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The Photolysis of Cyclopentanone

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The 326.1 nm direct photolysis and the cadmium-photosensitized reactions of cyclopentanone have been compared in order to clarify the role of the triplet state of cyclopentanone in the photolysis. The products observed in the both photolyses were carbon monoxide, ethylene, cyclobutane, and 4-pentenal. The results obtained in the direct photolysis were very similar to those obtained in the cadmium photosensitization. The ethylene/cyclobutane ratio was not affected by the pressure and temperature changes. The 4-pentenal/CO ratio increased with a decrease in the temperature. These similarities suggest that the decomposition of cyclopentanone takes place through the lowest triplet state in both the photolyses. The efficiency of cyclopentanone in quenching triplet cadmium was found to be about 0.8 times that of *cis*-2-butene.

The photochemistry of cyclopentanone has been the subject of active investigations for forty years.[1,2] It has been found that gaseous cyclopentanone decomposes to carbon monoxide and ethylene or cyclobutane, or rearranges to 4-pentenal, upon irradiation with 313.0 nm light, which corresponds to a weak n-π^* transition.[1,2] In the cases of aliphatic ketones, such as acetone, it is believed that the decomposition takes place through the triplet state. In spite of many investigations, however, there still remains considerable doubt about the role of the triplet state in the cyclopentanone photolysis.

Since Srinivasan could not observe the effects of oxygen, he proposed that the excited singlet states with various vibrational levels are responsible for the product formations.[3] Recently, Chup Yew Mok reinvestigated the system in detail and observed small effects of the addition of oxygen and 1,3-pentadiene. As he pointed out, the results could not be used either to prove or to disprove the role of the triplet state during the photolysis of cyclopentanone.[4] He explained his results in terms of the first excited singlet state.[4] On the other hand, Lee found that triplet benzene sensitized the 4-pentenal formation and suggested that the cyclopentanone triplet was important as a reaction intermadiate.[5] From their detailed studies of the fluorescence emission, they also suggested that the rate of intersystem crossing from the first excited singlet to the triplet is very fast.[6] Frey *et al.* examined the photolysis of *trans*-2,3-dimethylcyclopentanone and found that the products, such as cyclopentanone-, 4-pentenal-, and cyclobutane-derivatives, contained the *cis-trans* isomers.[7] They proposed that the reaction intermediate is a biradical form which can rotate freely. The biradical intermediate assumption had already been made by Benson and Kistiakowsky and by Blacet and Miller.[8,9]

Since a triplet cyclopentanone will be formed even in the triplet cadmium photosensitization, it is expected that a comparison with direct photolysis will give further information about the cyclopentanone photolysis. In the case of acetone photolysis, the method of cadmium photosensitization has been successfully applied to the investigation of the triplet state.[10]

Experimental

The cyclopentanone (Tokyo Kasei Ind.) was distilled bulb-to-bulb, with the middle third retained, after treating it with diphosphorus pentoxide. Gas-chromatographic analysis showed a trace amount of water as an impurity. Pure-grade *cis*-2-butene (Takachiho Shoji Co.,) was used as supplied. The cyclohexane (Tokyo Kagaku Seiki Co., pure-grade) was passed through a 2-m-silica gel column before use.

The quartz reaction cell used was 5.0 cm long and 4.8 cm in diameter, with a total volume, including access tubing, of about 90 m*l*; it was inserted in an electric furnace kept at the desired temperature within ±1°C by means of an electric controller. A home-made cadmium discharge lamp, with argon (2 torr) as the buffer gas, was heated in a furnace kept at 270±2°C by means of an electric controller. The 228.8 nm resonance line and visible lines were filtered out by means of a combination of a Toshiba UV-D25 filter and a Pyrex plate, so that the emerging light was mainly the 326.1 nm resonance line.

The reaction products obtained were analyzed by means of a gas chromatograph using a column of 5 m propylene glycol at 65°C, after removing the non-condensable gases at −196°C with a Toepler pump.

In the cadmium photosensitization, the light intensity absorbed by cadmium was measured by using the *cis-trans* isomerization of *cis*-2-butene as the actinometer. The quantum yield was assumed to be 0.5.[11]

Results and Discussion

Cadmium Photosensitization. In the case of the cadmium photosensitization, it is necessary to elevate the reaction temperature in order to increase the vapor

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[9] F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

[10] S. Sato, C. Takahashi, and S. Tsunashima, This Bulletin, **43**, 1319 (1970).

[11] S. Tsunashima and S. Sato, This Bulletin, **41**, 284 (1968); H. E. Hunziker, *J. Chem. Phys.*, **50**, 1288, 1294 (1969).

TABLE 1. QUANTUM YIELDS OF PRODUCTS IN THE CADMIUM PHOTOSENSITIZATION

Temp. °C	$P_{c\text{-}C_5H_8O}$ Torr	$P_{c\text{-}C_6H_{12}}$ Torr	Quantum Yields CO			
			CO	C_2H_4	c-C_4H_8	C_4H_7CHO
273	1.89	0	0.15			
273	2.81	0	0.15	0.17		0.020
273	3.55	0	0.15	0.15	0.038	0.030
273	7.50	0	0.16	0.20	0.045	0.055
273	8.76	0	0.16	0.18	0.042	0.043
273	11.0	0	0.17	0.18		0.038
273	13.1	0	0.18	0.23	0.053	0.053
273	34.3	0	0.19	0.24	0.052	0.064
273	50.6	0	0.18	0.21		0.047
273	81.2	0	0.19	0.25	0.063	0.075
273	38.7	0	0.17	0.21	0.038	0.048
273	43.3	222	0.16	0.20	0.04	0.063
273	40.0	504	0.15	0.17	0.032	>0.062
295	41.8	0	0.21	0.25	0.048	0.052
315	45.3	0	0.25	0.30	0.055	0.051
333	44.5	0	0.28	0.34	0.061	0.039
352	47.2	0	0.29	0.36	0.068	0.032
352	41.4	0	0.30	0.36	0.065	0.029

pressure of cadmium metal. The thermal reactions of cyclopentanone at 273°C were found to be negligibly small. The products in the cadmium photosentitization were identified as carbon monoxide, ethylene, cyclobutane, and 4-pentenal, which were the same as those obtained in the 313.0 nm direct photolysis. The quantum yields of the product formations are listed in Table 1 as functions of the pressure and the temperature. The rate of carbon monoxide formation was almost constant at pressures higher than 10 Torr. A comparison with the case of the acetone photolysis[10] suggests that the effect of the light other than the 326.1 nm resonance line on the cyclopentanone photolysis is negligibly small in the present experiment. The quantum yield of carbon monoxide formation was 0.18 at 273°C. The relative yields of carbon monoxide, ethylene, cyclobutane, and 4-pentenal were almost constant at pressures above a few Torr; they were, respectively, 1.0, 1.2, 0.3, and 0.3 at 273°C.

TABLE 2. QUANTUM YIELDS OF PRODUCTS IN THE CADMIUM PHOTOSENSITIZATION IN THE PRESENCE OF *cis*-2-BUTENE AT 270°C[a)]

$P_{cis\text{-}2\text{-}C_4H_8}$ Torr	Quantum Yields CO			
	CO	C_2H_4	c-C_4H_8	t-2-C_4H_8
0	0.19	0.24	0.064	0
1.0	0.17	0.22	0.057	0.021
1.7	0.19	0.25	0.054	0.044
2.2	0.17	0.22	0.057	0.049
3.0	0.16	0.20	0.036	0.089
4.1	0.17	0.21	0.051	0.087
5.2	0.12	0.15	0.035	0.13
6.8	0.16	0.22	0.048	0.17
7.7	0.17	0.20	0.048	0.17
9.5	0.13	0.15	0.041	0.14
11.0	0.13	0.16	0.039	0.18
12.3	0.13	0.16	0.040	0.20

a) $P_{c\text{-}C_5H_8O}$=22.6 Torr

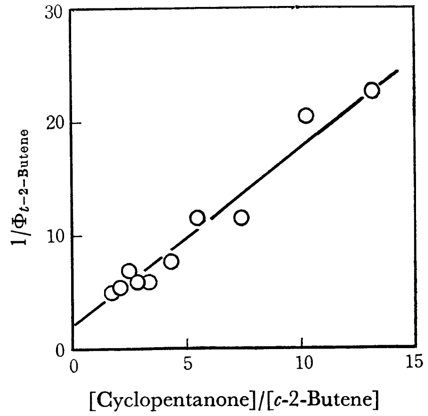

Fig. 1. Plots of the reciplocal of the quantum yield of *trans*-2-butene against the cyclopentanone/*cis*-2-butene pressure ratio.

When *cis*-2-butene was added to 22.6 Torr of cyclopentanone at 270°C, the quantum yields of the decomposition products (CO, ethylene, and cyclobutane) decreased with the increase in the quantum yield of *trans*-2-butene formation (Table 2). The reciprocal of the quantum yield of *trans*-2-butene is plotted against the cyclopentanone/*cis*-2-butene pressure ratio in Fig. 1. Obviously, a straight line was obtained. This result may be explained by the competitive quenching for triplet cadmium, as was discussed previously.[12)] From the slope of the straight line in Fig. 1, the relative quenching efficiency of cyclopentanone against that of *cis*-2-butene was calculated to be 0.8±0.2. The value is very large compared with that of paraffins and is close to that of olefins.[12)] This suggests that the cyclopentanone molecule interacts with triplet cadmium strongly and is excited to the triplet state:

$$\mathrm{Cd} + h\nu(326.1\,\mathrm{nm}) \longrightarrow \mathrm{Cd}^* \tag{1}$$

$$\mathrm{Cd}^* \longrightarrow \mathrm{Cd} + h\nu \tag{2}$$

$$\mathrm{Cd}^* + \mathrm{S}_0 \longrightarrow \mathrm{Cd} + \mathrm{T} \tag{3}$$

where Cd*, S_0, and T represent, respectively, triplet cadmium, and the ground state and the triplet state of cyclopentanone.

In the presence of *cis*-2-butene, the observed decrease in the quantum yield of the decomposition product agreed with that calculated assuming the competitive quenching for triplet cadmium within the limits of experimental error. That is, the reaction of the excited cyclopentanone is not affected by the presence of *cis*-2-butene.

As is shown in Table 1, the quantum yields of the products formation at lower pressures were slightly smaller than those at higher pressures. This difference may be explained in terms of Reaction (2).

The total quantum yields of CO and 4-pentenal were less than unity, even at the highest pressure examined. This suggests that a part of the triplet cyclopentanone formed loses its excitation energy without forming any product.

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12) S. Tsunashima and S. Sato, This Bulletin, **40**, 2987 (1967); S. Tsunashima, S. Satoh, and S. Sato, *ibid.*, **42**, 329 (1969).

In spite of the increase in the quantum yields of ethylene and cyclobutane formations with the increase in the temperature, the ethylene/cyclobutane ratio was independent of the temperature change. This suggests that the activation energy of the ethylene formation is slmost the same as that of the cyclobutane formation. It has been proposed that the tetramethylene diradical is an intermediate for the ethylene and cyclobutane formations:[7)]

$$\mathrm{T} \longrightarrow \mathrm{CO} + \dot{\mathrm{C}}\mathrm{H_2CH_2CH_2}\dot{\mathrm{C}}\mathrm{H_2} \qquad (4)$$

$$\dot{\mathrm{C}}\mathrm{H_2CH_2CH_2}\dot{\mathrm{C}}\mathrm{H_2} \longrightarrow 2\mathrm{C_2H_4} \qquad (5a)$$

$$\longrightarrow c\text{-}\mathrm{C_4H_8} \qquad (5b)$$

If the Process (4) occurs with a negligibly small activation energy, the Processes (5a) and (5b) should occur with an equal energy of activation.

The decomposition of cyclopentanone to carbon monoxide and ethylene is endothermic by 44.1 kcal/mol.[13)] The excess energy for the decomposition is 43.6 kcal/mol in the cadmium photosensitization. If the total spin is conserved during the reaction, one of the ethylenes formed should be in the triplet and should be almost in the perpendicular form, since the excitation energy of the lowest triplet ethylene decreases with an increase in the twisting angle around the C–C bond from about 106 to 43 kcal/mol.[14)]

In the presence of a large amount of cyclohexane, the quantum yield of the decomposition decreased, and that of 4-pentenal formation increased slightly; that is, the 4-pentenal/CO ratio increased. Since the products ratio of 4-pentenal/CO is independent of the competitive quenching of cyclohexane for triplet cadmium, the increase in the ratio suggests the presence of a collisional deactivation process for the 4-pentenal formation.

The results can, therefore, be explained in terms of the following simplified scheme:

$$\mathrm{T} \longrightarrow \mathrm{CO} + 2\mathrm{C_2H_4}(\text{or } c\text{-}\mathrm{C_4H_8}) \qquad k_d \qquad (6)$$

$$\longrightarrow \mathrm{C_4H_7CHO} \qquad k_i \qquad (7)$$

$$\longrightarrow \mathrm{S_0} \qquad k_s \qquad (8)$$

$$\mathrm{T} + \mathrm{M} \longrightarrow \mathrm{C_4H_7CHO} \qquad k_{mi} \qquad (9)$$

$$\longrightarrow \mathrm{S_0} + \mathrm{M} \qquad k_{ms} \qquad (10)$$

The steady-state treatment of the above mechanism gives the following equation:

$$\mathrm{R(4\text{-}pentenal)/R(CO)} = k_i/k_d + (k_{mi}/k_d)[\mathrm{M}] \qquad (11)$$

Using the data in Table 1, k_i/k_d is estimated to be 0.3 at 273°C. The value of k_{mi}/k_d may be very small, so that the second term on the right-hand-side of Eq. (11) is negligibly small, even at the pressure of 80 torr.

With the increase in the reaction temperature, the quantum yield of the decomposition increased and that of the 4-pentenal formation decreased; however, the decrease in the 4-pentenal formation was less than the increase in the quantum yield of the decomposition. The apparent activation energy for the 4-pentenal/CO ratio was estimated to be 9±3 kcal/mol. This may be explained by the difference in the activation energy between the Reactions (6) and (7) being 9 kcal/mol, on the assumption that the second term on the eight-hand-side of Eq. (11) is negligibly small. The second term is negligibly small at 273°C and at the pressures of cyclopentanone below 40 torr, as has been shown, and it is expected to decrease with an increase in the temperature, since the activation energy of Reaction (9) is probably smaller than that of Reaction (6).

326.1 nm Direct Photolysis. In the absence of cadmium vapor, carbon monoxide, ethylene, cyclobutane, and 4-pentenal were formed from cyclopentanone upon irradiation with the cadmium lamp. These products were the same as those obtained in the cadmium photosensitization, and also the same as those obtained in the 313.0 nm direct photolysis.[1,2)] The experimental conditions were the same except for the absence of cadmium. The rates of the product formation were less than those obtained in the cadmium photosensitization. The relative yields of the products are listed in Table 3.

Table 3. Relative Yields of the Products in the 326.1 nm Direct Photolysis

Temp. °C	$P_{c\text{-}\mathrm{C_5H_8O}}$ Torr	Relative Yields		
		$\mathrm{C_2H_4}/\mathrm{CO}$	$c\text{-}\mathrm{C_4H_8}/\mathrm{CO}$	$\mathrm{C_4H_7CHO}/\mathrm{CO}$
273	9.9	1.1	0.21	
273	37.9	1.5	0.21	
273	39.4	1.3	0.27	0.17
273	61.2	1.2	0.23	0.13
273	85.8	1.3	0.23	0.20
225	60.8	1.4	0.27	0.42
177	56.8	1.2	0.26	0.73

Assuming that the light intensity is the same as that in the cadmium photosensitization and that the value of ε is 4.7 l/mol cm,[15)] the quantum yield of the carbon monoxide formation was estimated to be about 0.6 at 273°C. This value may be an upper limit, since the light intensity absorbed has been underestimated in the above treatment.[10)]

The results obtained in the 326.1 nm direct photoolysis of cyclopentanone were very similar to those obtained in the cadmium photosensitization; *i.e.*, (1) the distributions of the products were almost the same at 273°C, (2) each product formation at 273°C was scarcely affected at all by the pressure change in either case, (3) the ethylene/cyclobutane ratios were constant whatever the pressure and temperature changes and were the same in both cases, and (4) the 4-pentenal/CO ratio decreased with the increase in the temperature, the apparent activation energy for the ratio in the direct photolysis being roughly 6 kcal/mol, slightly smaller than that obtained in the cadmium photosensitization. These similarities suggest that the precursor of the reaction products in the 326.1 nm direct photolysis is the same as that in the cadmium photosensitization.

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13) S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, New York (1968).

14) T. Terao, S. Hirokami, S. Sato, and R. J. Cvetanović, *Can. J. Chem.*, **44**, 2173 (1966).

15) C. Takahashi, S. Tsunashima, and S. Sato, unpublished data.

By the absorption of 326.1 nm light, the lowest excited singlet cyclopentanone may be formed in the direct photolysis. The excited singlet cyclopentanone will cross over to the triplet state or converge to the ground state with or without fluorescence emission. The triplet cyclopentanone thus formed will disappear through Reactions (6)—(10), as was assumed in the case of the cadmium photosensitization.

The small pressure effect on the 4-pentenal/CO ratio may be explained by the small value of k_{mi}/k_d. The apparent activation energy in the ratio can also be explained as in the case of the cadmium photosensitization.

The 4-pentenal/CO ratio at 273°C and the apparent activation energy in the ratio obtained in the direct photolysis were slightly smaller than those obtained in the cadmium photosensitization. These differences may arise from the difference in the excess energy of the triplet cyclopentanone formed.[16] This difference in the excess energy may be small, however, because only small differences were observed between the two photolyses.

Comparison with 313.0 nm Direct Photolysis. In the case of the 313.0 nm direct photolysis of cyclopentanone, almost the same results were obtained as in the 326.1 nm photolyses, except for the pressure effect upon the 4-pentenal/CO ratio.

In the 313.0 nm photolysis, the 4-pentenal/CO ratio increased with the increase in the pressure at 123.8°C.[3] Chup Yew Mok has explained the pressure dependence of the ratio by a relation which is essentially the same as Eq. (11), although the assumed the singlet cyclopentanone to be the precursor of the reaction products; he found that the rate-constant ratio, which corresponds to k_{mi}/k_d in Eq. (11), decreased with an increase in the temperature.[4] A similar temperature dependence of the k_{mi}/k_d ratio was considered in the 326.1 nm photolyses. The differences in the reaction temperature and in the excitation energy may be enough to explain the difference in the 4-pentenal/CO ratio. It is not necessary to assume a different reaction mechanism for the 313.0 nm photolysis.

Srinivasan assumed that the reaction products were formed from the first excited singlet state, with various vibrational levels in the 313.0 nm photolysis.[3] His discussions were based on the fact that the effect of oxygen on the reaction was comparable to those of inert gasses.[3] Similar effects were obtained by Chup Ye Mok, using oxygen and 1,3-pentadiene.[4] These results cannot, however, conclusively exclude the presence of a triplet precursor for the reaction products, as was pointed out by Chup Yew Mok.[4] If oxygen and 1,3-pentadiene are inefficient in quenching the triplet cyclopentanone and/or if the lifetime of the triplet cyclopentanone is very short, the effect of oxygen or 1,3-pentadiene on the reaction can be expected to be small. If the excited singlet cyclopentanone is the precursor for the decomposition, the rate of the decomposition should be faster than that of the intersystem crossing. Lee *et al.* suggested that the rate of the intersystem crossing in cyclopentanone is very fast, as it is in acetone.[6] As was discussed in the previous sections, the assumption of the triplet precursor explains well the results of cyclopentanone photolyses.

Consequently, it may be said that the triplet state is responsible for the reaction products in the cyclopentanone photolysis, as is in the case of acetone.

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[16] D. C. Montague and F. S. Rowland, *J. Amer. Chem. Soc.*, **91**, 7230 (1969).