square formed by four Te(2) atoms and forms four bonds 3.293 Å. long to these atoms; directly beneath the La atoms is a Te(2) at 3.260 Å. which completes a square pyramid with the other four Te(2); four Te(1) atoms at 3.381 Å. from La form a square 2.52 Å. above La, and this square is rotated 45° with respect to the square pyramid formed by the Te(2) atoms, Figure 2. The shorter La–Te(2) bonds can be ascribed to the more ionic nature of this bond, and the lengthening of La–Te(1) is due to the quite different character of the metalloid in the basal plane of the unit cell. Figure 3 shows the atomic configuration in this structure.

The environment of Te(2) consists of a nearly regular pyramid formed by four La atoms in the base and one La atom at the apex. The 4.036-Å. distance between Te(1) and Te(2) indicates that very little bonding exists between these tellurium layers. The higher temperature factor observed for Te(1) agrees also with the concept that these atoms are different from the tellurium found in sites 2(e) of the space group.

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The Photolysis of Carbon Suboxide

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At room temperature C_3O_2 absorbs light in the region 2492–2700 Å. to give CO and a photopolymer which is the same as the thermal polymer except that ketenyl groups are present. Photopolymerization is shown to be a combination of photonucleation and thermal polymerization on the nuclei; the polymer precipitates from the gas phase and also forms on the cell windows. The presence of O_2 during photolysis eliminates the ketenyl band from the photopolymer spectrum, reduces both the amount of polymer and CO that are formed, and increases the ratio of C_3O_2 used to CO produced. No CO_2 is formed either with or without the presence of O_2. The proposed reaction mechanism features an electronically excited C_3O_2 molecule which may dissociate to give a C_2O radical and CO or be deactivated by a suitable third body (O_2 or C_3O_2), a typical carbene attack by the C_2O radical on C_3O_2 to give C_4O_2, and a nucleation reaction of C_4O_2 with C_3O_2.

Introduction

Recent papers[1,2] have discussed the photolysis of C_3O_2 in the presence of a large excess of ethylene, under which conditions the principal products are allene and CO. Also, it was reported[3] that the photopolymer which is produced by irradiation of C_3O_2 with ultraviolet light is different from the thermal polymer. This paper reports on the photolysis of C_3O_2 without admixture of other gases and in the presence of O_2.

Experimental Section

C_3O_2 was prepared as described earlier.[3] Photolyses were carried out in evacuable Pyrex cells which were 14 mm. long and 25 mm. in diameter, with 3-mm. thick BaF_2 windows sealed at each end with Kronig cement. The 13-cm. lead of 4-mm. tubing between the cell and the stopcock was bent so that the bend could be immersed in liquid N_2 and so that the cell and stopcock could be placed in the cell compartment of a Cary Model 14 spectrophotometer. The filtered radiation from a Hanovia 673A mercury vapor lamp was used for photolysis. The filter was composed of two solutions contained in silica cells: (a) 46 g. of $NiSO_4 \cdot 6H_2O$ and 14 g. of $CoSO_4 \cdot 7H_2O$ in 100 ml. of H_2O, and (b) 0.108 g. of I_2 and 0.155 g. of KI in 1 l. of H_2O. The energy distribution calculated to be incident on the photolysis cell was determined using the lamp manufacturer's rated energy output at each wave length and an experimentally determined absorption curve for the filter. The percentage distribution at the most intense wave lengths in this region was 1.6% at 3341, 27.7% at 3130, 4.8% at 3025, 1.2% at 2967, 1.6% at 2700, 16.9% at 2652, 11.3% at 2571, 29.9% at 2537, and 3.5% at 2482 Å. By combining these values with the molar extinction coefficients of C_3O_2 it was calculated that 90% of the absorbed radiation lay between 2652 and 2537 Å., or 96.5% between 2700 and 2482 Å. In the few measurements made at 3130 Å. a filter was used in which solution (b) above was replaced by one containing 0.5 g. of potassium hydrogen phthalate per 100 ml. Calculations and experiments similar to those just described showed that 88% of the photolytic radiation transmitted by this filter was at 3130 Å. and 12% was at 3341 Å. One of the main products of irradiation is a tan photopolymer which deposits in part on the windows and soon prevents the further absorption of more light; photolysis ceases. The spectrum of this photopolymer was determined with Cary Model 14 and Perkin-Elmer Model 21 spectrophotometers after first removing all gases for analysis. In an effort to minimize the volume and to exclude Hg vapor (and the possibility of Hg photosensitization) all gas pressures were measured with an all-glass spiral gauge which, together with the optical lever, had an over-all sensitivity of ±0.08 mm.

In analyzing for CO, the bend in the stem of the photolysis cell was immersed in liquid N_2 to freeze out any C_3O_2 and CO_2. When CO was the only noncondensable gas, it was allowed to expand from the cell to a small volume which included the spiral gauge; calibration measurements related the observed pressure to the CO pressure which had existed in the cell before expansion. When CO was mixed with O_2, the two gases were drawn through a 4-mm. tube tightly packed with Pt gauze and heated electrically to 500°; the CO thus converted to CO_2 was frozen out in a small U tube while the remaining O_2 was completely removed from the system by pumping. The CO_2 (formerly CO) was transferred with the aid of liquid N_2 to a small finger trap attached to the small-volume system, its pressure was measured at room tem-

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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); (d) *Bull. soc. chim. Belges*, **71**, 724 (1962).

[2] R. T. Mullen and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 3214 (1962).

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

perature with the spiral gauge, and it was then discarded. Calibration measurements related the observed CO_2 pressure to the CO pressure which had existed in the cell before expansion. In those experiments where a very small amount of O_2 had been used in photolysis, additional O_2 was provided before expansion through the Pt gauze.

A variety of methods were used to check on the presence of CO_2 in the reaction products. The presence of large amounts of C_3O_2 made this determination more difficult than would normally be the case. In the most unequivocal check, the mixture of C_3O_2 and CO_2 remaining after removal of CO (and O_2 when present) was transferred to the finger trap by means of liquid N_2. Then, isolated in the small-volume system, the finger trap was raised to the melting point of *n*-pentane (−129.9°). At this temperature the vapor pressure of CO_2 is 2.2 mm. and that of C_3O_2 is 0.027 mm., well below the limit of detection of the spiral gauge (0.08 mm.). As a check on this procedure, it was shown that 1.15 mm. of CO_2 was completely recoverable and measurable in the presence of 98 mm. of C_3O_2; this corresponds to about 14 μg. of CO_2 in the presence of about 2 mg. of C_3O_2. If CO_2 is formed during photolysis it lies below this limit of detection; in this study it was considered that CO_2 is not a product of photolysis. This finding was supported by infrared examination of the combined photolysis products in the photolysis cell with BaF_2 windows. Separate measurements with known amounts of CO_2 showed a limit of detection of about 0.1 mm. by this method.

The unused C_3O_2 was determined after removal of CO (and O_2, when present) by transferring it to the finger trap with liquid N_2, isolating it in the small-volume system, and then measuring its pressure at room temperature with the spiral gauge. Calibration measurements related the observed pressure to the C_3O_2 pressure which had remained in the cell after photolysis.

The O_2 used in these experiments was taken from the vapor of liquid O_2 condensed from tank O_2 by liquid N_2. In some of the preliminary experiments photolyses were carried out in fused silica cells because of the advantages that the cell itself could be immersed in liquid N_2 and at the end of a run the whole cell could be filled with O_2 and heated with a torch to burn the photopolymer to CO_2; after pumping, the cell was again ready for another run. In order to correlate gas product formation with polymer formation, it was necessary to use the BaF_2 windows, which had to be removed and cleaned after each run. A 10-cm. cell was employed in those runs in which a 100-fold excess of O_2 or He was used. In this way the same amount of C_3O_2 at low pressure could be made available in the absorbing light path as was available in the 1.4-cm. cell at higher pressures.

TABLE I

RESULTS FROM THE PHOTOLYSIS OF C_3O_2 AT ROOM TEMPERATURE AND IN THE WAVE LENGTH REGION 2482–2700 Å.[a]

O_2 press., mm.	Initial C_3O_2 press., mm.	C_3O_2 used, mm.	CO produced, mm.	$\frac{C_3O_2 \text{ used}}{\text{CO produced}}$
...	199.6[b]	41.0	23.4	1.75
...	199.3[c]	16.3	10.8	1.51
...	193.0[d]	32.5	12.8	2.54
...	118.1	21.8	15.8	1.38
...	92.7[c]	20.4	11.2	1.82
...	41.6	14.2	10.9	1.30
...	41.6	12.9	10.7	1.21
...	40.9[c]	11.6	5.3	2.15
...	40.0[c]	9.0	4.9	1.83
...	37.6[b]	18.2	8.2	2.22
...	10.0	5.3	4.6	1.15
1.1	100.2	9.9	2.0	4.95
1.1	97.5	11.1	2.5	4.43
5.0	94.9	11.1	2.0	5.55
91.4	97.6	15.5	4.3	3.60
104.3	97.1	8.6	2.3	3.74
602.6	62.7	3.1	0.6	5.17
617.6	60.7	12.3	4.2	2.93
602.4	6.2[e]	1.8	0.5	3.60
600.1	6.0[e]	2.1	0.6	3.50

[a] Unless otherwise indicated, exposure time is 30 min. in a 14-mm. long cell with BaF_2 windows. [b] Exposure time 40 min. [c] In 10-mm. long silica cell. [d] Exposure time 35 min. [e] Exposure time 90 min. in 100-mm. long silica cell.

Results

CO and photopolymer are the only products formed in the photolysis of pure C_3O_2 at room temperature and over the range of pressures used (10 to 200 mm.). Photopolymerization commences immediately on irradiation, while thermal polymerization under the same condition has an induction period of several days. Photopolymer forms on the windows and homogeneously in the gas phase; in all runs there was a heavy layer of polymer at the bottom of the cell which had settled out of the gas phase and none on the top side. In most respects the photopolymer is identical with the thermal polymer[3,4]; it turns red when exposed to H_2O vapor; it further polymerizes to the larger red and purple polymers when heated *in vacuo;* and its ultraviolet, visible, and infrared spectra are virtually identical with those of the thermal polymer with but one exception. This exception, an important one, is a small absorption band at 4.48 μ which varies in intensity from run to run and which is characteristic of the ketenyl group (=C=C=O). This peak is *not* observed with the thermal polymer under comparable conditions of C_3O_2 pressure and cell size. In the study of the properties and structure of the C_3O_2 thermal polymer, the authors did observe a small ketenyl band at 4.5 μ, but the difference is that in the former study massive opaque films were used and the ratio of the 4.5 μ peak to the strong 7.3 μ peak was of the order of 0.03, while in the present study the films were transparent and the ratio of the 4.5 μ peak to the 7.3 μ peak is of the order of 0.2 to 0.4. At times, depending on the amount of film that appears on the window, the ketenyl band may be equivalent to as much as 0.3 mm. of C_3O_2 monomer in the same cell. The 4.5 μ peak was observed to be comparable in size and shape when the polymer was produced by radiation at 3130 Å. The spectrum of the photopolymer is not altered when it alone is irradiated for several hours. The fact that the ketenyl band of the photopolymer does not diminish in intensity by irradiation at the wave lengths used in the photolysis may indicate greater photostability of these ketenyl groups or simply the fact that the films are relatively opaque to ultraviolet light. Just as was observed in the study of the thermal polymer, the ketenyl peak of the photopolymer was observed to disappear only after prolonged (~18 hr.) hard pumping (10^{-5} to 10^{-6} mm. pressure); the spectra were normally obtained after 0.5 hr. of hard pumping (the total cell volume was approximately 5.8 ml.). Addition of C_3O_2 monomer to a deketenylized photopolymer, followed by pumping, did not cause the reappearance of the ketenyl band, and it was thus judged that the ketenyl band is not an artifact caused by the strong physical adsorption of C_3O_2

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(4) A. R. Blake, W. T. Eeles, and P. P. Jennings, *Trans. Faraday Soc.*, **60**, 691 (1964).

monomer. The course of the photolysis and the nature of the product are not affected when the photolysis is carried out in the presence of an initial preponderance of CO. The results, summarized in Table I, show that the experiments are not reproducible with regard to the number of C_3O_2 molecules consumed per molecule of CO produced.

When oxygen is added to C_3O_2 and the mixture photolyzed, CO and photopolymer are still the only products formed, but with some interesting changes: the number of molecules of C_3O_2 used per molecule of CO produced increases, and as little as 1 mm. of O_2 in the presence of 100 mm. of C_3O_2 will eliminate the appearance of the ketenyl band in the photopolymer at 4.48 μ. With increasing ratio of O_2 to C_3O_2, the amount of photopolymer visibly decreases until, with a ratio of 100:1, practically no photopolymer at all is observed; the production of CO is also greatly reduced. The photolysis of a comparable mixture using He instead of O_2 produced photopolymer in the usual manner. The spectrum of the photopolymer is not altered by simple addition of O_2.

Discussion

The following reaction mechanism will account for the results observed in the photolysis of C_3O_2.

$$C_3O_2 + h\nu \longrightarrow C_3O_2^* \tag{1}$$

$$C_3O_2^* + M \longrightarrow C_3O_2 + M^* \tag{2}$$

$$C_3O_2^* \longrightarrow C_2O + CO \tag{3}$$

$$C_2O + C_3O_2 \longrightarrow C_5O_3 \tag{4}$$

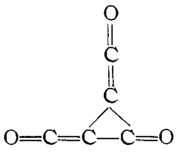
$$C_5O_3 \longrightarrow C_4O_2 + CO \tag{5}$$

$$C_2O + P' \longrightarrow P'' + CO \tag{6}$$

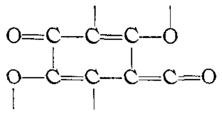
$$C_4O_2 + (C_3O_2)_n \longrightarrow P' \tag{7}$$

$$C_3O_2 + (C_3O_2)_n \longrightarrow P \tag{8}$$

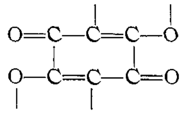
Deferring for the moment a discussion of $C_3O_2^*$, it should be pointed out that the over-all effect of steps 1 and 3 to form C_2O and CO has been previously suggested by Bayes and by Mullen and Wolf to explain their findings with C_3O_2–C_2H_4 mixtures. The C_2O^+ *ion* has been observed as a major fragment in a mass spectral study[5] of C_3O_2, but C_2O itself has not yet been directly observed in any study. At the wave lengths used (2482–2700 Å.) it has been judged that C_2O is produced in the singlet state, reactive to a carbon–carbon double bond as in step 4. Steps 4 and 5 are typical of a singlet carbene attack on a double bond and similar to that suggested by Bayes for the reaction of C_2O with C_2H_4. The activated complex, C_5O_3, is the expected cyclopropane compound



These steps are also very probable in view of the preponderance of C_3O_2. Unlike allene, the product of the reaction of C_2O with C_2H_4, C_4O_2 is not stable and has never been isolated. It is reasonable to assume that the C_4O_2 disappears by reaction with the ever-present C_3O_2, as in step 7 with $n = 1$, forming the basic unit ring structure for the photopolymer (P′)



which is the same as the six-membered polylactonic basic ring unit of the thermal polymer (P) formed in step 8



This accounts for the similarity in properties and the near identity of the spectra of the photo- and thermal polymers, as well as for the presence of the ketenyl band that is found in the photopolymer but not in the thermal polymer. Step 7 (with $n = 1$) is basically a nucleation process for further thermal polymerization. It has long been observed that once nucleation has set in (*i.e.*, after a long induction period) thermal polymerization continues very easily. Both photonucleation and thermal polymerization (step 8) were shown to be involved in the over-all photopolymerization by alternating periods of radiation (at 2537 Å.) with periods of dark (thermal) reaction. During the periods of dark reaction the rate of increase in polymer thickness on the cell windows was measured at 3700 Å., radiation rather strongly absorbed by the polymer, but not at all by the monomer. For each period of dark reaction the rate of thermal polymerization remained essentially constant, but each succeeding period of dark reaction had a higher rate than the preceding one. For example, in a cell filled initially with 100 mm. of C_3O_2, the rates of thermal polymerization relative to the rate on a very transparent initial film (65% transmission at 2537 Å.) became 6.5, 9.5, and 22 times faster as the films decreased in their transmissions to 33, 11, and 2% at 2537 Å. It required about 12 hr. under the same conditions and starting with a similar film to build up to the same film thickness by thermal polymerization alone, all at a fairly constant rate throughout the entire period.

The actual situation which exists during the course of photolysis is not nearly as simple as that which exists for thermal polymerization at an interface such as a cell window. During photolysis polymeric nuclei and small particles are continuously generated and distributed throughout the cell volume and are readily accessible for reaction with C_3O_2, the reaction intermediates, or each other. The data indicate that the rate of nucleation is highest in the early stages of the photolysis when the windows are the most transparent to the photolytic radiation, and that the rate of thermal incorporation of C_3O_2 into these nuclei increases during the photolysis as the number of nuclei and the surface area of the resulting polymeric particles increases.

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

TABLE II

SOME OF THE CONSEQUENCES OF DIFFERENT PROPORTIONS OF THE INTERMEDIATE C_2O REACTING WITH MONOMER BY STEP 4 OR WITH POLYMER BY STEP 6[a]

Molecules of C_3O_2 used			Molecules of CO produced			
in step 4	in step 8	Total	in step 5	in step 6	Total	C_3O_2 used / CO produced
100	100	300	100	0	200	1.5
100	200	400	100	0	200	2.0
75	75	250	75	25	200	1.25
75	150	325	75	25	200	1.62
60	60	220	60	40	200	1.1
60	340	500	60	40	200	2.5

[a] The effect of incorporating C_3O_2 into the polymer by thermal reaction in step 8 is also shown. The calculations are based on absorption of 100 light quanta to produce C_2O and CO as in step 1 followed by step 3.

Considering the high degree of dispersion of this heterogeneous reaction system and the ready availability of the polymeric particles, it seems reasonable to believe that the C_2O radicals might as easily react with the ketenyl groups of the polymeric particles in step 6 as with the ketenyl group of C_3O_2 in step 4. The resulting ketenyl group would be one carbon atom farther removed from the ring than the one which was displaced.

Table II shows the interlocked dependence of the ratio of C_3O_2 used to CO produced on the amount of C_3O_2 used in thermal polymerization (step 8) and on the relative amounts of C_2O used in reaction with monomer (step 4) or with polymer (step 6). Each calculation is based on the absorption of 100 light quanta according to step 1 followed by step 3. The calculated ratios of C_3O_2 used to CO produced, based on this mechanism, satisfactorily cover the range of observed ratios (Table I), but at the same time it is obvious that there is an almost unlimited number of other combinations that will achieve the same result.

Bayes postulated the production of two different intermediates in the primary act: (1) a triplet C_2O formed on dissociation at the longer wave lengths, and (2) either a singlet C_2O formed on dissociation or an electronically excited $C_3O_2^*$ molecule. He found evidence for the existence of both at the shorter wave lengths (2537 Å.), and he favored a singlet C_2O over an electronically excited $C_3O_2^*$. The results in Table I indicate that for photolysis in the presence of O_2 the total amount of C_3O_2 used *and* CO and polymer produced is greatly reduced, even though for the same period of irradiation the total number of light quanta available for absorption is greater due to much less absorption by polymer on the windows; this is especially pronounced when O_2 is present in very large excess. This effect must involve more than a simple reaction of O_2 with C_2O radicals, for though this would reduce the amount of polymerization it would not reduce the amount of CO formed. Furthermore, C_2O, being in a singlet state, should not react with O_2. The present work seems to favor the view that in the primary act there is first formed an excited $C_3O_2^*$ molecule which may subsequently dissociate to form a singlet or a triplet C_2O (depending on the energy of excitation) or be deactivated by collision with a suitable molecule (M in step 2) such as O_2. By this means the production of both CO and polymer would be diminished, as observed, when O_2 is added. The effect of adding increasing amounts of O_2 is to decrease the rate of formation of nuclei and to shift the balance between photonucleation and thermal polymerization in favor of the latter so that the polymer will have a smaller "ketenyl content" at the same time it is being produced at a lower rate; both of these effects are observed. The fact that the ketenyl band is "eliminated" may mean only that it is reduced below the limit of spectral detection used in the experiments. It appears that C_3O_2 itself may be a reasonably effective molecule for deactivation (M in step 2), for when photolysis is attempted in pure C_3O_2 at a high pressure of 560 mm., only a very small amount of photopolymerization takes place. This may account also for the fact that Thompson and Healey[6] did not observe fluorescence when they irradiated C_3O_2. Helium is ineffective as a third-body deactivator since the presence of a 100-fold excess of He has no appreciable effect on the normal path of photolysis.

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(6) H. W. Thompson and N. Healey, *Proc. Roy. Soc.* (London), **A157**, 331 (1936).