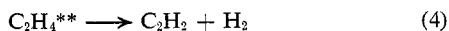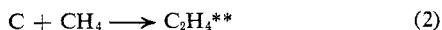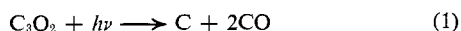# Photolysis of Carbon Suboxide at 1470 Å in the Presence of Methane. Collisional Deactivation of Excited Ethylene

## L. J. Stief[1a] and V. J. DeCarlo[1b]

*Contribution from the Research Division, Melpar, Inc.,
Falls Church, Virginia. Received August 12, 1968*

Abstract: A quantitative study has been made of the collisional deactivation of excited ethylene formed in the photolysis of C_3O_2 at 1470 Å in the presence of methane. The results are interpreted in terms of the existence of two excited states of ethylene, of which only one is capable of dissociating. By comparison with other systems in which excited ethylene is formed, it is estimated that the excitation energy of ethylene formed in this system is 5.4 eV. Possible sources of excited ethylene are carbon atom insertion into methane and reactions of vibrationally or electronically excited C_2O. An approximate application of the theory of unimolecular reactions suggests that C_2O containing sufficient vibrational energy (2.9 eV) to produce ethylene containing 5.4 eV would not survive long enough to experience collision with other molecules under the conditions of these experiments. It is concluded that the presently available results are best explained by reactions of free carbon atoms or electronically excited C_2O and not by vibrationally excited C_2O.

Photolysis of C_3O_2 in the presence of CH_4 at 2537 Å produces ethylene,[2] while at 1470 Å both ethylene and acetylene are formed.[3] The latter has been explained[3a] in terms of the production of atomic carbon in the primary photodecomposition process at 1470 Å, followed by carbon atom insertion into methane to form excited ethylene. The latter may be collisionally deactivated or decompose to acetylene and hydrogen.

$$C_3O_2 + h\nu \longrightarrow C + 2CO \quad (1)$$

$$C + CH_4 \longrightarrow C_2H_4^{**} \quad (2)$$

$$C_2H_4^{**} + M \longrightarrow C_2H_4 + M \quad (3)$$

$$C_2H_4^{**} \longrightarrow C_2H_2 + H_2 \quad (4)$$

An alternate mechanism[3b] involving excited C_2O radicals

$$C_3O_2 + h\nu \longrightarrow C_2O^* + CO \quad (5)$$

$$C_2O^* + CH_4 \longrightarrow C_2H_4^{**} + CO \quad (6)$$
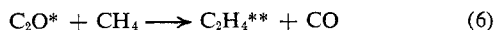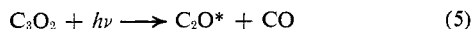
would also be consistent with formation of both ethylene and acetylene. Contribution from secondary photolysis of ethylene to form acetylene appears to be minor for these experiments (4% maximum conversion) based on the absorption coefficients at 1470 Å for C_3O_2 (1140 cm^{-1})[1a] and C_2H_4 (375 cm^{-1}).[4b]

In an attempt to evaluate the potential roles of $C(^3P)$, $C(^1D)$, and C_2O^* in the formation of excited ethylene, a quantitative study has been made of the collisional deactivation of excited ethylene formed in the $C_3O_2 + CH_4$ system at 1470 Å.

Recent experiments on the 1470 Å photolysis of matrix-isolated C_3O_2[5] have led to the spectroscopic identification of the C_2O radical. The latter is also observed in the photolysis of matrix-isolated cyanogen azide in the presence of CO.[5] Reactions of N_9, H_2, and D_2 with atomic carbon, presumably formed from secondary photolysis of trapped C_2O, have been studied at 4.2 °K in an argon matrix.[6]

Experimental Section

The Xe resonance lines (1470 and 1295 Å) were excited in an electrodeless discharge in the pure gas maintained by a Raytheon 2450-Mc/sec microwave generator. A sapphire window eliminates the 1295-Å line. Carbon suboxide was prepared by dehydration of malonic acid at 140°[7] and purified by low-temperature distillation. Mass spectrometric analysis[8] indicated that the only detectable impurity was CO_2. Methane was Phillips research grade and purified as described previously.[9] The ratio CH_4/C_3O_2 was kept large in order to minimize formation of carbon suboxide polymer. The photolysis cell was a 250-cc spherical Pyrex bulb (8-cm i.d.) equipped with a 25-mm LiF window and a finger for condensing the carbon suboxide. The LiF window was attached to the bulb with epoxy cement. All experiments were performed at 25° and, in any one experiment, 0.5–4% of the carbon suboxide was decomposed.

Analysis for the products C_2H_4 and C_2H_2 was performed in a CEC 21-130 mass spectrometer. No attempt at separation of reactants and products by low-temperature distillation was made, since tests with standard mixtures having low concentration of C_2H_4 and C_2H_2 in CH_4 showed that attempted removal of even some of the CH_4 resulted in drastic loss of both C_2H_4 and C_2H_2. Blank experiments showed that neither acetylene nor ethylene was produced on mixing C_3O_2 and methane for periods comparable to those of the photolyses.

Results

The product ratio C_2H_4/C_2H_2 has been examined as a function of photolysis time at pressures of 10, 90, 200, and 300 torr, and the results are shown in Figures 1 and 2. The ratio CH_4/C_3O_2 was maintained at approx-

(1) (a) National Aeronautics and Space Administration, Code 616, Goddard Space Flight Center, Greenbelt, Md. 20771; (b) Xerox Corporation, Rochester, N. Y. 14603.

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

(3) (a) L. J. Stief and V. J. DeCarlo, *J. Chem. Phys.*, **43**, 2552 (1965); (b) Abstracts, 151st National Meeting American Chemical Society, Pittsburgh, Pa., 1966, No. N75.

(4) (a) H. H. Kim and J. L. Roebber, *J. Chem. Phys.*, **44**, 1709 (1966); J. L. Roebber, J. C. Larrabee, and R. E. Huffman, *ibid.*, **46**, 4594 (1967); (b) M. C. Sauer and L. M. Dorfman, *ibid.*, **35**, 497 (1961).

(5) M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, *ibid.*, **43**, 3735 (1965).

(6) N. G. Moll and W. E. Thompson, *ibid.*, **44**, 2684 (1966).

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

(8) K. D. Bayes, *J. Am. Chem. Soc.*, **84**, 4077 (1962); T. J. Hirt and J. P. Wightman, *J. Phys. Chem.*, **66**, 1756 (1962); R. Botter, *Advan. Mass Spectry.*, **2**, 540 (1962).

(9) L. J. Stief, V. J. DeCarlo, and J. J. Hillman, *J. Chem. Phys.*, **43**, 2490 (1965).
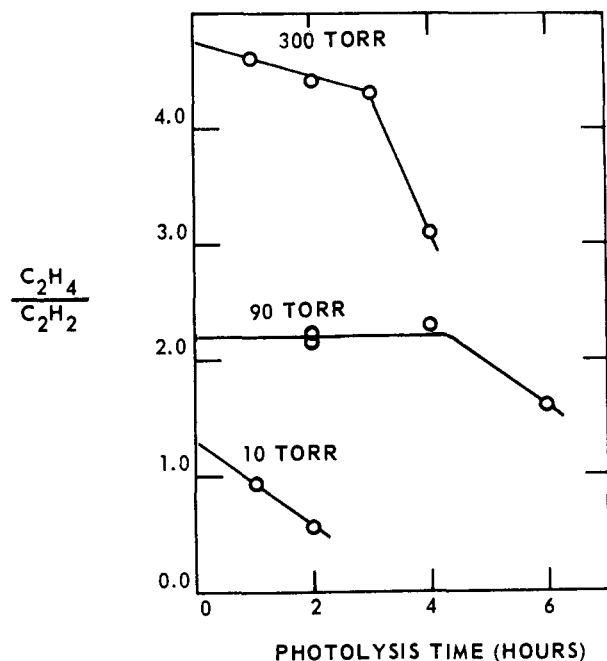
Figure 1. Ratio of C_2H_4 to C_2H_2 formed during the photolysis of C_3O_2 at 1470 Å in the presence of CH_4 at total pressures of 10, 90, and 300 torr.

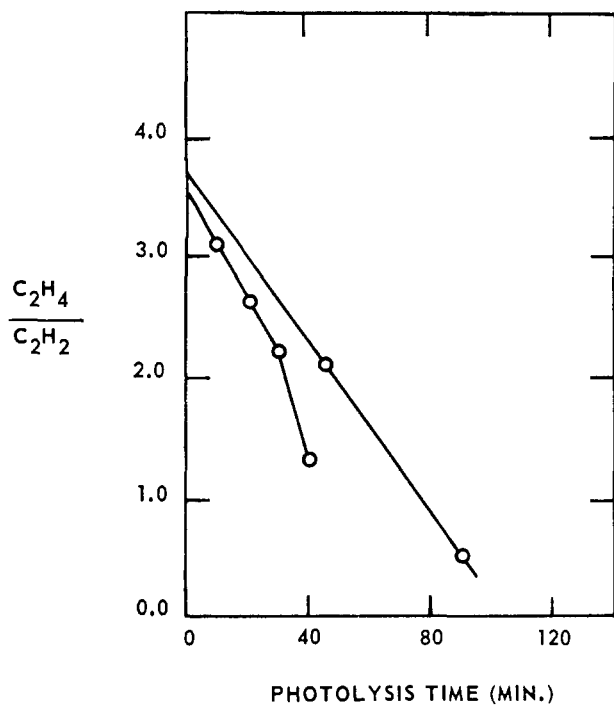Figure 3. Ratio of C_2H_4 to C_2H_2 as a function of total pressure.

Figure 2. Ratio of C_2H_4 to C_2H_2 formed during the photolysis of C_3O_2 at 1470 Å in the presence of CH_4 at total pressure of 200 torr.

imately 100; even at this ratio, methane absorbs somewhat less than 1% of the 1470-Å radiation. For the 10-, 90-, and 300-torr experiments, a total of 1, 3, and 4% of the C_3O_2 was decomposed. For the 200-torr experiments the total conversion was 2% for the upper line and 1% for the lower. The rate of loss of C_3O_2 was higher at the higher pressure because of more extensive polymerization.

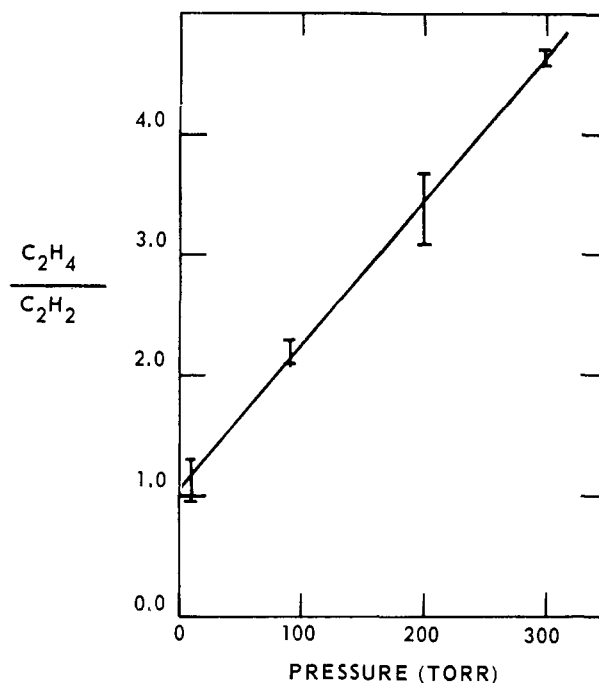A decrease in the C_2H_4/C_2H_2 ratio with photolysis

time was observed at all pressures, although there was no initial decrease at 90 torr. Either C_2H_4 is being consumed or there is an additional source of C_2H_2. While there seems to be no plausible secondary source of C_2H_2, C_2H_4 could be consumed by reaction with some undetected intermediates such as atomic oxygen. A unique explanation cannot be given at the present time. Secondary photolysis of C_2H_4 may apparently be neglected.[4a]

We have taken the extrapolated value of C_2H_4/C_2H_2 at zero photolysis time as the upper limit for the ratio at each pressure. The lower limit of the ratio is taken as that measured at the shortest photolysis time. Since there seems to be little effect of time for the first three 90-torr experiments, we have used the range of values for these experiments regardless of the photolysis time. The relationship between the C_2H_4/C_2H_2 ratio, determined as described above, and the total pressure is shown in Figure 3. The least-squares line for the points at the center of the bars has a slope of 0.012 torr^{-1} and an intercept of 1.05.

Discussion

A. Stabilization/Decomposition Ratio for Excited Ethylene. If the reactions of excited ethylene, whether formed by carbon atom insertion into methane or *via* excited C_2O radicals, are to be described simply by the sequence of reactions

$$C_2H_4^{**} + M \longrightarrow C_2H_4 + M \qquad (3)$$
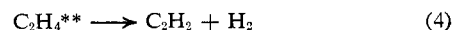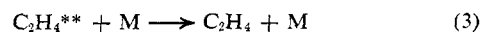
$$C_2H_4^{**} \longrightarrow C_2H_2 + H_2 \qquad (4)$$

it follows that

$$\frac{C_2H_4}{C_2H_2} = \frac{k_3}{k_4}[M] \qquad (I)$$

This relationship requires that a plot of the ratio of ethylene to acetylene as a function of pressure should
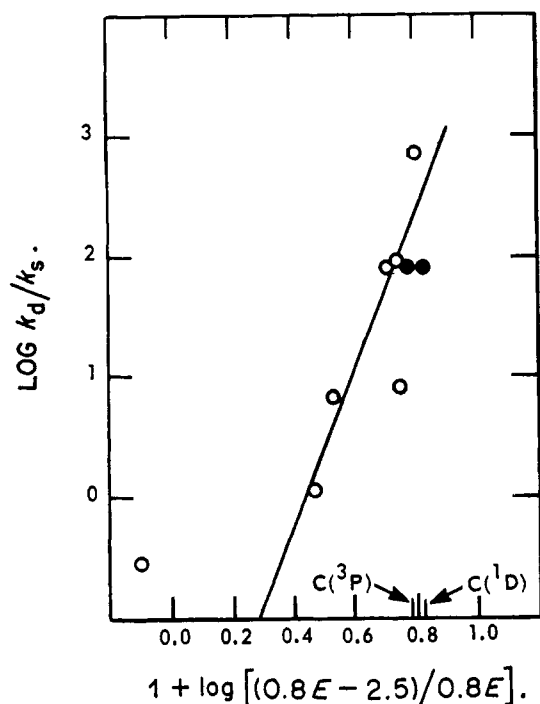
$$1 + \log\left[(0.8E - 2.5)/0.8E\right].$$

Figure 4. Relationship between lifetime and energy content of excited ethylene species: O, systems considered by Hampson and McNesby;[11] ●, carbon atom insertion into methane.

yield a straight line having zero intercept and slope equal to k_3/k_4. While a linear relationship is observed between the ratio C_2H_4/C_2H_2 and the pressure, a positive intercept is obtained (Figure 3). This positive intercept indicates the participation of a state of ethylene which is not capable of dissociation. This is to be expected if either or both of the following occur.
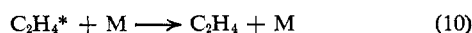
(1) C_2O radicals are formed in the system and react with CH_4 to form C_2H_4 in the manner suggested by Bayes.[2]

$$C_3O_2 + h\nu \longrightarrow C_2O + CO \qquad (7)$$

$$C_2O + CH_4 \longrightarrow C_2H_4 + CO \qquad (8)$$
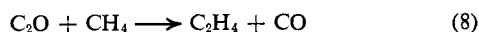
This leads to the relationship

$$\frac{C_2H_4}{C_2H_2} = \frac{\varphi_7}{\varphi_1} + \left(1 + \frac{\varphi_7}{\varphi_1}\right)\frac{k_3}{k_4}[M] \qquad (II)$$

(2) There are two states of $C_2H_4{}^{**}$ formed in reactions 2 or 6, only one of which is capable of dissociating.

$$C_2H_4{}^{**} \longrightarrow C_2H_4{}^* \qquad (9)$$

$$C_2H_4{}^* + M \longrightarrow C_2H_4 + M \qquad (10)$$

Such a two-state theory has been proposed[10,11] for other systems involving $C_2H_4{}^{**}$. From these equations it follows that

$$\frac{C_2H_4}{C_2H_2} = \frac{k_9}{k_4} + \frac{k_3}{k_4}[M] \qquad (III)$$

Interpreting the data in terms of reactions of C_2O leads to the conclusion that the ratio of the quantum yields of the primary processes yielding C_2O and C (φ_7/φ_1) is 1.05 and that the stabilization/decomposition

(10) A. B. Callear and R. J. Cvetanović, *J. Chem. Phys.*, **24**, 873 (1955).
(11) R. F. Hampson and J. R. McNesby, *ibid.*, **43**, 3592 (1965).

ratio for $C_2H_4{}^{**}$ is 0.006. Alternatively, use of the two-state theory leads to the conclusion that the rate of cross-over to the nondecomposing excited state of ethylene to the rate of decomposition of the initially formed excited ethylene is 1.05 and that the stabilization/decomposition ratio for $C_2H_4{}^{**}$ is 0.012. An unambiguous choice cannot be made between the two alternative interpretations. Since other systems involving the collisional deactivation of excited ethylene have been considered in terms of the two-state theory,[10,11] it will be convenient for us to do the same here for the purpose of comparison. Actually both mechanisms may be operative, and it seems safe to assume that the stabilization/decomposition ratio for $C_2H_4{}^{**}$ is within the range 0.010 ± 0.005.

B. Estimate of Excitation Energy of Excited Ethylene. A correlation has been achieved by Hampson and McNesby[11] between the stabilization/decomposition ratio (k_s/k_d) and the excitation energy of $C_2H_4{}^{**}$ produced in a variety of reactions with varying degrees of excitation. An approximate application of the theory of unimolecular reactions to the decomposition of excited ethylene was made assuming that, in those reactions where there was another product formed in addition to ethylene, 80% of the available excess energy is retained by the ethylene. The data were treated according to the following equation

$$k_d/k_s = A[(0.8E - E_0)/0.8E]^{S-1} \qquad (IV)$$

where E is the total excess energy of the process forming $C_2H_4{}^{**}$, E_0 is the minimum energy required for decomposition (estimated to be 2.5 eV), and S is the effective number of oscillators. From their plot (Figure 4), we estimate that our k_s/k_d value of 0.012 (two-state theory interpretation) corresponds to formation in this system of ethylene containing 5.4 eV excitation energy. With this estimate in mind, we can now examine the extent to which the potential sources of $C_2H_4{}^{**}$ (reactions of atomic carbon and reactions of excited C_2O) are consistent with this calculated excitation energy.

C. Carbon Atom Insertion into Methane. In the photolysis of C_3O_2 at 1470 Å, it is energetically possible to produce carbon atoms in either the $C(^3P)$ ground state or in the excited $C(^1D)$ state.[3] The exothermicities of the reactions

$$C(^3P) + CH_4 \longrightarrow C_2H_4{}^{**} \qquad \Delta H = -6.2 \text{ eV} \qquad (2a)$$

$$C(^1D) + CH_4 \longrightarrow C_2H_4{}^{**} \qquad \Delta H = -7.4 \text{ eV} \qquad (2b)$$

must completely reside in the excited ethylene. Thus, referring to the ordinate of Figure 4, these energies correspond to values of $1 + \log(E - 2.5)/E$ of 0.78 and 0.82, respectively. For the abscissa of Figure 4, our observed value of k_s/k_d is 0.012, corresponding to a value of $\log k_d/k_s$ of 1.92. These two points are represented by the filled circles of Figure 4. These points are not inconsistent with the line drawn for other systems involving excited ethylene. A clear choice cannot be made at this time between these two alternatives because of the necessary limitations of the analysis by Hampson and McNesby and the probable error in our data. Initial formation of $C(^3P)$ may be spin forbidden if the decomposition of C_3O_2 occurs from a singlet state.

D. Reaction of Excited C_2O. In the photolysis of

C_3O_2 at 1470 Å, the C_2O radical could be formed with considerable excess energy.

$$C_3O_2 + h\nu \longrightarrow C_2O^* + CO \qquad (5)$$
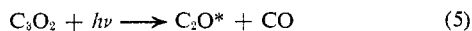
The C_2O^* formed in this manner could be either a highly vibrationally excited ground-state molecule or an electronically excited molecule. We will first estimate the degree of excitation in C_2O^* required to produce $C_2H_4^*$ with the observed level of excitation and then examine the consequences of vibrational and electronic excitation for such an excited C_2O molecule.

The heat of formation of C_2O has been estimated by Becker and Bayes[12] to be 4.0 eV. From this and the heats of formation of CH_4, C_2H_4, and CO (-0.78, 0.54, and -1.15 eV, respectively), the reaction

$$C_2O^* + CH_4 \longrightarrow C_2H_4^{**} + CO \qquad (6)$$
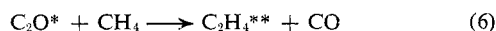
is calculated to be 3.8 eV exothermic for the nonexcited species. The ethylene produced in reaction 6 must contain 5.4 eV as excitation energy (see section B) if excited C_2O radicals are the source of excited ethylene. The difficulty here is to estimate the excitation in CO formed in (6).

For minimum excitation in C_2O, the excitation in CO should also be a minimum. In treating the data from the photolysis of methylketene[13]

$$CH_3CHCO + h\nu \longrightarrow C_2H_4 + CO \qquad (11)$$

the assumption[11] of the retention by C_2H_4 of 80% of the available excess energy resulted in a correlation between energy of ethylene species and the observed k_s/k_d ratio which was consistent with that observed for other systems in which excited ethylene was formed. For the lack of a better guide, we have assumed that in reaction 6, C_2H_4 retains 80% and CO retains 20% of the available energy.

$$C_2O + CH_4 \xrightarrow{} \underset{5.4\,\text{eV}}{\overset{80\%}{C_2H_4}} + \underset{1.3\,\text{eV}}{\overset{20\%}{CO}} \qquad (6)$$
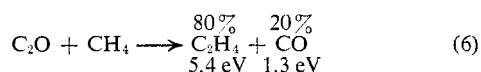
On this basis, the estimated excitation in C_2O required to produce $C_2H_4^{**}$ containing 5.4 eV is $(5.4 + 1.3) - 3.8$ or 2.9 eV. Now from the heats of formation of C_3O_2,[14] C_2O,[12] and CO (-1.02, 4.0, and -1.15 eV, respectively), the reaction

$$C_3O_2 \longrightarrow C_2O + CO \qquad (7)$$

is estimated to require 3.9 eV. Since the photon energy at 1470 Å is 8.4 eV, there is 4.5 eV excess energy to be distributed between C_2O and CO. The above requirement of C_2O containing 2.9 eV is thus not energetically unreasonable since this is only about 65% of the total 4.5 eV available.

If this 2.9 eV is present as excess vibrational energy in C_2O, the lifetime ($\tau = 1/k$) of such a vibrationally excited species may be estimated by an approximate application of the theory of unimolecular reactions to the decomposition of C_2O.

$$C_2O \longrightarrow C + CO \qquad (12)$$

The rate constant, k, is given by

$$k = A\left(\frac{E - E_0}{E}\right)^{S-1} \qquad (V)$$

where A is assumed to have a "normal" value of 10^{13} sec^{-1}, E is the excitation energy of C_2O (2.9 eV as derived above), E_0 is the minimum energy required for decomposition, and S is the effective number of oscillators. E_0 is estimated to be 2.3 eV, based on the heats of formation of $C(^3P)$, CO, and C_2O[12] (7.42, -1.15, and 4.0 eV, respectively). If C_2O is assumed to be a linear[5] triatomic molecule, the maximum value for S would be 4. Using these values in eq V yields a unimolecular rate constant $k = 9 \times 10^{10}$ sec^{-1} or a lifetime $\tau = 1.1 \times 10^{-11}$ sec. The range of pressure in these experiments was from about 0.01 to 0.5 atm, which corresponds to 10^7 to 5×10^8 collisions per sec, or to 10^{-7} to 2×10^{-9} sec between collisions. These times are two to four orders of magnitude longer than the calculated lifetime of vibrationally excited C_2O. This suggests that, if such an excited C_2O were formed in this system, it would not survive long enough to collide and react with CH_4.

The main uncertainties in this calculation are those in E, E_0, and the difference between them. The uncertainty in E arises from two sources: the heat of formation of C_2O and the partition of energy between C_2H_4 and CO in reaction 6. The uncertainty in E_0 is due solely to uncertainties in the heat of formation of C_2O. The question of the influence of an alternate value for the heat of formation of C_2O is discussed below and shown not to alter the conclusions. The principal uncertainty is therefore the partition of energy between C_2H_4 and CO. It can be readily shown that only if C_2H_4 contains more than 85% of the total available energy will the excitation in C_2O be sufficiently small to either preclude decomposition or result in a sufficiently long lifetime for C_2O^*. Any value less than 85% gives the same qualitative result that C_2O^* would not survive long enough in this system to experience collisions with other molecules. By analogy with the methyl ketene system, the assumption that C_2H_4 retains 80% of the energy seems the most reasonable at the present time. With due recognition of the present uncertainty in the partition of excess energy of reaction 6 between C_2H_4 and CO, it may tentatively be concluded that the formation of excited ethylene in this system is not attributable to the reaction of vibrationally excited ground-state C_2O.

The possibility exists, however, that electronically excited C_2O could be formed in this system and produce excited ethylene by reaction with CH_4. It should, however, be noted that the required excitation in C_2O (2.9 eV as derived above) is considerably higher than that for the predicted $^1\Delta$ and $^1\Sigma$ states, which are expected[15] to lie 0.5 and 0.8 eV, respectively, above the $^3\Sigma$ ground state.

Finally, it should be mentioned that a considerably lower value for the heat of formation of C_2O can be derived from the results of Palmer and coworkers[16]

(12) K. H. Becker and K. D. Bayes, *J. Am. Chem. Soc.*, **45**, 396 (1966); K. H. Becker and K. D. Bayes, *ibid.*, **48**, 653 (1968).

(13) D. P. Chong and G. B. Kistiakowsky, *J. Phys. Chem.*, **68**, 1795 (1964).

(14) B. D. Kybett, G. K. Johnson, C. K. Barker, and J. L. Margrave, *ibid.*, **69**, 3603 (1965).

(15) K. D. Bayes, *J. Am. Chem. Soc.*, **85**, 1730 (1963).

(16) H. B. Palmer and T. J. Hirt, *ibid.*, **84**, 113 (1962); T. J. Hirt and H. B. Palmer, *Carbon*, **1**, 65 (1963); H. B. Palmer and W. D. Cross, *ibid.*, **3**, 475 (1966).

on the thermal decomposition of C_3O_2. Use of their 2.5-eV value for the heat of formation of C_2O leads to the following: reaction 6 is 2.3 eV exothermic, the minimum excitation (E) in C_2O is 4.4 eV, and the minimum energy (E_0) required to decompose C_2O is 3.8 eV. If this 4.4 eV is present as vibrational energy in C_2O, the lifetime τ of this excited species would be 4×10^{-11} sec. While this is four times longer than the lifetime derived above, it is still 50 to 2500 times shorter than the time between collisions under the conditions of these experiments. Thus, this does not alter the tentative conclusion that vibrationally excited C_2O, if

formed in this system, would not live long enough to experience collisions with other molecules. Again, the possibility of the formation of electronically excited C_2O (4.4 eV in this case) must be recognized, as well as the fact that this energy now greatly exceeds that expected[15] for the $^1\Delta$ and $^1\Sigma$ states.

We therefore conclude that the presently available results on the formation and collisional deactivation of excited ethylene formed in this system are best explained by the reactions of free carbon atoms or electronically excited C_2O and not by vibrationally excited C_2O.

The Crystal and Molecular Structure of (1,3,5-Cyclooctatriene)diiron Hexacarbonyl[1,2]

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Received August 14, 1968*

Abstract: The crystal and molecular structures of the compound $(C_8H_{10})Fe_2(CO)_6$ obtained by reaction of cycloocta-1,3,5-triene with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ have been determined by three-dimensional X-ray crystallographic techniques. The intensities of 1898 independent reflections were collected on a counter-diffractometer, and the structure was solved by Patterson and Fourier methods. Full-matrix, least-squares refinement was carried out using 1206 statistically significant reflections and employing anisotropic thermal parameters to give a final unweighted discrepancy index of 0.067. The compound crystallizes in space group $P2_1/c$. Unit cell dimensions are $a = 13.39 \pm 0.01$ Å, $b = 7.684 \pm 0.004$ Å, $c = 14.31 \pm 0.01$ Å, $\beta = 92.83 \pm 0.04°$; density: ρ(obsd), 1.75 ± 0.01 g cm^{-1}; ρ(calcd), assuming $Z = 4$, 1.75 g cm^{-1}. The molecular structure is quite similar to that of $(C_8H_8)Ru_2(CO)_6$, which we recently reported, and permits us to give the compound the systematic name *cis*-(1,2,6-*trihapto*: 3,4,5-*trihapto*cycloocta-1,3,5-triene)hexacarbonyldiiron. The molecule does not have a plane of symmetry and the metal atoms are not structurally equivalent, one $Fe(CO)_3$ group being bound to three carbon atoms (3, 4, 5) forming an allyl group while the other is bound to one carbon atom (6) by a two-center bond and to the olefinic group formed by two others (1, 2). The two $Fe(CO)_3$ groups lie on the same side of the ring and are united by an Fe–Fe bond.

I t has been shown that from the reaction of 1,3,5-cyclooctatriene, C_8H_{10}, with either $Fe_3(CO)_{12}$[4] or $Fe_2(CO)_9$,[5] the red-orange, air-stable, crystalline compound $C_8H_{10}Fe_2(CO)_6$ can be isolated. King,[4] who first isolated the compound, proposed structure I for it. This structure, which has a mirror plane containing the iron atoms, is consistent with the infrared and proton nmr spectra which King also reported, and is, on the whole, a reasonable structure. It could not, however, be said to have been *proved* correct by the spectroscopic and chemical data cited by King.

A little later the same compound was prepared by Emerson, *et al.*,[5] who measured the Mössbauer spectrum. They concluded from the appearance of this spectrum that "the two iron atoms are chemically equiv-

alent" in this complex. If this is true, then structure I is clearly not admissible. As an alternative, these workers proposed structure II, also having a mirror plane, now perpendicular to the Fe–Fe line. Structure II is also consistent with the nmr and infrared data and contains chemically equivalent iron atoms.

A little later, Keller, Emerson, and Pettit[6] prepared a cyclooctatetraene complex, $(C_8H_8)Fe_2(CO)_6$, which has a proton nmr spectrum extremely similar to that of $(C_8H_{10})Fe_2(CO)_6$ and also has a Mössbauer spectrum which these authors considered to indicate "both iron nuclei to be chemically equivalent." It was natural, then, for them to propose structure III for the $(C_8H_8)Fe_2(CO)_6$ molecule. Certainly III, like II, is a reasonable structure and does not, at face value, seem unlikely.

Nevertheless, we have been led to doubt that structures II and III are correct by our studies of ruthenium carbonyl derivatives of cyclooctatetraene.[7,8] The compound $(C_8H_8)Ru_2(CO)_6$, with an nmr spectrum virtually

(1) Research supported by the National Science Foundation under Grant No. GP7034X.

(2) A systematic name (*cf.* F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968)) for this compound is *cis*-(1,2,6-*trihapto*:3,4,5-*trihapto*cycloocta-1,3,5-triene)hexacarbonyldiiron.

(3) National Institutes of Health Predoctoral Fellow, 1966–1968.

(4) R. B. King, *Inorg. Chem.*, **2**, 807 (1963).

(5) G. E. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *J. Am. Chem. Soc.*, **86**, 3590 (1964).

(6) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1388 (1965).

(7) F. A. Cotton, A. Davison, and A. Musco, *ibid.*, **89**, 6796 (1967).

(8) F. A. Cotton and W. T. Edwards, *ibid.*, **90**, 5412 (1968).