The Cadmium-photosensitized Decomposition of Acetaldehyde, Propionaldehyde, and *n*-Butyraldehyde

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The reactions of acetaldehyde, propionaldehyde, and *n*-butyraldehyde photosensitized by cadmium ($^3P_1$) have been investigated at 270 °C. The pressure dependence of the main products, CO, RH (R=CH_3, C_2H_5, and *n*-C_3H_7) and R_2, was well explained by the following reaction mechanism; Cd*+RCHO→R+CHO+Cd or RH+CO+Cd. R+RCHO→RH+RCO, RCO→R+CO, CHO→H+CO, H+RCHO→H_2+RCO, R+R→R_2 or RH+Olefin. Carbon dioxide was found to be a rather good quencher for triplet cadmium atoms, and was used for estimating the relative quenching efficiencies of the three aldehydes and acetone. The values obtained were 0.16, 1.0, 1.3, 1.2, and 1.4, respectively for carbon dioxide, acetone, acetaldehyde, propionaldehyde, and *n*-butyraldehyde, when the efficiency of *cis*-2-butene was assumed to be unity.

Since the available energy is only 87.7 kcal/mol in the cadmium($^3P_1$)-photosensitization, an appreciable bond scission cannot be observed in the reactions of hydrocarbons photosensitized by cadmium($^3P_1$).[1] When acetone[2] and cyclopentanone[3] were used, however, the decompositions could be observed and their quantum yields were estimated to be about 0.3 for both compounds.

The photolyses of the aldehydes including the mercury- and the acetone-photosensitizations, have long been studied by many investigators and their reaction mechanisms have almost completely been established.[4] However, no studies have been reported on the reactions of the aldehydes photosensitized by cadmium. In a previous paper,[1] were compared the quenching efficiencies of several hydrocarbons for Hg($^3P_1$), Cd($^3P_1$) and triplet benzene, and found that, although the energy transferred in the reaction with Cd($^3P_1$) is closer to that from triplet benzene ($^3B_{1u}$; 84.4 kcal/mol) than that from Hg($^3P_1$), the quenching efficiencies for Cd($^3P_1$) have more similar tendencies with those for Hg($^3P_1$) than those for triplet benzene.

The present authors hoped to ascertain whether the reaction mechanism previously proposed for the photolysis of the aldehydes can be applied also for the cadmium-photosensitization and, if possible, to find out the detailed mechanism of the energy transfer from Cd($^3P_1$) to the carbonyl compounds.

Experimental

The commercially available acetaldehyde (Wako Pure Chemical), and *n*-butyraldehyde (Koso Chemical) were used without purification. The gas chromatographic analysis showed that the impurity content was less than 0.5%. Since the propionaldehyde (Tokyo Kasei) contained a large amount of impurity, this reagent was purified by gas chromatography. All aldehydes were kept in traps at the temperature of liquid nitrogen after bulb-to-bulb distillations.

The *cis*-2-butene, carbon dioxide, ethane, ethylene, propane, and *n*-butane were purchased from the Takachiho Chemical Co. Metallic cadmium (5-nine) was the product of the Osaka Asahi Metal Co.

The experimental procedure was almost the same as described previously.[3] All runs were made at 270±1 °C, using two home-made resonance lamps. Since a combination of a Toshiba UV-25 filter and a Pyrex glass plate was used as a filter, the irradiating light mainly consisted of a 326.1 nm resonance line. The light intensities from the two resonance lamps were 0.21 and 0.34μ Einstein/min which were measured by using the *cis-trans* isomerization of *cis*-2-butene photosensitized by cadmium, the quantum yield being assumed to be 0.5.[5] The relative intensity of the light through the reaction vessel was also measured by the combination of a slit, a Toshiba M.S. 9SY photomultiplier and a micro-ammeter.

The columns used for the gas chromatographic analyses were 5m-polypropylene glycol for oxygenated compounds, 30m-dimethylsulfolane, and 5m-activated alumina for hydrocarbons.

Results

Before starting photochemical studies, the thermal decomposition of aldehydes was checked in the dark. Very small amounts of products were observed in the case of acetaldehyde. The amount was less than 10^{-3} times that of the photolysis. The results were not reproducible, probably because the reactions were not homogeneous.

The results of the cadmium-photosensitized reactions are summarized in Table 1. In order to obtain the accurate quantum yield of ethane in the case of acetaldehyde, another series of experiments were carried out. The result is shown in Fig. 1. In the cadmium-photosensitization, the direct light absorption by al-

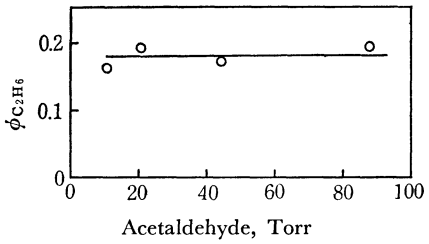


Fig. 1. The quantum yield of ethane in the Cd-photosensitized decomposition of acetaldehyde.

1) S. Tsunashima and S. Sato, This Bulletin, **40**, 2987 (1967).
2) S. Sato, C. Takahashi, and S. Tsunashima, *ibid.*, **43**, 1319 (1970).
3) S. Tsunashima, O. Ohsawa, C. Takahashi, and S. Sato, *ibid.*, **46**, 83 (1973).
4) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", John Wiley & Sons, Inc., 1967, p. 369.
5) S. Tsunashima and S. Sato, This Bulletin, **41**, 284 (1968).

Table 1. The quantum yields of CO, RH, R_2, H_2, and other products in the cadmium-photosensitized decomposition of three aldehydes

Acetaldehyde pressure (Torr)	Light intensity: 0.21 μ Einstein/min, Quantum yield			
	CO	CH_4	C_2H_6	H_2
22.4	5.33	4.95	n.d.[a]	0.19
46.3	13.58	12.62	0.2	n.d.[a]
113	32.80	30.88	0.4	n.d.[a]
264	83.70	82.92	n.d.[a]	n.d.[a]
482	133.3	139.5	0.5	0.68
Propionaldehyde pressure (Torr)	**Light intensity: 0.34 μ Einstein/min, Quantum yield**			
	CO	C_2H_6	n-C_4H_{10}	H_2
10.3	1.11	0.91	0.22	0.22
19.4	1.49	n.d.[a]	n.d.[a]	0.18
20.3	1.42	1.26	0.16	0.10
49.8	2.61	2.59	0.11	0.38
103	4.52	n.d.[a]	n.d.[a]	n.d.[a]
***n*-Butyraldehyde pressure (Torr)**	**Light intensity: 0.34 μ Einstein/min, Quantum yield**				
	CO	C_3H_8	C_2H_4	C_3H_6	H_2
10.0	1.06	0.89	0.01	0.003	0.14
20.2	1.70	1.35	0.04	0.014	0.19
21.1	2.03	1.65	0.06	0.015	0.03
48.9	3.08	2.97	0.07	0.023	0.25
96.6	5.53	3.88	0.04	0.024	0.25
144	7.64	7.41	0.08	0.047	0.34

a) n.d.: not determined.

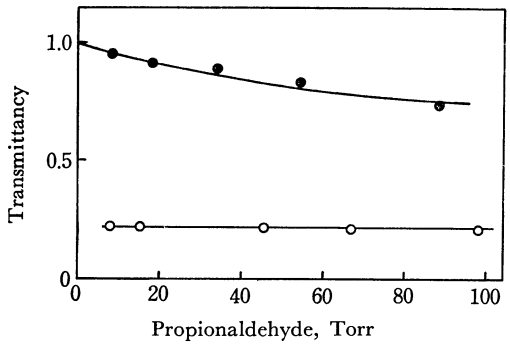


Fig. 2. The relative intensity of transmitted light as a function of propionaldehyde pressure in the presence (○) and in the absence (●) of cadmium vapor.

dehydes might play a role in the formation of the products. To estimate this contribution, we measured the relative intensity of the light which passed through the reaction vessel. As Fig. 2 shows, the relative light intensity in the presence of the cadmium vapor was independent of the pressure of propionaldehyde. This result suggests that the direct photolysis in this system is negligibly small compared with the decomposition induced by the $Cd(^3P_1)$.

In order to obtain the quenching efficiencies of the aldehydes for $Cd(^3P_1)$, a mixture of *cis*-2-butene and acetaldehyde was irradiated; however, the data obtained were much complicated by the reactions of the produced radicals. After several trials, carbon dioxide was found to be a rather good quencher for $Cd(^3P_1)$ without any products. Figure 3 shows the

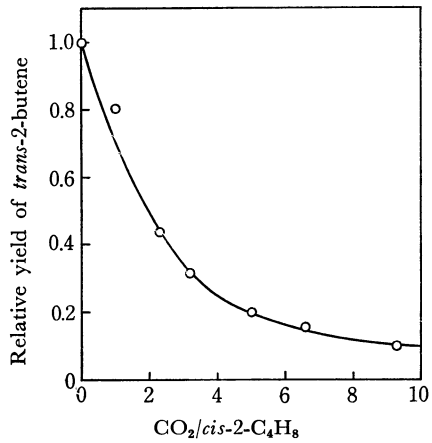


Fig. 3. The effect of carbon dioxide on the *cis-trans* isomerization of *cis*-2-butene photosensitized by cadmium.

effect of carbon dioxide on the relative rate of the formation of *trans*-2-butene from *cis*-2-butene photosensitized by $Cd(^3P_1)$. A simple kinetic analysis showed that the relative quenching efficiency of carbon dioxide for $Cd(^3P_1)$ is 0.16 ± 0.01, when the efficiency of *cis*-2-butene is assumed to be unity. The kinetic treatment will be shown later.

The similar experiments were carried out with the mixture of acetone and CO_2. The reciprocal of the relative rate of the formation of carbon monoxide was plotted in Fig. 4 as a function of the pressure ratio of CO_2 to acetone. The relative quenching efficiency of acetone was calculated to be 1.0 ± 0.1. Table 2

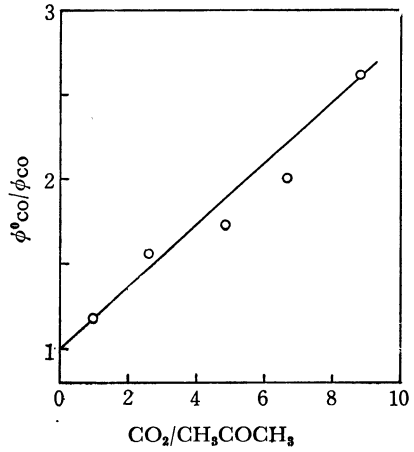


Fig. 4. The effect of carbon dioxide on the reaction of acetone.

TABLE 2. THE EFFECT OF CARBON DIOXIDE ON THE FORMATION OF CO IN THE CADMIUM-PHOTOSENSITIZED DECOMPOSITION OF THREE ALDEHYDES AND THAT ON THE FORMATION OF CH_4 IN THE CASE OF ACETALDEHYDE

The initial pressure of aldehyde is 20 Torr

CO_2/CH_3CHO	$\phi^0_{CH_4}/\phi_{CH_4}$	ϕ^0_{CO}/ϕ_{CO}
1.0	1.04	1.04
2.7	1.12	1.15
5.1	1.27	1.28
6.8	1.33	1.34
9.8	1.46	1.53

CO_2/C_2H_5CHO	ϕ^0_{CO}/ϕ_{CO}
1.0	1.04
2.6	1.22
5.1	1.26
7.6	1.63
9.9	1.88

CO_2/n-C_3H_7CHO	ϕ^0_{CO}/ϕ_{CO}
1.0	1.08
2.7	1.16
5.4	1.33
8.2	1.57
9.7	1.68
11.4	1.90

ϕ^0: the quantum yield in the absence of CO_2.

summarizes the results of the cadmium-photosensitized decomposition of the three aldehydes in the presence of CO_2.

In order to check the insensitivity of CO_2 to the radical reactions, the effect of CO_2 on the direct photolysis of propionaldehyde was also investigated. No effect was observed within the experimental error.

Discussion

As has been shown in the Results section, all of the aldehydes studied decomposed in chain mechanism, and the main products were CO, RH (R=CH_3, C_2H_5, and n-C_3H_7, respectively, for acetaldehyde, propionaldehyde, and n-butyraldehyde), and R_2. To explain the results of the cadmium-photosensitized reactions, we considered the following reaction scheme,

$$\begin{aligned}
Cd + h\nu &\longrightarrow Cd^* && I\\
Cd^* + RCHO &\longrightarrow CdH + RCO && \alpha \\
&\longrightarrow R + CHO + Cd && \beta \quad \Big\} \; k_q\\
&\longrightarrow RH + CO + Cd && \gamma \\
R + RCHO &\longrightarrow RH + RCO && k_1\\
RCO &\longrightarrow R + CO && k_2\\
R + R &\longrightarrow R_2 && k_3(1-\eta)\\
&\longrightarrow RH + Olefin && k_3\,\eta\\
CHO &\longrightarrow H + CO && k_4\\
CdH &\longrightarrow Cd + H && k_5\\
H + RCHO &\longrightarrow H_2 + RCO && k_6
\end{aligned}$$

Because of high temperature, the RCO, CHO, and CdH radicals were assumed to decompose unimolecularly.[4]

The steady state treatment gives the equations,

$$\phi_{CO} = (2\alpha+2\beta+\gamma) + \{(\alpha+\beta)/Ik_3\}^{1/2}k_1[RCHO] \quad (1)$$

$$\phi_{RH} = (\alpha+\beta) + \gamma + \{(\alpha+\beta)/Ik_3\}^{1/2}k_1[RCHO] \quad (2)$$

$$\phi_{R_2} = (1-\eta)(\alpha+\beta) \quad (3)$$

Here, ϕ_{CO}, ϕ_{RH} and ϕ_{R_2} denote the quantum yields of CO, RH and R_2. Figure 5 shows the predicted linear relationship between ϕ_{CO} and [RCHO], from which we can estimate the values of $(\alpha+\beta)$, γ and $k_1/k_3^{1/2}$ by assuming the η values. The quantum yield of ethane from the reaction of acetaldehyde has already been shown in Fig. 1. Since $\eta=0$ in this case,

$$\phi_{C_2H_6} = \alpha + \beta = 0.18 \pm 0.01$$

This value may be more accurate than that estimated using Eq. (1) or (2). In the case of n-butylaldehyde,

$$\phi_{C_3H_6} = \eta(\alpha+\beta) \quad (4)$$

By taking $\eta=0.16$,[6] we can calculate that $\alpha+\beta=0.14\pm 0.04$. Also in the reaction of n-butyraldehyde, the formation of ethylene was observed. This compound may be formed in the following initial process,

$$CH_3CH_2CH_2CHO + Cd^* \rightarrow CH_3CHO + C_2H_4 + Cd \quad \delta$$

The δ value is about 0.06. Table 3 summarizes all of the estimated values.

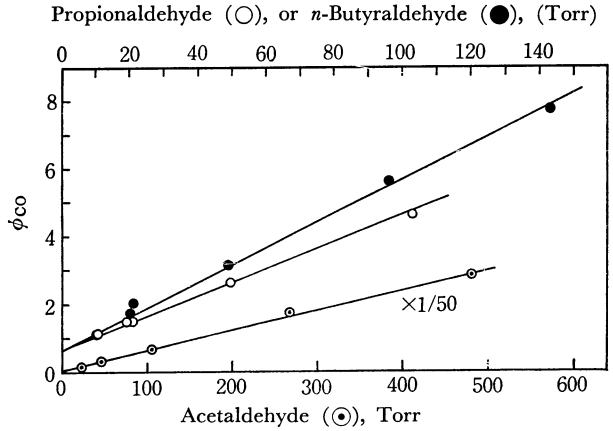


Fig. 5. The quantum yields of carbon monoxide in the cadmium-photosensitized decomposition of three aldehydes as functions of their pressures.

6) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," Vol. 1, edited by G. Porter, Pergamon Press, 1961, p. 105.

TABLE 3. THE QUANTUM YIELDS OF THE INITIAL PROCESSES, $\alpha + \beta$, γ AND δ

	$\alpha+\beta$	γ	δ
Acetaldehyde	0.18	0.1	—
Propionaldehyde	0.14[a]	0.4[a]	—
n-Butyraldehyde	0.14[a]	0.5[b]	0.06

a) Experimental error is ±20%. b) ±50%.

It is known that, in the direct photolysis at the wavelengths longer than 300 nm, the β process is the most prominent among the three initial processes, α, β and γ.[4] However, Table 3 suggests that, in the cadmium photosensitization, the γ process is one of the important processes, although the experimental errors preclude the quantitative estimation. Since the γ process contradicts the spin-conservation rule, the above result is not self-evident. Our reasoning for this is that, since CO is a good quencher for $Cd(^3P_1)$,[7] the intermediate complex between Cd* and CO may be formed in the course of the γ process,

$$RCHO + Cd^* \rightarrow \left(\begin{matrix} R \\ H \end{matrix}\!\!>\!C\!-\!O \atop \vdots\ Cd\right)^* \rightarrow RH + (CO\cdots Cd)^*$$

and then this complex decomposes into CO and Cd after crossing over the potential barrier between the triplet and the singlet states. This reasoning is obviously based on the assumption that the energy transfer from $Cd(^3P_1)$ to an aldehyde occurs through the interaction of $Cd(^3P_1)$ with a π electron in the C=O bond of the aldehyde. On the basis of this reasoning and of the smallness of the quenching efficiency of any alkanes to the $Cd(^3P_1)$ atom,[1] it may safely be said that the contribution of the α process to the decomposition of aldehydes is negligibly small compared with the β process.

The Competition between CO_2 and Other Molecules in Quenching $Cd(^3P_1)$ Atoms. When CO_2 is added into the system of the Cd-photosensitized isomerization of 2-butene, CO_2 compete with 2-butene in quenching $Cd(^3P_1)$. The reaction scheme may be described as follows:

$Cd + h\nu \longrightarrow Cd^*$	I
$Cd^* \longrightarrow Cd + h\nu$	k_0
$Cd^* + CO_2 \longrightarrow Cd + CO_2$	k_C
$Cd^* + cis \longrightarrow Cd + {}^3B$	k_{cis}
$Cd^* + trans \longrightarrow Cd + {}^3B$	k_{trans}
${}^3B + M \longrightarrow 1/2\,cis + 1/2\,trans + M$	

Here, *cis*, *trans* and ^3B denote *cis*- and *trans*-2-butene and the triplet state, respectively. The steady state treatment on the assumption that $k_{cis}=k_{trans}=k_B$ and that $k_0 \ll k_B$[butene] at butene pressures higher than 1 Torr,[1] gives the relation:

$$\frac{I\,t}{[\text{butene}]\,\log\left(\frac{C-T}{C_0-T_0}\right)} = 1 + \frac{k_C[CO_2]}{k_B[\text{butene}]} \qquad (5)$$

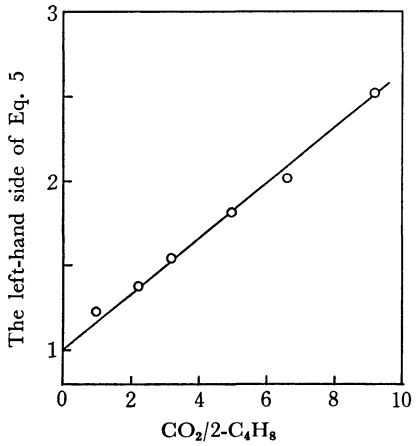


Fig. 6. The effect of carbon dioxide on the reaction of *cis*-2-butene.

Here, t is the reaction time, and C_0, C, T_0 and T are the initial and final concentrations of *cis*- and *trans*-2-butene. The predicted linear relationship between the left-hand side of Eq. (5) and the $[CO_2]$/[butene] ratio is shown in Fig. 6, from which we can calculate the quenching ratio of k_C/k_B to be 0.16±0.01 as has already been stated in the Results section.

The relative quenching efficiency of acetone was obtained by measuring the quantum yield of CO produced in the reaction of acetone in the presence of CO_2.

$$Cd^* + CH_3COOCH_3 \rightarrow 2\,CH_3 + CO \qquad k_A$$

The steady state treatment predicts the relationship:

$$\frac{\phi^0_{CO}}{\phi_{CO}} = 1 + \frac{k_A[\text{acetone}]}{k_C[CO_2]} \qquad (6)$$

The result has already been shown in Fig. 4.

In the case of three aldehydes, the kinetic treatment is not so simple, because these three compounds decompose in chain mechanism. Although it is a little complicated, a straight forward steady state treatment gives the relationship:

$$\phi_{CO} = \frac{2\alpha+2\beta+\gamma}{1+mx} + \sqrt{\frac{\alpha+\beta}{Ik_3(1+mx)}}\,k_1[RCHO] \qquad (7)$$

Here, $m=k_C/k_q$ and $x=[CO_2]/[RCHO]$. Then, using the notations:

$$y = \phi^0_{CO}/\phi_{CO}$$

and

$$c = \frac{1}{2\alpha+2\beta+\gamma}\sqrt{\frac{\alpha+\beta}{Ik_3}}\,k_1[RCHO]$$

which corresponds to the ratio between the ϕ_{CO} observed and the intercept obtained in Fig. 5, we can obtain

$$y = \frac{(1+c)(1+mx)}{1+c(1+mx)^{1/2}} \qquad (8)$$

This equation may be rewritten as follows:

$$1 + mx = \frac{y}{1+c} + \frac{1}{2}\left(\frac{cy}{1+c}\right)^2 + \left(\frac{cy}{1+c}\right)^2\left(\frac{1+c}{c^2y}+\frac{1}{4}\right)^{1/2} = z \qquad (9)$$

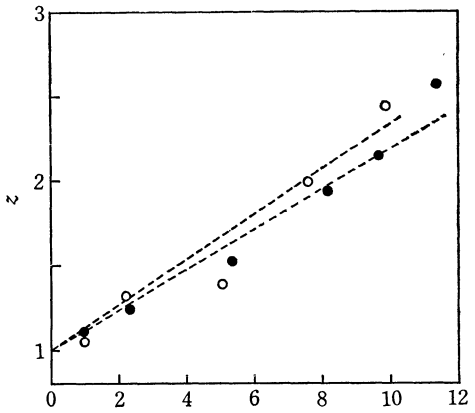
Since the right-hand side of Eq. (9), which is denoted

7) S. Tsunashima, T. Toyono, and S. Sato, This Bulletin, **46**, 2654 (1973).

by z, can be calculated from the observed values, the quenching ratio, m, can also be estimated from the plots of z as a function of x. In the case of acetaldehyde, the c value is much larger than unity, as has been shown in Fig. 5. Equation (8), therefore, may be simplified in the form:

$$1 + mx = y^2 \qquad (10)$$

Figures 7 and 8 show the plots for Eqs. (9) and (10). The relative quenching efficiencies thus obtained are listed in Table 4, together with those of other compounds previously obtained.



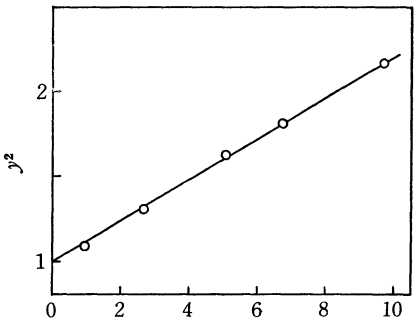
$CO_2/C_2H_5CHO(\bigcirc)$ or $CO_2/C_3H_7CHO(\bullet)$

Fig. 7. The Effects of carbon dioxide on the reactions of propionaldehyde and *n*-butyraldehyde.

Table 4. The relative quenching efficiencies for Cd ($^3P_1$)

cis-2-Butene	(1.00)
Ethylene	1.0
1,4-Butadiene	1.1
Propane	<0.001
Cyclopentanone	0.8[a)]
Acetone	1.0[a)]
Acetaldehyde	1.3[a)]
Propionaldehyde	1.2[a)]
Butyraldehyde	1.4[a)]
Carbon Dioxide	0.16

a) Experimental error is ±15%.



CO_2/CH_3CHO

Fig. 8. The effects of carbon dioxide on the reactions of acetaldehyde.