If equations 1 and 2 represent predominant reactions, then the decomposition of nitric oxide[4] also would be expected to occur, since only 162 kcal. are required to break the N—O bond, and 225 kcal. are evolved when nitrogen atoms recombine. Reaction 2, however, probably accounts for only a small percentage of the total decomposition since nitric oxide was not decomposed in a similar system.

The reaction

$$N + C_2H_6(W) \longrightarrow NH + C_2H_5 + 38 \text{ kcal.} \tag{9}$$

could proceed quite readily with ^2D and other excited nitrogen atoms, but the low concentration of these species in active nitrogen precludes their importance in the reactions studied.[5,6]

Metastable $A^3\Sigma$ nitrogen molecules have been postulated[7,8] as the species in active nitrogen which is responsible for the destruction of ammonia in the gas phase and probably accounts for the major process by which ammonia and the hydrocarbons are decomposed at −196°.

$$N_2(A^3\Sigma) + C_2H_6(W) \longrightarrow N_2(^1\Sigma) + C_2H_5 + H + 46 \text{ kcal.} \tag{10}$$

Ammonia and hydrogen cyanide then could be produced by reactions 4 to 9.

Since cyanogen was found as a product in the reaction of active nitrogen with hydrogen cyanide, CN radicals must have been formed. Thus either reaction 11

$$HCN(W) + N + N \longrightarrow CN + H + N_2 + 95 \text{ kcal.} \tag{11}$$

or reaction 12

$$HCN + N_2(A^3\Sigma) \longrightarrow CN + H + N_2(^1\Sigma) + 12 \text{ kcal.} \tag{12}$$

probably occurs. The cyanogen then would be produced by coupling of CN radicals.

Standards, Circular 467.
D(N–H) = 87 kcal. G. Pannetier and A. G. Gaydon, *J. Chem. Phys.*, **48,** 221 (1951).
D(NH–H) = 90 kcal. A. P. Altschuller, *ibid.*, **22,** 1947 (1954).
$D(NH_2\text{–}H)$ = 104 kcal. M. Swarcz, *Chem. Rev.*, **47,** 75 (1950).
$N_2(A^3\Sigma)$ = 142 kcal. K. D. Bayes, *Can. J. Chem.*, **39,** 1074 (1961).
D(H–CN) = 130 kcal. L. Brewer and A. W. Searcy, *Ann. Rev. Phys. Chem.*, **7,** 259 (1956).

(4) E. R. Zabolotny and H. Gesser, *J. Chem. Phys.*, in press.

(5) H. P. Broida and O. S. Lutes, *ibid.*, **24,** 484 (1956).

(6) H. I. Schiff, *Ann. N. Y. Acad. Sci.*, **67,** 518 (1957).

(7) K. D. Bayes, *Can. J. Chem.*, **39,** 1074 (1961).

(8) R. L. Nelson, A. N. Wright and C. A. Winkler, Symposium on Some Fundamental Aspects of Atomic Reactions, Sept., 1960, McGill University, Montreal.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES, CALIF.]

The Photolysis of Carbon Suboxide. I. Reaction with Ethylene

BY KYLE D. BAYES

RECEIVED JUNE 7, 1962

Carbon suboxide has been photolyzed in the presence of ethylene using the unfiltered radiation from a medium pressure mercury arc. The major products are allene, methylacetylene and carbon monoxide. In the limit of large ethylene to suboxide ratios, one mole of C_3H_4 is formed for every two moles of CO. The reactive intermediate is probably a CCO molecule. The intermediate can also react with carbon suboxide, resulting in polymer formation. The rate constant for the attack on suboxide is 1.4 times that for the attack on ethylene. It is suggested that if CCO is the reactive intermediate, it is formed initially in a low lying singlet state. The possible mechanisms which could yield two C_3H_4 isomers are discussed.

Introduction

The photolysis of carbon suboxide in the presence of an olefin results in a simple insertion of a carbon atom: *e.g.*, allene is formed from ethylene.[1] The nature of the reactive intermediate has not been established, but probably it is either a CCO molecule or a free carbon atom. Energy considerations, based on estimated heats of formation for carbon suboxide, favor the CCO molecule as the reactive intermediate.[2,3] Carbon atoms produced by nuclear transformations react with ethylene to give products different from those observed in the photolysis of carbon suboxide,[2] which further suggests that carbon atoms are not involved in the photolysis of carbon suboxide. The reaction with ethylene has been further studied in order to determine the nature of the reactive intermediate and the mechanism of attack on the hydrocarbon.

Experimental

The carbon suboxide was prepared by the low temperature dehydration of malonic acid.[4] After several bulb-to-bulb distillations, the suboxide was fractionated at reduced pressure on a Dry Ice–acetone cooled column, the middle third being collected and stored at liquid nitrogen temperature. The ultraviolet absorption spectrum was recorded on a Cary spectrometer, model 14, and is shown in Fig. 1. The spectrum shows the typical carbonyl band, with maximum absorption at 2650 Å., and part of the ethylenic absorption at shorter wave lengths. The intensity of the carbonyl absorption (ϵ_{max} 94 liter/mole cm.) is stronger than in other ketenes,[5] probably due to conjugation effects. Further purification did not alter the absorption coefficients. The peak intensities of the mass spectrum of the purified suboxide, taken with a CEC model 21-081A mass spectrometer using 70-volt ionizing electrons, are given in Table I. In addition to a small amount of CO_2 (mass 44 equals 0.21), the following peaks, probably due to impurities, were observed: 23(0.04), 27(0.04), 32(0.04), 56(0.05).

Research grade ethylene from Phillips Petroleum Co. was used. After removing non-condensable gases, the only impurities observed were approximately 0.1% CO_2 and a trace of acetylene. Commercial samples of allene, methylacetylene and carbon monoxide were used to calibrate the gas chromatograph.

The irradiations took place in a cylindrical quartz cell 3 cm. i.d. and 20 cm. long. At room temperature (23°) some decomposition of the suboxide was observed even in the ab-

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(1) K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).

(2) C. MacKay, P. Pollak, H. E. Rosenberg and R. Wolfgang, *ibid.*, **84**, 308 (1962).

(3) H. B. Palmer and T. J. Hirt, *ibid.*, **84,** 113 (1962).

(4) A. Klemenc, *Mh. Chem.*, **66,** 337 (1935); D. A. Long, F. S. Murfin and R. L. Williams, *Proc. Roy. Soc.* (*London*), **A223,** 251 (1954).

(5) G. B. Kistiakowsky and B. H. Mahan, *J. Am. Chem. Soc.*, **79,** 2112 (1957).

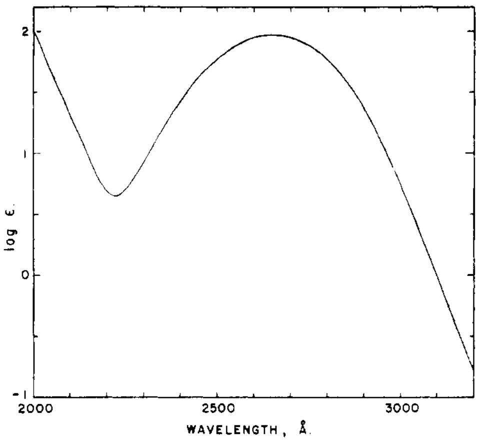

Fig. 1.—The common logarithm of the molar extinction coefficient, ϵ (liter/mole cm.), of carbon suboxide as a function of wave length. Measurements were made using a 10-cm. quartz cell at 11.5 mm. (for log $\epsilon > 1.0$) and at 125.0 mm. (for log $\epsilon < 1.3$) at 23°. Overlapping measurements agreed within 3%.

sence of ultraviolet light. However, lowering the temperature slightly eliminated this thermal decomposition, and all further experiments were made with the cell immersed in a constant temperature bath held at 0.0 ± 0.2°. A medium pressure 300 watt mercury arc was placed 10 cm. above the quartz cell. A 2-mm. thick sheet of Corning filter CS 9–54 prevented traces of light of wave length shorter than 2200 Å. from entering the cell. If the filter was not used, some decomposition of ethylene was observed.[6] The quartz cell was connected to a good vacuum system. Gases were added to the cell from storage bulbs, and the final pressure was measured with a mercury manometer to ±0.2 mm., or with a McLeod gage to ±0.02 mm., care being taken to prevent mercury vapor from entering the cell.

TABLE I

THE MASS SPECTRUM OF CARBON SUBOXIDE USING 70-VOLT IONIZING ELECTRONS

m/e	Intensity	m/e	Intensity
12	44.0	35	0.04
13	0.46	36	1.28
16	1.70	37	0.05
20	0.07	40	100.
24	14.5	41	2.22
25	0.34	42	0.23
26	0.47	52	2.16
28	20.4	53	0.09
29	0.23	68	77.2
30	0.05	69	2.75
34	6.17	70	0.36
34.5	0.22		

Gas from the cell was introduced directly into a gas chromatograph, which was equipped with a 2,4-dimethyl sulfolane on Chromosorb column and thermistor detectors. Samples were analyzed before and after irradiation and the areas on the chromatogram compared with runs using known amounts of the same gases. Duplicate analyses agreed within 3%. At least two analyses were made after each irradiation and the average reported.

Results

When carbon suboxide was photolyzed in the presence of excess ethylene ($C_2H_4/C_3O_2 > 100$), carbon monoxide, allene and methylacetylene were the major observable products.[7] With higher concentrations of carbon suboxide a brown polymer slowly formed on the walls of the cell during the photolysis, indicating that the reactive intermediate can also attack the parent suboxide molecules. Photolyzing a mixture of carbon monoxide, allene, methyl acetylene and ethylene under similar conditions resulted in no change in composition of the gas.

Using an excess of ethylene (1 mm. C_3O_2, about 150 mm. C_2H_4), the ratios of products were monitored and found not to be influenced by the following changes: 1, the surface-to-volume ratio was increased by more than a factor of five; 2, an impure sample of carbon suboxide (made by the high temperature pyrolysis of diacetyl tartaric anhydride[8] and having stronger absorption at longer wave lengths than that shown in Fig. 1) was used; 3, different samples of ethylene were used, before and after bulb-to-bulb distillation; 4, the extent of suboxide decomposition was varied from 1% to 95%.

A mechanism which is consistent with the experimental findings is given in eq. 1 through 3.

$$C_3O_2 + h\nu \longrightarrow CCO + CO \qquad (1)$$

$$CCO + C_2H_4 \xrightarrow{k_2} C_3H_4 + CO \qquad (2)$$

$$CCO + C_3O_2 \xrightarrow{k_3} \text{polymer} + n\text{CO} \qquad (3)$$

The CCO has been used as the reactive intermediate, although it is understood that this is not yet certain (see Discussion). The C_3H_4 in eq. 2 represents both allene and methylacetylene, so that 2 is probably a series of reactions and k_2 represents only the over-all rate of attack of CCO on ethylene. (A further discussion of the mechanism of formation of the two C_3H_4 isomers will be given below). The attack of CCO on the parent suboxide results in polymer formation and the release of an undetermined number, n, of CO molecules. The attack of CCO on C_3H_4 molecules, which might also result in polymer formation, has been neglected in the above treatment due to the small concentrations of C_3H_4 in these experiments. By assuming a steady state for the CCO concentration, and neglecting the variation of concentration of C_3O_2 and C_2H_4 with time, the following equation can be derived.

$$\frac{CO}{C_3H_4} = 2 + \frac{(n+1)k_3}{k_2}\frac{(C_3O_2)}{(C_2H_4)} \qquad (4)$$

In agreement with eq. 4, a plot of CO/C_3H_4 *vs.* $(C_2H_4)^{-1}$, for a constant initial pressure of suboxide of 0.9 mm., gave a straight line which extrapolated at infinite ethylene pressure to 2.04. The deviation from 2.0 is most likely the result of random errors, but it could be caused by the neglect of additional products. Very small amounts of a third product, with a retention time between that of ethylene and allene, were sometimes observed, but sufficient material could not be collected for identification.

Another test of eq. 4 was made by varying both the suboxide and the ethylene concentrations and

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[6] H. S. Taylor and H. J. Emeléus, *J. Am. Chem. Soc.*, **53**, 562 (1931).

[7] The small amounts of methylacetylene and its long retention time caused it to be overlooked in previous work.

[8] K. A. Kobe and L. H. Reyerson, *J. Phys. Chem.*, **35**, 3025 (1931).

plotting $(CO/C_2H_4 - 2)P(C_2H_4)$ against $P(C_3O_2)$. Since the partial pressures vary during a photolysis, the averages of the initial and final partial pressures were used. Less than 15% of the suboxide initially present was decomposed, except for the lowest pressure of suboxide where 30% decomposition was necessary to obtain sufficient product. The results are shown in Fig. 2 with the best straight line, restrained to go through the origin, fitted by the method of least squares. This method of plotting amplifies the errors of analysis: however, the reasonable fit supports the general mechanism given above. Figure 2 gives a value for $(n + 1) \cdot k_3/k_2$ of 2.82. By comparing the amount of CO formed for identical photolysis conditions, with an excess of ethylene and again with no ethylene present, a value of $(n + 1)$ of 2.0 was estimated. Therefore the relative rate of attack of the reactive intermediate on C_3O_2 is 1.4 times as fast as the rate of attack on ethylene.

The points in Fig. 2 appear to favor a straight line which does not go through the origin. Fitting a general straight line by least squares gives a slope of 2.50 and a $P(C_3O_2) = 0$ intercept of 3.1 mm. This non-zero intercept, if real, could be caused by the neglect of a small amount of an additional product or by some deactivation of the reactive intermediate (diffusion to the walls or electronic transitions) not included in the above treatment.

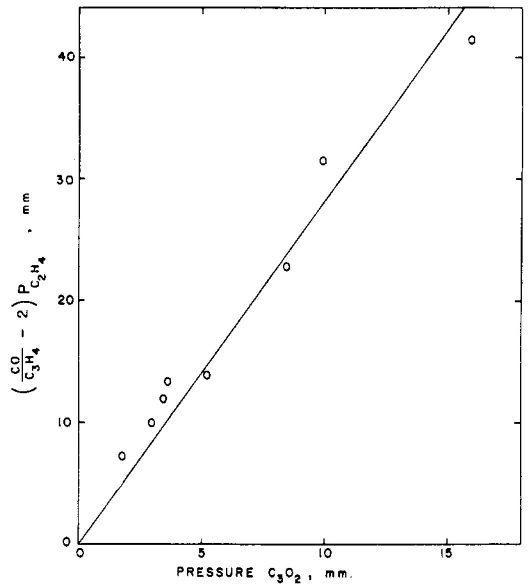

Fig. 2.—A test of eq. 4 using average values for the partial pressures of ethylene and carbon suboxide.

Discussion

It is expected that carbon suboxide will photolyze in a manner analogous to the other ketenes,[5] *i.e.*, initially

$$C_3O_2 + h\nu \longrightarrow CO + CCO \qquad (5)$$

It is not yet certain whether this CCO intermediate is sufficiently stable to undergo collisions with other molecules, or whether it decomposed rapidly to another CO molecule and a free carbon atom, the latter being the reactive intermediate. Unfortunately, the heat of formation of carbon suboxide is not known, but there is an estimated value of −8.3 kcal./mole.[3] Using this estimate along with 170 kcal./mole for the heat of sublimation of carbon, the ΔH for the over-all reaction

$$C_3O_2 \longrightarrow 2CO + C \qquad (6)$$

is 124 kcal./mole if the carbon atom is formed in its triplet ground state. If spin is conserved during the primary photolysis, any free carbon formed should be in a singlet state (the lowest triplet state of CO lies 139 kcal. above the ground state), which would require at least an additional 30 kcal. Since a quantum of wave length 2537 Å. provides only 112 kcal., it seems unlikely that the photolysis is producing a free carbon atom in the gas phase. However, the tentative nature of ΔH_f of carbon suboxide makes this conclusion less than certain.[9]

Carbon atoms produced by nuclear transformations react with ethylene to give some allene (18%), methylacetylene (4%), but the major hydrocarbon product is acetylene (38%).[2] Decreasing the translational energy of the carbon atoms with an inert gas did not drastically increase the production of allene or decrease the amount of acetylene formed. In contrast, photolyzing carbon suboxide with ethylene gives about 80% allene, 20% methylacetylene and no detectable acetylene. Because of these differences, it seems unlikely that a carbon atom is the reactive intermediate in the photolysis of carbon suboxide.

The suggestion has been made that the CCO radical, once formed, undergoes further photolysis to form a free carbon atom.[3] Because there is no initial lag in the production of allene compared to CO,[1] the CCO would have to reach its steady state concentration before 1% of the suboxide had been decomposed. This would require that the absorption coefficient of CCO be at least 100 times larger than that of C_3O_2. Although this possibility cannot be eliminated at the present time, it appears more reasonable to assume that the CCO itself reacts with the olefin.

It should be noted that if the CCO radical is the reactive intermediate, it probably has an excess of energy when first formed. Palmer and Hirt found an activation energy of 54 kcal./mole for the thermal decomposition of carbon suboxide.[3] This is most likely the energy required to cleave the molecule into a CCO radical and carbon monoxide. Light of 2537 Å. provides 112 kcal./mole, so the CCO could have 58 kcal./mole when first formed. Some, but probably not all, of this excess energy will be carried off by leaving the CO molecule. Molecular orbital considerations predict that a CCO molecule will be linear in its ground and lower excited states.[10] In addition, it is expected from Hund's rule that CCO will have a triplet ground state. The CCO could be first formed in a low-lying singlet state, thereby conserving spin in the initial cleavage (1) and absorbing some of the excess energy. The inertness toward oxygen and nitric oxide[1] supports an initial singlet state for the reactive intermediate.

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(9) An estimate by MacKay, *et al.*,[2] based on bond lengths and force constants, corresponds to a ΔH_f of at least −60 kcal./mole. This lower value strongly favors the CCO intermediate.

(10) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

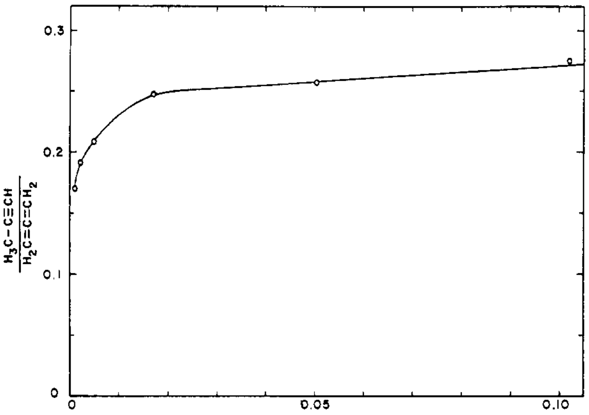
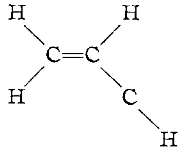


Fig. 3.—The ratio methylacetylene/allene as a function of the reciprocal of the initial total pressure for $C_2H_4/C_3O_2 \geqslant 10$.

When first formed, the C_3H_4 will also have excess energy, partly from the excess remaining on the intermediate, and partly from the energy released in bond formation. Therefore, isomerization is possible, and it is not surprising that at least two C_3H_4 isomers are formed. However, the dependence of the ratio of methylacetylene/allene on the total pressure is not that expected for a simple isomerization of a hot allene molecule to the thermodynamically more stable methylacetylene ($\Delta H_f^\circ = 44.32$ kcal./mole) in competition with collisional stabilization to allene ($\Delta H_f^\circ = 45.92$).[11] The ratio methylacetylene/allene plotted against the reciprocal of the total pressure is not a straight line, as can be seen in Fig. 3 (*cf.* the addition of CH_2 to propene to form hot methylcyclopropane molecules, which can isomerize to butenes or be stabilized by collisions).[12] Measurements up to several atmospheres total pressure will be required to determine whether allene is the exclusive C_3H_4 product in the limit of high pressures. The non-linearity of Fig. 3 might be caused by a multistep deactivation of the hot C_3H_4 molecules, or by a change in the nature of the reactive intermediate.

It is also possible that the two isomers are formed as the result of two different types of attack on the ethylene molecule. Attack on the carbon-carbon double bond could lead, by simple carbon insertion, to allene. Insertion into a carbon-hydrogen bond would give an intermediate of the form which could rearrange, by the migration of a hydrogen atom, to either of the observed C_3H_4 isomers. However, this mechanism alone cannot explain the observed pressure dependence. Isotopic labeling studies, especially on the methylacetylene, would be useful in establishing the nature of the processes responsible for the two products.[13]



It is a pleasure to thank Professor F. E. Blacet for the loan of equipment and the National Science Foundation for financial assistance. In addition, I wish to thank Professor R. Wolfgang for a prepublication copy of his manuscript.

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(11) F. D. Rossini, *et al.*, "Selected Values of Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44 (1953).

(12) J. N. Butler and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **82**, 759 (1960).

(13) NOTE ADDED IN PROOF.—An isotopic labeling study of the system C_3O_2–C_2H_4 has been published recently (R. T. Mullen and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 3214 (1962)). The observation of 8% end labeling in the product allene is consistent with some initial C–H bond insertion, although hot molecule isomerization could also be responsible.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CAN.]

The Reactions of Sulfur Atoms. I. The Addition to Ethylene and Propylene

BY OTTO P. STRAUSZ AND HARRY E. GUNNING

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Atomic sulfur, in the (^1D) metastable state, was generated, at 25°, by the *in situ* photolysis of gaseous carbonyl sulfide in the wave length region, 2550–2290 Å. Pure carbonyl sulfide yields CO and sulfur as the main reaction products. On addition of ethylene or propylene to the system, the corresponding cyclic sulfides are formed with a simultaneous decrease in the CO yield. This latter decrease approaches nearly 50% at sufficiently high pressures of added olefin. No major isomerization or cracking of the cyclic sulfide product was observed and its yield varied between 60% and 100% in the experiments. The value of the relative rate constant $k_{C_3H_6}/k_{C_2H_4}$ for the addition reaction was found to be 3.6, while the relative rate constants for the addition to olefin compared to the abstraction reaction from COS were found to be a function of the added olefin pressure. A mechanism is proposed for the reaction, and the roles of S(^1D) and S(^3P) therein are discussed.

Introduction

The renewed interest in atomic reactions in recent years is indicated by the increasingly large number of publications in that field. The success achieved in correlating rate constants to physicochemical properties of substrate molecules has led to a deeper understanding of elementary processes. Despite the progress made, there still exists a large number of reactions which have not yet received sufficient attention. The present investigation is the first in a series of studies to obtain insight into one such type of process, namely, the reactions of sulfur atoms.

Literature data indicated that the photolysis of carbonyl sulfide might be a convenient source of generating sulfur atoms at room temperature. It has been pointed out[1] that the energy available at the onset of the absorption continuum (*ca.* 2550 Å.)

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(1) W. Lochte-Holtgreven, C. E. H. Bawn and E. Eastwood, *Nature*, **129**, 869 (1932).