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The thermal and photochemical decomposition of *cis*-1,2-cyclobutanedicarboxylic anhydride in the vapour phase¹

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The thermal decomposition of *cis*-1,2-cyclobutanedicarboxylic anhydride (CBA) has been studied in a static system in the range 625–725 K. The major process observed was a homogeneous unimolecular decomposition to form ethylene and maleic anhydride, with first-order rate parameters $A = 1.14(\pm 0.1) \times 10^{14} \text{ s}^{-1}$ and $E = 55.1 \pm 1 \text{ kcal/mol}$. A very minor decomposition channel yielding butadiene, CO₂, and CO was also observed, with $A = 8.4 (\pm 0.1) \times 10^{14} \text{ s}^{-1}$ and $E = 67.5 \pm 1 \text{ kcal/mol}$.

The decomposition induced by a pulsed CO_2 laser was also studied briefly; the same two decomposition channels were observed and their dependence on fluence and pressure examined.

The ultraviolet photolysis of CBA was also investigated between 210 and 365 nm. In addition to the products found in the thermal reaction, cyclobutene was also a major product, and product ratios were measured as a function of wavelength and added CO_2 . Mechanisms in the three systems are discussed and compared.

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On a étudié la décomposition thermique de l'anhydride cyclobutanedicarboxylique-1,2 *cis* (ACB) dans un système statique avec un intervalle de température allant de 625 à 725 K. Le processus principal observé est une décomposition unimoléculaire homogène qui conduit à l'éthylène et à l'anhydride maléique, avec des paramètres de vitesse d'ordre un de $A = 1, 14(\pm 0, 1) \times 10^{14} \text{ s}^{-1}$ et de E = $55, 1 \pm 1$ kcal/mol. On a également observé une voie très secondaire de décomposition qui conduit au butadiène, au CO₂ et au CO avec $A = 8, 4 (\pm 0, 1) \times 10^{14} \text{ s}^{-1}$ et E = 67, 5 kcal/mol.

On a également étudié brièvement la décomposition induite par un laser à impulsion de CO_2 . On a observé les deux modes de décomposition et on a examiné l'effet de la fluence et de la pression sur ces voies de décomposition.

On a également étudié la photolyse dans l'ultraviolet du (ACB) entre 210 et 365 nm. En plus des produits trouvés dans la réaction thermique, le cyclobutane est également un produit principal et on mesure les rapports des produits en fonction de la longueur d'onde et du CO_2 ajouté. On discute et on compare les mécanismes de ces trois systèmes.

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Introduction

There have been few quantitative studies of the thermal decomposition of cyclic anhydrides of dicarboxylic acids, and except for a brief survey of a few mercury-photosensitized reactions (1), their gas-phase photochemistry has also been neglected. In a recent investigation of maleic anhydride in this laboratory (2), it was concluded that both the thermal and photochemical decomposition in the gas phase followed a simple concerted unimolecular path,

[1] Maleic anhydride $\rightarrow C_2H_2 + CO_2 + CO$

with E = 60.9 kcal/mol and $A = 2.14 \times 10^{14}$ s⁻¹ for the thermal process. With *cis*-1,2-cyclobutanedicarboxylic anhydride (hereafter CBA), the analogous decomposition would yield cyclobutene, but there is also the possibility of a second reaction path, cleavage of the cyclobutane ring. Simple two-channel unimolecular decompositions can be useful probes of energy distributions in thermal and photochemical reactions (3, 4). The present paper describes the thermal decomposition of CBA, a brief study of the decomposition induced by a

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pulsed CO_2 laser, and the photochemical decomposition in the ultraviolet region. Some of the results have been briefly presented elsewhere (3).

Experimental

The pyrolysis and uv photolysis were studied in simple static systems using apparatus and methods employed earlier with maleic anhydride (2). The uv light source was a Hg-Xe 1000 W lamp fitted with a monochromator. The infrared laser experiments were done in a cylindrical Pyrex vessel, 10 cm long and 4 cm in diameter, fitted with NaCl windows at each end. Radiation of 9.20 μ m from a Lumonics pulsed CO₂ TEA laser (4) was used unfocussed at a fluence of ~ 0.7 J/cm², or passed through a 2 m f. I. Ge lens placed 1 m from the reaction cell to give a slightly converging beam with a fluence in the reaction cell about 4 times higher. The reaction cell in all experiments was heated to 125°C to permit an adequate vapor pressure of CBA. CBA was obtained from Aldrich with a stated purity of 96% with the parent acid the main impurity; since the latter is much less volatile than the anhydride, the purity of the vapor used in our experiments was probably better than 99%. No other impurities could be detected by gas chromatography.

Results and discussion

The thermal decomposition

The only important primary product volatile at room temperature was ethylene, presumably formed by cleavage of the cyclobutane ring:

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Maleic anhydride was not positively identified as a product, but formation of C_2H_2 , CO_2 , and CO as secondary products as the reaction progressed was good evidence for its formation (2).

The only other primary hydrocarbon product found in significant amounts was 1,3-butadiene, which varied from about 0.15 to 0.03% of the ethylene. Comparable yields of CO and CO₂ were also observed, and there seems little doubt that these products come from cleavage of the anhydride ring:

$$[3] \qquad \bigcirc = C \xrightarrow{O} C = O \\ \longrightarrow C_4H_6 + CO_2 + CO$$

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It is not clear whether cyclobutene is an intermediate, as its thermal isomerization to butadiene is fast enough at the reaction temperatures to preclude its detection (5).

Figure 1 shows Arrhenius plots of k_2 , the firstorder rate constant based on C_2H_4 formation, and k_3/k_2 , given by C_4H_6/C_2H_4 . No significant variation with pressure was observed within the rather narrow range of pressure employed (2–7 Torr), nor when the surface/volume ratio was increased by a factor of 9 in a packed vessel. Reactions [2] and [3] thus appear to be occurring as homogeneous unimolecular reactions, and Arrhenius parameters of $A_2 = 1.14 (\pm 0.1) \times 10^{14} \text{ s}^{-1}$, $E_2 = 55.1 \pm 1$ kcal/mol, $A_3 = 8.40 (\pm 0.1) \times 10^{14} \text{ s}^{-1}$, and $E_3 =$ 67.5 ± 1 kcal/mol can be estimated from the plots in Fig. 1.

Reaction [2] is appreciably slower, with a lower A factor and higher E than the analogous decompositions (5) of cyclobutanecarboxaldehyde ($A = 2.7 \times 10^{14}, E = 53.3$) and of cyclobutylmethyl ketone ($A = 3.4 \times 10^{14}, E = 54.5$), both of which have carbonyl groups adjacent to the cyclobutane ring. This may reflect constraints on the resonance stabilization of the biradical imposed by the presence of the anhydride ring.

The activation energy of reaction [3] is 6.6 kcal/mol higher than that for the analogous decomposition of maleic anhydride; this is somewhat surprising since reaction [3] is only 14.1 kcal/mol endothermic² (to yield cyclobutene) compared with



FIG. 1. Arrhenius plots for k_2 (bottom) and k_3/k_2 (top) for the thermal decomposition of CBA. Solid points are for packed reaction vessel.

an endothermicity of 30.5 for reaction [1]. The higher activation energy is partially compensated by a higher frequency factor, about 4 times larger than for maleic anhydride. The energy required to open the almost strain-free anhydride ring (5) may be estimated as at least 75 kcal/mol, indicating that reaction [3], like reaction [1], probably proceeds by a concerted rather than a biradical mechanism, although the frequency factor is somewhat high. The rather high barrier to reaction may reflect the considerable distortion needed in the transition state for optimum incipient π bond formation in the cyclobutene product, which would require the two rings to lie normal to one another and the H atoms in the plane of the cyclobutane ring. Much less distortion would be required in the analogous decomposition of maleic anhydride.

The activation energy of reaction [2], and the *A*-factor, are compatible with a biradical process, but as with other cyclobutane derivatives, in the absence of firm evidence one way or the other, a concerted mechanism cannot be ruled out.

The infrared multiphoton decomposition

Products were the same as in the thermal reaction, with relatively more butadiene, between 0.1and 1% of the ethylene. The extent of decomposition, expressed as a probability of decomposition in a single pulse of a molecule in the laser beam, is

²Based on ΔH_l^0 for maleic anhydride of -96.8 kcal/mol and ΔH_l^0 for CBA of -98.6 (based on additivity relations), both in the vapour phase (6, 7).



FIG. 2. log-log plot of the probability of decomposition during a single laser pulse vs. the pressure of CBA. \Box , unfocussed beam; \bigcirc , converging beam with fluence increased by a factor of 4.

shown in Fig. 2 in a log-log plot as a function of pressure for the two fluences employed. A strong (\sim 5th-power) dependence on fluence is evident, and at both fluences the probability of decomposition fell off sharply with decreasing pressure. Figure 3 shows the variation with pressure of the ratio C_4H_6/C_2H_4 for the same experiments. The ratio at the highest pressures corresponds to effective "temperatures" of decomposition of 945 and 778 K at the high and low fluences respectively. At both fluences the C_4H_6/C_2H_4 ratio falls markedly with decreasing pressure, the decrease being more pronounced at the higher fluence. These trends are similar to those observed recently in the decomposition of cyclobutanone (8) and probably have similar causes; the small yields of C_4H_6 make the measurements too inaccurate to extend to the lower fluences and lower pressures required to see whether the similarity in the two systems is significant.

Photolysis in the ultraviolet

Figure 4 shows the absorption spectrum of CBA vapor measured at 3.02 Torr at 145°C in a cell 3.7 m long. The observed absorption almost certainly arises from a $\pi^* \leftarrow$ n transition. By analogy with the maleic anhydride spectrum (2) the broad absorption with $\varepsilon_{max} = 60$ at 230 nm and the very weak

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FIG. 3. Product ratio vs. pressure of CBA in the CO_2 laser induced decomposition. \Box , unfocussed beam; \bigcirc , converging beam with fluence increased by a factor of 4.



FIG. 4. Ultraviolet absorption spectrum of CBA vapor, measured at 3.02 Torr and 145°C, in units of $cm^{-1} M^{-1}$.

shoulder around 300 nm might be assigned to the $\pi^* \leftarrow n^+$ and $\pi^* \leftarrow n^-$ transitions respectively. However, the separation of 1.33 eV is much larger than might be expected from the photoelectric spectrum of succinic anhydride which shows a

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FIG. 5. Variation in product ratio with % reaction in the photolysis of CBA at 240 nm. Solid points are with added CO₂ at pressures of 10–100 Torr.

splitting of 0.81 eV, and it is difficult to see why the transition at 300 nm should be so much weaker. No structure was evident anywhere in the spectrum.

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Ethylene and butadiene again were products of the photodecomposition, and cyclobutene was also observed. The C₄ hydrocarbons were relatively much more important than in the thermal reaction, with the ratio (total C_4H_6)/ C_2H_4 ranging from 0.4 to 3.0, where total $C_4H_6 = 1,3$ -butadiene + cyclobu-tene. The yield of C_2H_4 was a linear function of photolysis time up to at least 5% conversion, but cyclobutene and butadiene have an unusual dependence on time (or % reaction) shown in Fig. 5 for the photolysis at 240 nm. The ratio cyclobutene/ $(total C_4H_6)$ fell sharply from a value of about 0.6 at the shortest photolysis time (7s), reached a minimum of about 0.3 after 1 or 2% reaction, and finally rose again to about its initial value. The ratio (total C_4H_6 /(total $C_4H_6 + C_2H_4$) showed a much smaller change; it appeared to rise slightly, then fall again, over the same range of photolysis times. Similar behaviour was observed at other wavelengths. The cause of these effects is obscure;³ it was discovered, however, that they essentially disappeared on the addition of CO₂ at pressures between 10 and 100 Torr.



F1G. 6. Product ratios vs. wavelength in the photolysis of CBA with added CO_2 .

For the photolysis at 240 nm under these conditions, values of cyclobutene/(total $C_4H_6) = 0.65$ and (total C_4H_6)/(total $C_4H_6 + C_2H_4$) = 0.69 were obtained, independent of CO₂ pressure, CBA pressure, and photolysis time. Similar measurements were made at other wavelengths from 210 to 366 nm, and the product ratios obtained are shown in Fig. 6.

The lack of pressure dependence of the product ratios in Fig. 6, and of the yield of decomposition, points to a short-lived excited state that decomposes before much stabilization by collision. Since there is no reason to expect an excited $\pi^* \leftarrow n$ state of a carbonyl compound to be dissociative itself, there must be fast internal conversion to high vibrational levels of the ground state which then rapidly dissociates.

The ratio (total C_4H_6)/(total $C_4H_6 + C_2H_4$) increases with increasing photon energy (Fig. 6) reaching a maximum of about 0.76 at 260 nm, then declines slightly. The frequency factors for reactions [2] and [3] in the thermal reaction would predict a maximum value of 0.88 for this ratio at infinite temperature. The observed values are probably compatable with a statistical decomposition of a highly excited ground-state molecule, the photon energy at 260 nm of 110 kcal/mol corresponding to excess energies of 55 and 42 kcal/mol for reactions [2] and [3] respectively. The slight decline in the product ratios at shorter wavelengths might suggest a different decomposition mechanism, favoring reaction [2], for photolysis in the $\pi^* \leftarrow \pi$ transition which probably begins to underlie the $\pi^* \leftarrow$ n transition at these wavelengths (Fig. 4).

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³To explain the observations, there must be a rapid secondary isomerization of cyclobutene to butadiene (which is then reversed at longer photolysis times) and which is eliminated by the addition of CO_2 . Gas phase thermal isomerization is too slow at 125°C; a surface process might be invoked if it could be inhibited by CO_2 adsorption on active sites. An isomerization of cyclobutene photosensitized by the maleic anhydride product building up in the system, which at 240 nm absorbs light much more strongly than CBA, and which could be quenched by CO_2 , is another possibility. It was not thought useful to pursue these effects further in the present study.

The ratio cyclobutene/(total C_4H_6) does not correspond to an equilibrium between cyclobutene and butadiene since at infinite temperature a maximum value of only 0.14 is predicted from the equilibrium constant at infinite temperature (5). It thus appears that cyclobutene is a primary product of a decomposition analogous to that of maleic anhydride. It also appears that butadiene is not formed by subsequent decomposition of vibrationally excited cyclobutene, since some pressure dependence would then have been expected, and a decrease in cyclobutene relative to butadiene with decreasing wavelength; it seems more probable that the two hydrocarbons are primary products of parallel unimolecular reactions. These may be the same reactions which occurred in the thermal decomposition, in which a concerted mechanism was favored on energetic grounds, and in which it was impossible to say whether butadiene, or cyclobutene, or both, were primary products, since any cyclobutene formed would have isomerized thermally to butadiene before analysis. The higher energy available in the photolysis, however, would permit biradical formation by opening of the anhydride ring, with subsequent decomposition to CO, CO_2 , and cyclobutene or butadiene, and such a biradical mechanism may well be operative.

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