Photolysis of cyclopentanone[1]

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The effect of wavelength and pressure on the distribution of products has been studied in the photolysis of cyclopentanone and cyclopentanone-2,2,5,5-d_4. At low pressures, C_2D_4 and C_2H_4 are formed in addition to the expected high pressure product $C_2H_2D_2$, confirming the intermediate formation of excited cyclobutane. The high pressure ratio of cyclobutane to ethylene is attributed to alternate reactions of the tetramethylene diradical which have equal energy sensitivity, and some evidence is presented for a further mechanism of ethylene formation at short wavelengths. Evidence is also presented for the formation of cyclobutane and ethylene following thermal re-excitation of the precursor of 4-pentenal.

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The vapor phase photolysis of cyclopentanone yields carbon monoxide, ethylene, cyclobutane (1), and 4-pentenal (2) and mechanisms, based on energetics (3), electronic states (4), and various diradical intermediates (1, 5), have been devised to explain these products. On the basis of quenching studies at 313 nm, Srinivasan (6) proposed a simple Stern–Volmer mechanism with unquenched species giving carbon monoxide (and ethylene and cyclobutane) and quenched species giving 4-pentenal. Recently, Mok (7) has elaborated this mechanism to include formation of 4-pentenal from both quenched and unquenched species. Srinivasan (3) also noted a temperature coefficient in the product yield, carbon monoxide being formed at the expense of 4-pentenal with increasing temperature. Since increased temperature has a marginal effect on the average energy of the absorbing molecules, this temperature effect must imply a re-excitation of that portion of the photo-excited species which had previously lost energy by collision. Carbon monoxide (and ethylene and cyclobutane) must therefore also have two origins, the original photo-excited and a thermally re-excited species.

Following the mechanisms of Srinivasan (6) and Mok (7), these species would be identified as different vibrational levels of the same electronic state. This would require collisional quenching and thermal excitation to occur simultaneously with the same molecule. Since this is clearly impossible it must be assumed that collisional quenching affects one species and thermal re-excitation another. The products of the photolysis may therefore be considered to arise from two separate precursors, one which bears the original photon energy and gives products according to the absorbed wavelength, and one which gives products according to the temperature. This doesn't imply that the former species is not transformed into the latter before product formation, but if it is, its lifetime precludes collision.

While positive identification of these two intermediates may be difficult, some evidence suggests that they may be the excited n,π^* singlet and triplet states. Rusbult and Lee (8) have estimated the non-radiative lifetime of the singlet to be 3×10^{-9} s and this species is, hence, an obvious choice for the collisionally quenchable species. The triplet, on the other hand, has been shown, by benzene triplet sensitization studies at room temperature, to give 4-pentenal (4) and is hence a possibility for the thermally excitable species. It is, however, reasonable to suppose that, by analogy with cyclohexanones (9–11), an acyl diradical, $\cdot CH_2CH_2CH_2CH_2CO\cdot$, may be the immediate precursor of stable products, and it is possible that this species has a sufficient lifetime for thermal excitation. The triplet might then be an alternate source, but not a necessary intermediate in the formation of the diradical. In solution, there is evidence for the intermediacy of the triplet in the diradical formation (12).

A further feature of the photolysis mechanism is the partitioning of the decomposition products between cyclobutane and ethylene. Above 5 Torr, this ratio is invariant with pressure, wavelength, and temperature (3), while below this pressure the ratio declines somewhat according to wavelength, presumably due to the decomposition of excited product cyclobutane to ethylene (13). The realization that cyclobutane arises from both a photo-excited and a thermally re-excited species

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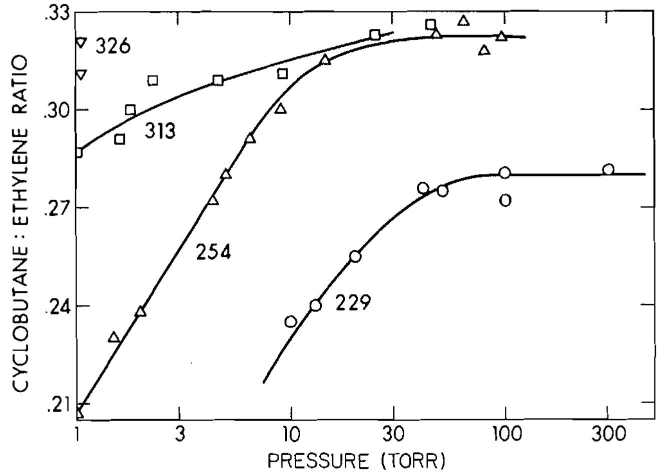

FIG. 1. Cyclobutane: ethylene ratio vs. pressure (Torr).

introduces the possibility that the constant high pressure ratio follows from the total formation of the products from the re-excited species under these conditions. To explore this mechanistic feature, the pressure effect has been examined in the photolysis of cyclopentanone-2,2,5,5-d_4 at 254 nm and in normal cyclopentanone from 326 to 229 nm, and the ratio of carbon monoxide to 4-pentenal has been examined from 326 to 254 nm.

Experimental

Commercial cyclopentanone was purified by preparative gas chromatography and was free of significant contaminants. Cyclopentanone-d_4 was prepared from this material by repeated exchange with D_2O (alkaline) and was shown by nuclear magnetic resonance spectroscopy to be better than 92% exchanged in the 2 and 5 positions. Heptane, used as an inert gas, was dried and distilled and was free of interfering contaminants.

Photolyses were carried out in a mercury-free metal–glass–teflon vacuum system. The photolysis cells were quartz, of volume 71 and 535 ml and were housed in aluminum block furnaces. The light sources were: (*a*) 229 nm: Osram low pressure cadmium with 1 cm Cl_2 filter; only absorbed impurities were 10% 227 nm and 0.5% 326 nm. (*b*) 254 nm: low pressure mercury arc with 1 cm Cl_2 and one 9-30 Corning filter, 0.5% other lines. (*c*) 307 nm: Osram low pressure zinc with one 0-53 Corning filter. (*d*) 313 nm: medium pressure mercury arc with one 0-54 filter, 2% at 302 nm. (*e*) 326 nm: Osram low pressure cadmium with four 0-54 filters, 0.2% at 313 nm. Photolysis times were several hours at both 229 and 326 nm due to very low extinction coefficients and were several minutes at the other wavelengths. Photolysis was carried to less than 2% conversion.

The products were separated at −80° into hydrocarbons (C_2H_4 and C_4H_8) and liquids (4-pentenal and cyclopentanone) and were then separately chromatographed on a 7 ft 1/4 in. diameter D.I.O.P. on Chromosorb *P* column, the hydrocarbons at room temperature and the liquids at 96°. In the photolysis of cyclopentanone-d_4, the product ethylenes were satisfactorily separated at −26° on a 75 ft 1/8 in. diameter nylon column packed with saturated $AgNO_3$ in ethylene glycol on Chromosorb *P*.

Results

Photolysis of cyclopentanone-2,2,5,5,-d_4 at 254 nm, 80°, and 11.2 Torr gave primarily $C_2H_2D_2$, with some C_2H_3D and C_2H_4 from less deuterated substrate. At 0.65 and 1.3 Torr, substantial yields of C_2D_4 and C_2H_4 in addition to $C_2H_2D_2$ were observed, suggesting approximately 14 and 10% cyclobutane decomposition at 0.65 and 1.3 Torr.

The effect of pressure on the ratio of the hydrocarbon products was investigated at 229, 254, 313, and 326 nm. This data, shown in Fig. 1, confirms the wavelength dependence previously noted (13) at 313 and 254 nm and shows the absence of the effect at 326 nm and the greater effect at 229 nm. Also, the constant high pressure ratio is confirmed in the range 326 to 254 nm, but a considerable decrease is noted at 229 nm at what is apparently the high pressure limit.

The relative yields of CO (i.e. C_4H_8 + 1/2 C_2H_4) and 4-pentenal were determined at 10 Torr and 25° and are listed in Table 1. The ratio at 313 nm is comparable to that reported by Srinivasan (3) and by Mok (7); the value at 254 nm is, however, considerably lower than their values, possibly because of a considerable contribution from longer wavelengths in their studies.

TABLE 1
Wavelength dependence of the product ratio

λ(nm)	4-Pentenal/CO
326	10.
313	1.4
307	1.0
254	0.02

Discussion

The observation of C_2D_4 and C_2H_4 in the photolysis of cyclopentanone-2,2,5,5-d_4 at 254 nm and at 0.65 and 1.3 Torr but not at 11.2 Torr confirms the partial decomposition of excited cyclobutane under conditions of low pressure and higher photon energy and hence qualitatively supports this reaction as the origin of the pressure effect in the cyclobutane–ethylene ratio. Quantitatively, the observed C_2D_4 would account for the ratio decrease at 1 Torr (see Fig. 1) if an isotope effect of 2 is assumed in the cyclobutane-d_4 decomposition.

The data in Fig. 1 confirm the wavelength dependence of the cyclobutane decomposition. At 326 nm and 1 Torr, the cyclobutane–ethylene ratio is at the high pressure value at longer wavelengths, suggesting no tendency for cyclobutane decomposition. This is in keeping with the exothermicity of the overall photo-reaction being just equal to the activation energy of the cyclobutane decomposition. The data at 313, 254, and 229 nm show a progressive trend to greater percentages of the cyclobutane decomposing at low pressures as the photon energy increases. At 229 nm, the high pressure limit is lower than observed with the longer wavelengths, and this suggests further complexity in the mechanism.

The effect of photon energy on the ratio of 4-pentenal to carbon monoxide (Table 1) fits the pattern that higher energy favors decomposition to carbon monoxide (3). The high ratio at 326 nm is reminiscent of the behavior of the benzene triplet sensitization system where the energy of the excited cyclopentanone is in the range of its triplet energy, 75 kcal/mole, and that of benzene, 85 kcal/mole. The small amount of carbon monoxide formed suggests that thermal re-excitation is not very important at room temperature. On the other hand, the almost trivial formation of 4-pentenal at 254 nm implies that the formation of that product directly from the photo-excited species, as observed by Mok (7) at 313 nm, is of little significance at shorter wavelengths. It also implies that at 10 Torr very little collisional deactivation of the excited singlet occurs and hence that the cyclobutane and ethylene arise from precursors bearing the full photon energy. Evidence from the cyclopentanone-d_4 and from Fig. 1 indicates that very little cyclobutane decomposition occurs under these conditions and hence it must be assumed that the cyclobutane to ethylene ratio in the products reflects the primary rates of formation from the highly excited species. At 313 nm, about the same ratio of cyclobutane to ethylene is obtained despite the 20 kcal/mole lower energy. It must therefore be assumed that cyclobutane and ethylene are formed in two parallel processes whose relative rates are insensitive to the energy of the precursor.

These aspects of the photolysis can be incorporated into a mechanism involving the several reactions of diradicals as is detailed in the approximate energy level diagram, Fig. 2.[2] The n,π^* excited singlet, as formed by photon absorption, presumably crosses over to a repulsive energy surface, potentially by way of the triplet, forming the acyl diradical $\cdot CH_2CH_2CH_2CH_2\dot{C}O$. Upon formation, this radical will bear excess energy characteristic of the absorbed energy, or of the thermally equilibrated excited state (n,π^*), minus the energy of the broken bond. Rearrangement of this biradical to 4-pentenal may then occur via a five-center cyclic transition state with a low Arrhenius A factor ($\sim 10^{11}$ s^{-1} due to loss of internal rotational degrees of freedom) and an activation energy determined primarily by the strain arising from formation of the five-member ring, >6 kcal/mole (15). Alternatively, the diradical may undergo a decarbonylation reaction, with an activation energy of 15 kcal/mole (by analogy with acetyl [16]) and a higher frequency factor, $\sim 10^{14}$ s^{-1}. This process would be expected to become increasingly significant with higher temperatures or decreasing wavelength of absorbed light, as is observed. The tetramethylene diradical so formed may then either decompose to ethylene or isomerize to cyclobutane; these processes occur with approximately equal activation energies (6.5 ± 1.5 kcal/mole) and frequency factors ($\sim 10^{12}$ s^{-1}) (14), in acceptable agreement with the observed

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[2] The heats of formation have been estimated from the group additivity tables of refs. 14 and 15.

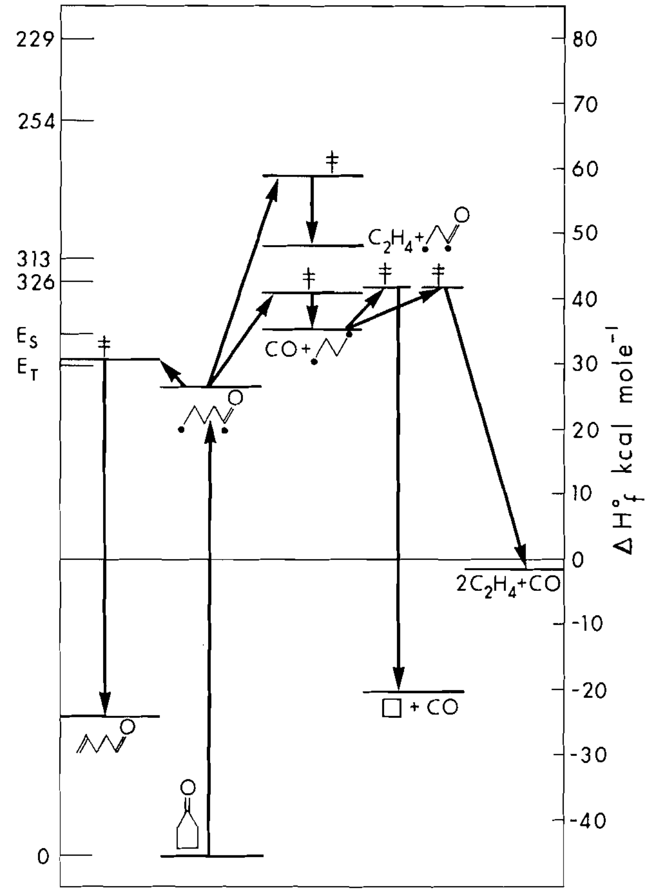

FIG. 2. The reaction mechanism (left-hand side: excited state energies and photon energies; right-hand side heats of formation).

high pressure ratio of cyclobutane: 1/2 ethylene of 0.64 (326 to 254 nm).

The increased yield of ethylene at 229 nm may be explained on the basis of a second decomposition reaction (eq. [1]) with an activation energy

$$[1] \quad \begin{aligned} &\underset{\cdot}{C}H_2CH_2CH_2CH_2\underset{\cdot}{C}O \rightarrow C_2H_4 + \underset{\cdot}{C}H_2CH_2\underset{\cdot}{C}O \\ &\underset{\cdot}{C}H_2CH_2\underset{\cdot}{C}O \rightarrow C_2H_4 + CO \end{aligned}$$

similar to that for the decomposition of *n*-butyl radical, ∼30 kcal/mole (17). Simple R.R.K. theory estimates of the relative rates of the decarbonylation, and this decomposition suggests, however, that this latter process must have an Arrhenius *A* factor in excess of 10^{15}; the reaction is hence somewhat unreasonable. The onset of a second primary reaction, such as the formation of the alternate diradical $\underset{\cdot}{C}H_2CH_2COCH_2\underset{\cdot}{C}H_2$, is possibly a more reasonable explanation of this feature. Current studies on the photolysis at shorter wavelengths (18) may further elucidate this aspect of the mechanism.

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