The Structure and Properties of Carbon Suboxide Polymer

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It is proposed that the carbon suboxide polymer is a polycyclic 6-membered lactone whose principal resonance form is a pyrilium-like aromatic ionic structure. This conclusion is based on studies of polymers made at a variety of temperatures in the range 25–400°. The polymer has been found to be much more stable than heretofore believed. At 100° the small amounts of observed CO_2 and CO are associated with the polymerization process and are not due to thermal decomposition of the monomer or polymer; at higher temperatures it is not possible to say with certainty that some of the CO and CO_2 does not come from the decomposition of the monomer. The polymer becomes increasingly unstable at temperatures above 300°; it rapidly turns to carbon at 500°. The principal gaseous decomposition product in the earlier stages is CO_2. The equivalent weight of the polymer is 68 ± 7 (the weight of one C_3O_2 unit), regardless of the temperature at which it is prepared. The visible and ultraviolet spectra indicate a polymer of relatively low molecular weight at room temperature, but one with increasing molecular weight (and size of resonance system) with increasing temperature of preparation. The infrared spectra are identical at all temperatures of preparation and thus indicate that, regardless of the size of the polymer, the unit structure is the same for all. Previously published X-ray data support the planar, graphitic, hexagonal ring nature of the proposed structure, as do previously published rate data on the hydrolysis of lactones. The ultraviolet photopolymer, which forms without any induction period, is unlike the thermal polymer. The main chemical and physical properties of the thermal polymer are summarized. A gas chromatographic method useful for the analysis of mixtures of CO, CO_2, and C_3O_2 is described.

Introduction

In studying the previously published work on carbon suboxide one is struck by the difficulties involved in the preparation of appreciable quantities of really pure C_3O_2, the problems of storage and handling once it is prepared, the great difficulties in preparing and handling the absolutely dry polymer, the limitations of the older analytical methods used in obtaining the results on which many of the presently accepted conclusions have been reached, and the speculative nature of the various proposed structures of the polymer and its mode of formation. This paper presents a large body of new work, discussed and correlated with the old, with the aim of setting the inorganic chemistry of carbon suboxide on a firmer foundation. Grauer[1] has published a brief review of the literature for the period 1873 to 1956.

Experimental

Preparation of Carbon Suboxide.—In spite of the poor yield involved, carbon suboxide was prepared by the method of Stock and Stolzenberg[2] with modifications by Long, Murfin, and Williams[3] and the present authors. Much better yields may be obtained from the pyrolysis of diacetyltartaric anhydride, but Long, Murfin, and Williams have shown that much of the earlier work on structure is invalidated by the presence of ketene which is simultaneously produced in appreciable quantities by this method and which is virtually impossible to remove by subsequent purification procedures. Carbon suboxide was made in batches from a mixture of 20 g. of malonic acid (Brothers Chemical Co., No. 2432), 40 g. of freshly dried sand (J. T. Baker), and 200 g. of phosphorus pentoxide (Baker and Adamson, No. 1148) which had been intimately mixed in a dry nitrogen atmosphere and rapidly transferred to a 1-l. flask. Immediately after closing the flask with a cap the dry mixture was outgassed

with a high vacuum system, often for as long as 24 hr. The C_3O_2 was generated by surrounding the reaction flask for 3 or 4 hr. with an oil bath whose temperature had already been raised to 145°. The crude mixture of gases (CO_2, C_3O_2, acetic acid, etc.) was first collected at −196°, then subsequently warmed to −78° to allow the CO_2 and C_3O_2 to pass through a lightly packed mixture of glass wool and CaO. The mixture of CO_2 and C_3O_2 was condensed in a LeRoy[4] low temperature fractionator; then with electrical heating and with continuous pumping, the temperature was raised to −110° for 0.75 hr. to purge the mixture of the bulk of the CO_2. The temperature was then lowered to −130° and after several days of pumping at this temperature, and after it had been ascertained that the equilibrium pressure in the fractionator was essentially that of pure C_3O_2, the C_3O_2 was transferred by distillation *in vacuo* to a reservoir closed by a vacuum stopcock. The yield of C_3O_2 from one batch was approximately 1 ml. of liquid. The infrared spectrum of this product showed no trace of CO_2 or ketene, even though each has a very strong characteristic absorption band. Except when in use, the liquid C_3O_2 was stored at Dry Ice temperature where, contrary to popular belief, it can exist indefinitely without polymerization. If the stem connecting the stopcock to the reservoir is not also kept at −78° (instead of room temperature) polymer will eventually form in it.

Thermal Decomposition Experiments.—In order to study the thermal decomposition of C_3O_2 monomer and polymer at various temperatures, C_3O_2 samples were sealed into special U-tubes made from carefully cleaned 7-mm. Pyrex tubing. Each U-tube, with a seal-off tip on one end of the U, was filled with C_3O_2 to a pressure of 174 mm. (the vapor pressure of C_3O_2 at −26°, the melting point of impure *m*-dichlorobenzene); then, while shut off from the rest of the system with a stopcock, the C_3O_2 was condensed with liquid nitrogen and the other end of the U sealed, leaving a seal-off tip on both ends of the U. When the tip had cooled, the U-tube was removed from the liquid nitrogen and placed in an oven or furnace at the desired temperature for the desired length of time. Mercury manometers were not used in pressure measurements for filling procedures, partly to minimize the volume of the filling section and partly to exclude mercury vapor, but primarily to avoid polymer formation which eventually occurred in the manometer. Separate measurements showed that each U-tube filled by this method contained approximately 3.7 mg. of C_3O_2. Analyses of the thermal decomposition

(1) R. Grauer, *Chimia* (Aarau), **14**, 11 (1960).
(2) A. Stock and H. Stolzenberg, *Ber.*, **50**, 498 (1917).
(3) D. A. Long, F. S. Murfin, and R. L. Williams, *Proc. Roy. Soc.* (London), **A223**, 251 (1954).
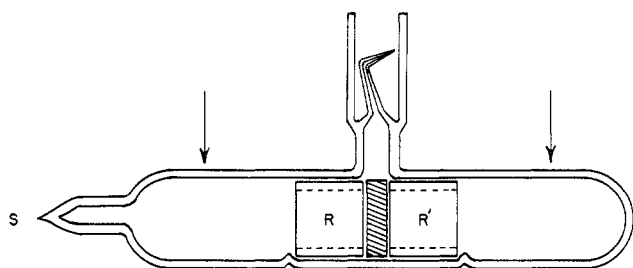(4) D. J. LeRoy, *Can. J. Res.*, **28B**, 492 (1950).

Fig. 1.—Special infrared absorption cell used in all studies made at temperatures above room temperature. The shaded portion is a NaCl window held in place by two Pyrex retaining rings.

products were made immediately following the thermal treatment by methods outlined below. In the few cases where this was not possible, the U-tubes were stored at Dry Ice temperature to prevent any further decomposition or polymerization. This method of study avoided all uncertainties due to stopcock grease or side effects due to traces of air, moisture, or mercury vapor. The color and nature of each polymer were also recorded.

Gas Chromatographic Procedures.—At the time the thermal decomposition of C_3O_2 was studied the gas chromatographic method of Hirt and Palmer,[5] using an Apiezon N impregnated firebrick column at room temperature, had not been published. As a consequence, the procedure described below was devised and used. This procedure depends on the fact that all of the decompositions were carried out in the sealed U-tubes which could, when desired, have their contents swept out with purified helium and subsequently analyzed gas chromatographically. Two independent streams of helium were used in this procedure; they will be referred to as the analytical stream and the sampling stream.

The analytical stream flowed at 35 ml./min. through the katharometer, a gas sample-changer which provided for a loop in which materials could be frozen from the sampling stream without interfering with the flow of the analytical stream, and a 35-cm. column of partially hydrated silica gel (Davison Chemical Co., Code 12, 28–200 mesh) in 0.25 in. copper tubing. The katharometer and column were housed in the furnace section of a Loenco Model 15 gas chromatograph with close regulation at 100° provided by a proportional temperature controller. The proper degree of hydration of the silica gel was determined by trial and error so as to give a retention time of about 5 min. for CO_2.

The sampling stream of helium had to be purified in order to prevent traces of condensable impurities (including CO_2) condensing in the sample-changer loop at the temperature of liquid nitrogen and then subsequently giving erroneous results. For this purification the helium was first passed through a large trap cooled to −196°, then through a U-tube of 3-mm. tubing also kept at −196°. An analysis was performed as follows: the U-tube containing the gas mixture to be analyzed was inserted into the purified sampling stream so as to avoid contamination by air, then the tips were broken so as to permit the contents to be swept into a gas train culminating in the loop at the gas sample-changer in the analytical stream. The gas mixture was carried first through an 8-cm. length of 7 mm. tubing filled with partially hydrated silica gel which removed the C_3O_2 by reaction with adsorbed water, second through a small U-tube of 3-mm. diameter tubing in which the CO_2 was frozen out at −196°, third through a 12-cm. length of 8-mm. tubing filled with I_2C_5 which quantitatively converted the CO to CO_2 at a temperature of 120°, and finally through the loop at the gas sample-changer where the CO_2 (which had originally been CO) was frozen out at −196°. After 20 min., a time sufficient to move all of the CO_2 through the silica gel with helium flowing at 35 ml./min. at room temperature, the sample-changer was changed and a beaker of boiling water put around the loop to cause immediate vaporization of the

(5) T. J. Hirt and H. B. Palmer, *Anal. Chem.*, **34**, 164 (1962).

CO_2 into the analytical stream. When the CO_2 peak had appeared on the recorder chart, the sample-changer was returned to its original position, liquid nitrogen replaced around the loop, and the original CO_2 vaporized to be condensed again in the loop. This operation, which required but a few minutes, was followed by a repetition of the boiling water procedure, and again a CO_2 peak appeared on the recorder chart.

By this technique both CO and CO_2 were analyzed as CO_2 and calibration was needed only for CO_2. Calibration was carried out with known amounts of CO_2 and checked with known amounts of CO. It was also verified that pure C_3O_2 did not give rise to spurious indication of CO or CO_2. Preliminary experiments showed that silica gel columns which separated CO, CO_2, and C_3O_2 and allowed them to pass in reasonable time were unsatisfactory because a certain amount of C_3O_2 would decompose at 100° or react with the column to generate additional CO and CO_2 over a relatively long period of time.

Infrared Spectra.—A Perkin–Elmer Model 21 double beam recording spectrophotometer was used for all infrared measurements. Most of the monomer and room-temperature polymer spectra were taken with simple evacuable cells having NaCl windows sealed to the ends with Kronig cement. When these were used, unpolymerized C_3O_2 was removed by several hours of pumping before making a spectrum determination. In order to prepare polymer films at higher temperatures and then to determine their spectra without contact with air, which causes an instantaneous change in color and alteration in structure due to reaction with water, it was necessary to make some rather elaborate cells which could be used only once. Such a cell is shown in Fig. 1. The cell body was made of 28-mm. Pyrex tubing and the side arm (with break-off tip) of 7-mm. tubing; the over-all length was about 15 cm. The following order of construction was used so as to assemble such a cell without fracturing the 1-in. diameter NaCl window: (1) The stem at S was connected to the cell body and left unsealed. (2) The dimple at the left end of R was located so as to position the NaCl window as shown. (3) The cylindrical notched retaining ring (R) of 25-mm. tubing was inserted into the dried, cooled cell, followed by the NaCl window and the second notched retaining ring (R'). (4) With the cell clamped vertically and a blowing tube connected to S at the bottom, a handle of Pyrex rod was quickly fastened to the very top of the cell body in such a way as to avoid moisture from the flame condensing inside the cell. The right end of the cell had been made excessively long in the first place so as to extend several inches beyond R'. The end of the cell was then quickly drawn off, with the flame directed upward, and sealed as shown, with the dimple at the right end of R' made quickly and immediately following. (6) The cell was allowed to cool slowly in its vertical position. (7) The cell was sealed at the left end to a stopcock and joint assembly for connection to a high vacuum system. (8) After thorough outgassing, the infrared cell was filled with C_3O_2 vapor to the desired pressure (usually 72 mm., its vapor pressure at −45°, the freezing point of impure chlorobenzene). With the stopcock closed, the right end of the infrared cell was immersed in liquid nitrogen to freeze out the C_3O_2, and the cell was sealed at S. The sealed cell could now be placed in an oven or furnace at any desired temperature for any length of time without concern for interference by greases, contamination by air or mercury vapor, or the differential expansion of NaCl and glass.

In order to determine the infrared spectrum of the polymer, a tip-breaker of glass rod was sealed into the side arm above the break-off tip and the whole side arm sealed to a three-way stopcock. This stopcock permitted the space above the break-off tip to be evacuated, and a stream of dry nitrogen to sweep all air out of the connecting tube right up to the other side of the stopcock. It was not possible to dry adequately a fast-moving stream of tank nitrogen by passing it through a liquid nitrogen trap. Instead, an electric heater inserted into a large dewar of liquid nitrogen provided extremely dry nitrogen at a rate determined by the heater current. A suitable pressure release was provided by a small slit in a piece of rubber tubing. With

everything in readiness at the spectrophotometer, nitrogen was admitted to the evacuated space above the break-off tip, the break-off tip was broken, a hot rod was applied to a file scratch located at the tip of one of the arrows in Fig. 1 in order to break off the end of the cell, and finally, a hot rod was applied to a file scratch located at the other arrow. The infrared spectrum was taken immediately with a heavy stream of nitrogen flowing out both ends of the cell. Prior to breaking off the ends of the cells the notches in the rings R and R′ were placed next to the NaCl window and adjacent to the side arm so as to encourage a free flow of nitrogen around the NaCl. On completion of the spectrum a stream of nitrogen saturated with moisture was played on the surface of the NaCl window and the cell again was swept out with a heavy stream of dry nitrogen while redetermining the spectrum.

Ultraviolet, Visible, and Near-Infrared Spectra.—These spectra were determined with a Cary Model 14 spectrophotometer. The samples were sealed in 1-cm. cylindrical quartz cells having quartz-to-Pyrex graded seals. They were filled in the same manner as the infrared cells, using a stopcock and a joint for connection to a high vacuum system. A convenient C_3O_2 pressure was 23 mm. (the vapor pressure of C_3O_2 at $-62°$, the freezing point of an impure $CHCl_3$ bath), for on complete polymerization the films had the proper transparency for good spectra. This low pressure caused inconveniently long polymerization times at the lower temperatures, but it ensured the absence of the monomer spectrum whch would accompany the polymer spectrum obtained in a short time with incomplete polymerization at higher pressure, or the opaque films obtained on complete polymerization. On completion of the spectra determined for films in the sealed cells, the cell side arms were broken open and nitrogen saturated with H_2O was swept through the cells. The excess water vapor was removed by evacuation and the spectra were redetermined.

Equivalent Weight Determination.—Polymer samples for this purpose were prepared by sealing a known weight of C_3O_2 monomer into Pyrex bulbs in the same manner used for the U-tubes and the absorption spectrum cells. The weight of C_3O_2 was calculated from the gas law, knowing the volume of the bulb and the temperature and pressure of the gas contained therein. The volume of each bulb was determined by calibration with water, and it included the volume of the stem connecting the stopcock to the bulb; the volumes were of the order of 60 ml. The bulbs were filled to a pressure of 72 mm. (the vapor pressure of C_3O_2 at $-45°$, the melting point of impure chlorobenzene); typical sample weights ranged from 14 to 19 mg. After sealing, the bulbs were heated at the desired temperature until polymerization was complete. After polymerization, the bulb stems were cracked off and a measured volume of standard base was added to the bulb. This base solution was heated to aid solution of the polymer (the 300 and 400° polymers are not very soluble in hot dilute NaOH and in this case it was the suspension that was titrated). After cooling, the excess base was titrated with standard HCl solution in a nitrogen atmosphere. The titrations were most simple and clear-cut when done with a pH meter, but the results were not significantly different if phenolphthalein was used as an indicator. The results were not precise, most probably due to a certain variation in the exact nature of the polymer from experiment to experiment and the varying amount of small decomposition which accompanies the polymerization. In this case, however, the precision of the results does not affect the important conclusion which may be drawn from the results.

A good many attempts were made to determine the saponification equivalent weight of the polymers, using KOH dissolved in ethylene glycol. The insolubility of the polymer in this mixture, the high temperature needed in its execution, and the great difficulty in determining end points led to extremely erratic results and this approach was dropped as impractical.

Discussion

General Characteristics of the Polymer and its Formation.—Before discussing the detailed conclusions

to be drawn from the experiments it will be helpful to summarize some of the important general properties of the polymer and its mode of formation.

(1) The rate of polymerization increases with increasing temperature and monomer pressure.

(2) Polymerization is preceded by an induction period which increases with decreasing temperature, but for any given temperature, it is very unpredictable.

(3) Polymerization is a heterogeneous process, the induction period being very dependent on the nature of the surface in contact with the monomer.

(4) The induction period is very short in the presence of strongly acidic sites. Walls coated with concentrated H_2SO_4 or contaminated with P_2O_5 cause very rapid polymerization; walls coated with paraffin have an extremely long (more than a week) induction period; glass and silica lie somewhere between these extremes. The polymer is thermally unstable on NaCl at much lower temperatures than it is on Pyrex. This was noticed particularly in the infrared experiments at 400° where it was difficult to obtain anything other than a gray carbon residue on the NaCl window even though the polymer which coated all of the interior Pyrex wall surfaces was relatively stable.

(5) Polymerization does not depend on photoinitiation. A sealed tube of C_3O_2 monomer, protected from light even when it was sealed, polymerized as easily in absolute darkness at room temperature as when exposed to room light.

(6) The polymers are intensely colored, varying from a rusty yellow when formed at room temperature to intense ruby red if formed at 100–300° and to violet if formed at 400°. The polymer often looks black because of intense coloration, but a bright light demonstrates the clear colors by transmission.

(7) The low-temperature polymers dissolve easily in water to give intensely red solutions. With increasing temperature of formation, the polymers become less water-soluble; the 400° polymer is almost completely insoluble.

(8) The polymers dissolve in dilute aqueous alkali hydroxide, but the high-temperature polymers do so only with difficulty. Hot concentrated alkali solutions are convenient for removing the polymers from glass.

(9) Acidification of aqueous or alkaline polymer solutions yields a red precipitate.

(10) The low-temperature polymers react immediately with the water vapor in the air to give a different colored polymer—one that contains H which cannot be removed by warm drying under high vacuum. High-temperature (400°) polymers are virtually unreactive to water vapor.

(11) Hydrated room-temperature polymer dried at 100° is water-insoluble, but if dried at room temperature it continues to be water-soluble.

(12) Polymers which are exposed to air fade to a pale yellow on long standing. This reaction is photochemical in nature since sections of tube protected from room light retain the original color of the water-reacted polymer.
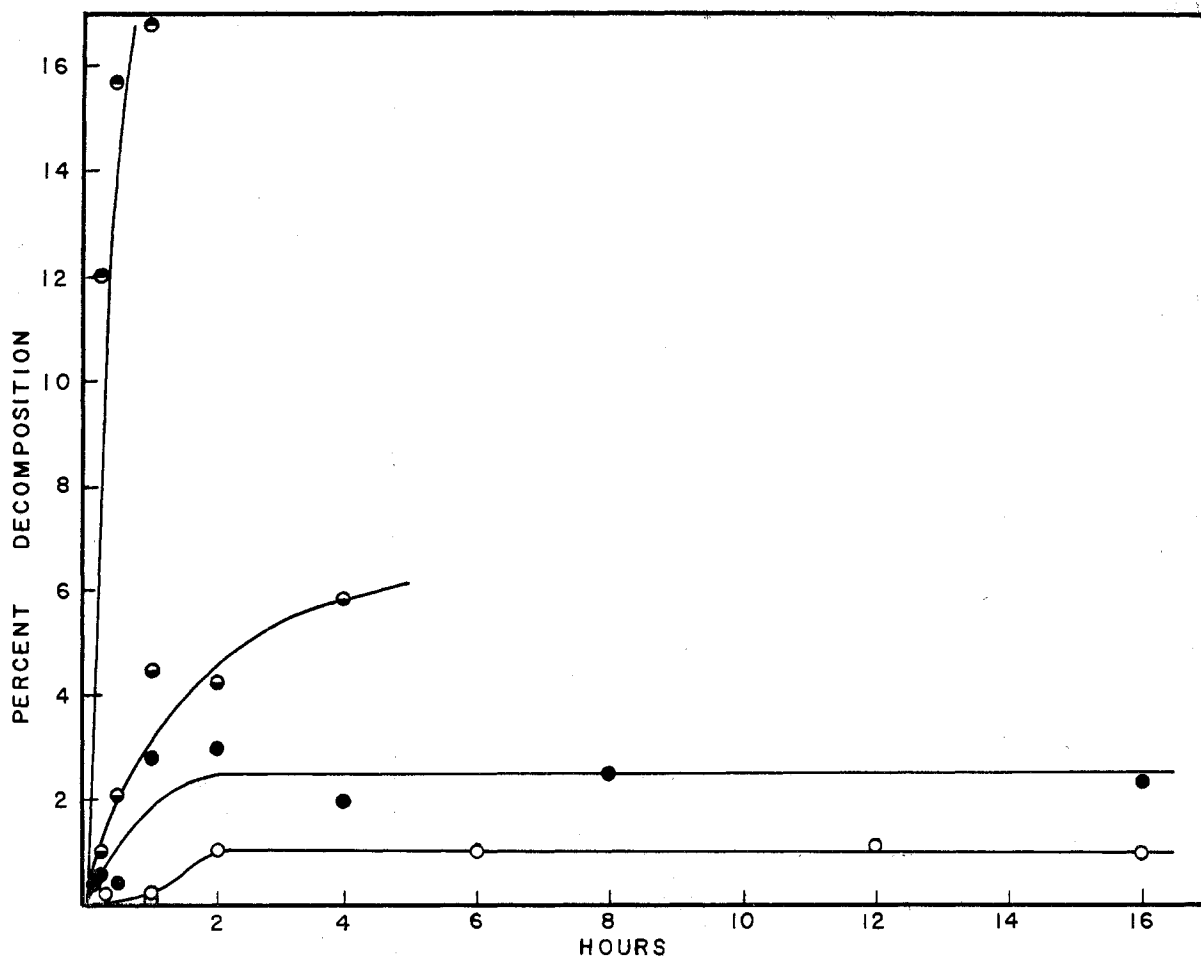
Fig. 2.—Rate of formation of CO_2 in the thermal decomposition of C_3O_2. The formation of CO_2 is expressed in terms of the percentage of C_3O_2 decomposed, assuming one CO_2 for each C_3O_2: O, 100°; ●, 200°; ◑, 300°; and ◓, 400°.

(13) Polymers which have not been opened to the air are not light sensitive.

(14) Carbon suboxide monomer is suffocatingly obnoxious and can be detected in traces by the nose. It is also a lachrymator.

(15) The polymer is insoluble in most organic solvents. Experience or published accounts include acetone, ethanol, chloroform, carbon tetrachloride, xylene, and benzene.

Thermal Decomposition.—The analytical results of some 60 sealed tube experiments are summarized in Fig. 2 and 3. A total of 3.7 mg. of C_3O_2 was used in each experiment. One is immediately struck by the great stability of the polymer up to 200° and the reasonably good stability at 300°. In terms of monomer, the percentage decomposition is about 1% at 100°, 2.5% at 200°, and 6% at 300°. In terms of the polymer, however, the result is much more striking. If one correlates visually the color and extent of polymerization with the analytical results, an interesting fact emerges. At 100 and 200° substantial polymerization is not evident until the plateau portion of the curve is reached in Fig. 3. During the time taken to reach this plateau portion at 100° the tubes show but slight coloration; they become increasingly dark in color during the period of sharp rise and after the

plateau portion is reached the color appears to remain dark and unchanged. At 100°, then, it appears that the bulk of the CO_2 and CO are produced *during* the process of polymerization and not after; *i.e.*, the polymer is stable, for on further standing no additional CO_2 or CO is found. At 200 and 300° it is not possible to say with certainty whether the bulk of the CO_2 and CO comes from the decomposition of the monomer or from the process of polymerization, for the induction period is relatively short. If the pattern at 100° is followed, the polymerization process would be the source. A small amount of decomposition continues after the polymerization at 300°. At 400° polymerization is very rapid and the subsequent decomposition of the polymer is fairly rapid. At 500° there is complete instability: in 15 min. the residue which remains is transparent and gray with no tinge of color at all, and as much decomposition has occurred as took place in 4 hr. at 400°. The general pattern of reaction seems to be (1) polymer nucleation at the walls (an induction period), (2) polymerization (accompanied by a small amount of decomposition yielding CO and CO_2), (3) decomposition of the polymer to give predominantly CO_2 at the beginning, but comparable amounts of CO in the latter stage.

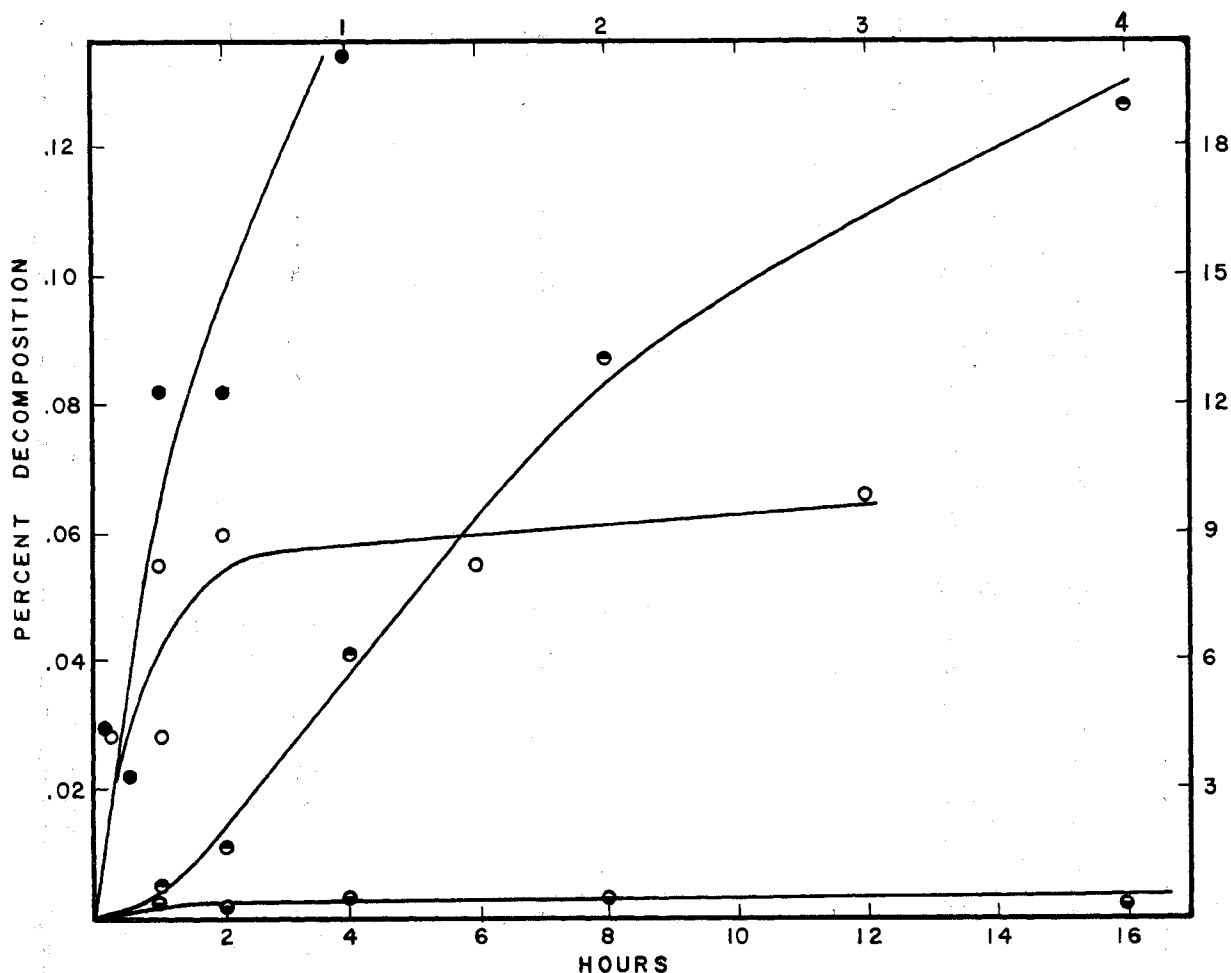Another point of interest is the relatively fixed ratio

Fig. 3.—Rate of formation of CO in the thermal decomposition of C_3O_2. The formation of CO is expressed in terms of the percentage of C_3O_2 decomposed, assuming two CO for one C_3O_2. For 100° (O) and 200° (●), the ordinate and abscissa values given at the left and bottom should be used. For 300° (◑) and 400° (◒), the ordinate and abscissa values at the right and the top should be used.

in which CO_2 and CO are produced at a given temperature. Rough values of the molar ratios at each temperature are: 10 to 1 at 100°; 15 to 1 at 200°; 10 to 1 at 300°; at 400° it steadily decreases from about 10 to 1 to about 1.5 to 1 with increasing time. These "fixed ratios" and predominance of CO_2 have been stressed in the earlier work of Klemenc, Wechsberg, and Wagner,[6,7] but the actual values are greatly different. For example, those workers found 14% decomposition at 200° and anywhere from 43 to 75% decomposition at 300°; the decomposition was too fast for measurement at 400°. Their molar ratios of CO_2 to CO varied from about 4 to 1 at 200° to about 2 to 1 at 400°. It is difficult to understand why there should be so great a difference between their results and the ones reported here. It is not certain which method of preparation was used for C_3O_2, but they did comment on the different characteristics of preparations obtained from malonic acid or from diacetyltartaric anhydride, and in one instance they commented on the properties of one C_3O_2 sample which polymerized

slowly at 400°. It seems likely that these authors did not use C_3O_2 of the highest purity. The analytical procedures which these authors used[8] were not as simple and straightforward as those available today and as a consequence their results were based on titrations and a complicated separation procedure which involved significant corrections. There is a remote possibility that their decompositions were influenced by mercury vapor or stopcock grease since a plug of mercury was used to keep the C_3O_2 from contact with the stopcock grease during the periods when C_3O_2 was heated. A great effort was made by these authors[6,7,9] to demonstrate that the decomposition of C_3O_2 occurred by the homogeneous gas phase equilibrium reaction

$$C_3O_2 \rightleftharpoons CO_2 + C_2$$
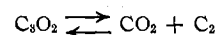
followed by the polymerization of C_2 to give graphite in red crystallites. The clinching argument put forward for this mechanism was the absorption spectrum taken of a decomposing mixture at 200°; the characteristic Swan band of red dicarbon gas was ob-

(6) A. Klemenc, R. Wechsberg, and G. Wagner, *Z. physik. Chem.*, **A170**, 97 (1934).

(7) A. Klemenc, R. Wechsberg, and G. Wagner, *Z. Elektrochem.*, **40**, 488 (1934).

(8) A. Klemenc, R. Wechsberg, and G. Wagner, *Monatsh.*, **65**, 405 (1935).

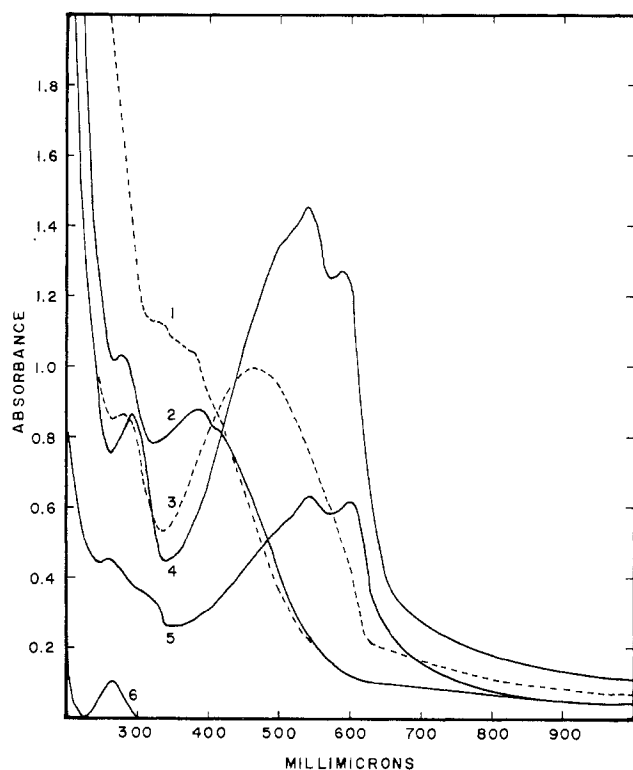(9) A. Klemenc and G. Wagner, *Z. anorg. allgem. Chem.*, **239**, 1 (1938).

Fig. 4.—Ultraviolet and visible spectra of the C_3O_2 polymers formed at different temperatures: 1, room temperature; 2, 100°; 3, 200°; 4, 300°; 5, 400°. For reference, curve 6 shows the spectrum of C_3O_2 monomer at 23 mm. pressure (1-cm. light path), the same pressure used in forming each of the polymers shown.

served. It seems very unlikely that this mechanism of polymer formation can be correct. Polymerization can occur at temperatures far too low for the possibility of this rearrangement to be a reality; polymerization can occur in organic solvents where gaseous C_2 is an unlikely intermediate; gaseous C_3O_2 can be stored at room temperature for hours or days without polymerization (depending on the walls and the pressure), yet there has never been any evidence of the red C_2 gas being produced in the establishment of the homogeneous gas phase equilibrium prior to the onset of polymerization. All evidence points to the initiation of polymerization at the wall, the induction period being determined by the rate of polymer nucleation. Finally, the polymer is not a polymer of C_2 but a polymer of C_3O_2, a fact which the earlier authors did not establish. The spectral observation on which the authors based their claim for the presence of C_2 was no doubt caused by the absorption of a bit of C_3O_2 polymer which when formed at 200° has a broad strong band centered at 4600 Å. (see Fig. 4).

Klemenc, Wechsberg, and Wagner suggested that the reaction

$$CO_2 + C \longrightarrow 2CO$$
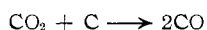
would account for the increased percentage of CO in the reaction mixture with increasing temperature in the range 300 to 650°. There is evidence[10,11] that this

(10) E. A. Gulbransen and K. F. Andrew, *Ind. Eng. Chem.*, **44**, 1048 (1952).

(11) E. M. Frey, *Proc. Roy. Soc.* (London), **A228**, 510 (1955).

reaction does not occur at a temperature below 600°, and hence some other reaction must be the cause. It seems likely that at these higher temperatures the C_3O_2 molecule may start to fall apart before polymerization and that one of the fragments may be CO, or that polymerization and polymer decomposition may be going on so rapidly and interdependently that separate steps cannot be simply separated.

It should be emphasized that the thermal decomposition described here corresponds to a much lower temperature range than the 713° used by Banerjee, Hirt, and Walker,[12] or the 900 and 1025° used by Palmer and Hirt,[13] for the preparation of pyrolytic carbon films.

The Equivalent Weight.—The equivalent weight of the polymers obtained at different temperatures was $68 \pm 10\%$. Though lacking in precision, they show the striking fact that, regardless of the type of polymer formed, there is one equivalent per C_3O_2 unit in the polymer. Pure C_3O_2 monomer possesses two equivalents per mole because it is the anhydride of malonic acid. If this information is taken along with the fact that the low-temperature polymers are water-soluble and the high-temperature ones are not, and that all of them will react with NaOH, the conclusion is that the low-temperature polymers are of low molecular weight and the high-temperature ones of higher molecular weight. The fact that a red polymer is reprecipitated from solution on addition of excess acid demonstrates the basic integrity of a polymer with acid–base properties which is soluble in its salt form. The work of Schmidt, Boehm, and Hofmann[14] shows very clearly the indefinite and variable nature of this polymer once it has been in solution. The variable composition resulting from slightly different treatments, the inability to account for all of the oxygen by quantitative functional group analysis, and unsuccessful efforts to obtain molecular weight values in molten acetamide lead one to the conclusion that once removed from solution and dried, the polymer undergoes a limited decomposition in a variety of unpredictable ways. Unpublished work from this Laboratory substantiates these findings.

Again, the work reported here is at variance with that reported by Klemenc, Wechsberg, and Wagner,[6] who state that "The polymer product obtained at 200° is colored a beautiful red. It readily dissolves in base and quantitatively forms malonic acid which corresponds exactly to the undecomposed C_3O_2."

Visible and Ultraviolet Spectra.—Figure 4 shows the visible and ultraviolet spectra of the polymers formed at different temperatures. For reference, and to emphasize that none of these spectra could be influenced by the presence of C_3O_2 if such should exist, the small lone peak at 2650 Å. which appears at a C_3O_2 pressure of 23 mm. (the starting pressure for all measurements) is also given. The colors corresponding to each of these temperatures are golden yellow at room

(12) P. K. Banerjee, T. J. Hirt, and P. L. Walker, *Nature*, **192**, 450 (1961).

(13) H. B. Palmer and T. J. Hirt, *J. Am. Chem. Soc.*, **84**, 113 (1962).

(14) L. Schmidt, H. P. Boehm, and U. Hofmann, *Z. anorg. allgem. Chem.*, **282**, 241 (1955).

temperature, orange-brown at 100°, rose-pink at 200°, and violet at 300 and 400°. The molar absorption coefficients (see Table I) at selected wave lengths of

TABLE I

WAVE LENGTHS OF MAXIMUM ABSORPTION IN VISIBLE AND ULTRAVIOLET REGIONS AND MOLAR ABSORPTION COEFFICIENTS, ϵ

| | | Temp. of polymer formation | | | |
	Room temp.	100°	200°	300°	400°
Wave length, Å.	2800	3800	2800	2950	2700
ϵ, cm.$^{-1}$ M^{-1}	1050	925	870	1950	450
Wave length, Å.	3350	4200 ?	4600	5100 ?	3100
ϵ, cm.$^{-1}$ M^{-1}	1230	820	1020	1490	306
Wave length, Å.				5450	5450
ϵ, cm.$^{-1}$ M^{-1}				1590	625
Wave length, Å.				5950	5950
ϵ, cm.$^{-1}$ M^{-1}				1380	615

maximum absorption were estimated by assuming that the known amount of C_3O_2 was uniformly polymerized over the walls of the sealed cell, and that the density of the polymers was the same as liquid C_3O_2 (1.1 g./ml.). The combined thickness of film on both windows was estimated as 1.4×10^{-3} cm. and the molar concentration of the solid polymer as 16 M. It is believed that the smaller absorbance observed for the 400° polymer at all wave lengths is the result of a certain amount of thermal decomposition leaving a thinner film on the window. In general, the polymers absorb very strongly in the ultraviolet, the onset of 99% absorption shifting to shorter wave lengths with increased temperature of polymer formation, as follows: room temperature polymer, 2600 Å.; 100° polymer, 2250 Å.; 200 and 300° polymer, 2100 Å.; and 400° polymer, 1920 Å. Also in the ultraviolet region it will be noticed that a second absorption peak appears in the region 2600–2950 Å. for the polymers made at 100° or higher. In addition, there is one major peak (possibly a doublet) that shifts to longer wave lengths as the temperature of polymer formation increases. This shift, from 3350 and 3700 Å. for room temperature polymer, to 3800 and 4200 Å. for 100° polymer, to 4600 Å. (a single peak only) for 200° polymer, and to 5450 and 5950 Å. for 400° polymer, accounts for the observed changes in color. These spectral observations are in contrast with those reported by Schmidt, Boehm, and Hofmann,[15,16] who state that there is no marked maxima in the visible and ultraviolet. They actually worked only with the hydrated polymer, but even so, their results would be at variance with those shown in Fig. 5. This shift in visible absorption maxima to longer wave lengths is characteristic of resonance systems which increase in size, and, again, this is in accord with the belief stated above that the water-soluble low-temperature polymers are of low molecular weight and the water-insoluble high-temperature polymers are of high molecular weight.

When the polymer films in the sealed cells are

(15) L. Schmidt, H. Boehm, and U. Hofmann, *Z. anorg. allgem. Chem.*, **296**, 246 (1958).

(16) L. Schmidt, H. Boehm, and U. Hofmann, Proceedings of the Third Conference on Carbon, Pergamon Press, Inc., New York, N. Y., 1959, pp. 235–240.
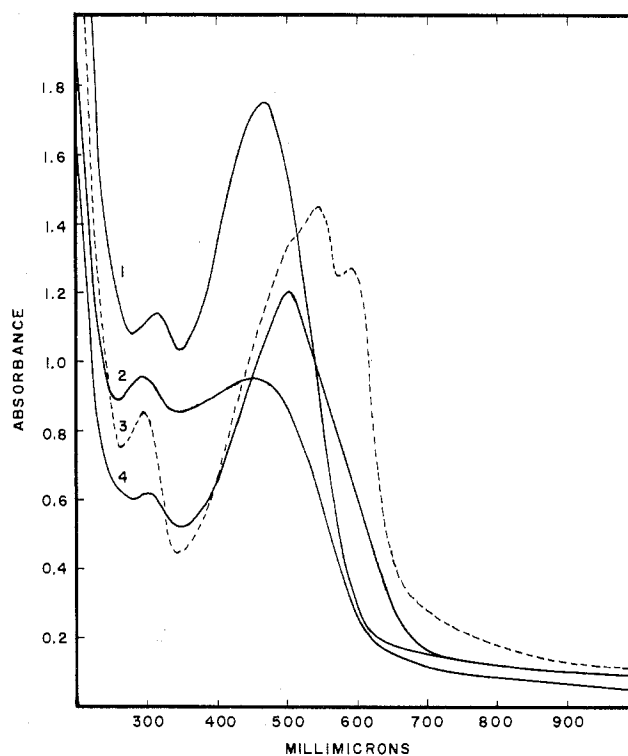

Fig. 5.—Ultraviolet and visible spectra of the same C_3O_2 polymer samples shown in Fig. 4 after treatment with water vapor at room temperature: 1, room temperature; 2, 100°; 3, 300°; 4, 200°. Curve 3 is identical with curve 4 in Fig. 4, and if the curve for 400° were also shown, it would be identical with that shown in curve 5, Fig. 4.

heated to temperatures above those at which they were originally polymerized, the spectra change and assume characteristics similar to those normally found at the higher temperatures. The 200° polymer differs most from this general behavior, tending to give an absorption maximum at 5050 Å. instead of 5450 or 5950 Å.; these spectra are not shown.

The absorption curves given in Fig. 5 show the spectral changes which occurred when the same samples used in Fig. 4 were treated with water vapor. At once it is seen that the spectra of the 300 and 400° polymers remain unchanged; for purposes of comparison at 300° see curve 4 of Fig. 4 and curve 3 of Fig. 5. The spectrum of the room-temperature polymer undergoes a major change; an entirely new peak appears at 4700 Å. which absorbs about five times more strongly than the untreated polymer at 3300 Å. For the 100 and 200° polymer the main absorption band also shifted to longer wave lengths (to 4600 and 5050 Å., respectively), but not with the dramatic increase in absorption coefficient. All of the polymers, regardless of the temperature at which they were made, show an absorption peak in the range 2900–3150 Å.

Infrared Spectra.—The infrared spectra of C_3O_2 monomer, C_3O_2 polymer, and the polymer exposed to water vapor and ammonia are shown in Fig. 6, 7, 8, and 9. The monomer spectrum has been carefully studied and discussed elsewhere.[3] Not included in these figures are (1) the broad bands at 11.2 and 12.9 μ with 40 and 21% transmission at 500 mm. pressure in
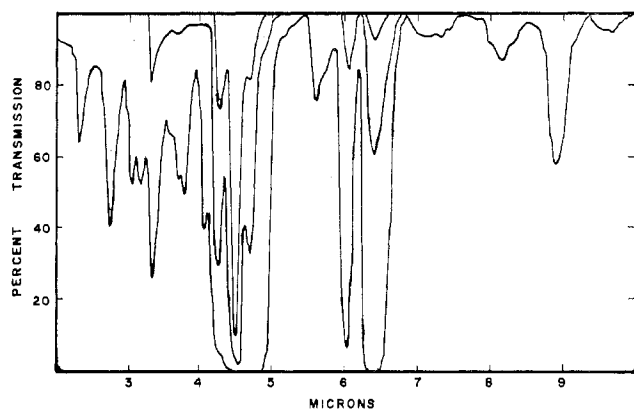
Fig. 6.—Infrared spectrum of C_3O_2 monomer at three pressures; 500, 15.1, and 2.4 mm.; cell length = 9.8 cm. Only two peaks (4.50 and 6.45 μ) at the lowest pressure.

Fig. 7.—Infrared spectrum of C_3O_2 polymer. The spectrum is the same for all temperatures of polymer preparation (25–400°).

the monomer spectrum, (2) the peak at 12.4 μ with 37% transmission for the polymer, and (3) the peak at 12.6 μ with 64% transmission for the water-treated polymer. It would appear that small amounts of C_3O_2 monomer are rather strongly adsorbed by the polymer at room temperature, for many hours of hard pumping are required to completely remove the last trace of the extremely strong spectral absorption at 4.5 μ, characteristic of the ketenyl group.[3,17] It is evident that there is little similarity between the monomer and polymer spectra. Also noteworthy is the fact that, in contrast to the visible and ultraviolet spectra, the infrared spectra for all polymers are identical, regardless of the temperature of preparation (25–400°).

Frequency assignments[18,19] for the polymer have not been as simple as might be expected for a compound composed of only two elements. The weak to medium absorption at 8.8 μ and the very strong absorption at 8.1 μ are probably due to =C—O— stretching vibrations; the very strong absorption at 6.0 μ to conjugated C=C; and the intense absorption at 5.8 and 5.6 μ to —C=O stretching frequencies, the latter being typical of a vinyl ester carbonyl, O=C—O—C=C. The two intense absorptions at 7.3 and 6.6 μ are seldom observed and have the resonant carboxylate ion as the nearest common example, the first frequency being assigned to the symmetric stretch of O–C–O and the second to the asymmetric stretch of O–C–O.

The great change which occurs with such ease when water vapor is added to the polymer seems to be due to the formation of a polymeric carboxylic acid, for one can assign the broad medium band around 3.3 μ to hydrogen-bonded O–H stretching, the very strong 5.8 μ band to —C=O stretching, the broad strong band at 6.9 μ and the broad medium band at 8.0 μ to C–O stretching vibrations or OH deformation vibrations.[18]

Although NH_3 does not react readily with the polymer (and apparently not at all at pressures of the order of 50 mm.), the polymer can be completely con-
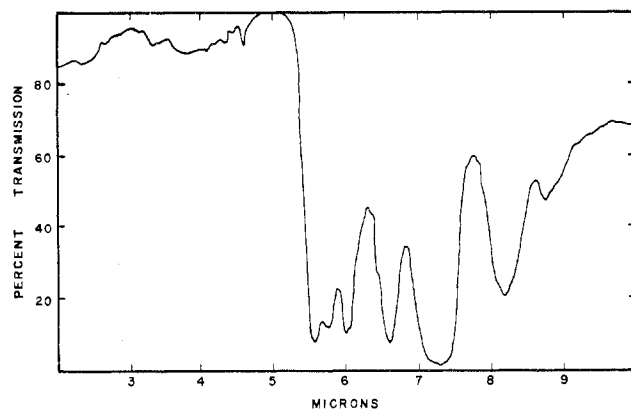
verted at an ammonia pressure of 1 atm. to a compound whose spectrum is typical of an amide (Fig. 9). This amide hydrolyzes rather readily in the air with concomitant evolution of NH_3.

Proposed Structure.—The following facts are of particular importance in proposing a satisfactory structure for the polymer·

(1) The polymer must be formed in a reasonable reaction process, using C_3O_2 as the building units, not C_2.

(2) The structure must be variable in size, being larger and less reactive to water and base if formed at higher temperature, but substantially the same unit bond structure at all temperatures.

(3) It must provide an equivalent weight of about 68 (the size of one C_3O_2 unit).

(4) On thermal decomposition it must tend to yield CO_2 as its principal gaseous product—at least in its earlier stage of decomposition. This requires that two oxygen atoms be attached to a given carbon atom.

(5) It must have a highly conjugated bond system to account for its intense color.

(6) The low molecular weight polymer must react readily with water to give a carboxylic acid type structure.

(7) It must be capable of forming an amide with NH_3.

It is possible to draw at least 16 different regular repetitive polymeric structures (not counting various resonance forms) which retain the over-all composition of C_3O_2 without taking into account an infinite variety of structures composed of random combinations of the various regular forms. Most of these regular structures can be ruled out because they do not fulfill all of the requirements just listed above, or would have other requirements which are not observed. For example, four of them would give rise to the extremely strong absorption band at 4.5 μ characteristic of the ketenyl group; four of them (including two just mentioned) would give rise to a strong absorption band at 9.6–10.4 μ, typical of four-member carbon ring compounds[20,21]; three others would require the absence of

(17) D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946).

(18) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1958.

(19) R. N. Jones, C. Sandorfy, and A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. IX, "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 4.

(20) J. D. Roberts and H. E. Simmons, *J. Am. Chem. Soc.*, **73**, 548 (1951).

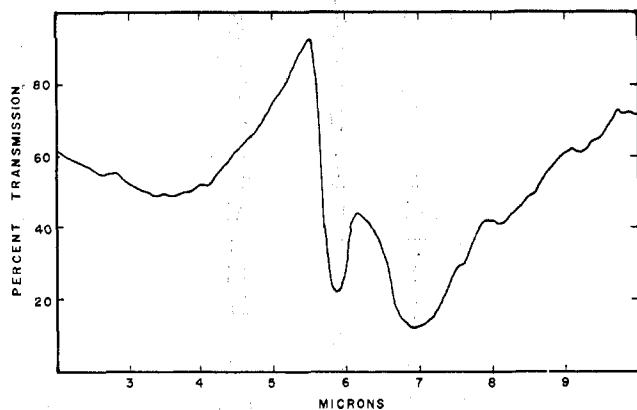(21) L. W. Marrison, *J. Chem. Soc.*, 1614 (1951).

Fig. 8.—Infrared spectrum of room temperature C_3O_2 polymer after treatment with water vapor at room temperature. The 300 and 400° polymer spectra show very little change after treatment with water vapor from that shown in Fig. 7.

Fig. 9.—Infrared spectrum of room temperature C_3O_2 polymer after treatment with NH_3 gas at 680 mm. pressure and room temperature for 24 hr. Treatment with 50 mm. NH_3 pressure produces very little change in spectrum from that shown in Fig. 7.

the characteristic carbonyl frequency; and at least five of them (including three mentioned above) would be completely unreactive to water. Ten of the 16 structures would find it difficult to eliminate CO_2, and 13 of them do not possess any type of simple conjugated bond system.

Three of the 16 structures, all lactones, seem to fit the general requirements, but only the polycyclic 6-membered lactone structure shown in Fig. 10 appears to give a unique solution to the problem. One of these lactones consists of a series of β-propiolactone rings connected by double bonds (or unsaturated β-propiolactone rings connected by single bonds); it should give a strong carbonyl absorption at about 5.4 μ and possibly an absorption at 10.2 μ characteristic of trimethylene oxide, but neither is observed. The second consists of bicyclic 5-membered lactones connected in a chain by single or double bonds, depending on whether the two lactone rings are fused at a common double bond or whether each is an unsaturated γ-lactone fused at a common single bond. In the formation of this 5-membered lactone polymer there is the requirement that as the C_3O_2 molecules add to each other they would have to react alternately by two different mechanisms, a much more demanding and unlikely situation than exists for the formation of the polycyclic 6-membered lactone where each C_3O_2 molecule adds like every other one. There is also the usual argument that a 6-membered ring has less strain than a 5-membered ring. There is the further interesting fact that β-valerolactone (a 6-membered ring) is tremendously unlike other lactones in its reactivity to water. It is very hygroscopic; it also has a rate constant at 0° for alkaline hydrolysis (in 60% dioxane–water solution) of 5.5 sec.$^{-1}$ M^{-1} compared to values of 0.15, 0.26, and 0.35 for lactones having 5-, 7-, and 8-membered rings, or values of 0.012, 0.000022, and 0.000055 for lactones having 9-, 10-, and 11-membered rings.[22] Another attractive feature of the polycyclic 6-membered lactone structure is the possibility of the ionic pyrilium-like resonance form shown in Fig. 10c;

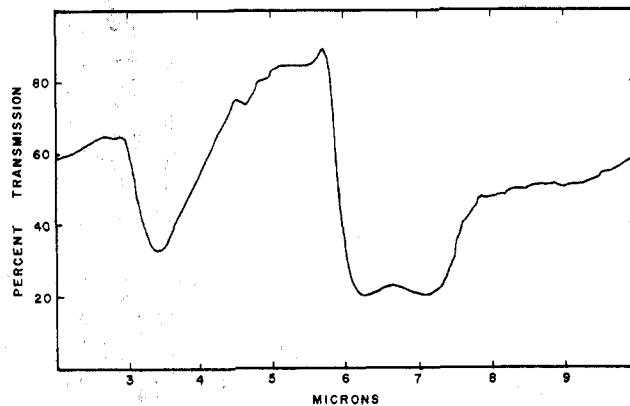(22) R. Huisgen and H. Ott, *Tetrahedron*, **6**, 253 (1959).

in fact, this may be the most important of the resonance forms. This ionic form is highly aromatic in character and should possess considerable stability and color. It is also possible that the resonance interaction of the two oxygen atoms bound to the same carbon in the forms shown in Fig. 10 may lead to the appearance of the two strong absorption bands at 7.3 and 6.6 μ, similar to that observed for the carboxylate ion where the two oxygen atoms are exactly equivalent. The variation in the color of the polymers, ranging from yellow to red to violet with increasing temperature of formation, is accounted for by postulating that the size of the polymer increases with the temperature of formation. Also in keeping with this variation in polymer size with temperature of formation is a concomitant decrease in reactivity to water and base. One could also use the X-ray data of Schmidt, Boehm, and Hofmann[15] to support this structure, for they find that "the X-ray interference bands support the conclusion that the 'red coal' consists of graphite-like layers of about 10 Å. across and composed of hexagonal rings. Like microcrystalline carbon, the layers are arranged parallel to one another, but they do not possess a common orientation in the direction of the a- and b-axes." They also conclude, because of their inability to account for all of the oxygen present, that much of the oxygen must lie in the planes as part of the hexagonal rings. Some caution must be used in connection with these X-ray data, however, for they were obtained on polymers which had been exposed to water vapor.

The structure proposed by Schmidt, Boehm, and Hofmann[15] is very unlikely. Not only does it not fulfill all the requirements given above, but inspection shows that 11 of the 15 rings are different from each other and that there are present 3 non-lactonic carbonyl oxygens, 12 lactonic oxygens, 4 ketenyl oxygens, and 11 cyclic ether oxygens. There is only one ingenious way by which the 15 C_3O_2 units can be added together, and the structure does not allow for adding more C_3O_2 units or for possessing less than 15. The authors describe it as self-limiting. The structure proposed by
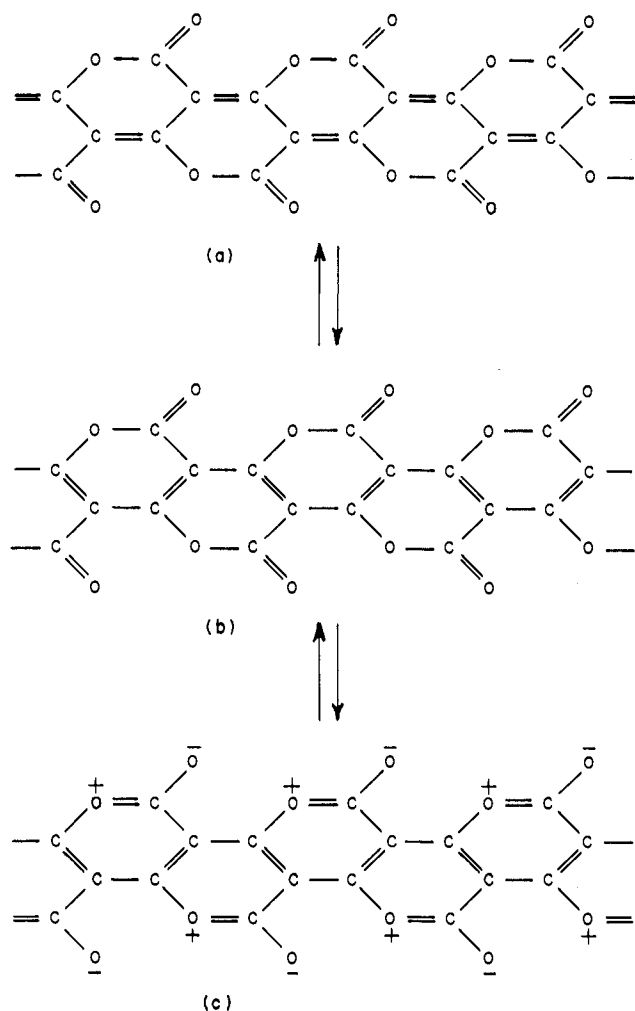
Fig. 10.—Three resonance forms of the proposed structure of the C_3O_2 polymer.

Diels, Beckmann, and Tonnies[23] is, like that of Schmidt, Boehm, and Hofmann, based on experiments with polymers which contained at least 2% hydrogen and which had been precipitated from organic solvents and exposed to water vapor in the air. They propose a polymeric cyclobutadione structure with ketenyl end groups—a structure which does not meet the requirements outlined above. The complicated peroxidic dimeric structure proposed by Hartley[24] is one of conjecture only, and it cannot account for the observed properties.

There are many possibilities for chain termination, but a reasonable suggestion is the 1,2 or 2,3 addition

of a C_3O_2 molecule at either end of the polymer (Fig. 10a,b) to make 5-membered terminal rings with dangling ketenyl groups. At the left end the rings would be α,β- or α,γ-cyclopentenedione, while at the right end the rings would be a furanone or a γ-lactone. If the latter were present the equivalent weight for the group would be 34 because both the lactone and the ketenyl would be hydrolyzable, but in all of the other cases the equivalent weight would be 68, due in each case to the ketenyl group. There is also the possibility that the long induction period is required to attach a terminal C_3O_2 molecule to the wall in some heterogeneous fashion that permits the further continued addition of other C_3O_2 molecules.

Photopolymerization.—The photopolymer appears to be a different molecule formed by a mechanism different from that involved in the thermal polymerization. There is no induction period, for polymerization starts as soon as the monomer is exposed to ultraviolet light. The photopolymer looks gray and its visible and near-infrared spectrum shows a generally increasing absorption at shorter wave lengths with but one broad ill-defined absorption shoulder at about 3500 Å. This spectrum is similar to that observed for a thin carbon film. Recent papers[25-27] concerning the ultraviolet photolysis of small amounts of C_3O_2 ($P = 1$ mm.) in the presence of large amounts of C_2H_4 ($P = 50$ to 750 mm.) have led Mullen and Wolf to the tentative conclusions that the initial act after absorbing a light quantum is the splitting of a $C{=}C$ bond to give CO and a C_2O radical. If this is indeed the case, then the photopolymer might be the result of C_2O radicals reacting with C_3O_2. Bayes suggested in his first paper that the postulated intermediate C_2O radical might possibly spontaneously decompose to carbon atoms and another CO molecule. This, if true, might indicate that the photopolymer was simply a carbon film. In his second paper, however, Bayes felt that spontaneous decomposition was unlikely in the homogeneous gas phase, though this feeling would not necessarily preclude the possibility of heterogeneous decomposition of C_2O at the surface to give a carbon film.

(23) O. Diels, R. Beckmann, and C. Tonnies, *Ann.*, **439**, 76 (1924).
(24) W. H. Hartley, *Chem. News*, **94**, 40 (1906).

(25) K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).
(26) R. T. Mullen and A. P. Wolf, *ibid.*, **84**, 3214 (1962).
(27) K. D. Bayes, *ibid.*, **84**, 4077 (1962).