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The Cadmium-photosensitized Decomposition of Acetone

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The cadmium-photosensitized decomposition of acetone has been studied and compared with the 3261 Å direct photolysis at 270±1°C. The data could be consistently explained by the following reaction mechanism:

$$Cd(^3P_1) + CH_3COCH_3 \longrightarrow Cd + {}^3A^* \quad (1)$$
$$^3A^* \longrightarrow 2CH_3 + CO \quad (2)$$
$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2 \quad (3)$$
$$2CH_3 \longrightarrow C_2H_6 \quad (4)$$
$$CH_3 + CH_3COCH_2 \longrightarrow C_2H_5COCH_3 \quad (5)$$
$$2CH_3COCH_3 \longrightarrow (CH_3COCH_2)_2 \quad (6)$$

The mechanism from (2) to (6) is exactly the same as that proposed for the 3130 Å direct photolysis at temperatures higher than 100°C. By using the *cis-trans* isomerization of 2-butene as the actinometer, the quantum yield of the photosensitized decomposition of acetone was estimated to be 0.3. Kinetic analysis showed that the energy-rich ethane produced by the recombination reaction (4) has the lifetime of 2×10^{-8} sec at 270°C.

In a previous series of papers,[1] we have reported the reactions of various hydrocarbons photosensitized by cadmium ($^3P_1$). Since the electronic energy tranferred in the cadmium photosensitization is only 87.7 kcal/mol, most of the hydrocarbons investigated did not decompose appreciably. The chemical changes observed thus far have been the *cis-trans* isomerizations of 2-butene and 2-pentene, the hydrogen-atom scrambling of dideuteroethylene, and the formations of vinylacetylene and benzene from acetylene.

In this paper, we have experimented with acetone as the reactant in the expectation that its decomposition may take place because of the low dissociation energy of the C–C bond attached to the carbonyl. The photochemistry of acetone has extensively been studied, and its reaction mechanism has almost been completely established.[2] Therefore, acetone was thought to be a suitable subject for the first application of the cadmium photosensitization of compounds containing oxygen atoms.

Experimental

Acetone (Koso Chemical Co.) was distilled bulb-to-bulb, with the middle third retained. Gas-chromatographic analysis showed no measurable impurities. Pure-grade *cis*-2-butene (Matheson Ltd.) was used as supplied.

The quartz reaction cell mounted in a furnace was 9.0 cm long and 4.8 cm in diameter, with a total volume, including acess tubing, of 175 m*l*. The cell was attached to the vacuum line through a greaseless stopcock equipped with a Viton diaphragm.

A home-made cadmium discharge lamp, with argon (2 mmHg) as the buffer gas, was used. The lamp was heated in another furnace which was kept at 270°C (within ±2°C) by an electric controller. The 2288 Å resonance line was filtered out by a UV-29 Toshiba glass filter, so that the emitting light was mainly the 3261 Å resonance line.

Products from the photolyses were analyzed by gas chromatography after removing the noncondensable gases at 77°K (carbon monoxide and methane) with a Toepler pump. The amounts of carbon monoxide and methane were measured using a gas buret attached to a cuprous oxide furnace at 280°C. In this furnace carbon monoxide is selectively oxidized to carbon dioxide, which is condensable at 77°K.

Since the extinction coefficient of acetone is strongly dependent on the temperature, it was measured using a combination of a set of slits, a photomultiplier (Toshiba MS-9SY), and a micro-ammeter. In the cadmium photosensitization, the light intensity absorbed by cadmium atoms was measured by using the *cis-trans* isomerization of 2-butene as the actinometer. The quantum yield was assumed to be 0.5.[1,3]

Results

Extinction Coefficients of Acetone. Since a monochromator was not used, the impinging light

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[1] S. Tsunashima and S. Sato, This Bulletin, **40**, 2987 (1967); **41**, 284, 2281 (1968); S. Tsunashima, S. Hirokami and S. Sato, *Can. J. Chem.*, **46**, 995 (1968); S. Tsunashima, S. Satoh and S. Sato, This Bulletin, **42**, 329, 1531 (1969).

[2] E.W.R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Co., New York (1954).

[3] H.E. Hunziker, *J. Chem. Phys.*, **50**, 1288, 1294 (1969).

was not only the 3261 Å resonance line, but was contaminated by the lights which were not absorbed by acetone. To estimate the molar extinction coefficient, therefore, the following equation was used:

$$I^{\text{obs}} - I = (I_0^{\text{obs}} - I)10^{-\varepsilon[A]l}$$

Here, I^{obs} and I_0^{obs} are the light intensities obtained in the presence and in the absence of acetone respectively. I is the intensity in the presence of a large amount of acetone. ε is the molar extinction coefficient, [A] is the concentration of acetone, and l is the length of the cell. Table 1 summarizes the obtained values. Although the 3261 Å resonance line is contaminated by weak lines at 3466 and 3613 Å,[4] which are in the absorption band of acetone, the extinction coefficients obtained are in fair agreement with the reported value[5] (about 0.6 l mol^{-1} cm^{-1} at 3261 Å at 25°C).

TABLE 1. EXTINCTION COEFFICIENTS OF ACETONE AT 3261 Å.*

Temperature °C	Extinction Coefficient ε $l$mol^{-1}cm^{-1}
36	0.57
85	0.67
117	0.80
165	1.02
212	1.32
224	1.42
255	1.67
270	1.80
281	1.91

* The light is from a Cd resonance lamp through a Toshiba UV-D25 glass filter.

Direct Photolysis. The results are summarized in Table 2. The products observed were carbon monoxide, methane, ethane, methyl ethyl ketone, and a compound with a high melting point which was not identified. The formations of ethylene, hydrogen, ketene, and biacetyl were not observed. Since the quantum yield of carbon monoxide is believed to be unity above 100°C,[5] the light intensity at 3261 Å of this lamp was estimated using the data of Table 1 and those of Runs No. 2, 13, 12, 11 and 10 in Table 2, their acetone concentrations being almost constant in the cell ($3.02 \pm 0.02 \times 10^{-3}$ moll^{-1}). The estimated value was 0.55 ± 0.03 μEinstein min^{-1}.

TABLE 2. THE 3261 Å DIRECT PHOTOLYSIS OF ACETONE

Run No.	Acetone mmHg	Temperature °C	Products μmol min$^{-1}\times10^2$			
			CO	CH_4	C_2H_6	MEK*
6	2.46	270	0.25	0.26	0.06	0.05
4	5.11	270	0.40	0.55	0.06	0.12
8	7.68	270	0.59	0.88	0.10	0.14
3	10.1	270	0.74	1.07	0.08	0.20
9	15.1	270	1.20	1.42	0.11	0.31
1	19.1	270	1.27	1.90	0.22	0.25
5	47.7	270	2.63	4.47	0.19	0.58
7	62.3	270	3.48	5.96	0.15	n.d.
2	102	270	5.68	10.2	0.27	1.10
13	103	270	6.00	9.97	0.17	1.07
12	89.8	202	4.36	5.67	0.55	1.71
11	80.6	155	3.30	2.78	1.26	1.48
10	74.1	108	2.37	1.01	1.88	0.58

* Methyl ethyl ketone

Cadmium-sensitized Photolysis. In order to check the thermal reaction, a few mmHg of acetone were kept in the cell at 270°C for several hours in the presence of cadmium, but no decomposition was detected. The photolysis results are summarized in Table 3. The products observed were the same as those obtained in the direct photolysis. The light intensity absorbed by cadmium atoms was estimated to be 0.21 ± 0.01 μEinstein min^{-1}. Figure 1 shows the quantum yield of carbon monoxide as a function of the acetone pressure. The curve A was obtained from the data shown in Table 3. Obviously the quantum yield above 10 mmHg increases linearly with the increase in the pressure of acetone. The curve B shows the results of another series of experiments using a different lamp, the light intensity absorbed by cadmium being 0.12 μ-Einstein min^{-1}. In the latter case, the increase in the quantum yield of carbon monoxide was not appreciable. This discrepancy will be discussed in the next section.

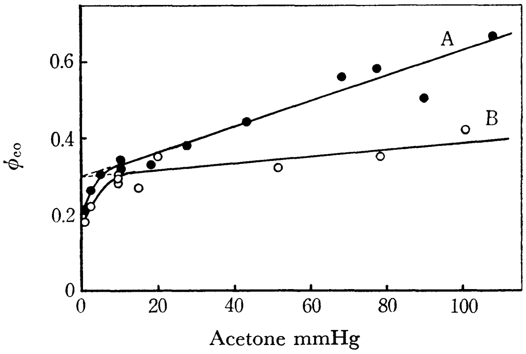

Fig. 1. The quantum yield of carbon monoxide in the cadmium photosensitized decomposition of acetone. For A and B, see the text.

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[4] S. Tsunashima, Ph. D. Thesis, Tokyo Institute of Technology (1968).

[5] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York (1966).

[6] S. W. Benson, "Advances in Photochemistry," Vol. 2 ed. by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., Interscience Publishers, New York (1964).

Table 3. The cadmium-photosensitized decomposition of acetone at 270°C.

Run No.	Acetone mmHg	Products μmol min$^{-1}\times 10^2$			
		CO	CH_4	C_2H_6	MEK
25	1.14	4.44	1.87	2.36	0.3
23	2.38	5.38	2.68	3.62	1.10
18	4.90	6.20	4.00	3.28	1.59
21	10.1	7.14	6.86	2.57	2.82
29	10.1	6.65	6.00	2.14	2.50
26	18.6	6.89	7.50	1.77	2.51
22	27.4	7.90	9.48	1.35	3.16
20	43.0	9.33	12.0	1.32	2.94
27	68.3	11.8	17.5	1.03	3.65
19	77.5	12.2	17.2	0.67	2.95
28	89.9	10.4	16.5	0.52	n.d.
24	108	14.0	21.8	0.98	3.73

Discussion

The first absorption band of acetone extends from 3500 Å to 2200 Å. Therefore, if the broadening of the 3261 Å resonance line is large, direct photolysis will take place even in the presence of a large amount of cadmium vapor. The broadening of the resonance line is known to be very sensitive to the pressure of the buffer gas, the shape of the lamp, and the condition of discharge. In this experiment, we prepared two cadmium resonance lamps. The data presented here were obtained with the one of the higher intensity except for the curve B in Fig. 1. As has been stated in the Results section, the light intensity absorbed by acetone was 0.55 μEinstein min^{-1}, while that used for the cadmium photosensitization was 0.21 μEinstein min^{-1}. This difference may be attributed mainly to the broadening of the resonance line from the lamp. Thus, the increase in the quantum yield of carbon monoxide with the increase in the pressure of acetone can be interpreted in terms of the direct photolysis by the light which is not absorbed by cadmium. The difference in the slope between the curves A and B is explained by the difference in the broadening of the resonance line from the two lamps. The true quantum yield of carbon monoxide formed by the cadmium photosensitization is, therefore, obtained by extrapolating the curve obtained at higher pressures of acetone to zero pressure. Obviously the two curves point to the same value, 0.3.

The 3130 Å direct photolysis of acetone at temperatures higher than 100°C has been established to occur through the following reaction mechanism:[2)]

$$CH_3COCH_3 + h\nu \longrightarrow {}^1A^* \qquad (1)$$

$$ {}^1A^* \longrightarrow {}^3A^* \qquad (2)$$

$$ {}^3A^* \longrightarrow 2CH_3 + CO \qquad (3)$$

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2 \qquad (4)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (5)$$

$$CH_3 + CH_3COCH_2 \longrightarrow C_2H_5COCH_3 \qquad (6)$$

$$2CH_3COCH_2 \longrightarrow (CH_3COCH_2)_2 \qquad (7)$$

The quantum yield of the decomposition through the excited singlet state is known to be small.[5)] The fluorescence and the phosphorescence, which are not shown in the above mechanism, are also known to be very small compared with the decomposition.[5)] The quantum yield of carbon monoxide, therefore, is believed to be nearly unity. Although, in the present study of the 3261 Å direct photolysis, the quantum yields have not been measured, the products observed correspond well with the mechanism described above. In the cadmium photosensitization, the formation of the excited state of acetone may be written as follows:

$$CH_3COCH_3 + Cd({}^3P_1) \longrightarrow {}^3A^* + Cd \qquad (8)$$

The successive reactions will, then, be the same as has been described above from the reactions (3) to (7). We will show below that the data presented in the previous section can be consistently explained by this mechanism.

Since the quantum yields calculated from the data have some ambiguities, the relative yields will now be discussed. Figure 2 shows the relative rates of the formation of methane, ethane, and methyl ethyl ketone against that of carbon monoxide as a function of the pressure of acetone. The curves obtained in the two photolyses, direct and cadmium-photosensitized, are obviously different from each other. However, the material balance:

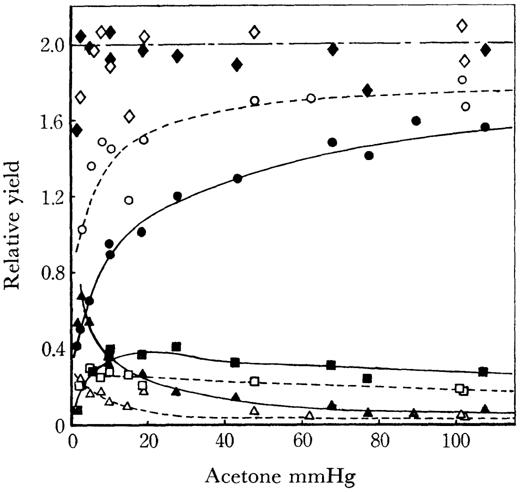

Fig. 2. Relative yields of products as a function of the pressure of acetone; open signs for the direct photolysis and filled signs for the cadmium photosensitization.

○, ● for CH_4

△, ▲ for C_2H_6

□, ■ for $C_2H_5COCH_3$

◇, ◆ for $[CH_4]+2[C_2H_6]+[C_2H_5COCH_3]$

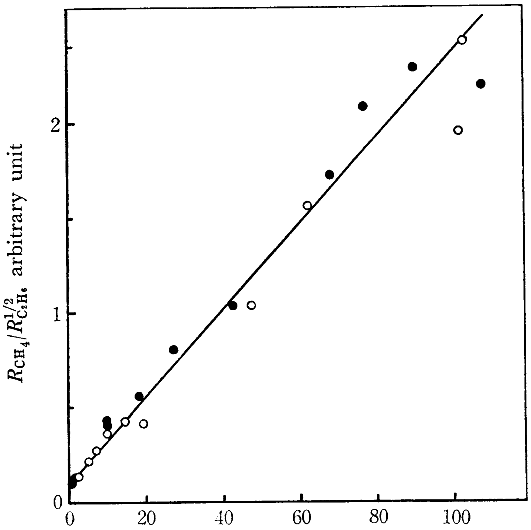

Fig. 3. The plots for $R_{CH_4}/R^{1/2}_{C_2H_6}$ against the pressure of acetone.

○ for the direct photolysis

● for the cadmium photosensitization

$$2[CO] = [CH_4] + 2[C_2H_6] + [C_6H_5COCH_3]$$

which is derived from the reaction mechanism proposed, holds rather nicely. This is also shown in Fig. 2. Moreover, the plots of the $[CH_4]/[C_2H_6]^{1/2}$ ratio against the pressure of acetone coincide with each other on a single straight line. This is shown in Fig. 3. The following equation is obtained by the steady-state treatment of the reaction mechanism proposed:

$$R_{CH_4}/R^{1/2}_{C_2H_6} = (k_4/k_5^{1/2})[A] \qquad [I]$$

Here, R_{CH_4} and $R_{C_2H_6}$ are the rates of the formation of methane and ethane, and k_4 and k_5 are the rate constants of the reactions (4) and (5). From the slope of the linear relationship in Fig. 3, the value for $(k_4/k_5^{1/2})$ is calculated to be 0.25 $l^{1/2}$ $(\text{mol sec})^{-1/2}$. The literature values for k_4 and k_5 are $10^{8.88}\exp(-10.0/\boldsymbol{RT})$ and $10^{10.5}\ l\ (\text{mol sec})^{-1}$.[6] Therefore, the value for $(k_4/k_5^{1/2})$ at 270°C 0.58 $l^{1/2}$ $(\text{mol sec})^{-1/2}$, a value which is in reasonable agreement with the value obtained in the present experiment. From the above discussion, it can be concluded that the apparent discrepancy between the two types of photolysis in the relative rate of the formation of the products is not essential, but is due to the difference in the concentrations of radicals in the steady states of the two photolyses. The light intensity used for the decomposition in the cadmium photosensitization is constant, while in the direct photolysis the intensity depends upon the pressure of acetone.

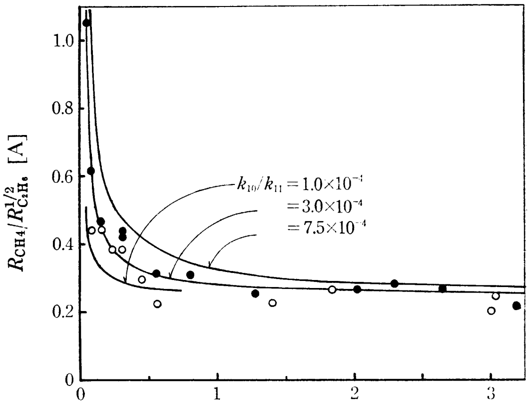

Fig. 4. The plots for the estimation of the lifetime of the energy-rich ethane molecule.

○ for the direct photolysis

● for the cadmium photosensitization

According to Eq. [I], the linear relationship in Fig. 3 should not have a definite intercept at the zero pressure of acetone. However, if the following mechanism:

$$2CH_3 \longrightarrow C_2H_6^* \qquad (9)$$

$$C_2H_6^* \longrightarrow 2CH_3 \qquad (10)$$

$$C_2H_6^* + CH_3COCH_3 \longrightarrow C_2H_6 + CH_3COCH_3 \qquad (11)$$

is assumed in place of the reaction (5), the existence of the intercept can be understood. Moreover, the lifetime of the energy-rich ethane formed in the reaction (9) can be estimated. If the reactions (9), (10) and (11) are included, the steady-state treatment gives Eq. [II] instead of [I]:

$$\frac{R_{CH_4}}{R^{1/2}_{C_2H_6}[A]} = \frac{k_4}{k_9{}^{1/2}}\left(1 + \frac{k_{10}}{k_{11}[A]}\right)^{1/2} \qquad [II]$$

In Fig. 4, the left-hand side of Eq. [II] is plotted against the concentration of acetone, [A]. Obviously at higher concentrations, the value of Eq. [II] remains around 0.25, but as the concentration of acetone decreases the value is rapidly increased. As is shown in Fig. 4, the best fit-curve is obtained by assuming the k_{10}/k_{11} ratio to be 3×10^{-4}. If every collision between energy-rich ethane and acetone is effective for the stabilization, then, by assuming the collision frequency to be $10^{11.3}\ l\text{mol}^{-1}\ \text{sec}^{-1}$,[6] the lifetime of energy-rich ethane molecules at 270°C can be calculated to be 2×10^{-8} sec.