³ whether given molecules should be aromatic, nonaromatic, or antiaromatic. Indeed, until the development of our SCF-MO procedures,^{1,4,6} the PMO method was the only one which could be used satisfactorily in this connection, and recently it has been shown¹³ that a similar procedure can be used to account in a rather simple way for the course of electrocyclic reactions. This success raises a rather puzzling point; how can the PMO method be superior to the HMO method, given that the former is but a first approximation to the latter? The success of our half-electron treatment of open-shell systems seems to provide an answer to this conundrum.

The PMO treatment compares the energies of related even conjugated hydrocarbons by constructing them by union of common odd fragments. For example, the π energies of benzene and hexatriene can be compared by estimating the changes in π energy when two allyl radicals unite to form one or other of the two even species; *viz.* eq 7. To a first approximation, the change in π energy during union of two such odd-alternant radicals arises from mutual interaction of their NBMO's, which, in the



HMO approximation, are degenerate. The interaction energy can be calculated in a very simple manner by first-order perturbation theory, since the coefficients of AO's in the NBMO of an odd-alternant hydrocarbon radical can be found at once by a procedure of Longuet-Higgins.¹⁴ Now the special properties of NBMO's in the HMO method do not carry over into the open-shell SCF-MO treatment; in particular, the singly occupied MO's of different odd-alternant hydrocarbon radicals (allyl, benzyl, etc.) do not have identical energies. It therefore seems at first sight that the PMO treatment must indeed be based on the HMO approximation and so should not be superior to it.

However, the odd systems introduced in the PMO treatment do not need to be normal chemical species. All we need are suitable common building blocks that can be used to construct the pairs of even systems we are comparing. We are therefore at liberty to use "closed-shell" radicals for this purpose, in which the unpaired electrons are replaced by pairs of half-electrons. It is very easily shown that odd-alternant hydrocarbon radicals of this type obey the pairing theorem, and in particular that the half-electrons in them occupy MO's of identical energies, the coefficients in which are given by the usual Longuet-Higgins¹⁴ procedure. The PMO treatment can therefore be regarded as a first approximation not to the HMO method, but to the Pople SCF-MO method that has been developed in earlier papers of this series. Since this procedure is known to give very satisfactory values for the heats of formation of conjugated hydrocarbons of all kinds, it is not surprising that the PMO method should lead to a correspondingly satisfactory picture.

(13) M. J. S. Dewar, *Tetrahedron, Suppl.* 8, [I] 75 (1966).

(14) H. C. Longuet-Higgins, *J. Chem. Phys.*, 18, 265, 275, 283 (1950).

The Reactivity of C₂O

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Contribution No. 2067 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received September 5, 1967

Abstract: Carbon suboxide has been photolyzed in mixtures of ethylene and one other gas. The relative reactivities determined by this direct competition support the values found by another method and disagree completely with an independent set of reactivities. Photolyzing at 3000 and at 2500 Å produces two different intermediates which are thought to be C₂O($\dot{X}^3\Sigma$) and C₂O($\dot{a}^1\Delta$). The reactivity of these intermediates with the olefins is compared with that of other singlet and triplet species. It is concluded that C₂O($\dot{X}^3\Sigma$) is electrophilic, similar to O(3P) and S(3P). In contrast, C₂O($\dot{a}^1\Delta$) is quite indiscriminate. The differences in reactivity found for C₂O($\dot{X}^3\Sigma$) are primarily the result of differences in activation energy, although some steric effects are present.

Carbon suboxide, C₃O₂, undergoes a simple photochemical reaction with olefins.¹ A single carbon atom is inserted into the carbon-carbon double bond,

giving an allene and two molecules of CO. The reactive intermediate is thought to be the C₂O molecule.²

(1) K. D. Bayes, *J. Am. Chem. Soc.*, 84, 4077 (1962).

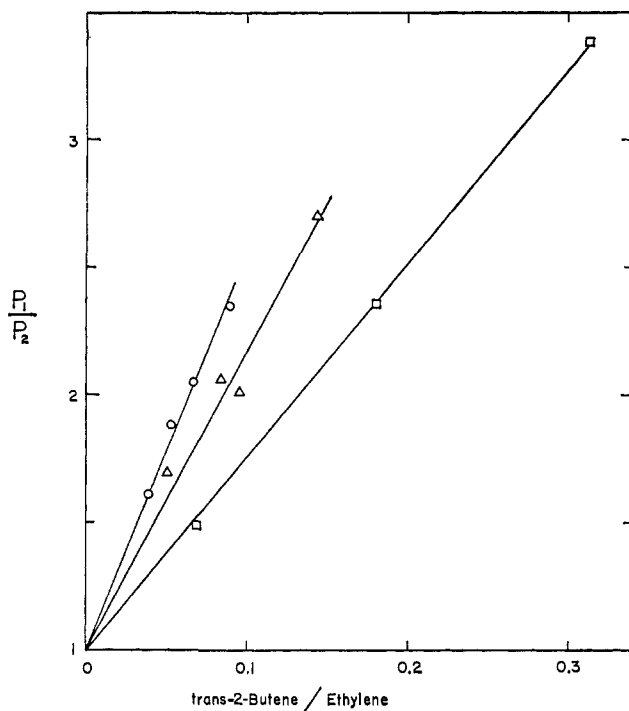


Figure 1. The ratio of the C_3H_4 yields in cell 1 (P_1) and in cell 2 (P_2) as a function of the *trans*-2-butene/ethylene ratio in cell 2, for three different temperatures: \circ , 273.2°K; Δ , 303.7°K; \square , 327.7°K.

When the C_3O_2 is labeled in the central position, the newly inserted atom is found primarily in the central position of the allene.³ The kinetic behavior of the reaction shows that one of the steps leading to allene formation is inhibited by collisions.⁴ This pressure effect is relatively unimportant for ethylene but becomes more and more significant as methyl groups are added to the carbon-carbon double bond.

The C_2O molecule has been identified in a low-temperature matrix by its infrared absorption spectrum.⁵ Its electronic absorption spectrum may have been observed in the gas phase during flash photolysis of carbon suboxide.^{6,7} Molecular orbital considerations predict that C_2O should be linear⁸ and, like O_2 , should have a $^3\Sigma$ ground electronic state and low-lying $^1\Delta$ and $^1\Sigma$ states.² The behavior of the intermediate which is formed by long-wavelength photolysis, namely great sensitivity to O_2 and NO , suggests that $C_2O(\tilde{X}^3\Sigma)$ is formed for $\lambda \geq 2900 \text{ \AA}$. In contrast, the photoreaction at 2500 \AA is not effected by O_2 or NO , and consequently $C_2O(\tilde{a}^1\Delta)$ has been proposed as the intermediate.² Some doubt has been cast on this interpretation by the recent observation that in the isoelectronic molecule, NCN , it is the $\tilde{a}^1\Delta$ state that is destroyed rapidly by O_2 , while the ground $\tilde{X}^3\Sigma$ state is not affected.⁹

The relative reactivities of C_2O have been measured by two different methods, with drastically different re-

sults. Willis and Bayes photolyzed mixtures of C_3O_2 , O_2 , and various olefins at 3000 \AA , and measured the amount of allene-type product formed as the O_2 /olefin ratio was changed.⁴ Since the competing reaction was always $C_2O + O_2$, the relative reactivities of C_2O with the olefins were determined. It was found that the reactivity increased as more methyl groups were added to the double bond, which is characteristic of electrophilic agents.

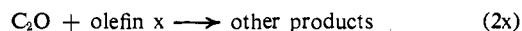
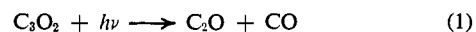
In contrast, Baker, Kerr, and Trotman-Dickenson concluded that C_2O was a nucleophilic agent.¹⁰ They measured the allene-type products and CO for various pressures of a given C_3O_2 -olefin mixture. They concluded that C_2O shows approximately the same relative reactivity in both of its electronic states (*i.e.*, at 2537 and 3130 \AA), and that the reactivity decreases as methyl groups are added to the olefin double bond.

The present study uses a third method to measure relative reactivity, namely the direct competition between ethylene and a second olefin for C_2O . By measuring only the C_3H_4 yield, which comes from the reference reaction, $C_2O + C_2H_4$, the complicating pressure effects are minimized. The relative reactivities determined by this method are compared with the previous studies.

Results

Competition experiments consisted of the simultaneous photolysis of two gas mixtures. Both cells contained the same partial pressure of C_3O_2 and ethylene, but the competing olefin x was added to cell 2 only. After photolysis, the amounts of C_3H_4 formed in the reference cell 1, P_1 , and in cell 2, P_2 , were measured. The products formed by C_2O reacting with olefin x were ignored. The experimental data are collected in Table I for the photolyses at 3000 \AA . Values of P_1 in torr and the ratios P_1/P_2 are given. Similar competition experiments using 2500- \AA radiation are reported in Table II.

If there is a simple competition between the two olefins for the reactive intermediate, indicated by reactions 2e and 2x, then there should be a simple depen-



dence of P_1/P_2 on the composition of cell 2. Equation I can be derived by assuming equal light absorption and a steady state for the C_2O concentration within each cell.

$$P_1/P_2 = 1 + k_{2x}(\text{olefin } x)/k_{2e}(\text{ethylene}) \quad (I)$$

The data in Tables I and II obey equations of this type, within their experimental error. For example, Figure 1 shows the competition plots for *trans*-2-butene-ethylene mixtures at three different temperatures, and Figure 2 is a similar plot for 2,3-dimethyl-2-butene. The slopes of these straight lines then give the ratios of k_{2x}/k_{2e} directly. The values of k_{2x}/k_{2e} derived by fitting the data of Tables I and II to eq I by the method of least squares are collected in Table III.

The ratio k_{2x}/k_{2e} did not depend on the light intensity or on the extent of conversion. Therefore, the reaction of C_2O with itself or with products was evidently unim-

- (2) K. D. Bayes, *J. Am. Chem. Soc.*, **85**, 1730 (1963).
- (3) R. T. Mullen and A. P. Wolf, *ibid.*, **84**, 3712 (1962).
- (4) C. Willis and K. D. Bayes, *ibid.*, **88**, 3203 (1966).
- (5) M. E. Jacox, D. E. Milligen, N. G. Moll, and W. E. Thompson, *J. Chem. Phys.*, **43**, 3734 (1965).
- (6) C. Devillers, *Compt. Rend.*, **262C**, 1485 (1966).
- (7) T. Morrow and W. D. McGrath, *Trans. Faraday Soc.*, **62**, 3142 (1966).
- (8) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).
- (9) H. W. Kroto, *J. Chem. Phys.*, **44**, 831 (1966).

- (10) R. T. K. Baker, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc., A*, 975 (1966).

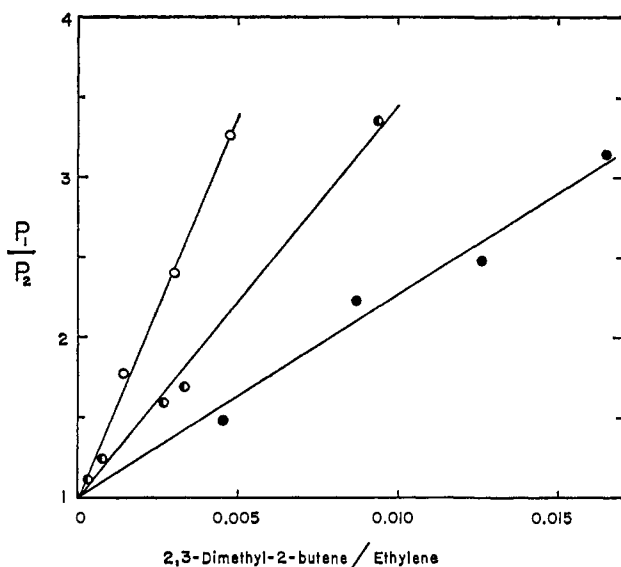


Figure 2. The ratio of the C_3H_4 yields in cell 1 (P_1) and in cell 2 (P_2) as a function of the 2,3-dimethyl-2-butene/ethylene ratio in cell 2, for three different temperatures: \circ , 273.2°K; \bullet , 301.4°K; \bullet , 326.2°K.

portant under the present experimental conditions. As shown in Table III the reaction of C_2O with allenes appears to be slower than the reaction with the corresponding olefins. Secondary attack of C_2O on the allene products can therefore be ruled out at the low conversions used.

Table II. The Direct Competition between Ethylene and an Added Gas for the Reactive Intermediate Formed at $2500 \pm 100 \text{ \AA}$ ^a

Olefin x Cell 2	Ethylene Cell 2	Both cells C_3O_2	Both cells O_2	Product P_1	P_1/P_2
Propylene					
18.4	64	5.6	13.3	0.12	1.31
34.6	53	5.5	12.5	0.12	1.82
46.9	37	5.6	12.4	0.11	2.42
cis-2-Butene					
55.5	158	5.5	9.6	0.12	1.68
105	105	5.4	11.0	0.12	2.90
129	88	5.5	11.7	0.13	3.75
2,3-Dimethyl-2-butene					
22.9	63	5.6	18.6	0.14	1.66
25.5	41.7	5.8	17.0	0.14	2.33
35.1	38.2	5.6	18.1	0.16	3.04
1,3-Butadiene					
23.5	113	5.6	12.6	0.25	1.59
23.2	56	5.5	29.9	0.15	1.94
40.2	106	5.4	32.8	0.17	1.96
22.2	56	5.7	29.7	0.19	1.96
37.2	98	5.5	14.3	0.11	2.06
25.6	43	5.9	28.7	0.37	2.27
87.0	111	5.6	14.9	0.16	2.74
43.2	60	5.7	30.2	0.18	2.86

^a All runs done at 303.6°K. The ethylene pressure in cell 1 was approximately equal to the sum of the ethylene and olefin x pressures in cell 2. All pressures are given in torr.

A few runs were made to measure the CO yields in the *cis*-2-butene- C_2O reaction. Again the double cell was employed with identical pressures of C_3O_2 in each side. A constant pressure of ethylene was used in cell 1 as a reference, and varying pressures of *cis*-2-butene were

Table III. Values of k_{2x}/k_{2e} Derived from the Data of Tables I and II by the Method of Least Squares

Reactant x	k_{2x}/k_{2e} at 3000 \AA			k_{2x}/k_{2e} at 2500 \AA 304°K
	273 °K	302 \pm 2°K	326 \pm 2°K	
Propylene	7.3	6.0	5.2	1.15
1-Butene	9.2	6.9	5.4	...
<i>cis</i> -2-Butene	13.5	9.7	8.0	1.88
<i>trans</i> -2-Butene	15.6	11.7	7.6	...
Cyclopentene	26.0	19.1	14.3	...
Isobutene	89.5	56.7	37.0	...
2-Methyl-2-butene	186	95.8	58.1	...
2,3-Dimethyl-2-butene	477	245	127	2.17
1,3-Butadiene	325	210	132	2.38
Acetylene	...	0.34
2-Butyne	...	8.9
2,4-Dimethyl-2,3-penta- diene	...	110
O_2^a	245	152	94	<1 ^b

^a The O_2 -ethylene competition at 262°K gave $k_{2x}/k_{2e} = 350$.

^b Reference 2.

added to cell 2. After photolysis, the CO formed in each cell was measured. The hydrocarbon products were not measured for these experiments. The results are given in Table IV.

Table IV. Measurements on the CO Yield in the Reaction of C_3O_2 and *cis*-2-Butene at 304°K and $3000 \pm 100 \text{ \AA}$ ^a

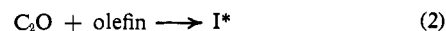
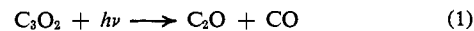
C_4H_8 Cell 2	C_3O_2 Both cells	$(CO)_1$	$(CO)_2/(CO)_1$
3.9	1.2	0.18	1.28
10.5	1.2	0.16	1.18
14.6	1.2	0.17	1.19
21.3	1.2	0.18	1.05
100	1.1	0.17	0.74
312	1.3	0.19	0.67
20.0	6.2	0.15	0.87
42.4	6.2	0.19	0.75
91.3	6.5	0.16	0.66
236	5.9	0.18	0.56
326	5.7	0.18	0.56
469	6.0	0.20	0.53

^a The reference cell 1 contained 207 ± 8 torr of C_2H_4 in all runs. All pressures are in torr.

Discussion

The following discussion will refer to the reactive intermediate formed by photolyzing C_3O_2 at 3000 \AA as $C_2O(\bar{X}^3\Sigma)$, and the intermediate formed at 2500 \AA as $C_2O(\bar{a}^1\Delta)$, with the understanding that this assignment is still tentative.

Mechanism. The mechanism proposed in a previous study⁴ of the carbon suboxide photolysis at 3000 \AA is given by reactions 1-4. Postulation of an intermediate



I^* , supposedly an energy-rich adduct of C_2O with the olefin, was necessary to explain the observed suppression of the allene yields at higher pressures. Step 4 was thought to be a removal of vibrational energy, rather than a reaction, since argon, nitrogen, isobutane, and *cis*-2-butene were of comparable effectiveness in in-

hibiting allene formation. Evidence for the "other products" being (olefin-C₂O) has been observed.⁴

The competition method used in this study assumes that the added olefin *x* has no effect on the C₃H₄ yield except by the direct removal of C₂O, reaction 2*x*. Since there is usually a different total pressure in the two cells, the added olefin could be causing a pressure-quenching effect also. As measured previously,⁴ the ratio k_4/k_3 for ethylene is 5.8×10^{-4} torr⁻¹. The maximum excess pressure in cell 2 was about 50 torr, which means that the C₃H₄ yield is being unbalanced by no more than 3% due to reaction 4. Such a small effect could not be detected for the experimental errors involved.

Additional evidence for the proposed mechanism comes from the CO yield measurements given in Table IV. It has been reported recently that the CO yield from the photoreaction of C₃O₂ and *cis*-2-butene at 3130 Å is not pressure dependent, although the pressure range studied was not stated.¹¹ The data of Table IV, plotted in Figure 3, show that there is a significant pressure effect on the CO yield. In the limit of low butene pressures, the ratio (CO)₂/(CO)₁ extrapolates to 1.36 ± 0.1 , while at higher butene pressures the ratio approaches a limiting value approximately half the low-pressure limit. This decrease in CO production by a factor of 2 as the pressure increases is expected when reaction 4 dominates over reaction 3. The solid line in Figure 3 is the predicted behavior, using the zero pressure limit of 1.36 and the value of $k_4/k_3 = 5.05 \times 10^{-2}$ torr⁻¹ determined previously.⁴ The general agreement between the solid line in Figure 3, which is determined from the measurements of the 2,3-pentadiene yield alone, and the CO production is a confirmation of the proposed mechanism. The absence of a pressure effect in the CO yield reported by Cundall, *et al.*,¹¹ suggests that they were working at a pressure above 100 torr where the variation is weak.

There are two features of these CO yield experiments which are not explained by the mechanism. The CO yields at high butene pressures are a bit lower than predicted. Similarly, the runs with 6 torr of C₃O₂ are consistently below the runs with 1.2 torr of C₃O₂. The other difficulty, perhaps related to the first, is the fact that (CO)₂/(CO)₁ does not extrapolate to near unity at low butene pressures. Actually, the above mechanism predicts an extrapolated value of 1.05, due to the operation of reaction 4 in cell 1. The observed value of 1.36 indicates that at least one additional effect has been ignored.

In spite of its simplicity, the mechanism given above is capable of explaining the complex behavior of products in mixtures of olefins⁴ and of predicting the dependence of CO yields on pressure (Figure 3). Until a more complicated mechanism becomes necessary, reactions 1-4 will be assumed correct. Consequently, the values of k_{2x}/k_{2e} given in Table III for $\lambda = 3000$ Å are interpreted as the primary reactivities of C₂O($\dot{X}^3\Sigma$) with the added gases.

Relative Reactivities of C₂O($\dot{a}^1\Delta$). In contrast to the large differences in k_{2x}/k_{2e} values for C₂O($\dot{X}^3\Sigma$), the values measured at 2500 Å are all about the same. Among the olefins tested, 1,3-butadiene is the most re-

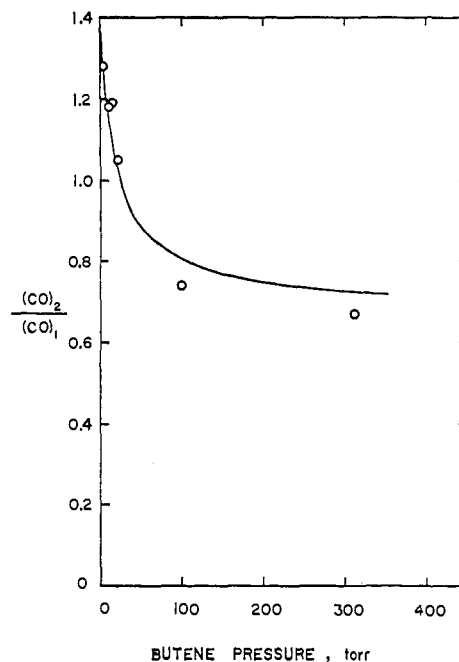


Figure 3. The decrease in the yield of CO as the pressure of *cis*-2-butene in cell 2 is increased.

active with C₂O($\dot{a}^1\Delta$), and is only 2.4 times more reactive than ethylene.

The results given in Table II show that there is a direct competition between the two olefins, rather than just a pressure effect. Plots of P_1/P_2 against (olefin *x*)/(ethylene) are linear, while plots of P_1/P_2 against pressure of olefin *x* are not linear. Since the reactivities are so similar at 2500 Å, it was necessary to add large pressures of olefin *x*. In an attempt to reduce the effects of pressure quenching of the C₃H₄ yield, the total pressure, rather than just the ethylene pressure, was kept approximately constant.

It might be argued that the more highly substituted olefins are really much less reactive with C₂O($\dot{a}^1\Delta$) than is ethylene, and that the reduction in C₃H₄ yield is just the result of pressure quenching, as indicated by reaction 4. For this to be the case, the efficiency of the higher olefins in reaction 4 would have to be approximately 100 times as great as the efficiency of C₂H₄; although not impossible, the available evidence shows that gases as different as argon and isobutane differ in efficiency by only a factor of 4.

Another possibility is that the larger olefins are not reacting directly with C₂O($\dot{a}^1\Delta$), but only deactivating it to the ground state (reaction 5). Then on subsequent



collisions the C₂O($\dot{X}^3\Sigma$) will react predominantly with the more highly substituted olefin. If this is the case, the slopes of the competition plots represent the ratio of sums of rate constant for reaction and deactivation. Clearly there must be some direct reaction of C₂O($\dot{a}^1\Delta$) with the olefins, for if there were only deactivation, by both ethylene and the higher olefins, then the competition plots would have the same slopes as when C₂O($\dot{X}^3\Sigma$) is formed directly. In the case of propylene, the absence of positive curvature in the plot of P_1/P_2 vs. (C₃H₆)/(C₂H₄) at 2500 Å requires that reaction, rather than deactivation, occurs in the majority of collisions be-

(11) R. B. Cundall, A. S. Davies, and T. F. Palmer, *J. Phys. Chem.*, 70, 2503 (1966).

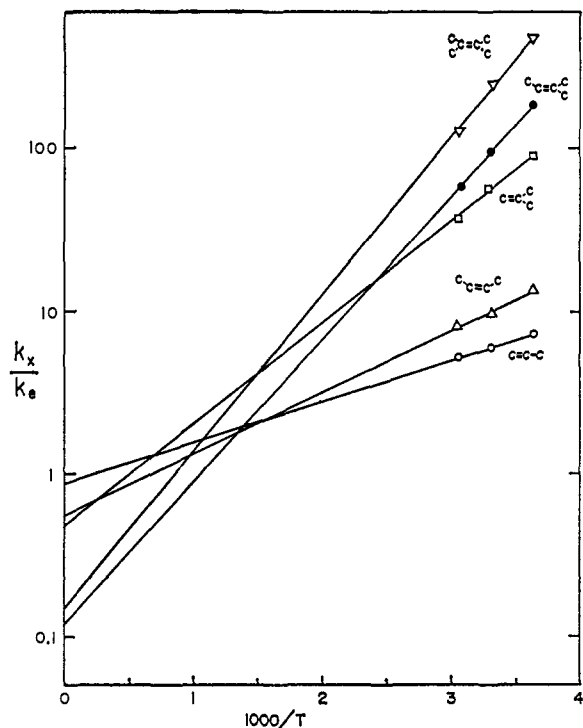


Figure 4. An Arrhenius plot of the relative rate constants for $C_2O(\tilde{X}^3\Sigma)$. The solid lines have been derived from a least-squares treatment of $\ln(k_x/k_e)$ and $1000/T$, using the values given in Table IV.

tween $C_2O(\tilde{a}^1\Delta)$ and C_3H_6 . Also the fact that O_2 and NO do not have a large effect on the C_3H_4 yield at 2500 Å indicates that electronic deactivation is not an easy process. For these molecules, reaction 5 would be spin allowed, which is not the case for deactivation by the olefins. It is concluded that the values of k_{2x}/k_{2e} reported at 2500 Å are primarily reactivities, although some contribution from electronic deactivation may be present.

Temperature Effects. If both reactions 2e and 2x obey a simple Arrhenius-type temperature dependence, then the ratio of rate constants should obey an equation of the form

$$\ln(k_{2x}/k_{2e}) = \ln(A_x/A_e) - (E_x - E_e)/RT \quad (II)$$

where A_x and A_e represent the preexponential factors, E_x and E_e are the activation energies for the two reactions, R is the gas constant, and T is the absolute temperature. A test of eq II is shown in Figure 4. The Arrhenius parameters derived by a linear least-squares fit of the data of Table I to eq II are collected in Table V. For comparison the corresponding values derived from $O(^3P) + \text{olefin}$ experiments¹² are included in Table V.

Most of the observed differences in reactivity are due to differences in activation energy. In going from ethylene to 2,3-dimethyl-2-butene, the activation energy decreases by 4.4 kcal/mole while the A factor decreases by a factor of approximately 10. In the vicinity of 300°K, the change in E dominates, making the heavier olefins more reactive. A similar although smaller decrease in activation energy is responsible for the trend of reactivities observed in oxygen atom reactions.

Even though the differences in activation energy for C_2O reactions have been determined, no single value of

(12) R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

Table V. Arrhenius Parameters Derived by Fitting the Values of k_{2x}/k_{2e} at 3000 Å to eq II^a

	$C_2O(\tilde{X}^3\Sigma)$		$O(^3P)$	
	A_x/A_e	$E_e - E_x$	A_x/A_e	$E_e - E_x$
Ethylene	1.0	0	1.0	0
Propylene	0.9	1.2
1-Butene	0.4	1.8	0.7	1.2
<i>cis</i> -2-Butene	0.6	1.7
<i>trans</i> -2-Butene	0.2	2.3
Isobutylene	0.5	2.8	0.7	2.1
2-Methyl-2-butene	0.1	4.0	1.2	2.5
2,3-Dimethyl-2-butene	0.2	4.4	1.2	2.6
1,3-Butadiene	1.5	2.9	1.1	1.8
Oxygen	0.4	3.5

^a Energy is given in kcal/mole. Values of $O(^3P)$ are taken from ref 12.

E is known. A lower limit for the largest activation energy, $E_e \geq 4.4$ kcal/mole, can be set by assuming that $C_2O(\tilde{X}^3\Sigma) + 2,3\text{-dimethyl-2-butene}$ has no activation energy. A somewhat larger value results by assuming that the reaction $C_2O(\tilde{X}^3\Sigma) + NO$, which is 2×10^4 times faster than $C_2O(\tilde{X}^3\Sigma) + C_2H_4$ at 300°K,¹³ has no energy of activation and a frequency factor similar to that of ethylene. This gives a value of E_e of approximately 6 kcal/mole. Both of these estimates are considerably higher than the corresponding value for $O(^3P) + C_2H_4$, which is approximately 2.5 kcal/mole.¹²

Because of the narrow range of absolute temperature used in this study, the values of A_x/A_e shown in Table V are not accurate to better than a factor of 2. For example, the apparent differences in frequency factors among the butenes may not be significant. However, the over-all trend to lower values as methyl groups are added is outside the experimental error. It is concluded that $C_2O(\tilde{X}^3\Sigma)$ is sensitive to steric effects in a cumulative fashion.

In contrast, the reactions of $O(^3P)$ with olefins show no steric effects, the preexponential factor being the same for 2,3-dimethyl-2-butene as for ethylene. It has been proposed that this absence of a steric effect indicates a very loosely bound transition state, perhaps with some charge-transfer character.¹² Applying this reasoning to C_2O , the occurrence of steric effects then implies a tighter transition state, which is in agreement with the higher activation energies. C_2O being larger than atomic oxygen may contribute to this effect also. The only olefin found to have a value of A_x/A_e larger than unity is 1,3-butadiene. Since there are two double bonds which the C_2O may attack, the large preexponential factor is reasonable.

Comparison with Other Measurements. The present results confirm the relative reactivities measured previously using $C_2O(\tilde{X}^3\Sigma) + O_2$ as the reference reaction: the more highly substituted olefins have the greater reactivity. The agreement is not perfect, for the present k_{2x}/k_{2e} values are somewhat greater (15–40%) than the values reported previously.⁴ Since there is a strong temperature effect on the reactivities, and since the cell used in ref 4 was not thermostated, it was suspected that the previous measurements were made at a temperature somewhat above room temperature. Indeed, if it is assumed that the cell in ref 4 was at an effective

(13) D. G. Williamson and K. D. Bayes, *J. Am. Chem. Soc.*, **89**, 3390 (1967).

Table VI. A Comparison of the Relative Reactivity of C_2O with Olefins as Reported by Baker, Kerr, and Trotman-Dickenson¹⁰ and in the Present Work

Olefin	$\lambda \geq 3000 \text{ \AA}$		$\lambda \cong 2500 \text{ \AA}$	
	BKTD 273°K	Present work 301 ± 2°K	BKTD 273°K	Present work 304°K
Ethylene	1.00	1.00	1.00	1.00
Propylene	0.287	6.0	0.321	1.2
1-Butene	0.072	6.9	0.096	...
<i>cis</i> -2-Butene	...	9.7	0.157	1.9
2,3-Dimethyl-2-butene	...	245	0.019	2.1

Table VII. A Comparison of Relative Reactivities

Reactant	$O(^3P)^a$ 25°	$S(^3P)^b$ 25°	$C_2O(\tilde{X}^3\Sigma)$ 25°	$CH_2(\tilde{X}^3\Sigma)^c$ 24°	$CH_2(^1A_1)^c$ 24°	$C_2O(\tilde{a}^1\Delta)$ 30.5°
Ethylene	1.0	1.0	1.0	1.0	1.0	1.0
Propylene	5.8	6.8	6.1	1.0	1.3	1.2
1-Butene	5.8	9.7	7.0	1.6	1.6	...
<i>cis</i> -2-Butene	24	16	10.1	0.94	1.4	1.9
<i>trans</i> -2-Butene	28	19	11.4	0.89	1.4	...
Isobutylene	25	51	58	2.9	2.0	...
2-Methyl-2-butene	79	92	100	1.8	2.1	...
2,3-Dimethyl-2-butene	102	128	250	2.7	2.2	2.1
1,3-Butadiene	24	93	210	19	3.9	2.4
Cyclopentene	30	18	19
2,4-Dimethyl-2,3-pentadiene	113 ^d
Acetylene	0.21 ^e	...	0.3 ^d
2-Butyne	8.5 ^d
Benzene	0.04	...	<1
Oxygen	135	≤0.5
Nitric oxide	2 × 10 ⁴

^a Reference 12. ^b Reference 16. ^c S. Krzyzanowski and R. J. Cvetanović, *Can. J. Chem.*, **45**, 665 (1967). ^d 30.5°. ^e D. Saunders and J. Heicklen, *J. Phys. Chem.*, **70**, 1950 (1966).

temperature of 320°K, the agreement with the present results is excellent. Since the nonthermostated cell was approximately 20 cm from the 1-kW lamp, which was air-cooled, this amount of heating is not unreasonable. Direct heating by the photolysis reaction itself was not significant.¹⁴

Both of the above sets of reactivities are in severe disagreement with the relative reactivities reported by Baker, Kerr, and Trotman-Dickenson (BKTD).¹⁰ By competing allene formation against the reaction $C_2O + C_3O_2$, BKTD concluded that the more highly substituted olefins reacted less readily with C_2O than did ethylene. Their reactivities were essentially the same when the photolysis was done at $\lambda > 3000$ and at 2537 Å, as shown in Table VI. Although the experiments were done at slightly different temperatures, there is no doubt that the disagreement is complete.

Another difference between the results of BKTD and the present interpretation is the effect of pressure. In the experiments of BKTD, pressure had no effect on the relative reactivities, even though the allene yields were used as a measure of the reaction. It seems probable that this different pressure dependence and the opposite trend of reactivities shown in Table VI are closely connected. However, the exact cause for the completely opposite results is not evident at the present time.¹⁵

(14) S. W. Benson, *J. Chem. Phys.*, **22**, 46 (1954).

(15) One experimental difference that might be of importance is the cell arrangement. BKTD illuminated all of their cell with the photolyzing light, while in the arrangement used above the light struck only part of the front and back windows of the cell. If the other products

The results shown in Figure 2 are incompatible with the relative reactivities proposed by BKTD. In the photolysis at 3000 Å and 273°K, the addition of 0.5% of 2,3-dimethyl-2-butene to ethylene decreases the amount of C_3H_4 product by more than a factor of 3: independent of kinetic interpretation, 2,3-dimethyl-2-butene is a strong inhibitor of product formation in the reaction of $C_2O(\tilde{X}^3\Sigma)$ with C_2H_4 .

Because of the agreement between the reactivities measured using both $C_2O + O_2$ and $C_2O + C_2H_4$ as reference reactions, and probable confirmation of these values by flash photolysis,⁶ the relative reactivities mea-

sured here, rather than those of BKTD, will be adopted as representing the primary k_{2x}/k_{2e} . It should be emphasized, however, that the disagreement remains unresolved.

The Nature of C_2O . The large difference in behavior of the intermediates formed by photolyzing C_3O_2 at 3000 and 2500 Å justifies the classification made previously on the basis of the effect of O_2 and NO .² At wavelengths longer than 2900 Å, the carbon insertion reaction is easily inhibited by O_2 and NO , and the intermediate shows great selectivity among the olefins. At about 2500 Å, O_2 and NO have little effect on the allene production, and the intermediate is indiscriminate in its reactions with olefins. The two intermediates are thought to be $C_2O(\tilde{X}^3\Sigma)$ for $\lambda \geq 2900$ Å and $C_2O(\tilde{a}^1\Delta)$ at 2500 Å, the expected ground and first excited states of C_2O . The verification of these assignments must await more convincing spectroscopic studies.

The relative reactivities for various triplet- and singlet-state reagents are collected in Table VII. The general trend shown by $C_2O(\tilde{X}^3\Sigma)$ is similar to that of $O(^3P)$ and $S(^3P)$ ¹⁶ and very different from the trend of the singlet-state reactants. Most remarkable is the close similarity of the reactivities of $S(^3P)$ and C_2O -

formed in reaction 4 deposit on the cell walls (which happens in at least one of the reactions⁴), the arrangement of BKTD might have led to more secondary photolysis than in the present study. Another factor contributing to secondary photolysis in the BKTD experiments is their use of light of wavelength 3100 Å, which is absorbed only very weakly by C_3O_2 .

(16) H. E. Gunning, *et al.*, quoted by R. J. Cvetanović and R. S. Irwin, *J. Chem. Phys.*, **46**, 1694 (1967).

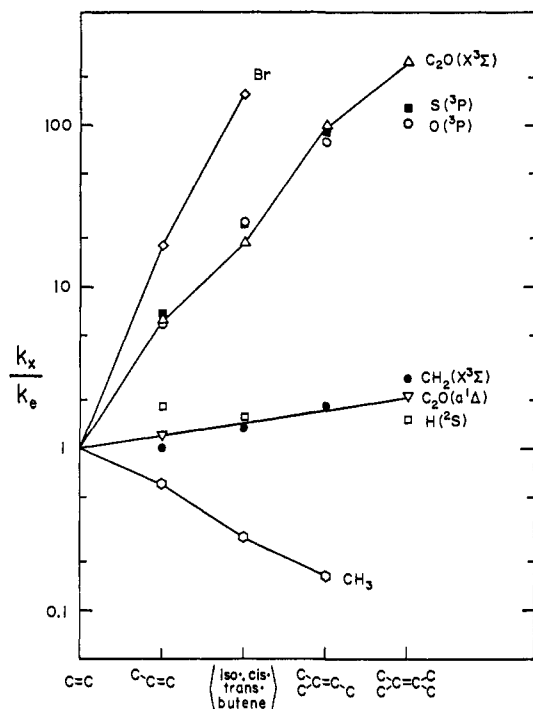


Figure 5. The relative rate constants for various reactants as a function of the degree of substitution on the carbon-carbon double bond.

($\bar{X}^3\Sigma$): the trend from *cis*- to *trans*-butene to isobutylene is identical for the sulfur atom and triplet state C_2O , and distinct from the behavior of $O(^3P)$. It will be most interesting to see if the reactivity of $S(^3P)$ is the result of the same combination of preexponential factors and activation energies that is responsible for the C_2O -($\bar{X}^3\Sigma$) reactivities. Since in the sulfur atom work it was certain that ground-state 3P atoms were involved, the almost perfect correlation between the two reactivities is assurance that a triplet-state intermediate is formed in the long wavelength photolysis of carbon suboxide.

These trends in reactivity are displayed in Figure 5. The logs of the relative rate constants have been plotted against the number of alkyl groups attached directly to the double bond. Since the butenes show a considerable variation in reactivity for some reagents, but not for others, the geometric means of the relative reactivities of *cis*- and *trans*-butene and isobutylene have been used in Figure 5. This average has no theoretical basis and is used only to give smoothly varying functions. The approximate straight lines in Figure 5 are equivalent to the common Hammett ρ - σ relationship. It is clear from Figure 5 that $O(^3P)$, $S(^3P)$, and C_2O ($\bar{X}^3\Sigma$) show a similar electrophilic trend.

The reactive intermediate which is formed by photolyzing C_3O_2 at 2500 Å, here called $C_2O(\bar{a}^1\Delta)$, belongs to the class of reactants which might be called indiscriminate. These include both singlet- and triplet-state CH_2 , as well as hydrogen atoms. $S(^1D)$ probably belongs in this class also.¹⁶ Little change in reactivity is observed in going from ethylene to the fully substituted double bond.

Another generality distinguishes the two classes of reactants. All of the electrophilic species show a slight decrease in reactivity in going from 2,3-dimethyl-2-butene to 1,3-butadiene, while the indiscriminate

reactants all show an increase, by a factor of 1.1 for $C_2O(\bar{a}^1\Delta)$, 1.8 for $CH_2(^1A_1)$, 6.6 for $H(^2S)$, and 22 for $CH_2(\bar{X}^3\Sigma)$. Methyl radicals, which show the least electrophilic character, undergo the largest increase in reactivity between 2,3-dimethyl-2-butene and 1,3-butadiene, a factor of about 600. Reasons for these trends have been discussed before and will not be repeated here.¹² It is only intended to point out the completely different behavior of $C_2O(\bar{X}^3\Sigma)$ and $C_2O(\bar{a}^1\Delta)$.

It has been argued that any differences in the reactions of singlet- and triplet-state CH_2 are the result of the different energy contents of the adducts, rather than the specific state of electron spins.¹⁷ Since the major part of the selectivity shown by $C_2O(\bar{X}^3\Sigma)$ is the result of a significant activation energy, such an interpretation could explain the lack of selectivity observed at 2500 Å. The ($\bar{a}^1\Delta$) state is estimated to have an excitation energy of about 12 kcal/mole,² which is probably larger than the activation energies involved in the $C_2O(\bar{X}^3\Sigma)$ -olefin reactions. However, if the energy requirements of the reaction are satisfied by the excitation energy of $C_2O(\bar{a}^1\Delta)$, then the reactivities should be determined primarily by the preexponential factors. A comparison of the A_x/A_e factors of Table V with the relative reactivities for $C_2O(\bar{a}^1\Delta)$, as given in Table VII, suggests that this may not be the case. Either there is a small activation energy still present in the reactions of $C_2O(\bar{a}^1\Delta)$, which just compensates for the preexponential factors, or else the electronic configuration of the C_2O molecule plays a role in determining its kinetic behavior. However, it should be remembered that the uncertainties in the A_x/A_e values are large and so the above argument is only tentative.

Experimental Section

The simultaneous runs were made in a quartz double cell consisting of two hemicylindrical compartments, each with a volume of 18 cm³. The two cells were completely immersed in a water bath whose temperature was kept constant to within $\pm 0.2^\circ$ by a thermostat. The light source was a 1-kW high-pressure mercury arc (BH6) situated at the entrance slit of a small grating monochromator (Bausch and Lomb 33-86-25-01). Light from the exit slit passed through a quartz window on the side of the water bath, and approximately equal intensities entered the two cells. One-quarter of the front cell windows and one-half of the rear windows were illuminated by the beam. Photolysis times were typically 15 min. Calibrations of the ratio of the absorbed light intensities were made by photolyzing identical mixtures at least every four runs. With some reactants (cyclopentene, 1,3-butadiene), polymer formation on the window made it necessary to do a calibration on every other run. The cells were cleaned frequently by heating in air.

Pressures under 100 torr were measured to ± 0.2 torr with a Wallace and Tiernan diaphragm gauge. A mercury manometer was used for higher pressures. Gases were added to the photolysis cells after the cells had been equilibrated at the reaction temperature: the rest of the gas-handling system was at room temperature, approximately 25°. The very reactive compounds were diluted with He or N₂ so that small concentrations could be added to the cells accurately.

Analyses were done with a Loenco H-15B gas chromatograph equipped with thermistor detectors. Propadiene and propyne were separated with a 3-m column of 20% dimethyl sulfolane on firebrick with 0.5-m terminal section of 20% squalene on Chromosorb W. Carbon monoxide was analyzed using a 1.5-m molecular sieve column (Linde 13X). Chromatograph sensitivities were determined with authentic samples.

(17) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, 2, 219 (1964).

Less than 10% of the carbon suboxide was decomposed in any one experiment. For the most reactive olefins, the amount of suboxide decomposed was sometimes a significant fraction of the olefin pressure. For these cases, the pressure of added olefin given in Table I is an average value, calculated by assuming that every C_2O which did not form C_3H_4 in cell 2 removed one molecule of olefin x . These corrections, being important only at the lowest ratio of (olefin x)/(ethylene), had little effect on the relative reactivities.

The carbon suboxide was generated as described previously.⁴ After several trap-to-trap distillations under vacuum, the only impurity detected by gas chromatography was a fraction of a per cent of CO_2 . All hydrocarbons were degassed under vacuum before using. The olefins were Phillips Research Grade, with the excep-

tion of the following: 1,3-butadiene, Matheson Instrumental Grade; isobutylene and *trans*-2-butene, Matheson CP Grade; 2,3-dimethyl-2-butene, 2,4-dimethyl-2,3-pentadiene, and 2-butyne, Columbia Organic Chemicals, 99.5%; acetylene, Matheson, 99.66%, passed through a cold trap. The following gases were used directly from the tanks: oxygen, Gordon Duff, 99.8%; nitrogen, Matheson, 99.997%; helium, Matheson, 99.99%.

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A Floating Spherical Gaussian Orbital Model of Molecular Structure. IV. Hydrocarbons¹

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Abstract: The FSGO model is applied to a series of hydrocarbons: methane, ethane, ethylene, acetylene, and cyclopropane. Bond lengths and bond angles are obtained with an average absolute deviation of 1.7 and 1.0%, respectively, from observed values. The barrier to internal rotation of ethane is calculated.

The floating spherical Gaussian orbital (FSGO) model is discussed in detail in paper I^{2a} of this series. As currently applied, the model predicts the electronic and geometric structure of singlet ground states of molecules with localized orbitals without the use of any arbitrary or semiempirical parameters. The localized orbitals are constructed by using single normalized spherical Gaussian functions

$$\phi_i(\vec{r} - \vec{R}_i) = \left(\frac{2}{\pi \rho_i^2} \right)^{3/4} \exp[-(\vec{r} - \vec{R}_i)^2 / \rho_i^2]$$

with orbital radius, ρ_i , and position, \vec{R}_i . A single Slater determinant represents the total electronic wave function. If S is the overlap matrix of the set of non-orthogonal localized orbitals $\{\phi_i\}$ and $T = S^{-1}$, then the energy expression for a molecule is

$$E = 2 \sum_{j,k} (j|k) T_{jk} + \sum_{k,l,p,q} (kl|pq) [2T_{ki} T_{pq} - T_{kq} T_{lp}]$$

where $(j|k) = \int \phi_j h \phi_k dv$ (h = one-electron operator) and $(kl|pq) = \int \phi_k(1) \phi_l(1) (1/r_{12}) \phi_p(2) \phi_q(2) dv_1 dv_2$. The energy is minimized by a direct search procedure with respect to all parameters: orbital radii, ρ_i , orbital positions, \vec{R}_i , and nuclear positions.

Previous work with the FSGO model^{2b,3} indicated that the model works best for elements in the middle of

the second row of the periodic table. So in choosing larger and more complicated molecules to which to apply the model, the hydrocarbons were a natural selection. Simple hydrocarbons present a variety of molecular structure, double and triple bonds, ring compounds, and several interesting energetic quantities.

Results

Methane provides a simple example for detailed consideration of the application of the FSGO model to the hydrocarbons. In order to make the calculation most efficient, tetrahedral symmetry is imposed, thus allowing identification of symmetrically related integrals which are calculated only once. This in effect places a symmetry constraint on the minimization; *i.e.*, while the orbital positions and radii are varied, they are varied in such a way that the symmetry is maintained. Parameters were defined so that the four C-H orbital radii are varied together; the twelve orbital positions (x , y , and z for four C-H bonding orbitals) formed another parameter. The carbon 1s orbital radius was another parameter, but the orbital was held at the origin to maintain symmetry. The 12 hydrogen positions were defined by the fourth and final parameter with the carbon being held at the origin.

This symmetry constraint is not as serious as one might suspect. Several calculations were made with relaxed symmetry with LiH and BH_3 , and the results were essentially the same as corresponding symmetry-constrained calculations. The remainder of the results reported here have the indicated symmetry imposed and presumably no error is introduced by such tactics.

The results for methane were presented in paper III³ along with other first-row hydrides but are reproduced here for comparison with the other hydrocarbons. As-

(1) Portions of this paper were presented at the Computers in Chemistry Symposium, San Diego, Calif., June 1967, and at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(2) (a) A. A. Frost, *J. Chem. Phys.*, **47**, 3707 (1967) (paper I); (b) **47**, 3714 (1967) (paper II).

(3) Paper III: A. A. Frost, *J. Phys. Chem.*, **72**, 1289 (1968); also see the preliminary communication: A. A. Frost, B. H. Prentice, III, and R. A. Rouse, *J. Am. Chem. Soc.*, **89**, 3064 (1967).