atom has unoccupied d orbitals. The polarity of the ClF bond due to the electronegativity difference between the chlorine and fluorine atom may be compensated to some extent by the formation of partial double bonds. The bond order calculations also show that the bond order of ClF_2^- (0.92) is considerably lower than that of ClF and ClF_2^+ and is best explained by the semiionic 3c–4e bond model. This is in good agreement with theoretical expectation,[32,33] predicting for localized covalent bonds a bond order of about 1, and for 3c–4e bonds bond orders of about 50% of the single-bond value. If it is realized that the N values calculated for ClF, ClF_2^+, and ClF_2^- are all somewhat too high, the force constants seem to be a useful method for distinguishing between these two different types of bonding. A positive or negative charge on the central chlorine atom will obviously also have some influence on the type of bonding. Whereas a negative charge will favor the contribution of ionic structures to the bond energy and thus the formation of semiionic bonds, a positive charge will increase the electronegativity of the central chlorine atom and increase the covalent contribution.

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Photoinduced Reactions in Solid Carbon Suboxide

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The infrared spectrum of the photolysis products of C_3O_2 in a solid film at ~100°K has been analyzed for clues to the mechanism of photopolymerization of C_3O_2 This spectrum consists of several sharp bands with the most characteristic features centered at 2060, 1822, 1716, and 1697 cm^{-1}. The richness of the spectrum combined with the insensitivity of band positions or relative intensities to either extent of photolysis or the wavelength of photolytic radiation hints at a single reaction path initiated by cleavage of C_3O_2 and culminating in a tricyclic ring compound $C_{13}O_8$. Upon warming, the $C_{13}O_8$ molecules then act as nucleation sites for polymerization.

Introduction

The photoinduced gas-phase reaction of C_3O_2 with ethylene has been interpreted by Bayes[1] as resulting from cleavage of C_3O_2 to give the carbene, C_2O, which subsequently attacks the ethylene double bond. The resultant ring compound then rearranges to give the observed reaction products. The attractiveness of this mechanism has further increased since Jacox, *et al.*,[2] detected C_2O in the photolysis products of C_3O_2 trapped in an inert gas matrix at liquid helium temperatures. The latter study also indicated that C_2O is mobile in such matrices at temperatures greater than ~20°K.

One might thus expect that photolysis of a pure thin film of C_3O_2 at 100°K would yield mobile C_2O species, which, by analogy with Bayes' proposal, would attack neighboring C_3O_2 molecules to give the three-membered ring compound C_5O_3. In a very recent paper Smith, *et al.*,[3] suggest C_5O_3 as an intermediate in the gas-phase photopolymerization of C_3O_2 but the species has not been detected. We report here the results of spectral studies of the products of photolysis of thin films of pure C_3O_2 at ~100°K.

Experimental Section

C_3O_2 was prepared by allowing P_2O_5 and malonic acid to react at 140°. The product mixture was distilled through an Ascarite column and purified by several single-state vacuum distillations until no impurity bands were detectable in the infrared spectrum of a thick solid film. Initially we planned to conduct the photolysis with the C_3O_2 molecules isolated in a CO_2 matrix at 100°K using various $CO_2{:}C_3O_2$ ratios to sort out the reaction steps which occur. However, consistent with the observation of Moll and Thompson at 4.2°K,[4] no detectable reaction could be induced while using a medium-pressure mercury lamp as a source of photolytic radiation as long as the ratio was 5 or greater. Therefore, our attention was directed primarily to pure thin films of C_3O_2.

The pure C_3O_2 was thus slowly deposited on a cold (100°K) sodium chloride window suspended in a standard low-temperature infrared cell. Deposition rates were controlled by throttling through a needle valve such that deposition times varied from a few minutes to 1 hr, depending upon the film thickness desired. After an infrared scan of the pure thin film, photolysis was initiated using a medium-pressure mercury lamp mounted flush against one portal of the low-temperature cell. In several instances the lamp output was filtered using solution filters. A given deposit was alternately photolyzed and scanned with succeeding photolysis periods of increasing length. Thus monitoring of samples photolyzed for periods ranging from 0.5 to 27 hr was possible. In a few instances the effect of warming the photolyzed C_3O_2 was followed spectroscopically. All infrared spectra were recorded on a Beckman IR-7 spectrometer.

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[1] (a) K. D. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961); (b) *ibid.*, **84**, 4077 (1962); (c) *ibid.*, **85**, 1730 (1963).

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

[3] R. N. Smith, R. A. Smith, and D. A. Young, *Inorg. Chem.*, **5**, 145 (1966)

[4] N. G. Moll and W. E. Thompson, *J. Chem. Phys.*, **44**, 2684 (1966).

Results

The effect of ultraviolet radiation on pure solid C_3O_2 at ~100°K is shown by the infrared spectra in Figure 1. Curve B, from a sample photolyzed using the unfiltered lamp, is typical of those obtained throughout this study. In addition to a tan coloring, evidence for reaction included the sharp, well-defined infrared bands (curve B, Figure 1) at 2060, 1822, 1697, and 1405 cm^{-1} together with weaker diffuse absorption at 1792, 1744, 1716, 1475, 1342, 1052, 900, and 715 cm^{-1}. These features appear in the spectra of thick C_3O_2 films after less than 0.5 hr of photolysis.

Extended photolysis of the relatively thick C_3O_2 films (up to 10 hr) acts to increase the intensity of product bands without introducing new spectral features or altering relative intensities significantly. However, long-term photolysis of thin films eventually depletes the C_3O_2 supply and is thus accompanied by the appearance of broad polymer-type absorption bands (curve A, Figure 2).

A concentrated effort to alter the product (and thus the product spectra) by varying the wavelength of the photolysis energy over the range 3100–2500 A was unsuccessful. Filters composed of pure *m*-xylene, N,N-dimethylformamide, and benzene, or mixtures thereof, were selected so as to admit photolytic energy of progressively shorter wavelengths with no effort made to regulate the longer wavelength radiation. Photolysis was first detectable following 15 min of irradiation while using a benzene–dimethylformamide solution which transmitted approximately 25% at 2750 A. The product spectrum was not detectably altered by admitting shorter wavelengths or by complete elimination of the filters. In fact, the only significant variation from the spectra in Figure 1 was obtained from the photolysis product of a solid mixture of C_3O_2 and CO_2 (1:1) which gave a comparatively weak absorption at 1822 cm^{-1}.

Warming of thick film samples resulted in apparent thermal polymerization of unreacted C_3O_2 on the deposition window seemingly induced by the photolysis product. The result was a thick red film for which the room-temperature spectrum was identical with that in Figure 7 of Smith's paper.[5] Figure 2 depicts the changes which occur in the 1200–2000-cm^{-1} range accompanying warmup of an extensively photolyzed thin film. A broad, intense absorption at 1780 cm^{-1} is replaced by numerous broad bands at lower frequencies. In all cases the ketenyl band near 2200 cm^{-1} disappeared quickly with warming and pumping.

Discussion and Conclusions

The sharpness of product bands and their insensitivity to photolysis procedures seemed to indicate that photolysis of solid films of C_3O_2 yields a single major product. Guided by the studies of Bayes[1] and Jacox,[2] we originally expected this product to be the ring compound C_5O_3 formed by the process

$$C_3O_2 \xrightarrow{\text{ultraviolet}} C_3O_2^*$$

$$C_3O_2^* \longrightarrow C_2O + CO$$

$$C_2O + C_3O_2 \longrightarrow C_5O_3$$

and either trapped or kinetically stabilized in the low-temperature film. However, the spectrum of the actual product was surprisingly rich in bands (particularly in the 6-μ region). We therefore transferred Urey–Bradley force constants to C_5O_3 and roughly estimated its infrared spectrum by a normal coordinate calculation. The calculated frequencies (Table I) matched observed values at 2060, 1822, 1405, and 715 cm^{-1} satisfactorily, but left several unexplained bands.

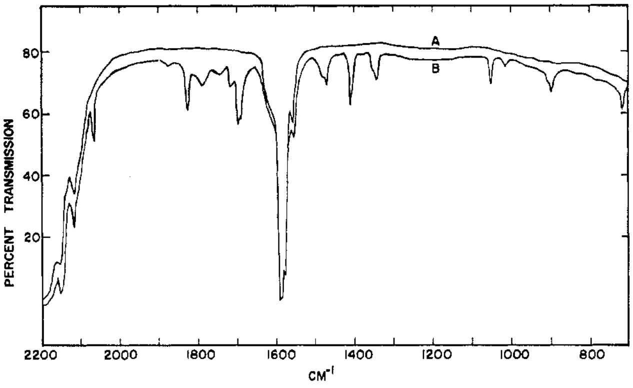

Figure 1.—Infrared spectra of thick C_3O_2 film at ~100°K: A, pure film; B, same film after 1.5 hr of photolysis using a medium-pressure mercury lamp.

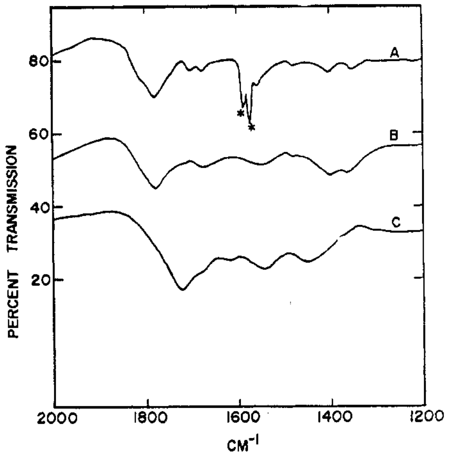

Figure 2.—Infrared spectra of C_3O_2 photopolymer: A, nearly completely photolyzed thin C_3O_2 film at ~100°K; B, same film at 173°K; C, same film at 273°K (asterisk indicates unreacted C_3O_2).

However, a reaction scheme based on C_5O_3 can be imagined which gives products more compatible with the observed spectrum as well as the colored nature of the reaction product. Smith, *et al.*,[3] propose that C_5O_3 is an intermediate in the gas-phase reaction which includes the steps

$$C_5O_3 \longrightarrow C_4O_2 + CO$$

$$C_4O_2 + C_3O_2 \longrightarrow (C_7O_4)$$

where (C_7O_4) represents the basic unit ring structure for the photopolymer

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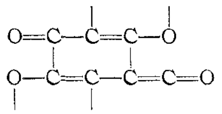
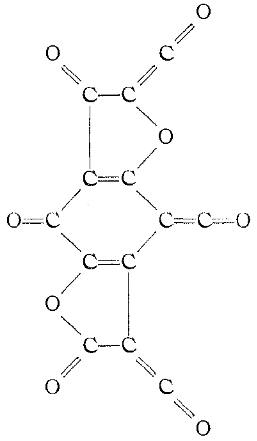
(5) R. N. Smith, D. A. Young, E. N. Smith, and C. C. Carter, *Inorg. Chem.*, **2**, 829 (1963).



Assuming that C_5O_3 is unstable in the C_3O_2 matrix at 100°K, then (C_7O_4) would most likely form and immediately bridge to two neighboring C_3O_2 molecules, thus forming one of three quite similar molecules having the empirical formula $C_{13}O_8$ and exemplified by



Since this species contains the following groups (frequency in parentheses estimated from Bellamy): (a) γ-lactone, β,γ-unsaturated (~1800); (b) dieneone (~1680); (c) α,β-unsaturated five-membered ring ketone (1716); and (d) ketenyl, the observed spectrum is reasonably compatible with that expected from such products. Further, the spectrum shows definite doubling of bands at 1697, 1475, 1342, and 900 cm^{-1}, consistent with the presence of two or more highly similar products as would result from the reaction of (C_7O_4) with C_3O_2.

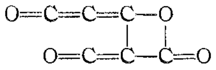
Table I

Transferred Urey–Bradley Force Constants[a] and Calculated Planar Fundamental Frequencies (cm^{-1}) for C_5O_3

Force constants		Calcd frequencies	
		a_1 symmetry	b_1 symmetry
$K_{C=O}$	12.8	2063	2052
$K_{C=C}$	7.6	1882	1212
K_{C-C}	2.3	1314	763
$H_{C=C=O}$	0.57	788	661
$H_{C=C-C}$	0.31	521	390
H_{C-C-C}	0.28	459	176
$H_{C-C=O}$	0.31	108	
F_{OC}	0.10		
F_{CC}	0.10		

[a] Stretching and nonbonded force constants, K and F, are in units of mdynes per angstrom while bending constants have units of 10^{-11} erg/rad^2.

The most disturbing feature in the above scheme is the relatively strong band at 1822 cm^{-1}, slightly high for a β,γ-unsaturated γ-lactone absorption. There remains a faint possibility that this band and the features at 2060, 1405, and 715 cm^{-1}, all comparatively sharp and reasonably consistent with the calculated frequencies of C_5O_3, are produced by trapped C_5O_3 molecules. Another alternative is that $C_3O_2^*$ reacts through an entirely independent route, dimerizing to give C_6O_4



a β-lactone which absorbs characteristically near 1820 cm^{-1}. This possibility has some appeal since ketene is known to condense in this manner[6] and such a reaction would be particularly sensitive to dilution, thus explaining the low intensity of the 1822-cm^{-1} band in the photolyzed solid mixture of C_3O_2 and CO_2. However, it is particularly curious that no reaction was observed using radiation of greater than 2700-A wavelength, whereas Smith, *et al.*, report photopolymerization using 3130-A radiation. This observation is most readily interpreted if one assumes that all reaction is *via* C_2O. Then it can be argued that, although the 3130-A radiation may produce C_2O in the solid C_3O_2, there is insufficient energy to eject the CO* from the reaction site so that recombination rather than reaction dominates. This viewpoint rules out dimerization as an important reaction process. One might then conclude, quite tentatively, that $C_{13}O_8$ is the dominant product. If reaction is all *via* C_2O, then C_5O_3 and $C_{13}O_8$ are logical end points. The spectrum is not that of C_5O_3 alone so some C_5O_3 must react to give $C_{13}O_8$. Since it is difficult to imagine some stabilized and some reactive C_5O_3, $C_{13}O_8$ remains as the most logical product.

Certain rather definite conclusions can be reached concerning the low molecular weight photolysis products in the solid C_3O_2 films at 100°K: (1) since C_2O is believed to be formed,[1,2,4] either C_5O_3 or $C_{13}O_8$, but probably not both, is a likely product (we favor $C_{13}O_8$); (2) if C_5O_3 is produced, it is not the only major product; (3) C_2O is not trapped in detectable amounts; and (4) the isolated photolysis products serve as nucleation sites for polymer growth when the thin films are warmed. The latter fact is obvious since warming such films without photolysis yields no polymer on the deposition window. Similar studies at liquid hydrogen temperatures should further clarify the situation.

The prolonged photolysis of certain thin films at 100°K produced a polymer with a spectrum radically different from that obtained by Smith for the room-temperature photopolymer.[3] The reason is quite clearly that we have suppressed thermal polymerization which accompanies photolysis at room temperature. As a result, spectrum A in Figure 2 is that of the true photopolymer. The spectrum is dominated by an intense, broad band near 1790 cm^{-1} most likely indicative of extensive lactone structure. This polymer is unstable, however, and rearranges upon warming to a structure having a spectrum similar to that of the room-temperature photopolymer (Figure 2).

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(6) F. A. Miller and S. D. Koch, Jr., *J. Am. Chem. Soc.*, **70**, 1890 (1948).