High Pressure Mass Spectra and Ion Chemistry of Carbon Suboxide

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Abstract: Subjecting carbon suboxide, C_3O_2, to electron bombardment in the ion source of a mass spectrometer results in formation of a great variety of positive ions from ion–neutral reactions at sample pressures up to 0.3 Torr. Secondary and higher order ions identified include C_xO^+ ($x = 3, 4, 5, 6$), $C_yO_2^+$ ($y = 3, 4, 5, 6, 7, 8, 9$), and $C_zO_3^+$ ($z = 5, 7$). From consideration of the pressure dependence of ionic abundances, possible reactions are suggested. Insertion of carbon atoms from C_3O_2 into reactant ions seems to be an important process. Ion–neutral reactions may provide a path for formation of elemental carbon, but there is no evidence here that they lead to polymerization of C_3O_2. The rate constant for reaction of C_2O^+ with C_3O_2 is $(2.1 \pm 0.2) \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1}.

Previous mass spectrometric studies of C_3O_2, carbon suboxide or dioxopropadiene, are those of Hirt and Wightman,[1] Botter,[2] and Bayes,[3] who obtained "low" pressure spectra. Botter reported small quantities of the ions $C_4O_2^+$ and $C_5O_3^+$, which he attributed to ion–neutral reactions. Ionic processes have been invoked to account for the gaseous polymerization of C_3O_2 upon γ radiolysis,[4] but no systematic investigation of the ion chemistry of C_3O_2 or the pressure dependence of its mass spectrum has been reported.

The present study was undertaken to examine the behavior of C_3O_2 under ionizing conditions and to extend the work in this laboratory on ion–neutral reactions in oxides of carbon.[5] The method used consists of subjecting C_3O_2 at pressures up to 0.3 Torr to electron bombardment in the ion source of a mass spectrometer and measuring the relative abundances of the resulting positive ions. From this, information about the kinetics and mechanisms of the ionic reactions is obtained.

Experimental Section

The C_3O_2 sample was furnished by Professor J. E. Kilpatrick (Rice University). Before each experiment the sample was vacuum distilled trap to trap. The vapor above the liquid in an acetone–solid CO_2 bath entered the mass spectrometer through a variable leak.

The "high" pressure ion source, quadrupole mass filter, and operating conditions have been described.[5] Spectra were scanned from *m/e* 12 to 140, the upper mass limit of the instrument, with up to 0.3 Torr of C_3O_2 in the ion source. Typically the electron energy is 150 eV. The repeller potential of +6 V gives a field of 12 V cm^{-1}. The residence time of an ion in the source is about 10^{-6} sec. The source, which is heated by the electron-emitting filament, operates at a temperature of about 340°K.

Ions were identified by mass number and isotope ratios, which permitted an ion $C_xO_y^+$ to be distinguished from a possible ion $C_{x\pm4}O_{y\mp3}^+$ at the same nominal mass.

Results

Primary Ions. Ions formed in unimolecular processes are the parent, $C_3O_2^+$, and the fragments C^+, C_2^+, C_3^+, O^+, CO^+, C_2O^+, and C_3O^+. Some of the C^+, O^+, and CO^+ may arise from carbon monoxide formed in the ion source by decomposition of C_3O_2.[2] The abundances of these ions at pressures below 10^{-2} Torr approach those previously reported,[1–3] although quantitative comparisons are difficult because of a strong dependence on repeller potential, observed here and reported by Botter.[2] As the repeller potential is decreased, the residence time of ions in the source increases and the observed intensity of the parent $C_3O_2^+$ decreases relative to that of the fragment ions. The pressure dependence of the ion abundances is strong also.

Ions of Higher Order. The mass spectra at higher pressures are characterized by a large variety of new ions formed in second order and higher order reactions. The pressure dependence of the abundances of the more important ions is shown in Figures 1 and 2 for a typical experiment. Except at the lowest pressures where C_2O^+ or CO^+ is most abundant, $C_3O_2^+$ dominates up to about 0.025 Torr; then $C_4O_2^+$ to about 0.05 Torr; $C_5O_2^+$ to 0.16 Torr; then $C_7O_2^+$. Other ions identified are C_3O^+ (maximum abundance 10% at 0.010 Torr), C_4O^+ (2.3% at 0.015 Torr), C_5O^+ (1.7% at 0.03 Torr), C_6O^+ (0.5% at 0.04 Torr), $C_5O_3^+$ (12% at 0.04 Torr), and $C_7O_3^+$ (14% at 0.10 Torr). The four species $C_6O_2^+$, $C_7O_2^+$, $C_8O_2^+$, and $C_9O_2^+$ are formed with their abundances in the proportion 35:65:0.4:0.2 at all pressures considered. There is no evidence for formation of $C_6O_4^+$, corresponding to a dimer of C_3O_2; higher polymeric ions could not be sought because of the mass limitation of the instrument.

Discussion

The lability of C_3O_2 in the ion source, where it presumably polymerizes[6] or decomposes to carbon[7] on the chamber walls and on the filament, makes the acquisition of quantitative kinetic data difficult. Nevertheless, there are some features of the kinetics of this system which are reproducible and believed reliable. A summary of the reactions supposed to occur is shown below (eq 1–14). Reactant ions shown with continuous underscore are primary ions. Those with broken underscore are formed in both primary and secondary processes. The rationale for this scheme will now be considered.

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(1) T. J. Hirt and J. P. Wightman, *J. Phys. Chem.*, **66**, 1756 (1962).

(2) R. Botter in "Advances in Mass Spectrometry," Vol. 2, R. M. Elliot, Ed., Pergamon Press Ltd., Oxford, 1963, p 540.

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

(4) A. R. Blake and K. E. Hodgson, *J. Chem. Soc., A*, 533 (1966).

(5) S. M. Schildcrout and J. L. Franklin, *J. Chem. Phys.*, in press.

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

(7) T. J. Hirt and H. B. Palmer, *Carbon*, **1**, 65 (1963).

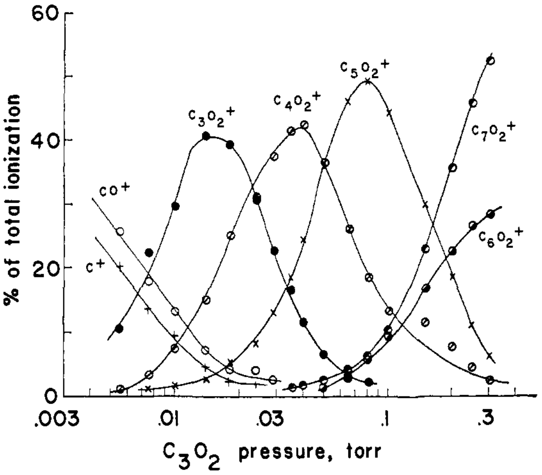

Figure 1. Pressure dependence of relative abundances of some of the more important ions formed from 150 eV electron impact in C_3O_2. Ion-repeller potential is 6.1 V; repeller field is 12 V cm^{-1}.

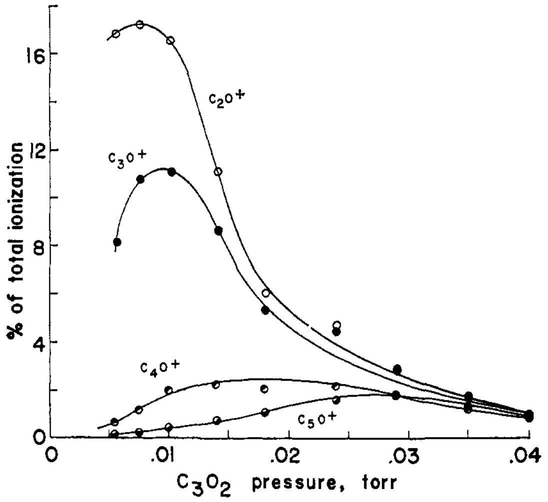

Figure 2. Pressure dependence of relative abundances of C_xO^+ ions formed from 150 eV electron impact in C_3O_2.

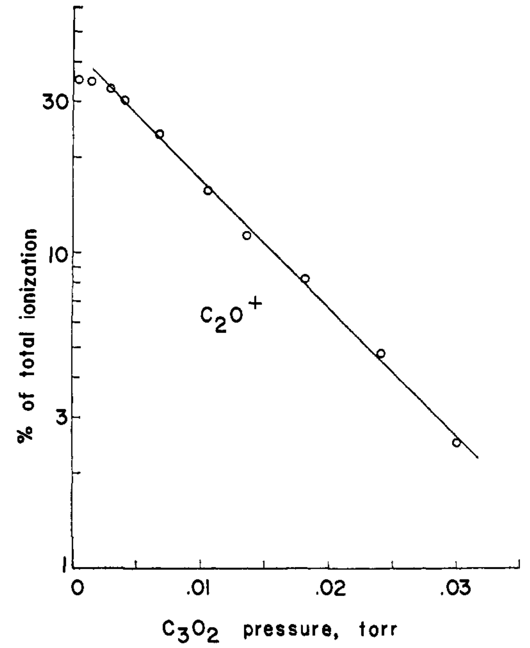

Figure 3. Semilogarithmic plot of pressure dependence of relative abundance of C_2O^+ formed from 150 eV electron impact in C_3O_2. Nonlinearity at low pressure may be caused by formation of C_2O^+ in secondary processes. Rate constant for reaction of C_2O^+ is determined from slope of linear portion.

All the primary ions except $C_3O_2^+$ and C_3O^+ decrease in abundance as the pressure is increased, indicating that they react with C_3O_2. The fact that $C_3O_2^+$ and C_3O^+ increase with pressure implies that they are formed in secondary as well as primary processes. Although the purely primary ions react at roughly comparable rates, the only rate constant that could be determined with confidence is that for C_2O^+, namely (2.1 ± 0.2) × 10^{-9} cm^3 $molecule^{-1}$ sec^{-1}. This number is obtained from the slopes of plots such as that shown in Figure 3, assuming that the available reaction time is that for an ion in free flight between the electron beam and the exit orifice of the ion source.[5] The rate constant is the same at 24 eV as at 150 eV ionizing energy, and at 3 V as at 6 V repeller potential.

$$\underline{CO^+} + C_3O_2 \longrightarrow C_3O_2^+ + CO \tag{1}$$
$$\underline{C^+} + C_3O_2 \longrightarrow C_3O_2^+ + C \tag{2}$$
$$\underline{C_2O^+} + C_3O_2 \longrightarrow C_3O_2^+ + C_2O \tag{3}$$
$$\longrightarrow C_3O^+ + 2CO \tag{4}$$
$$\underline{C_3O^+} + C_3O_2 \longrightarrow C_4O^+ + 2CO \tag{5}$$
$$C_4O^+ + C_3O_2 \longrightarrow C_5O^+ + 2CO \tag{6}$$
$$C_5O^+ + C_3O_2 \longrightarrow C_6O^+ + 2CO \tag{7}$$
$$\underline{C_3O_2^+} + C_3O_2 \longrightarrow C_4O_2^+ + 2CO \tag{8}$$
$$\longrightarrow C_5O_3^+ + CO \tag{9}$$
$$C_4O_2^+ + C_3O_2 \longrightarrow C_5O_2^+ + 2CO \tag{10}$$
$$C_5O_2^+ + 2C_3O_2 \longrightarrow C_6O_2^+ + 2CO + C_3O_2 \tag{11}$$
$$\longrightarrow C_7O_2^+ + 4CO \tag{12}$$
$$\longrightarrow C_8O_2^+ + 2CO + CO_2 \tag{13}$$
$$\longrightarrow C_9O_2^+ + 2CO_2 \tag{14}$$

Since the extent of CO production by thermal processes in the ion source was variable and not readily controllable, the abundances of C^+, O^+, and CO^+ ions which may arise from CO as well as from C_3O_2 have limited significance for determination of rate constants.

The formation of $C_3O_2^+$ in secondary processes presumably occurs by charge transfer from primary ions. Since the ionization potential of C_3O_2 (10.6 eV)[8] is less than those of CO (14.0 eV)[9] and C (11.2 eV),[9] charge transfer could occur from CO^+ and C^+ by reactions 1 and 2.

It is not known whether charge transfer from C_2O^+ to C_3O_2 is energetically allowed and the present results do not resolve this problem. The heat of formation of C_2O is estimated at 92 ± 5 kcal $mole^{-1}$ by Becker and Bayes,[10] and an upper limit of 353 kcal $mole^{-1}$ on that of C_2O^+ is obtained from Botter's[2] appearance potential of C_2O^+ from C_3O_2 and from Čermák and Herman's[11] appearance potential of C_2O^+ from ion–neutral reaction in CO. From these numbers, the upper limit of the ionization potential of C_2O is 11.5 eV. Thus reaction

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(8) C. Baker and D. W. Turner, *Chem. Commun.*, 400 (1968).

(9) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice Hall, Inc., Englewood Cliffs, N. J., 1965, pp 303, 310.

(10) K. H. Becker and K. D. Bayes, *J. Chem. Phys.*, **48**, 653 (1968).

(11) V. Čermák and Z. Herman, *Coll. Czech. Chem. Commun.*, **30**, 1343 (1965).

3 is tentatively considered reasonable, although confirmation of its exoergicity is lacking.

For an ion–neutral reaction $A^+ + mN \rightarrow B^+ + \ldots$, the ratio $(B^+)/[(A^+) + (B^+)]$, where (A^+) and (B^+) are the observed relative abundances of A^+ and B^+, should be proportional to the mth power of the pressure of the neutral N, if the pressure is sufficiently low and if other reactions involving A^+ and B^+ are negligible. Accordingly, the ratios $(C_{x+1}O^+)/[(C_xO^+) + (C_{x+1}O^+)]$, where $x = 3, 4, 5$, were considered over pressure ranges where (C_xO^+) was no longer increasing significantly and $(C_{x+1}O^+)$ had not yet begun to decrease. Examples are shown in Figure 4. The ratios are proportional to the first power of pressure, suggesting the occurrence of reactions 5, 6, and 7. Reaction 4 is suggested since C_3O^+ must be formed from one of the more abundant primary ions, and since it is analogous to (5)–(7). Since the sum of the relative abundances of all C_xO^+ ions decreases as pressure increases above 0.01 Torr, these ions may react to form ions with two or three O atoms, also.

Similarly, formation of $C_4O_2^+$ and $C_5O_3^+$ seems to occur directly from $C_3O_2^+$ by reactions 8 and 9, respectively. The rate of (8) exceeds that of (9) by a factor of about 4, which is indicated also by Botter's results.[2] Reaction 10 accounts for formation of $C_5O_2^+$.

The analogs of (8) and (10), by which carbon atoms are added one at a time to $C_xO_2^+$, do not occur after $C_5O_2^+$ is formed. The ratio $(C_6O_2^+)/[(C_5O_2^+) + (C_6O_2^+)]$ increases as the square of pressure (Figure 4), suggesting reaction 11; and $C_7O_2^+$, $C_8O_2^+$, and $C_9O_2^+$ grow in abundance in proportion to $C_6O_2^+$, indicating parallel reactions 12–14, with (11) and (12) occurring much faster than (13) and (14).

It is not clear from the present results how $C_7O_3^+$ is formed or destroyed. A possible precursor is $C_5O_3^+$. The fates of the minor primary ions C_2^+, C_3^+, and O^+ are not known except that they react rapidly.

Considering the complexity of this system, the results do not necessarily rule out other conceivable reactions involving the ions discussed, although such reactions are presumably of less importance than those given. Also, especially at the higher pressures studied, reactions involving ions of masses beyond the upper limit of the present instrument ($m/e \sim 140$) may be significant.

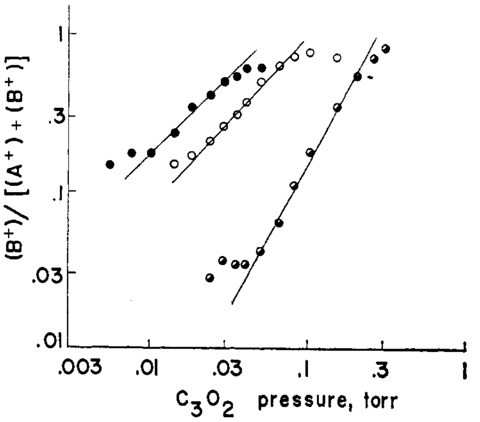

Figure 4. Logarithmic plots of $(B^+)/[(A^+) + (B^+)]$ *vs.* pressure. Slope of linear portion is taken as m in the reaction $A^+ + mC_3O_2 \rightarrow B^+ + \ldots$. ●: $A^+ = C_4O^+$, $B^+ = C_5O^+$, $m = 1.0$; ○: $A^+ = C_4O_2^+$, $B^+ = C_5O_2^+$, $m = 1.1$; ◑: $A^+ = C_5O_2^+$, $B^+ = C_6O_2^+$, $m = 1.9$.

Conclusions

Reactions 4, 5, 6, 7, 8, and 10 are of interest in that C_3O_2 seems to add one of its carbon atoms to the ion in each reaction. It is known that under photolysis C_3O_2 inserts its central carbon atom into olefinic carbon–carbon double bonds to form an allene and two molecules of CO.[12] Therefore, it seems reasonable to suppose that many of the ions in the present system have carbon–carbon double bonds, as does C_3O_2 itself, into which C_3O_2 inserts carbon atoms stepwise, to cause lengthening of cumulene-type carbon chains to form the heavy, carbon-rich ions observed. Most of these reactions are quite rapid; nearly every gas phase collision is a reactive one. Reactions of this kind provide a possible mechanism for the deposition of elemental carbon by ionized C_3O_2, but they do not provide a route to polymerization as had been supposed.[4]

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[12] D. G. Williamson and K. D. Bayes, *J. Am. Chem. Soc.*, **90**, 1957 (1968), and references therein.