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THE PHOTOLYSIS OF ETHYLENE CARBONATE AND VINYLENE CARBONATE IN THE GAS PHASE

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(Received May 18, 1982)

Summary

The photolysis of ethylene carbonate vapour was studied at 206.2 nm at pressures from about 5 to 30 Torr and at temperatures from 120 to 160 °C. The major products were CO_2 and ethylene oxide, while the minor products were H_2, CO, CH_4 and CH_3CHO. The quantum yields for the production of CO_2 increased sharply at higher pressures, reaching values as high as 200, and there is evidently an unusual photo-initiated chain reaction occurring to produce CO_2, ethylene oxide polymer and smaller amounts of ethylene oxide.

The thermal decomposition was also studied briefly between 150 and 500 °C; CO_2 and ethylene oxide were major products, apparently formed in a surface reaction.

The photolysis of vinylene carbonate vapour around 220 - 240 nm at pressures from 1 to 5 Torr and a temperature of 60 °C gave CO and H_2 as the major products in a 3 to 1 ratio. Ketene and CO_2 were also observed in rather smaller yields.

Mechanisms are discussed and absorption spectra are reported for both compounds.

1. Introduction

Except for dimethyl carbonate, which has been studied in several laboratories [1 - 3], the photolysis of carbonate esters in the gas phase has been largely neglected, probably because of their low volatility and lack of absorption at convenient wavelengths. Cyclic carbonates are of interest for comparison both with the dialkyl carbonates and with other simple carbonyl ring compounds. In the present paper, brief studies of the photolysis of ethylene carbonate (1,3-dioxolan-2-one) and vinylene carbonate (1,3-dioxol-2-one) in the vapour phase are described.

2. Experimental details

The photolyses were studied in a cylindrical quartz vessel 10 cm long and 5 cm in diameter. The carbonates were stored as liquids at about 20 °C and warmed when required to give the desired pressure of vapour. The pressure was measured with a quartz spiral gauge, and the entire vacuum line, pressure gauge, photolysis cell etc. were enclosed in an air thermostat at a temperature high enough to avoid condensation of the carbonate vapour. After the photolysis, non-condensable gases (CO, CH_4 and H_2) were removed through a liquid nitrogen trap measured in a gas burette and analysed by gas chromatography. Gases volatile at 0 °C were then removed through a trap and analysed by gas chromatography using a variety of columns. No analysis was made for higher products.

The light sources employed were an iodine resonance lamp with a liquid water filter which gave essentially monochromatic 206.2 nm radiation [4], a cadmium resonance lamp at 228.8 nm and a medium pressure mercury arc with and without a Vycor filter. The photolysis of azomethane was used for actinometry, on the assumption of a nitrogen quantum yield of unity. Absorption spectra, not previously reported for the carbonate vapours, were measured in a spectrophotometer and are shown in Fig. 1.

Some thermal decomposition was observed with both compounds, and a brief study of this was made with ethylene carbonate, using the photolysis
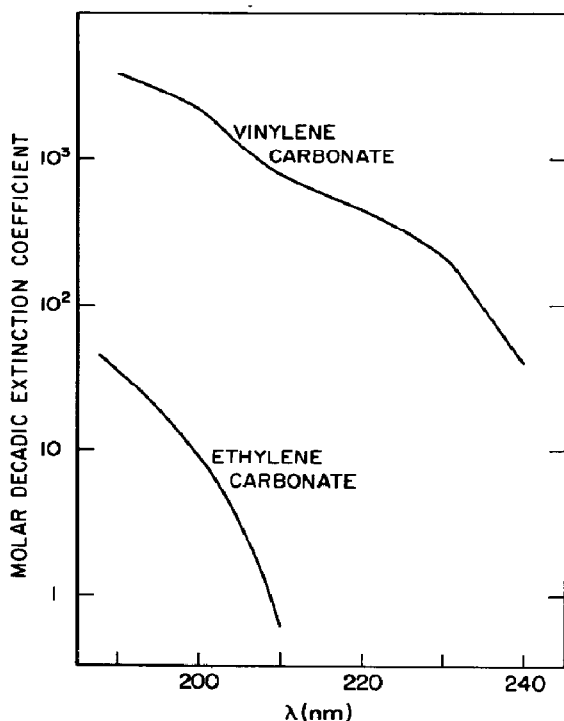

Fig. 1. Absorption spectra of ethylene carbonate and vinylene carbonate vapour, measured at 20 Torr and 140 °C and at 0.4 Torr and 30 °C respectively.

vessel, and corrections were made to the photolysis yields. Further experiments at higher temperatures were made in sealed Pyrex tubes.

The carbonates were obtained from Aldrich Chemical Co. with a stated purity of about 99% and were used after rigorous degassing and several trap-to-trap distillations. No impurities were detected using gas chromatography.
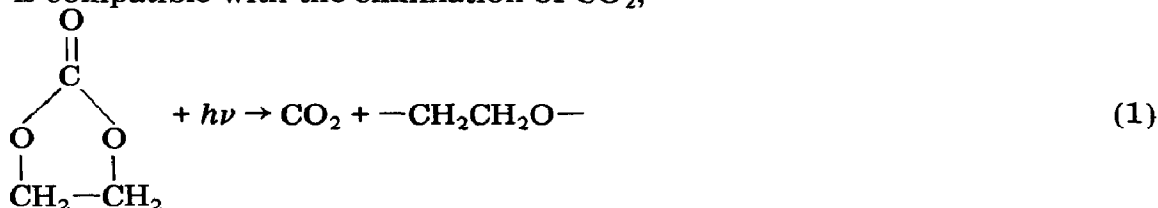
3. Results and discussion

3.1. Absorption spectra

Absorption spectra for the two carbonates are shown in Fig. 1 and differ remarkably, with the extinction coefficient for vinylene carbonate 100 - 1000 times larger than that for ethylene carbonate. An explanation can be found in the photoelectron spectra of the two molecules, from which it has been concluded that, while the highest occupied orbital in ethylene carbonate is the n_0 lone pair orbital on the carbonyl oxygen, the highest occupied orbital in vinylene carbonate is a π orbital largely localized on the two ring oxygen atoms [5]. Thus the absorption in ethylene carbonate is probably the usual weakly allowed $\pi^* \leftarrow n_0$ transition of a carbonyl compound; in contrast, the first absorption band in vinylene carbonate probably arises from an allowed $\pi^* \leftarrow \pi$ transition. There is evidence for two transitions in the vinylene carbonate spectrum in Fig. 1 and, since the photoelectron spectrum shows no occupied orbital that could account for this, a second upper orbital is probably involved. No vibrational structure is evident in either spectrum, indicating that Rydberg states are not excited in these transitions, as these would be expected to show a vibrational structure comparable with that in the photoelectron spectra.

3.2. Ethylene carbonate photolysis

The photolysis was studied at 206.2 nm at pressures from 1 to 25 Torr and temperatures from 120 to 160 °C. The volatile products observed were CO_2, ethylene oxide, H_2, CO, CH_3CHO and CH_4. The variations in quantum yields with pressure at 140 °C were typical and are shown in Figs. 2 and 3. While the yields of the products shown in Fig. 2 were fairly reproducible, the yields of ethylene oxide and CO_2 (Fig. 3), especially the latter, were not, partly because of a sizable and irregular thermal dark reaction but also apparently because of irreproducibility in the photolysis process itself.

The production of the minor products, H_2, CO, CH_3CHO and CH_4, is compatible with the elimination of CO_2,

$$\begin{array}{c} O \\ \parallel \\ C \\ \diagup \diagdown \\ O \quad\quad O \\ | \quad\quad | \\ CH_2 - CH_2 \end{array} + h\nu \rightarrow CO_2 + -CH_2CH_2O- \qquad (1)$$
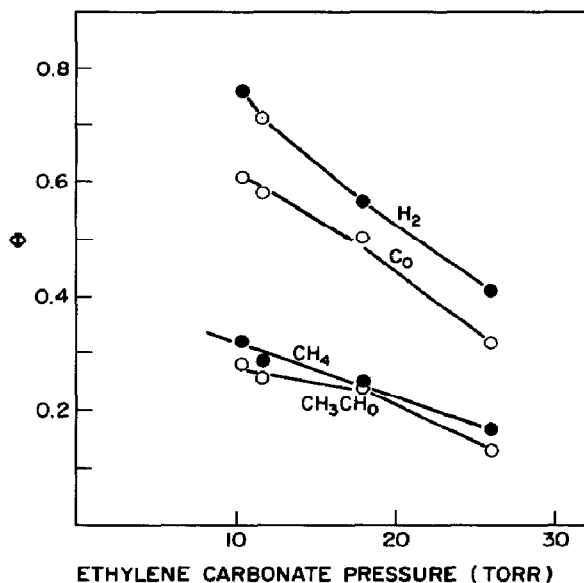
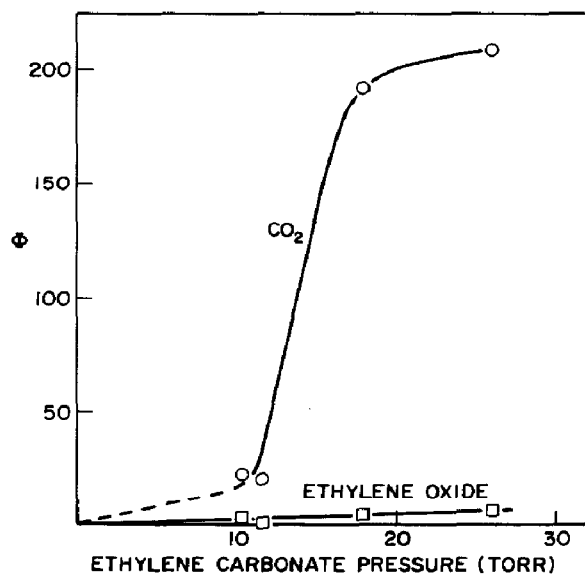Fig. 2. Quantum yields of minor products in the photolysis of ethylene carbonate at 206.2 nm and 140 °C.

Fig. 3. Quantum yields of CO_2 and ethylene oxide from the photolysis of ethylene carbonate at 206.2 nm and 140 °C.

with a quantum yield perhaps near unity at low pressures, followed by the same reaction sequence postulated for the $-CH_2CH_2O-$ biradical in the decomposition of ethylene oxide [6],
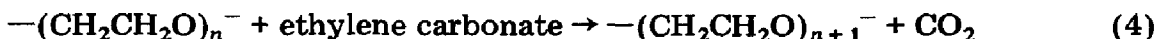
$$-CH_2CH_2O- \rightarrow CH_3CHO^* \rightarrow CH_3 + H + CO$$
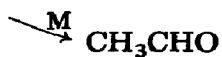
$$\searrow^M CH_3CHO$$

(2)

and abstraction reactions of H and CH_3. The addition of CO_2 or C_2F_6 reduced the yields of CH_4, CO and H_2 systematically, as might be expected from the stabilization of CH_3CHO^*. The addition of small amounts of O_2 eliminated CH_4 and H_2, while an ethylene pressure of a few torrs reduced the yield of H_2 close to zero and slightly reduced the CH_4 production. These observations support the suggestion that H and CH_3 are precursors of H_2 and CH_4.

The formation of the major products, CO_2 and ethylene oxide (Fig. 3), follows a very different pattern. At pressures of 10 or 12 Torr, $\Phi(CO_2)$ was found to be already about 15 or 20 in the series of experiments shown in Fig. 3, and at higher pressures it rose sharply to a value of over 200 at 26 Torr. While these data were not very reproducible, yields of the same order of magnitude were always obtained; at pressures below 10 Torr, yields of CO_2 were scattered between 2 and 10, well above unity, and it seems clear that under all conditions an efficient chain reaction was occurring to produce CO_2. Yields of ethylene oxide, while scattered, were also generally greater than unity and rose with increasing pressure, although less sharply than those of CO_2; although ethylene oxide must also be a chain product the yield was much less than expected from a stoichiometric decomposition of ethylene carbonate into CO_2 + CH_2CH_2O. A polymer was observed to form on the surface of the reaction vessel and apparently must account for the missing ethylene oxide. These observations point to an unusual polymerization reaction of ethylene carbonate, yielding not an ethylene carbonate polymer but an ethylene oxide polymer with the liberation of CO_2. Such a polymerization might be initiated by $-CH_2CH_2O-$ biradicals from reaction (1) or by CH_3 or another monoradical derived from reaction (2). The latter possibility was ruled out by generating methyl radicals in the system by the photolysis of azomethane at 366 nm where ethylene carbonate is transparent. Yields of CH_3 were ten times larger than in the direct photolysis, yet no polymerization or decomposition of ethylene carbonate was observed. Initiation was therefore probably by biradicals,

$$-CH_2CH_2O- + \text{ethylene carbonate} \rightarrow -CH_2CH_2OCH_2CH_2O- + CO_2 \qquad (3)$$
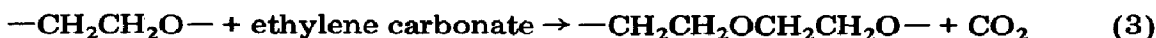
followed by a general propagation step,

$$-(CH_2CH_2O)_n^- + \text{ethylene carbonate} \rightarrow -(CH_2CH_2O)_{n+1}^- + CO_2 \qquad (4)$$

The occasional loss of CH_2CH_2O units from the propagating polyradicals could account for the minor chain production of ethylene oxide. The decrease in the quantum yields of all the minor products, including CH_3CHO, with increasing pressure of ethylene carbonate (Fig. 2) can now be explained by a competition between reactions (2) and (4) for $-CH_2CH_2O-$ radicals (simple collisional deactivation of CH_3CHO^* would have decreased H_2, CH_4 and CO but *increased* CH_3CHO).

The polymer formed was a clear transparent film deposited fairly uniformly on all surfaces of the vessel, suggesting either condensation on the surface as a liquid or a surface polymerization; the temperature in all

these experiments was well above the melting point of 60 - 65 °C reported for poly(ethylene oxide). Polymerization on the surface could account for the irreproducibility of the formation of CO_2 and ethylene oxide and the dependence on surface condition and the presence of deposits from previous experiments. The polymer was found to be completely water soluble, as expected for an ethylene oxide polymer [7].
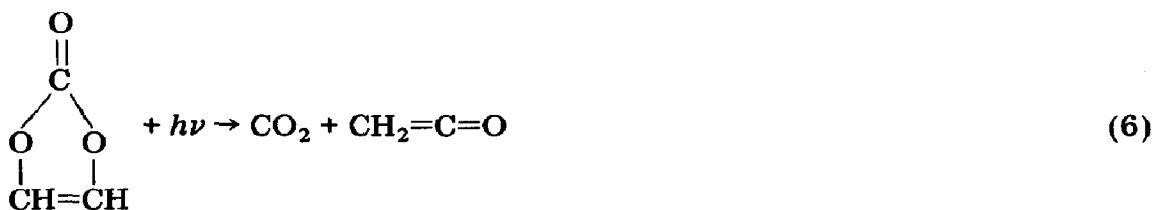
3.3. Thermal decomposition of ethylene carbonate

The thermal decomposition was also studied briefly, at temperatures up to 350 °C in the photolysis vessel and from 250 - 500 °C in sealed Pyrex vessels which permitted higher pressures of reactant, up to about 400 Torr. The only primary products of importance were CO_2 and ethylene oxide, with CH_3CHO, CH_4, CO and H_2 appearing as secondary products at higher temperatures and conversions, obviously from the secondary pyrolysis of ethylene oxide. Below about 230 °C the decomposition was almost independent of temperature, while from 230 - 500 °C an activation energy of about 20 kcal mol^{-1} was observed. The yields of CO_2 were rather scattered and consistently two or three times larger than those of ethylene oxide. These observations suggest a surface decomposition and some ethylene oxide polymer formation, as in the photolysis.

3.4. Photolysis of vinylene carbonate

The photolysis was studied briefly, using either a cadmium resonance lamp at 228.8 nm or a medium pressure mercury arc with a Vycor filter. Thermal decomposition and polymerization were a more severe problem than with ethylene carbonate; most experiments were done around 60 °C where these problems were not serious and the vapour pressure was sufficiently high to permit experiments from 1 to 5 Torr. The major photolysis products were CO and H_2, formed in about a 3 to 1 ratio. The addition of O_2 had little effect on these products and, since vinylene carbonate itself should also be a good scavenger for hydrogen atoms, it appears that molecular hydrogen was formed directly:

$$
\begin{array}{c}
O \\
\parallel \\
C \\
\diagup \diagdown \\
O \quad O \\
\vert \quad \vert \\
CH{=}CH
\end{array}
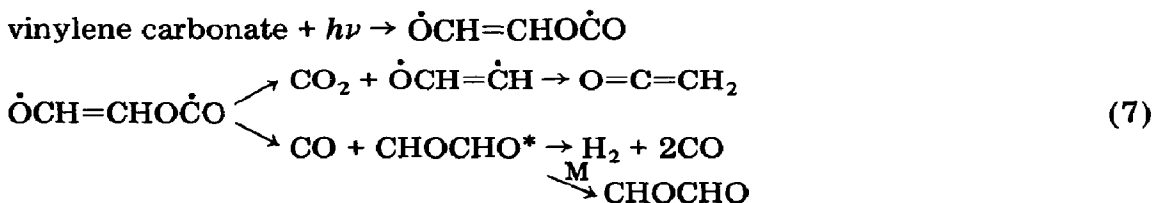\quad + \; h\nu \rightarrow H_2 + 3CO \tag{5}
$$

Approximate quantum yield measurements showed a value for reaction (5) in the range 0.5 - 0.9. A second important process, with smaller and somewhat scattered yields, was

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{C} \\
\diagup \quad \diagdown \\
\text{O} \qquad \text{O} \\
\mid \qquad \mid \\
\text{CH=CH}
\end{array}
\quad + h\nu \rightarrow CO_2 + CH_2{=}C{=}O
\qquad (6)
$$

Ketene was identified by mass spectrometry, and its rapid secondary photolysis to give CO and some ethylene complicated the product measurements.

The mechanism of reactions (5) and (6) is of some interest. The direct elimination of H_2 from vinylene carbonate would leave a highly strained ring which could decompose to three CO molecules and this may indeed occur. The C_3O_3 intermediate might also decompose to $CO_2 + C_2O$. To test this possibility, ethylene was added to the system, and a careful search was made for allene, known to be formed efficiently by the reaction of C_2O with ethylene [8]; none was found. An alternative path for reaction (5) might be a primary formation of CO and glyoxal, followed by elimination of H_2 from vibrationally or electronically excited glyoxal. Molecular hydrogen has been reported as a product of the glyoxal photolysis at short wavelengths [9] and it is also interesting that Torres *et al.* [10] have recently found glyoxal as a major product in the matrix photolysis of vinylene carbonate at low temperatures. They also observed ketene and CO_2 as products in the matrix, confirming the occurrence of reaction (5). A mechanism for reactions (5) and (6) proceeding through a common biradical intermediate can be written as

$$
\text{vinylene carbonate} + h\nu \rightarrow \dot{O}CH{=}CHO\dot{C}O
$$

$$
\dot{O}CH{=}CHO\dot{C}O
\begin{cases}
\nearrow CO_2 + \dot{O}CH{=}\dot{C}H \rightarrow O{=}C{=}CH_2 \\
\\
\searrow CO + CHOCHO^* \rightarrow H_2 + 2CO \\
\qquad\qquad\quad \searrow^{M} CHOCHO
\end{cases}
\qquad (7)
$$

Glyoxal was not detected in the present experiments and, while small yields might have been missed in the analysis, the 3 to 1 ratio of CO to H_2 suggests that these were not important. The CHOCHO* species in reaction (7) may be a vibrationally or electronically excited glyoxal molecule, or a biradical, with enough energy to prevent much stabilization in the present gas phase photolysis but which was stabilized to some extent in the matrix at 8 K. Reaction (7), with its common biradical intermediate, is indistinguishable experimentally from two primary processes directly extruding molecular CO_2 and CO. It is interesting that, in the ethylene carbonate photolysis, analogous loss of CO would have given a CH_2OCH_2O intermediate which would be expected to decompose to two CH_2O molecules. Formaldehyde was not observed, and apparently only the loss of CO_2 was important in the primary process. This difference between vinylene and ethylene carbonate may reflect the fact that different electronic transitions are involved, as discussed earlier,

with the $\pi^* \leftarrow \pi$ excitation of vinylene carbonate leading to a more direct disruptive dissociation of the ring. It might also be noted that acetylene and ethylene were not observed as products of these photolyses, indicating that primary formation of CO_3 and the corresponding hydrocarbon did not occur.

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