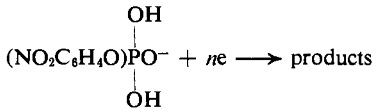
metric reduction, which occurs over about 30 min, reduction 3 goes essentially to completion, and four electrons per molecule of TNP are consumed. This scheme also accounts for the esr results. It is also possible that reaction 3 involves the formation of bis(nitrophenyl) phosphate liberating a nitrophenyl radical which then dimerizes. However, the absence of evidence for the formation of nitrobenzene, which would also probably form in this scheme, makes us prefer a mechanism in which both nitrophenyls come from the same TNP molecule.

Since the current function of wave 3 decreases with increasing scan rates, it probably involves a product of the chemical reaction, which follows the charge transfer (3), such as



$$(NO_2C_6H_4O)\overset{OH}{\underset{OH}{P}}O^- + ne \longrightarrow \text{products} \tag{6}$$

On the other hand, the current function of wave 4 increases with increasing scan rate, so that wave 4 can be ascribed to

$$(NO_2C_6H_4O)_3PO^{2-} + ne \longrightarrow \text{products} \tag{7}$$

Wave 5 can be ascribed to a reaction such as

$$NO_2C_6H_4C_6H_4NO_2^- + ne \longrightarrow \text{products} \tag{8}$$

since 4,4′-dinitrobiphenyl has a reduction wave at these potentials (Table IV).

The formation of 4,4′-dinitrobiphenyl indicated that the reaction occurs by the cleavage of the oxygen–carbon bond, while the energy-rich phosphorus–oxygen bond remains intact. A similar cleavage of oxygen–carbon has been proposed by Mitteil[14] in the reduction of diphenyl phosphate. Our results differ from his, however, in that we did not observe nitrobenzene as the cleavage product.

Experimental Section

The general experimental methods and purification techniques are the same as those previously described.[9] A multipurpose instrument employing operational amplifier circuitry with a three-electrode configuration was used in the voltammetric experiments. Controlled-potential coulometry was carried out using a previously described apparatus.[9] Cyclic polarograms were taken with a platinum disk working electrode (area = 0.031 cm^2). The reference electrode was an aqueous sce connected *via* an agar plug and sintered-glass disk to a salt bridge containing the test solution and closed at the end by a fine porosity sintered-glass disk. A platinum gauze electrode was used in controlled-potential experiments. The auxiliary electrode was silver. The esr spectra were obtained with a Varian Associates V4502 spectrometer employing 100-kc field modulation. A Varian V-153C klystron (output 300 mw) was used; attenuation levels represent attenuation of the output of this klystron *in* a standard Varian bridge. Samples were contained in the flat Varian aqueous cell. Calculations were performed on a Control Data Corporation 1604 computer. Theoretical simulated spectra were plotted on a CDC 160 plotter.

Tris(*p*-nitrophenyl) phosphate (TNP) was obtained from Aldrich Chemical Co.; analysis by thin layer chromatography and mass spectrometry established that its purity was over 98%. 4-Nitrophenylphosphoric acid was prepared by passing an aqueous solution of the disodium salt through a cation-exchange resin solution and recrystallizing it twice from water (mp 105–107°). Other nitro compounds were obtained from Aldrich and were used without further purification. Tetra-*n*-butylammonium iodide (TBAI) was polarographic grade, obtained from Southwestern Analytical Chemicals (Austin, Texas).

Acknowledgment. This work was performed under Contract DA-18-035-AMC-715(A), U. S. Army Edgewood Arsenal.

[14] I. Mitteil, *Ber.*, **72**, 2129 (1939).

The Reaction of C_2O with Oxygen and Nitric Oxide

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Abstract: Products from the photolytic reaction of C_3O_2 with O_2 and NO have been measured for a variety of conditions. The reaction of C_2O with O_2 appears to form CO, CO_2, and oxygen atoms. The reaction of oxygen atoms with C_3O_2, producing mainly CO with only small amounts of CO_2 and C_2O, has a rate constant of $(4 \pm 2) \times 10^8$ l./mole sec. Two additional experiments confirm the presence of oxygen atoms in the C_2O–O_2 reaction. Nitric oxide is a very effective inhibitor of C_2O reactions, being more than 10^4 times as reactive with C_2O than is ethylene. The C_2O–NO reaction produces CO, N_2, N_2O, and CO_2. It has not been possible to construct a satisfactory mechanism to explain these products.

The existence of C_2O has now been established. Jacox, Milligan, Moll, and Thompson[1] have observed the infrared absorption of matrix-isolated C_2O. The observed isotope shifts and the modes of formation, either by photolysis of C_3O_2 or by the reaction of atomic carbon with CO, establish the structure as linear CCO. Flash photolysis of C_3O_2 in the gas phase produces a transient absorption between 5000 and 6350 A which is too complex to be a diatomic molecule.[2] A vibrational spacing of 1980 ± 20 cm^{-1} in the electronic spectrum, compared to 1978 cm^{-1} observed in the matrix-isolated C_2O, identifies the transient in the flash-photolysis experiments as ground-state C_2O. The matrix-isolated C_2O also has a broad absorption "near 5000 A."

Photolysis of C_3O_2 at 3000 A produces an intermediate which can insert a carbon atom into a carbon–carbon

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

[2] C. Devillers, *Compt. Rend.*, **262C**, 1485 (1966).

double bond.[3,4] The reaction with ethylene produces

$$C_3O_2 + C_2H_4 + h\nu \longrightarrow C_3H_4 + 2CO \qquad (1)$$

mainly allene with smaller amounts of methylacetylene. The intermediate in this photolytic reaction is also ground-state C_2O, since its relative reactivity with various olefins[4] agrees quantitatively with the ability of these olefins to consume C_2O in the flash-photolysis experiments.[2]

Molecular orbital theory predicts that C_2O, like diatomic oxygen, will have a $^3\Sigma$ ground state, with low-lying $^1\Delta$ and $^1\Sigma$ excited states.[5] Because of its high reactivity with O_2 and NO, the intermediate formed at wavelengths longer than 2900 A was tentatively identified as $C_2O(X^3\Sigma)$. Although the triplet nature of C_2O has not been demonstrated directly, the isoelectronic molecules, NCN and CNN, do have $^3\Sigma$ ground states.[6] Photolysis of C_3O_2 at wavelengths shorter than 2900 A produces an intermediate of different reactivity,[5] which is probably singlet-state C_2O.

A recent study has questioned the above interpretation.[7] Cundall and co-workers, on the basis of measured quantum yields and the observation of *cis–trans* isomerization in the photolysis of carbon suboxide–*cis*-2-butene mixtures, have concluded that triplet states are involved at all wavelengths. However, they did not take into account the known effects of pressure on the yield of products, and so their conclusions must be considered tentative.

The rate of reaction of C_2O with O_2 has been used as a standard for measuring the relative reactivities of various olefins with C_2O.[4] Since another method of measuring the same relative reactivities seems to give drastically different results,[8] it was desirable to investigate the reference reaction more carefully. The C_2O–O_2 reaction is probably also important in many hydrocarbon–oxygen flames[9] and in radiation chemistry.[10] The following study investigates the course of this and related reactions.

Experimental Section

Most photolysis experiments were performed in a double cell, as described previously.[4] Each compartment, of 18-cm³ volume, received approximately equal intensities of light at the exit slit of a small grating monochromator (Bausch and Lomb No. 33-86-25-01) used in the first order. The light source was a 1-kw, high-pressure mercury arc (General Electric BH-6). Carbon suboxide photolyses were done at 3080 ± 100 A unless stated otherwise. Less than 10% of the C_3O_2 was decomposed in any one experiment, and no effects of photolysis time were observed, except for the butadiene-NO reaction noted below. Both compartments contained equal partial pressures of C_3O_2, one compartment serving as a reference cell to compensate for variations in light intensity.

The mercury-sensitized decomposition of N_2O was carried out at room temperature in cells containing a drop of liquid mercury. The quantitative results did not depend on which of two low-pressure mercury lamps were used (UV Products, SL 2537, 9 w, or Pen Ray neon-mercury, 25 w). A Vycor filter was used in all experiments to eliminate the 1849-A line. Direct absorption of the 2537-A light by C_3O_2 was negligible at the pressures used.

Products were analyzed by mass spectrometry (CEC 21-081 A) and by gas chromatography (Loenco H 15-B equipped with thermistor detectors). Most separations were made on a 3-m column of 20% dimethylsulfolane on 60–80 firebrick, with a terminal section of 0.5-m 20% squalene on 60–80 Chromosorb W in order to reduce column bleeding. Permanent gases were separated with a 1.5-m molecular sieve column (Linde 13X) operated at room temperature. Small quantities of CO_2 were separated from N_2O on a 4.5-m Perco Poropak Q column. Nitrogen dioxide may have been formed under some conditions but was not determined. No decomposition of C_3O_2 to give CO or CO_2 was observed on any of the columns used. However, when small amounts of NO_2 were present with C_3O_2, some CO_2 was formed, apparently by a reaction on the column.

All quantitative measurements are corrected for the slightly different light absorption in the two cells and for gas chromatographic response, as determined with authentic samples. In a few runs it was necessary to correct for the small amounts ($\leq 5\%$) of C_2O that reacted with C_3O_2, using previously determined rate constants.

Results

Only CO and CO_2 could be detected as products of the photolysis of C_3O_2–O_2 mixtures at 3080 A. Polymer formation was not observed as long as significant amounts of oxygen were present. These two products are expected if the photolysis mechanism involves reaction 2 followed by 3. However, the measured ratio of

$$C_3O_2 + h\nu \longrightarrow C_2O + CO \qquad (2)$$

$$C_2O + O_2 \longrightarrow CO_2 + CO \qquad (3)$$

CO/CO_2 was 8.1 ± 0.8, and not 2.0 as predicted by the above reactions. In addition, $\phi(CO_2)$, the yield of CO_2 relative to the C_3H_4 yield in reaction 1, was 0.48 ± 0.04. The above mechanism requires $\phi(CO_2)$ to be unity. These results suggest that not every C_2O formed results in a CO_2 molecule.

Since reaction 3 is exothermic by 170 to 215 kcal/mole, it is possible that the newly formed CO_2 retains sufficient energy to decompose. If reaction 4 were in competition with the collisional stabilization of the hot CO_2,

$$(CO_2)^* \longrightarrow CO + O \qquad (4)$$

$$(CO_2)^* + M \longrightarrow CO_2 + M \qquad (5)$$

reaction 5, then the yield of CO_2 should be strongly pressure dependent. No significant change in $\phi(CO_2)$ could be observed over the range 30 to 300 torr when pressurizing with isobutane (see Table I). It is concluded that reaction 3 cannot explain the observed CO and CO_2 yields.

As an alternative to reaction 3, the direct formation of atomic oxygen, reaction 6, is energetically possible also. The oxygen atom could then react with additional C_3O_2

$$C_2O + O_2 \longrightarrow O + 2CO \qquad (6)$$

to form CO and CO_2. This possibility was investigated by studying the reaction of oxygen atoms with C_3O_2 in a separate system.

Ground-state oxygen atoms were generated by the mercury-sensitized decomposition of N_2O. Ratios of $N_2O/C_3O_2 > 200$ were used to avoid the sensitized decomposition of C_3O_2. Since the primary step is reaction 7 exclusively,[11] the formation of N_2 serves as an internal actinometer. The major reaction prod-

$$Hg(^3P_1) + N_2O \longrightarrow Hg(^1S) + N_2 + O(^3P) \qquad (7)$$

uct was CO, with the observed ratio CO/N_2 being 3.01 ± 0.17 (standard deviation from nine runs). These results were not influenced by the surface-to-

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

[4] C. Willis and K. D. Bayes, *ibid.*, **88**, 3203 (1966).

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

[6] E. Wasserman, L. Barash, and W. A. Yager, *ibid.*, **87**, 2075 (1965).

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

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

[9] K. H. Becker and K. D. Bayes, *J. Chem. Phys.*, **45**, 396 (1966).

[10] P. Harteck and S. Dondes, *ibid.*, **23**, 902 (1955).

[11] R. J. Cvetanović, *ibid.*, **23**, 1203, 1208 (1955).

Table I. The Measured Yield of CO_2 in Cell 2 Compared to the Yield of C_3H_4 (Allene and Methylacetylene) in Cell 1[a]

Both cells C_3O_2	Cell 1 C_2H_4	Cell 2			$\frac{CO_2\text{(cell 2)}}{C_3H_4\text{ (cell 1)}}$
		O_2	C_4H_{10}	CO_2 formed	
5.1	110	19.9	0	0.040	0.48
5.2	89	6.7	0	0.091	0.45
5.0	89	10.0	0	0.14	0.60
5.1	89	13.3	0	0.11	0.47
5.9	86	10.0	0	0.053	0.47
5.4	107	5.3	0	0.16	0.48
2.2	123	15.8	0	0.16	0.48
5.6	104	2.6	0	0.088	0.52
5.6	119	12.2	0	0.16	0.48
5.6	105	16.5	0	0.10	0.46
5.5	110	17.5	335	0.18	0.48
5.4	110	17.6	22.0	0.13	0.47
4.8	98	6.1	15.2	0.12	0.45
5.3	100	6.8	7.7	0.11	0.56
5.5	100	7.0	17.0	0.21	0.52
5.2	103	7.2	57	0.32	0.53
5.1	103	7.4	86	0.20	0.57
5.5	99	7.4	300	0.23	0.46
5.4	98	7.7	232	0.22	0.45

[a] All pressures given in torr. Mixtures photolyzed for approximately 60 min at 25 ± 4°.

volume ratio of the reaction vessel or the choice of mercury resonance lamp. The stoichiometry thus indicates that reaction 8 is of primary importance. However, some CO_2 was formed ($CO_2/N_2 = 0.024 \pm$

$$O(^3P) + C_3O_2 \longrightarrow 3CO \tag{8}$$

$$O(^3P) + C_3O_2 \longrightarrow CO_2 + C_2O \tag{9}$$

0.004) indicating that reaction 9 occurs to a small extent. Assuming that reaction 9 is followed by reaction 10 in this system, then the ratio of rate constants,

$$C_2O + C_3O_2 \longrightarrow CO + \text{polymer} \tag{10}$$

k_8/k_9, equals 42 ± 8 at 25°.

The reaction of oxygen atoms with C_3O_2 can account for the large yields of CO observed in the C_3O_2–O_2 system, but cannot account for the CO_2 formation. The dominance of reaction 8 over reaction 9 prevents reaction 6 from being the exclusive primary step.

If *both* reactions 3 and 6 are important, then the observed products can be explained quantitatively.

Considering only reactions 2, 3, 6, 8, and 9, and assuming steady-state concentrations for atomic oxygen and C_2O, eq I and II can be derived. The rate constant

$$\frac{(CO)}{(CO_2)} = \frac{2k_3k_8 + 2k_3k_9 + 6k_6k_8 + 2k_6k_9}{k_3k_8 + k_3k_9 + k_6k_9} \tag{I}$$

$$\phi(CO_2) = \frac{k_3k_8 + k_3k_9 + k_6k_9}{k_3k_8 + k_3k_9 + k_6k_8} \tag{II}$$

subscripts refer to the corresponding reactions, and $\phi(CO_2)$ is defined as the total molecules of CO_2 formed divided by the molecules of C_2O formed in reaction 2. Using the value for k_8/k_9 given above, and the experimental value for CO/CO_2 of 8.1, eq I can be solved to give the ratio $k_6/k_3 = 1.04$. Inserting these two rate constant ratios into eq II results in the prediction $\phi(CO_2) = 0.51$, which is in good agreement with the observed value, 0.48 ± 0.04. Thus, if the primary reactions 3 and 6 occur with comparable frequency, the products of photolysis of C_3O_2–O_2 mixtures can be explained.

Two features of the above mechanism were tested by additional experiments. The reaction of oxygen atoms with C_3O_2, eq 8 and 9, should result in a greater rate of consumption of C_3O_2 when O_2 is present, as compared to the photoreaction with an olefin. This possibility was tested with the double cell, using equal pressures of C_3O_2 on both sides, but with O_2 added to one cell and C_2H_4 to the other. Both cells were pressurized with N_2 to 360 torr total pressure. Since only about 5% of the C_3O_2 was normally decomposed during a run, isobutane was used as an internal standard. The isobutane was inert toward both reactions and had a convenient retention time. Two experiments gave 57 ± 15 and 55 ± 15% greater C_3O_2 consumption in the cell containing O_2, whereas the above mechanism and rate constants predict 52% greater consumption with oxygen. Although there could be complications in such experiments,[12] the excellent agreement supports the proposed mechanism.

The presence of oxygen atoms in the C_3O_2–O_2 system was tested by the addition of a substance which could react with oxygen atoms. If the above mechanism is correct, this should cause a decrease in the production of CO. *cis*-2-Butene was selected for several reasons. It reacts rapidly with ground-state oxygen atoms,[13] forming only small amounts of CO. However, C_2O reacts much more rapidly with molecular oxygen than with *cis*-2-butene.[4] Therefore *cis*-2-butene can scavenge oxygen atoms without interfering with the primary reactions 3 and 6.

First the relative reactivity of ground-state oxygen atoms with C_3O_2 and *cis*-2-butene was determined by direct competition. Oxygen atoms, generated by the mercury-sensitized decomposition of N_2O, were allowed to react with known mixtures of C_3O_2 and *cis*-2-butene, and the resulting N_2 and CO were determined. Assuming that there is a direct competition between the butene and the suboxide for the oxygen atoms, that $O + C_3O_2$ forms three CO molecules, while $O + C_4H_8$ forms β CO molecules, then the usual steady-state

$$O(^3P) + C_4H_8 \longrightarrow \beta CO + \text{other products} \tag{11}$$

approximation results in eq III. The neglect of reaction

$$\frac{3 - (CO/N_2)}{(CO/N_2) - \beta} = \frac{k_{11}(C_4H_8)}{k_8(C_3O_2)} \tag{III}$$

9 compared to reaction 8 has no significant effect on eq III except when (CO/N_2) approaches 0. Using the value of 0.038 for β,[13] the data of Table II are plotted in Figure 1 according to eq III. The slope of the straight

Table II. The Competition between *cis*-2-Butene and C_3O_2 for $O(^3P)$[a]

C_3O_2	C_4H_8	N_2O	N_2 formed	CO/N_2
4.8	0.638	413	0.024	0.83
4.8	0.372	408	0.028	1.14
4.9	0.175	391	0.020	1.84
4.5	0.088	400	0.020	2.21
4.6	0	424	0.027	3.07

[a] All pressures given in torr.

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[12] D. G. Williamson, Thesis, University of California, Los Angeles, Calif., 1966.

[13] R. J. Cvetanovic, *Can. J. Chem.*, **36**, 623 (1958).

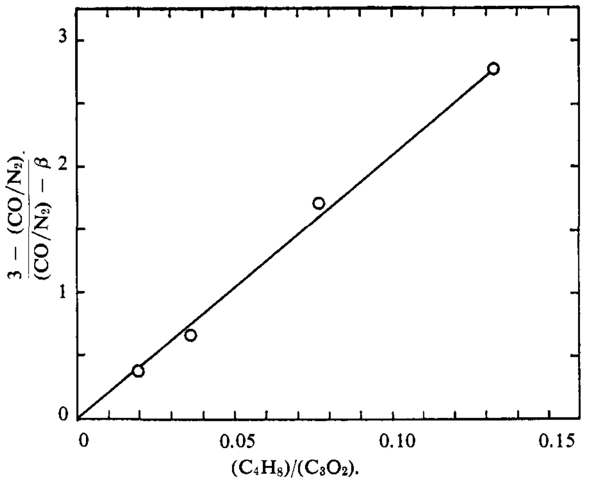


Figure 1. The competition between *cis*-2-butene and carbon suboxide for oxygen atoms.

line gives $k_{11}/k_8 = 21$. Using the accepted value[14] for k_{11}, $(8 \pm 4) \times 10^9$ l./mole sec, the absolute value of k_8 is $(4 \pm 2) \times 10^8$ l./mole sec. Since oxygen atoms react 21 times more rapidly with *cis*-2-butene than with C_3O_2, the butene can be used to test for the presence of oxygen atoms in the C_3O_2–O_2 photolysis.

The addition of small amounts of *cis*-2-butene to suboxide–oxygen mixtures resulted in a decrease in the CO production. The results given in Table III are plotted in Figure 2 by comparing the CO production in the two cells as *cis*-2-butene is added to one. The solid line gives the calculated behavior. The excellent agreement between the predicted and observed behavior is confirming evidence for the formation of oxygen atoms in the primary reaction of C_2O with O_2.

Table III. The Effect of Adding *cis*-2-Butene on the CO Production during Photolysis of C_3O_2–O_2 Mixtures[a]

Both cells		Cell 2	Cell 1	CO (cell 2)/CO	Total pressure of
C_3O_2	O_2	C_4H_8	CO produced	(cell 1)	each cell[b]
5.0	61.1	0.142	0.19	0.897	405
5.0	55.1	0.248	0.20	0.837	354
5.2	40.0	0.576	0.37	0.776	420
5.0	24.3	0.648	0.12	0.750	268
4.0	49.6	0.874	0.066	0.697	403
4.9	40.6	1.74	0.14	0.676	400

[a] All pressures given in torr. [b] Both cells pressurized with N_2O.

The reactivity of NO with C_2O was determined by competition with the 1,3-butadiene–C_2O reaction. Since the reactivity of butadiene is known[12] relative to the other olefins and to O_2, the reactivity of NO was determined on the same scale.

For direct competition between reactions 12 and 13, the steady-state approximation results in eq IV, where

$$C_2O + NO \longrightarrow \text{products} \tag{12}$$

$$C_2O + C_4H_6 \longrightarrow C_5H_6 + CO \tag{13}$$

$(yield)_1$ and $(yield)_2$ represent the production of C_5H_6

$$\frac{(yield)_1}{(yield)_2} = 1 + \frac{k_{12}(NO)}{k_{13}(C_4H_6)} \tag{IV}$$

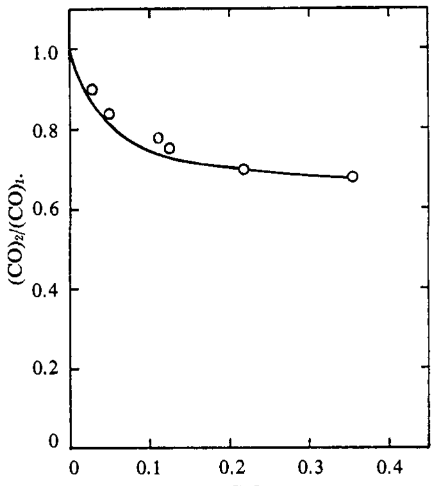


Figure 2. The effect on the CO production of adding *cis*-2-butene to the C_2O–O_2 reaction. The butene was added to cell 2 only.

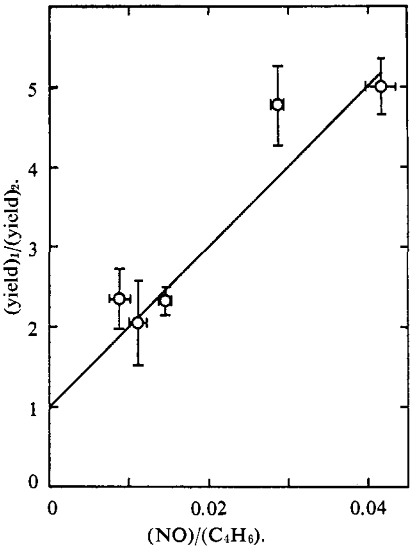


Figure 3. The competition between NO and 1,3-butadiene for C_2O.

in the two cells having equal partial pressures of C_3O_2 (7.5 torr) and C_4H_6 (50 or 100 torr), but with NO added to cell 2 only. The total pressure in each cell was adjusted to 175 torr with N_2. Since only small partial pressures of NO were used, and since 1,3-butadiene is not very susceptible to yield quenching[12] (step 4 of ref 4), the C_5H_6 yields are a good measure of the reactivities in reactions 12 and 13.

A test of eq IV is shown in Figure 3. There is considerable uncertainty in these points, because the cell calibration changed by 20 to 30% during the runs. A thin polymer film could be seen in the cell containing NO. It was necessary to calibrate the light absorbed within the cells before and after each run by photolyzing identical mixtures of C_3O_2 and C_4H_6. An average calibration factor was used when calculating the ratio $(yield)_2/(yield)_1$. The vertical error limits shown in Figure 3 result from using the prerun and postrun calibration factors to calculate $(yield)_2/(yield)_1$. A smaller uncertainty involving the consumption of NO during a run is indicated by the horizontal error limits.[12]

The least-squares line shown in Figure 3, restrained to have unit intercept, gives the value $k_{12}/k_{13} = 100 \pm$

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

Table IV. The Measured Yield of N_2 from the Reaction of C_2O with NO, Relative to the Yield of CO from Reaction 1[a]

Both cells C_3O_2	Cell 1 C_2H_4	Cell 2 NO	Cell 2 He	Cell 2 N_2 formed	$2\frac{N_2(\text{cell 2})}{\text{CO (cell 1)}}$
3.6	100	17.1	349	0.17	0.62
3.6	90	25.4	227	0.16	0.54
3.5	93	25.7	271	0.26	0.58
3.5	94	169	21	0.23	0.67
3.6	90	173	159	0.21	0.71
3.6	92	168	288	0.22	0.73
6.0	93	92	0	0.17	0.63
5.5	97	50.4	518[b]	0.23	0.70
5.9	92	48.7	625[b]	0.16	0.67

[a] All pressures given in torr. [b] Carbon dioxide was used instead of He.

Table V. The Effect of NO, C_3O_2, and Total Pressure (torr) on the Ratio of Products, (CO)/(N_2)

C_3O_2	NO	He	CO_2	N_2 produced	CO/ N_2
2.5	49	0	0	0.18	5.33
2.5	49	0	46	0.18	4.83
2.4	48	0	107	0.14	4.38
2.4	48	0	163	0.12	4.36
3.5	133	0	54	0.60	3.73
3.4	157	0	424	0.32	3.05
5.2	24.7	0	0	0.12	5.90
5.3	50	0	0	0.17	5.58
5.3	50	0	89	0.15	4.87
5.4	50	0	211	0.20	4.66
5.4	50	0	313	0.18	4.45
5.3	50	0	437	0.26	4.17
10.1	50	0	0	0.20	5.57
10.5	47	0	73	0.20	5.27
10.5	48	0	148	0.45	4.87
10.5	48	0	302	0.22	4.78
10.5	47	0	315	0.20	4.45
10.5	48	0	344	0.37	4.51
10.5	48	0	457	0.11	4.63
10.5	49	0	609	0.18	4.31
10.3	97	0	0	0.16	5.17
10.3	97	0	196	0.14	4.70
3.5	15.9	0	0	0.28	5.34
3.6	17.1	349	0	0.23	4.38
3.6	25.4	227	0	0.21	4.70
3.5	25.7	271	0	0.35	4.44
3.4	163	0	0	0.26	3.53
3.5	169	21	0	0.26	3.90
3.1	181	54	0	0.29	3.41
3.6	173	159	0	0.28	3.34
3.4	189	216	0	0.26	3.50
3.1	181	272	0	0.71	3.18
3.6	168	288	0	0.30	3.33

20. Since $(k_3 + k_6)/k_{13}$ has been measured[12] as 0.74 ± 0.09, then $k_{12}/(k_3 + k_6) = 135 \pm 30$. Thus NO is by far the most effective scavenger for $C_2O(X^3\Sigma)$, being 135 times more reactive than O_2 and approximately 10^4 times more reactive then ethylene.

The products from the C_3O_2–NO photolysis at 3080 A were observed to be N_2, N_2O, CO, and CO_2. No analysis for NO_2 was attempted. The yield of N_2 was determined relative to the CO production in the C_3O_2–C_2H_4 reaction. Values of $\phi(N_2)$ of 0.54 to 0.73 were observed, with at most a slight dependence on (NO) and total pressure (see Table IV). The average, $\phi(N_2) = 0.65 \pm 0.08$, indicates that not all C_2O molecules react to form N_2. Similarly, four measurements gave $\phi(N_2O) = 0.36 \pm 0.03$. (The yield of N_2O had to be corrected, by 15% in some cases, for the N_2O originally present in the NO.) The ratio of CO to N_2 was found to depend on both the total pressure and on the NO pressure (see Table V).

Discussion

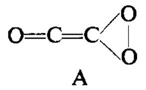
The experimental data from the oxygen–carbon suboxide photoreaction require a mechanism involving two primary steps (eq 3 and 6). Other reactions having

$$C_2O + O_2 \longrightarrow CO_2 + CO \tag{3}$$

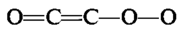
$$C_2O + O_2 \longrightarrow 2CO + O \tag{6}$$

four- and five-atom transition states are thought to involve two or more reaction paths leading to different products,[15,16] or to the same products in different electronic states.[17] It is possible that both of the above reactions form CO_2 initially, but in different electronic states, one of which always dissociates in the pressure range studied here. If this is the case, then the lack of a significant pressure effect on $\phi(CO_2)$ requires that the lifetime of this excited CO_2 be less than 10^{-10} sec.

An approximate calculation was made to test the possibility that the two reaction paths are the result of two different geometries in the transition state. Assuming that geometry A results exclusively in reaction



A



O=C=C—O—O

B

3 and geometry B results in reaction 6, the ratio k_6/k_3 was calculated by the transition state theory.[18] The following approximate values were used in the calculation: bond lengths for C=C and C=O were taken from C_3O_2,[19] while the sums of covalent radii were used for C—O and O—O[19]; the vibrational frequencies of B were approximated by those of C_3O_2[20]; the lowest bending mode of A was taken to be 250 cm^{-1}, and higher energy vibrations were neglected; the energy barriers for the formation of A and B were assumed equal. Using these values and a temperature of 300°K in the transition-state formula for the rate constants gives $k_6/k_3 = 1.35$. This is to be compared to the experimental value 1.04. The agreement between the calculated and observed ratios is only a demonstration that a geometrical origin of the two reaction paths is not unreasonable and is not a confirmation of such a mechanism. Although the parameters used in the calculation are very crude, it seems unlikely that better bond lengths or vibrational frequencies will alter the above conclusion.

Reactions 3 and 6 are sufficiently exothermic so that electronically excited products could be formed. The exact exothermicities depend on the heat of formation of C_2O, which is still uncertain. The following discussion is valid for either of the two values currently favored.[4]

Since O_2 and probably C_2O are in their triplet ground states, both singlet and triplet state products may be formed without violating the spin conservation rule.

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The formation of an oxygen atom in its ^1D excited state, but not in the ^1S state, is energetically possible in reaction 6. However, the addition of a saturated hydrocarbon (isobutane), which should react with $O(^1D)$ on nearly every collision,[21] to the C_2O-O_2 reaction did not result in a decrease in the CO production. Therefore $O(^3P)$ rather than $O(^1D)$ must be formed in reaction 6. This conclusion is confirmed by Figure 2, where the predicted scavenging of $O(^3P)$ by *cis*-2-butene agrees with the observed decrease in CO production.

Reaction 3 is sufficiently exothermic to form either CO or CO_2, but not both, in their first excited triplet states. The fate of such triplet-state molecules in the $C_3O_2-O_2$ mixture is uncertain; they would probably be deactivated to their ground states by energy transfer to C_3O_2 or O_2, which would in turn probably dissociate to give additional C_2O or oxygen atoms. In view of the observed quantum yields and the rate of consumption of C_3O_2, such a chain does not appear to be significant. Either the excited-state molecules are being deactivated without dissociation of the collision partner, or reaction 3 forms only ground-electronic-state CO and CO_2.

The reaction of $O(^3P)$ with C_3O_2 to form three CO molecules is exothermic by 115 kcal/mole,[22] which is not sufficient to excite the first triplet state of CO at 138 kcal/mole.[23] It is surprising then that reaction 8, which is spin forbidden as written, dominates the alternate spin-allowed reaction 9. It is generally accepted that a spin-allowed reaction involving only light atoms (small spin-orbit coupling) will dominate a spin-forbidden reaction.

One possible resolution of this difficulty would be for reaction 8 to proceed in two steps. The first step might be reaction 14, which could be fast since it is spin allowed. The C_2O_2 excimer could then decay to two

$$O(^3P) + C_3O_2 \longrightarrow C_2O_2(^3A) + CO(X^1\Sigma) \quad (14)$$

ground-state molecules at a slower rate. Alternatively, a triplet-state C_3O_3 adduct, analogous to the $O(^3P)$–olefin reactions, could be formed rapidly, followed by a slow decomposition step. The experimental data now available do not allow a choice between the one-step and two-step mechanisms for reaction 8.

No experimental finding from these experiments resolves the disagreement between the two sets of C_2O–olefin relative reactivities.[4,8] A significant reaction of the product allenes with oxygen atoms or excited molecules, formed by the reaction of C_2O with O_2, can be rejected since the relative reactivities found in ref 4 do not depend on the amount of product formed or on the O_2/olefin ratio.

A satisfactory mechanism for the C_2O–NO reaction has not been uncovered. The fact that the sum of $\phi(N_2)$ and $\phi(N_2O)$ is close to unity suggests that again there are two primary steps, one forming N_2 and the other forming N_2O. A straightforward method of forming N_2 would be reaction 15 followed by reaction 16. Although the rate of nitrogen atom attack on C_3O_2 is not known, the excess of NO over C_3O_2 and

$$C_2O + NO \longrightarrow N + 2CO \quad (15)$$

$$N + NO \longrightarrow N_2 + O \quad (16)$$

the large value[24] of k_{16} should make (16) the dominant reaction of a nitrogen atom in these experiments. The same products could be derived *via* NCO or CNO radicals instead of atomic nitrogen.

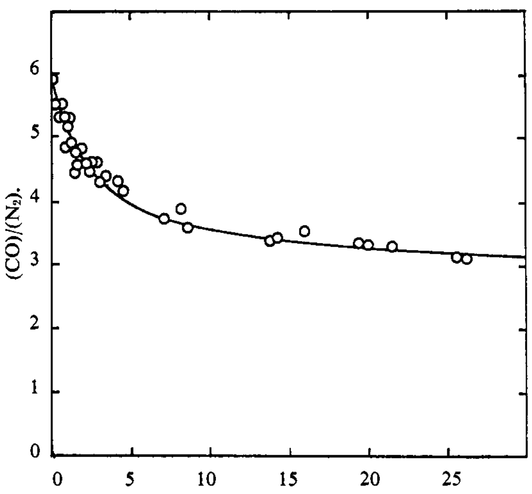

Figure 4. The dependence of the ratio of products $(CO)/(N_2)$ on the nitric oxide (NO), carbon suboxide (C_3O_2), and total (M) pressures.

If reaction 15 were the exclusive fate of C_2O in this system, then the production of CO could be explained. The ratio $(CO)/(N_2)$ approaches 6 at low pressures and 3 at high pressure (see Table V). The variation of $(CO)/(N_2)$ between these two limits is a function of the variable $(NO)(M)/(C_3O_2)$, where (M) represents the total pressure (see Figure 4). This variation and the observed $(CO)/(N_2)$ limits are compatible with the expected behavior of an oxygen atom in this system, namely reaction 8 in competition with reaction 17.

$$O + C_3O_2 \longrightarrow 3CO \quad (8)$$

$$O + NO + M \longrightarrow NO_2 + M \quad (17)$$

However, when the measured $(CO)/(N_2)$ values are treated according to this interpretation, the derived value of k_{17}/k_8 is approximately a factor of 10 larger than what is calculated from the accepted value[25] for k_{17} and the value of k_8 determined above. Photolysis of newly formed NO_2 was probably not important, since its absorption coefficient[26] is small near 3000 A, and since runs at different per cent conversions led to the same $(CO)/(N_2)$ ratios.

Another defect of the above interpretation comes from associating all of the CO production to the N_2-forming reactions, which leaves no CO to accompany N_2O formation. This is a major criticism which makes it necessary to reject a mechanism centered on reactions 15–17 and 8. Proposal of a complete and consistent mechanism for the C_2O–NO reaction cannot be made at the present time.

The very high reactivity of NO with C_2O is of importance for the C_2O–olefin reactions. Assuming that NO reacts with C_2O no faster than the gas kinetic collision frequency, then the reaction of 1,3-butadiene with C_2O occurs in only one in 10^2 or more collisions. Similarly, C_2O reacts no faster than approximately one

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in 10^3 collisions with the butenes and one in 10^4 collisions with ethylene. If the newly formed C_2O contains excess translational or rotational energy, then on the average this excess should be lost by collisions before reaction can occur. If vibrational relaxation of C_2O is similar to that of CO_2 or N_2O,[27] then C_2O should have thermal energies before it reacts, except possibly for the most reactive molecules. These conclusions mean that relative reactivity measurements of $C_2O(X^3\Sigma)$ with the olefins should be the same regardless of the source of C_2O.

Acknowledgments. The financial support of the National Science Foundation through Grant GP-2489 is gratefully acknowledged. We wish to thank Dr. Clive Willis for helpful encouragement.

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Inversion Barriers of Pyramidal (XY_3) and Related Planar (=XY) Species[1]

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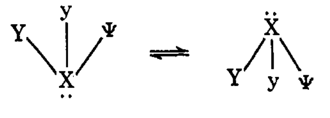
Abstract: Barriers to inversion, V_i, of 46 pyramidal (XY_3) ions and molecules have been evaluated by the method of Costain and Sutherland, and Weston. A valence force field is used, and the potential function has the form $V = 1.5k_1(\Delta l)^2 + 1.5k_\delta(\Delta\alpha)^2$. The input data for this model are the vibration frequencies (ν_1, ν_2) and bond parameters (l_{XY}, α). Some of the values of V_i in kcal/mole are: $(CH_3)_3N$, 7.5; H_3O^+, 1–2; $(CH_3)_3O^+$, 11–26; CH_3^-, 6–12; $(CH_3)_3C^-$, 8–14; ClO_3^-, 49; SO_3^{2-}, 62. These barriers turn out to be most sensitive to changes in ν_2 and the YXY angle (α). Our results indicate why it has not been possible to prepare optically active carbanions and provide a rationale for the existence of configurationally stable phosphines, arsines, etc. The model has tentatively been extended to nonplanar cyclic species, and planar species which can undergo in-plane inversion (wagging). Thus, ethylenic, cyclopropyl, and cyclobutyl anions, as well as their isoelectronic nitrogen analogs, have been examined. Applications to mechanistic problems are discussed.

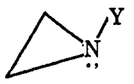
Barriers to intramolecular motions which lead to inversion are intimately related to the configurational identity of a molecule. The inversion barrier between two potential energy minima with the concomitant energy splitting, ΔE_n, of the vibrational energy levels in ammonia is a familiar example.[2,3] Of course, when different groups are attached to an atom X in a pyramidal-like molecule $XyY\Psi$, we can write D and L forms[4]



(1)

Besides the ammonia analogs, *e.g.*, PF_3, $SbBr_3$, there are anions, *e.g.*, CH_3^-, $(CH_3)_3Si^-$, ClO_3^-, TeO_3^{2-}, and cations, *e.g.*, $(CH_3)_3S^+$, H_3O^+, in which three groups and one electron pair are attached to one atom. We presume that all of these species are pyramidal and possess barriers to inversion. In respect to the configuration of the trivalent atom, some small ring species (**1–4**), *e.g.*, cyclopropyl anions, aziridines, protonated ethylene oxides, or sulfides, etc., are obviously close kin to these pyramidal species. And it does no real violence to the notion of inversion to include types **5** and **6**,

1



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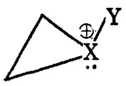
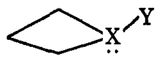
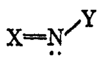


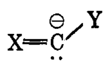
3, X = O, S



4a, X = C
b, X = N
c, X = P



5



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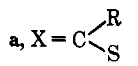
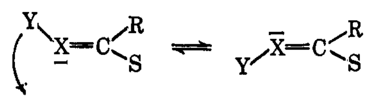


a, $X = C\begin{smallmatrix}R\\S\end{smallmatrix}$
b, X = NR

or alkenides, imines, oximes, imido ethers, azoxy and azo compounds, etc., provided that they isomerize by in-plane wagging,[5] *e.g.*



(2)

The barrier restricting inversion, V_i, has been associated both with the tunneling of the apical electron pair and with the deformation required to make the pyramid coplanar.[2,3,6-10] Both aspects of the process

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[1] Supported in part by the Petroleum Research Fund of the American Chemical Society; inquiries should be addressed to S. I. M.

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