The Reaction of Carbon Suboxide with Oxygen Atoms and Active Nitrogen[1]

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Abstract: A study has been made of the reaction of C_3O_2 (carbon suboxide) with O atoms, active nitrogen, and a mixture of O atoms plus active nitrogen. A time-of-flight mass spectrometer was used to observe the reaction products and to determine their concentration. The spectra of the flames of the reactions were recorded with emission spectrographs. The results showed the following reactions to occur: $C_3O_2 + O \rightarrow 3CO$, $(5.2 \pm 2) \times 10^{-13}$ cm^3/particle sec (1); $C_3O_2 + O \rightarrow CO_2 + C_2O$, $(4.1 \pm 2) \times 10^{-14}$ cm^3/particle sec (2); $C_2O + O \rightarrow CO$ $(A^1\Pi, d^3\Delta, e^3\Sigma) + CO$ (4); $C_2O + N \rightarrow CN\,(B^2\Sigma) + CO$ (6).

The formation of C_3O_2 from CO and the reactions of C_3O_2 have generated considerable interest in the past few years. Recently, studies using C_3O_2 have been conducted in several areas.

(a) In the radiation chemistry of CO, a polymer of C_3O_2 is one of the main products.[2,3] Here it is important to know how the C_3O_2 is formed and, once it is made, how it polymerizes. Evidence exists for a building up of C_3O_2 from C to C_2O to C_3O_2.[4] This mechanism has been shown to be correct in the photochemistry of CO.[5] In addition, a reaction between a C atom and C_2O has been suggested to explain the excitation of the C_2 high-pressure bands observed in the radiation chemistry studies of helium + CO mixtures.[6]

(b) From the work of Willis and Bayes[7] and Mullen and Wolf[8] on the photolysis of C_3O_2, it appears that a species is primarily produced which reacts with a variety of foreign gases such as olefins where a C atom is inserted into the double bonds. It seems certain that this species is the radical C_2O.

(c) Low-pressure work in fast flow systems[9,10] has shown that C_3O_2 reacts with O atoms in a fast reaction, yielding CO and CO_2 as products. In addition, a chemiluminescence of CO excited with as high as ~9 ev is observed. It has been postulated[9,10] that this high energy originates from the reaction of C_2O with O atoms.

In all the above examples, the radical C_2O seems to play a most important role, either as a building block for C_3O_2 or as a reactive intermediate from the decomposition of C_3O_2, either photolytic or chemical. A knowledge of the chemical reactions of this intermediate is of importance in the general understanding of the radiation chemistry of CO.

In this study we will discuss the results obtained by treating C_3O_2 with either O atoms or active nitrogen, or a mixture of O atoms and active nitrogen.

The reaction of C_3O_2 with O atoms has been shown to proceed in two ways[9,10]

$$C_3O_2 + O \longrightarrow 3CO \tag{1}$$

$$C_3O_2 + O \longrightarrow C_2O + CO_2 \tag{2}$$

We have reinvestigated this reaction and the rate of the over-all reaction. Also the individual reactions have been measured with a time-of-flight mass spectrometer.

The reaction of C_3O_2 with active nitrogen provides information on some of the reactions leading to the formation of excited CN. This reaction is simpler than reactions of active nitrogen with hydrocarbons since all reactions associated with hydrogen are avoided.

Extensive work has been done on the reactions of active nitrogen with other carbon-containing compounds and on the origin of the CN luminescence (red and violet systems) which is usually associated with these reactions.[11,12] The mechanism of the CN emission has been shown to be pressure dependent in that crossings from the higher vibrational levels of the $A^2\Pi$ state to the $B^2\Sigma$ state have been shown to take place.[13,14] Whatever the mechanism for the emission, the energy necessary to excite the levels emitting must be available from the chemical reactions taking place. An alternative mechanism has also been proposed[15] where the excitation to the higher vibrational levels of the $B^2\Sigma$ state occurs through energy transfer to the CN radical by collision with energetic species, possibly produced in course of the reaction of active nitrogen with the carbon-containing compounds.

Experimental Section

C_3O_2 was prepared by the dehydration of malonic acid at 150° and purified by fractional distillation.[16] Active nitrogen was made by flowing nitrogen through a Woods-Bonhoeffer discharge tube. For most of the experiments the O atoms were made by adding NO to the active nitrogen. The reaction of N atoms in the active nitrogen with NO is very fast and produces oxygen atoms in the ground state.

$$N + NO \longrightarrow N_2 + O(^3P) \tag{3}$$

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[1] This research was supported by the U. S. Atomic Energy Commission under Contract AT(30-3)-321.

[2] For a general description of the radiation chemistry of CO, see S. C. Lind, "Radiation Chemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1961.

[3] A. R. Anderson, J. V. F. Best, and M. J. Willett, *Trans. Faraday Soc.*, **62**, 595 (1966).

[4] S. Dondes, P. Harteck, and H. von Weyssenhoff, *Z. Naturforsch.*, **19a**, 13 (1964).

[5] G. Liuti, S. Dondes, and P. Harteck, *J. Chem. Phys.*, **44**, 4051, *ibid.*, 4052 (1966).

[6] C. Kunz, S. Dondes, and P. Harteck, *ibid.*, **46**, 4157 (1967).

[7] C. Willis and K. D. Bayes, *J. Am. Chem. Soc.*, **88**, 3203 (1966).

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[9] H. von Weyssenhoff, S. Dondes, and P. Harteck, *J. Am. Chem. Soc.*, **84**, 1526 (1962).

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

[11] H. G. V. Evans, G. R. Freeman, and C. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).

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[13] E. Radford and H. P. Broida, *J. Chem. Phys.*, **38**, 644, (1963).

[14] R. L. Brown and H. P. Broida, *ibid.*, **41**, 2053 (1964).

[15] D. W. Setser and B. A. Thrush, *Nature*, **200**, 864 (1963).

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

By titrating the active nitrogen with NO in the usual manner the amount of N atoms produced was measured, and flow rates of 4 × 10^{18} to 9 × 10^{18} atoms/sec were found. By producing O atoms in this manner (reaction 3), a known amount determined from the NO added was readily available. For the mass spectrometric determination of the CO to CO_2 ratio obtained from the reaction of O atoms with C_3O_2 (reactions 1 and 2), the O atoms were produced by flowing oxygen through the discharge tube. This was necessary since the CO formed could not be readily determined mass spectrometrically in the presence of nitrogen.

The nitrogen was purified by passing the gas over copper oxide at ~400°. The exiting gas was then bubbled through a chromous chloride solution and finally passed through a series of cold traps cooled with liquid oxygen. The oxygen used for the preparation of O atoms was passed through cold traps cooled with Dry Ice and acetone.

For the emission spectroscopic measurements, the C_3O_2 was added through a jet to the active gases flowing through a quartz tube of 3.2 cm i.d. and 2 m long. NO was added to the active nitrogen 40 cm upstream from the jet. The total pressure of the gas was between 0.3 and 0.6 torr, and flow rates of approximately 8 × 10^3 cc/sec were used. Glass and quartz Hilger medium spectrographs were used. Kodak spectroscopic plates 103a-F were used and developed as outlined by Kodak.

The kinetics of the reactions were studied using a Phillips–Schiff[17] reactor in conjunction with a Bendix time-of-flight mass spectrometer as previously described. Pressures and flow rates were the same as used in the emission spectroscopic experiments.

Results and Discussion

A. C_3O_2 + O Atoms. The fast reaction of C_3O_2 with O atoms has been studied by von Weyssenhoff, Dondes, and Harteck,[9] who observed the products CO and CO_2 together with the emission of the CO triplet bands ($d^3\Delta \rightarrow a^3\Pi$) indicating that a reaction is taking place that is unusually exothermic. Becker and Bayes[10] confirmed the high exothermicity and in addition found emissions from the $A^1\Pi$ state and $e^3\Sigma$ state, all at about 9 ev above the ground state. The mechanism that best satisfies these observations is expressed by

$$C_3O_2 + O \longrightarrow 3CO \tag{1}$$

$$C_3O_2 + O \longrightarrow CO_2 + C_2O \tag{2}$$

$$C_2O + O \longrightarrow CO^* + CO \tag{4}$$

von Weyssenhoff, *et al.*,[9] measured the CO/CO_2 ratio and found an average value of 13. The ratio of the rates of reaction 1 and 2 is then about 3.6. Using the time-of-flight mass spectrometer instead of the technique used by von Weyssenhoff, *et al.*,[9] we reinvestigated the C_3O_2 + O reaction and measured the rate constant for the disappearance of C_3O_2 at room temperature at total pressures of 0.4, 0.5, and 0.6 torr and an initial partial pressure of O atoms of about 0.034 torr. The initial concentration of C_3O_2 was much lower than that of the O atoms (~0.0015 → 0.002 torr).

The data have been fitted into the integrated first-order rate equation

$$-0.434k[\mathrm{O}]t = \log \frac{[C_3O_2]_t}{[C_3O_2]_0}$$

where $[C_3O_2]_0$ is the initial C_3O_2 concentration and $[C_3O_2]_t$ is the measured concentration at time t. The O atom concentration was taken as constant for the time interval examined. Table I shows the results obtained from a typical run at 0.5 torr. The remarkable stability of k for different values of the residual C_3O_2 can be taken as good evidence that the O atom concentration is constant and the reaction can be treated as first order with respect to C_3O_2.

Table I

C_3O_2 signal (arbitrary units)	$t \times 10^3$, sec	$k \times 10^{13}$, cc/particle sec
240	0	
49	2.12	6.7
35	3.06	5.6
25	3.55	5.7
18	4.00	5.8
14	4.48	5.6
12	4.95	5.4

The ratio CO/CO_2 was measured by treating C_3O_2 with O atoms obtained from an O_2 discharge because of the difficulty of measuring small variations of the mass spectrometer peak for CO at m/e 28 in the presence of large amounts of N_2. Here, the concentration of O atoms was also in large excess over the concentration of suboxide to assure complete reaction prior to entering the mass spectrometer. Values of CO/CO_2 of 33, 36, and 39 were obtained. Taking into account the entire mechanism, and the average value for CO/CO_2 of 36, a ratio of k_1/k_2 equal to 11.3 ± 1.0 is obtained.[18] These values are larger by a factor of ~3 compared with the results of von Weyssenhoff.[9]

The over-all rate for the reaction of O atoms with C_3O_2 and the rates for the two specific reactions are

$$C_3O_2 + O \longrightarrow \text{products} \qquad (5)^{19}$$
$$k_5 = (5.6 \pm 2) \times 10^{-13}\ \text{cm}^3/\text{particle sec}$$

$$C_3O_2 + O \longrightarrow CO \tag{1}$$
$$k_1 = (5.2 \pm 2) \times 10^{-13}\ \text{cm}^3/\text{particle sec}$$

$$C_3O_2 + O \longrightarrow CO_2 + C_2O \tag{2}$$
$$k_2 = (4.1 \pm 2) \times 10^{-14}\ \text{cm}^3/\text{particle sec}$$

The limit of error given is to allow for inaccuracies in determinating the O-atom concentration and to compensate for any possible systematic errors. It should be noted that it was not necessary to know the actual C_3O_2 concentration since the ratio of the mass spectrometric signals for C_3O_2 over the time interval for the reaction was used in calculating the rate constant. This ratio could be determined within a limit of error that was small in relation to the other measurements.

B. C_3O_2 + Active Nitrogen. When C_3O_2 is added through a jet to active nitrogen, a moderately intense glow of pink color is noticed which extends from the jet down the length of the tube to the cold trap before the pump. A slow deposition of a brown substance is formed on the walls of the reaction tube. The glow appears brighter and more violet at the jet, while the pink color extends downstream with an intensity not substantially decreased even 1 m from the jet. The nitrogen afterglow which remained after the addition of C_3O_2 also contributes to the appearance of the glow.

A spectrum of the glow of C_3O_2 and active nitrogen taken at the jet, where the pressure was 0.3 torr and the flow rate was about 3 × 10^{17} particles/sec, is shown in Figure 1. A spectrum of C_2N_2 and active nitrogen

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(17) L. F. Phillips and H. L. Schiff, *J. Chem. Phys.*, **36**, 1509 (1962).

(18) To assess the role of O_2 in the following possible reactions

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

$$(\longrightarrow 2CO + O \text{ also possible}) \tag{b}$$

an argon–oxygen mixture (90:10) as well as pure oxygen was used. There was no substantial change in the ratio of CO/CO_2 produced indicating that reactions a and b cannot play a major role.

(19) Reaction 5 is first order in respect to atomic oxygen.

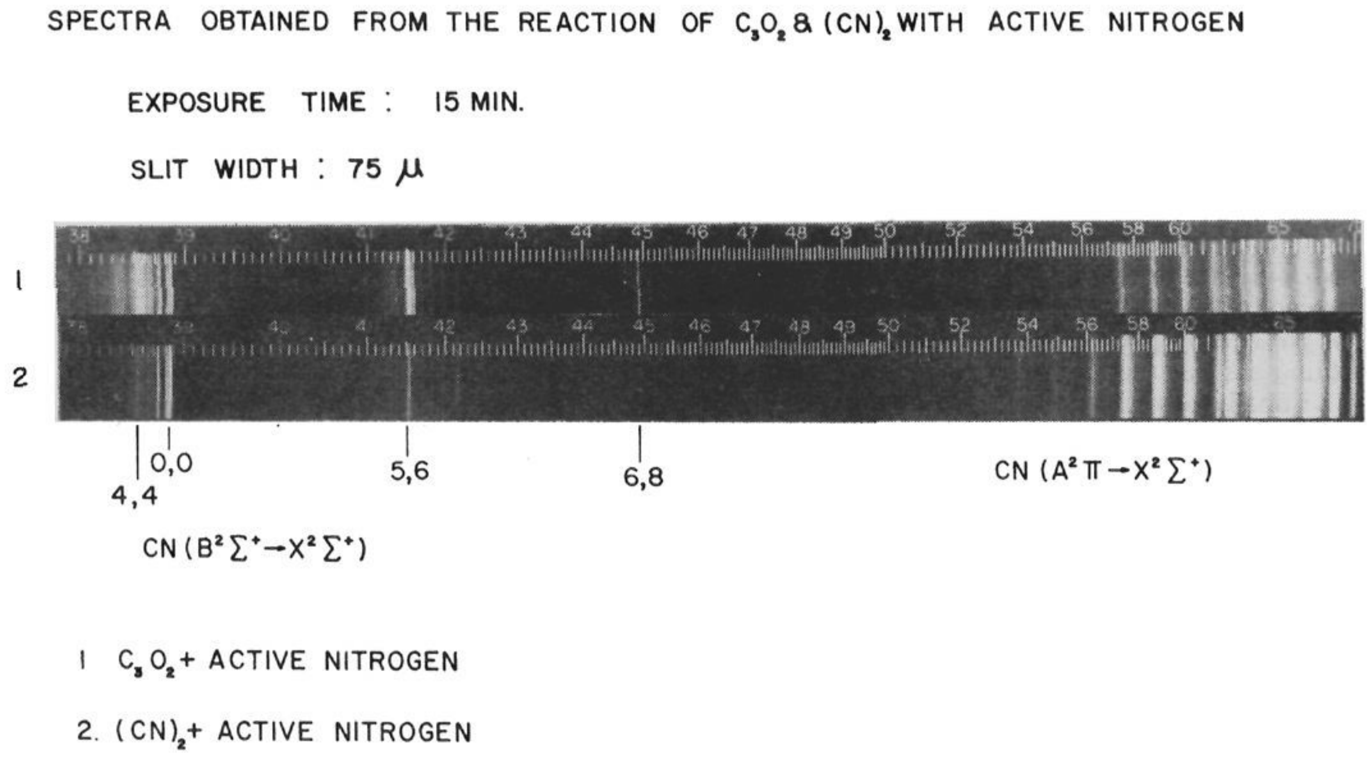

Figure 1.

under similar conditions is shown for comparison. In both cases, the emissions observed are from the CN violet ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) and CN red ($A^2\Pi_i \rightarrow X^2\Sigma^+$) systems.

In the case of C_3O_2 plus active nitrogen, the violet system is relatively more populated. In the case of C_2N_2 plus active nitrogen, the lower vibrational levels of both the red and violet systems are more populated. Changes in the flow rate of either C_3O_2 or active nitrogen did not basically alter the appearance of the spectrum.

Mass spectrometric measurements showed only a relatively small consumption of C_3O_2 (5 to 7% in 20 msec) and dicyanogen as the only product observed in the gas phase. Assuming that the only process which takes place is a bimolecular reaction between N atoms of the active nitrogen and C_3O_2, a second-order rate constant equal to $(2.3 \pm 1) \times 10^{-15}$ cc/particle sec can be calculated from the measured N atom concentration (0.04 torr) and the variation of the C_3O_2 signal. However, it is difficult to ascertain whether the over-all reaction occurring is simply the one indicated above. The nitrogen afterglow contains active species other than the ground-state atoms, although in much lower concentration. The most abundant of these may be N_2 ($A^3\Sigma$), possibly vibrationally excited, which is originated both in the discharge and in the afterglow itself following N-atom recombination. Therefore a process of energy transfer from N_2 ($A^3\Sigma$) to C_3O_2 could occur followed by dissociation of C_3O_2 to CO and C_2O. The violet luminescence which appears at the jet may then be due to a reaction between N atoms and C_2O as follows

$$N + C_2O \longrightarrow CN^* + CO \qquad (6)$$

where CN would be excited preferentially to the intermediate vibrational levels of the $B^2\Sigma$ system. The CN radical in turn could dimerize to form C_2N_2, contribute to the formation of higher polymers, and take part in reactions giving rise to the weak pink luminescence observed downstream. Reactions of the type[12,14]

$$N + CN + M \longrightarrow NCN + M \qquad (7)$$

$$N + NCN \longrightarrow N_2 + CN^* \qquad (8)$$

have been postulated to account for the CN emission in reactions of active nitrogen with chlorinated hydrocarbons.

The direct reaction between N atoms and C_3O_2 can only proceed as follows (taking $D(\text{C–N}) = 173$ kcal/mole,[20] $D(\text{C–O}) = 256$ kcal/mole, and the heat of formation from the atoms of C_3O_2 = 655 kcal/mole.[21]

$$C_3O_2 + N \longrightarrow CN + 2CO + 30 \text{ kcal/mole} \qquad (9)$$

Formation of molecules such as NCO and C_2O or NO and C_3O can be excluded on energetic grounds. The exothermicity of reaction 9 is not enough to excite CN to the observed levels; therefore, some other process must be operative to account for the relative energetic emissions.

C_3O_2 + N + O Atoms. To investigate the possibility of direct chemical excitation of CN in a strongly exothermic reaction, we performed the study of the reaction of C_3O_2 with a mixture of N and O atoms. It should be possible through the fast reaction of O atoms with C_3O_2 to form the C_2O radical (reaction 2) and under the proper conditions observe any reaction of the N atoms with the C_2O.

When a small amount of NO is added to active nitrogen before it is mixed with C_3O_2, a much brighter violet flame develops from the C_3O_2 jet extending for about 10 cm. As the amount of NO (*i.e.*, the amount of O atoms) is increased, the flame reaches a maximum luminosity and then with further increase fades to a weak luminescence at the equivalence point (only O atoms present). Figure 2 shows spectrograms of the flame obtained from various mixtures of N and O atoms with C_3O_2 taken on the same spectroscopic plate, same exposure time, same initial C_3O_2 flow, and at approximately the same total pressure (the total pressure changes because of the introduction of NO, but not by more than 10%). By comparing spectrogram no. 3 with spectrogram no. 4 it can be seen that a small amount of O atoms causes both the violet and red systems of CN to be considerably intensified. When the O atom concentration

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(20) J. Berkowitz, *J. Chem. Phys.*, **36**, 2533 (1962).

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

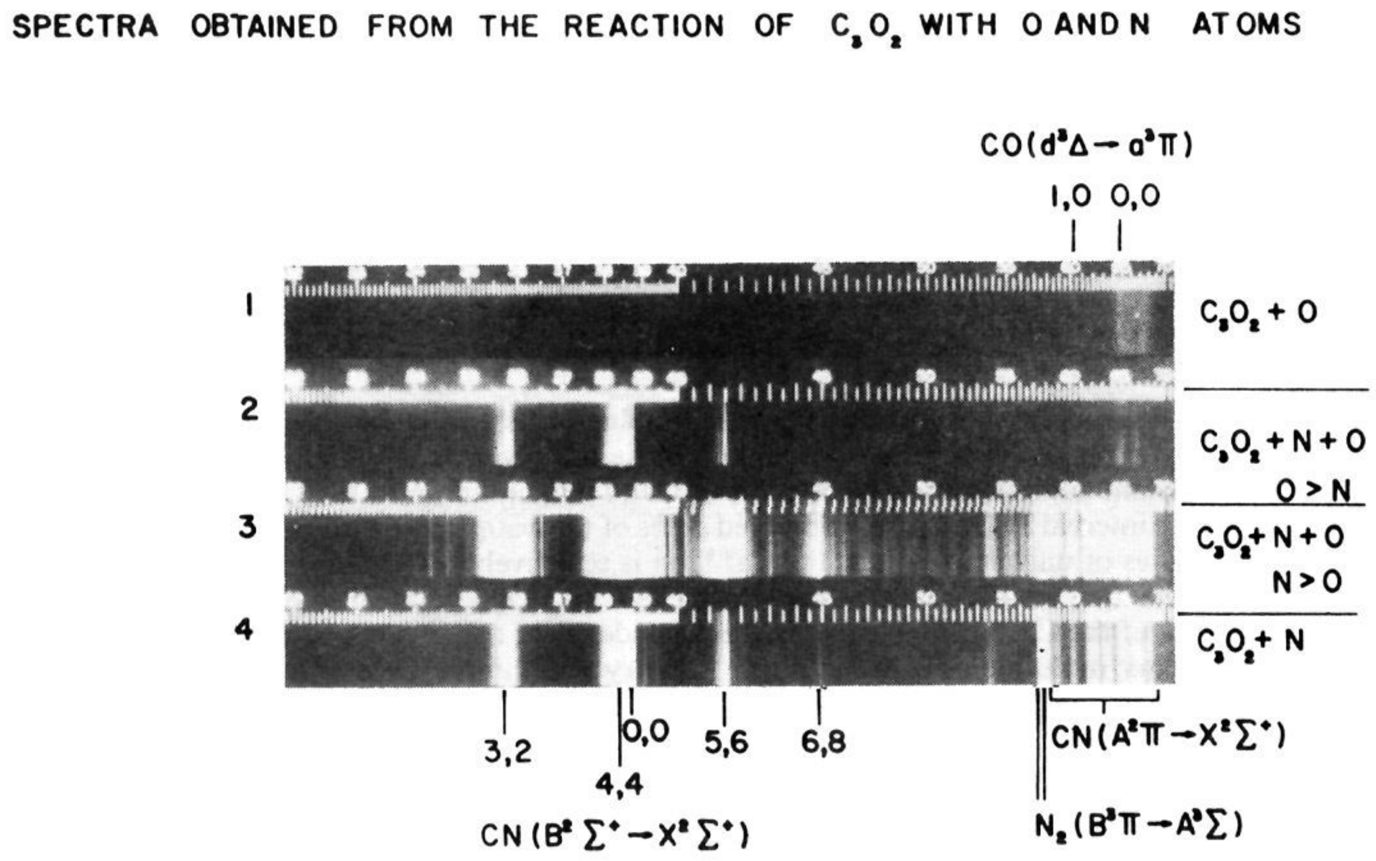

Figure 2.

is increased to the point where it is equal to or somewhat greater than the N atom concentration, the total intensity is decreased. However, the higher vibrational levels of the violet system are intensified in relation to the other CN emissions (compare spectrograms 2 and 4). At the same time the CO triplet bands appear partially superimposed on the CN red bands. At the equivalence point, where only O atoms are present, only the CO triplet bands are seen (spectrogram no. 1).

Repeating the same experiment but using the mass spectrometer, we observed that by increasing the NO flow the production of C_2N_2 increased to a maximum which corresponded to the maximum light emission and then decreased to a very low value. For both, the maximum CN light emission and the maximum C_2N_2 production, the amount of O atoms reacting was approximately equal to the amount of C_3O_2 added, while the N atoms were in excess. This behavior, coupled with the information obtained from the $C_3O_2 + O$ reaction, can be accounted for by the following reaction scheme.

$$C_3O_2 + O \longrightarrow 3CO \qquad (1)$$
$$k_1 = (5.2 \pm 2) \times 10^{-13}\ \text{cm}^3/\text{particle sec}$$

$$C_3O_2 + O \longrightarrow CO_2 + C_2O \qquad (2)$$
$$k_2 = (4.1 \pm 2) \times 10^{-14}\ \text{cm}^3/\text{particle sec}$$

$$C_2O + O \longrightarrow CO\ (A^1\Pi,\ d^3\Delta,\ e^3\Sigma) + CO \qquad (4)$$

$$C_2O + N \longrightarrow CN\ (B^2\Sigma) + CO \qquad (6)$$

When the concentration of O atoms is approximately the same as the C_3O_2, a rapid reaction according to (1) and (2) will occur. The C_2O formed *via* reaction 2 will predominantly react with N atoms (which are in a large excess) according to reaction 6, producing CN excited to the intermediate vibrational levels of the $B^2\Sigma$ system. With only O atoms present, the C_2O reacts with them *via* reaction 4, and the CO triplet bands ($d^3\Delta \rightarrow a^3\Pi$) are observed with weak intensity.

In experiments where simply O atoms were treated with C_3O_2, the profile of the flame indicated that the rate-determining step in the over-all mechanism was reaction 5. Therefore the rate of reaction 4 must be faster than 5.6×10^{-13} cm³/particle sec. Also when equal concentrations of O and N atoms (both in excess of C_3O_2) were available to react with the C_2O, emissions from both the CN violet and CO triplet systems were observed, indicating that reactions 4 and 6 are competitive and that their rates cannot be very different.

The results also indicate that the CN red system [which was observed in the high vibrational levels (predominantly $v' = 5$ to $v' = 8$)] and the lowest levels of the violet system (predominantly from $v' = 0$) are excited by tertiary reactions which involve CN radicals formed from previous processes. This was determined by assuming that the relative amounts of C_2N_2 measured with the mass spectrograph corresponded to the amount of CN radicals present and relating these results to the emission spectroscopic observations. For example, in Figure 2, spectrogram no. 2, the C_2N_2 measured mass spectrometrically was very low (note that the CN red system is almost not observable). This supports reactions 7 and 8 as a mechanism for the excitation of the red system and the lowest vibrational levels of the violet system.[22]

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[22] Note Added in Proof. After submission of this article, a paper by D. G. Williamson and K. D. Bayes (*J. Am. Chem. Soc.*, **89**, 3390 (1967)) appeared in which they measured the rate of reaction 1. The rate constant they obtained of $6.7 \pm 3 \times 10^{-13}$ cc/particle sec is in good agreement with the value in this article.