Mercury- and Cadmium-Photosensitized Reactions of β-Propiolactone

Shunzo YAMAMOTO,* Rinko GOHDA, Rie MORIKAWA, Hiroshi TAKAHOSO, Yoshimi SUEISHI, and Norio NISHIMURA
Department of Chemistry, School of Science, Okayama University, 3-1-1, Tsushima-naka, Okayama 700
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The mercury- and cadmium-photosensitized reactions of β-propiolactone (PL) have been investigated. The gaseous products from the mercury-photosensitized reaction were carbon dioxide, ethylene, carbon monoxide, ethylene oxide, acetaldehyde, and methane, while the products obtained in the cadmium-photosensitized reaction were carbon monoxide, ethylene oxide, and acetaldehyde. In the mercury-photosensitized reaction, the quantum yields of the products were independent of the lactone pressure at pressures higher than 1500 Pa, while in the cadmium-photosensitized reaction, the quantum yields of the products decreased with the increase in the lactone pressure. Several possible reaction schemes have been proposed to explain the above kinetic behavior. The mercury- and cadmium-photosensitized reactions proceed through different intermediates, that is, a triplet lactone in the former and an excited complex between an excited cadmium atom and a lactone molecule in the latter.

Recently we have studied the mercury- and cadmium-photosensitized reactions of γ-butyrolactone(BL) and found that the mercury-photosensitized reaction gives carbon dioxide, cyclopropane, and propylene, while the cadmium-photosensitized reaction gives carbon monoxide, and ethylene.[1] We concluded that the mercury-photosensitized reaction proceeds through a lactone triplet state, while the cadmium-photosensitized reaction proceeds through an excited complex between an excited cadmium atom and a lactone molecule.

The present study was undertaken to see whether other simple lactones behave similarly.

Experimental

The mercury-photosensitized reaction was carried out at 100° C in a conventional cylindrical quartz vessel, 10 cm long and 4 cm in diameter, fitted with plane quartz windows at each end. A low pressure mercury lamp (Toshiba Electric Co., germicidal lamp) made from a quartz tube was used. The 184.9 nm resonance line was filtered out by means of a Vicor filter. The light intensity absorbed by mercury atoms at 253.7 nm was determined by means of *cis*-2-butene actinometry.[2]

The cadmium-photosensitized reaction was carried out at 235° C in a cylindrical Pyrex cell, 2 cm in diameter and 20 cm long. A U-shaped cadmium discharge lamp made of Pyrex, filled with 670 Pa Ar, was used. The light intensity absorbed by cadmium atoms at 326.1 nm was determined by means of *cis*-2-butene actinometry.[3]

Product analysis was done by fractionation at −196 and −89° C, and messurement by gas buret and gas chromatography. The first portion, non-condensable at −196° C, was collected by the use of a Toepler pump. This portion consisted of carbon monoxide and methane, and it was analyzed by combustion over copper oxide at 250° C. The products in the second portion, which was not condensable at −89° C, were analyzed by means of gas chromatography, using a 6-m column of Gasukuro-pack 55 (Gasukuro Kogyo Co., LTD) at 100°C. The third portion, which was condensable at −89 °C, contained a large amount of PL; it was not analyzed.

β-Propiolsctone(PL)(Sigms Chem. Co., Grade II) was dried over a molecular sieve 4A and purified by means of trap-to-trap distillation. A known amount of liquid propiolactone was injected into a capillary by the use of a microsyringe, fully degassed by many careful freeze-pump cycles, and completely transfered to the cell. The pressure of PL in the cell was calculated by means of the perfect-gas equation.

Results and Discussion

The Mercury-Photosensitized Reaction. Since the vapor pressure of PL is low at room temperature, it is necessary to elevate the reaction temperature in order to obtain sufficient vapor pressure. As was been mentioned above, the mercury-photosensitized reaction was studied at 100° C. The thermal decomposition at this temperature and the direct photolysis at 253.7 nm were found to be negligible. The major volatile products observed in the mercury-photosensitized reaction of PL were carbon dioxide, ethylene, carbon monoxide, acetaldehyde, ethylene oxide, and methane. The yields of these products increased linearly with increase in the resction time and the light intensity, showing that they are primary products. The quantum yields of all products except for carbon monoxide and methane increase with the increase in the lactone pressure up to 1500 Pa, while they are independent of the lactone pressure above 1500 Pa. The increase in the rate of product formation with the increase in the lactone pressure at pressures below 1500 Pa may be explained in terms of the increase in the rate of the energy transfer from $Hg(^3P_1)$ to lactone with the increase in the lactone pressure and/or in terms of the increase in the absorption intensity by mercury atoms as a results of the pressure broadening of the absorption line. The relative yields of products are shown in Fig. 1 as a function of the lactone pressure. Ethylene is always formed in amounts equimolar with carbon dioxide. The relative yields of ethylne oxide and acetaldehyde reach a constant value of about 0.12 above 1500 Pa, and fall slightly at lower pressures, while that of carbon monoxide decreased rapidly with the increase in the lactone pressure below 1500 Pa and reaches an almost constant value of at pressures higher than 1500 Pa. (Methane was found at pressures lower than 5000 Pa. The yield of methane decrease with the increase in the

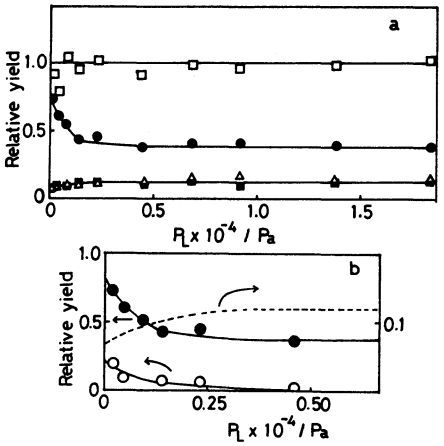


Fig. 1. Pressure dependence of relative quantum yields of products in the mercury-photosensitized reaction of PL.
a; ethylene (□), CO (●), ethylene oxide (△), and acetaldehyde (■). b; CO (●) and methane (○). Dashed line in b shows pressure dependence for ethylene oxide and acetaldehyde.

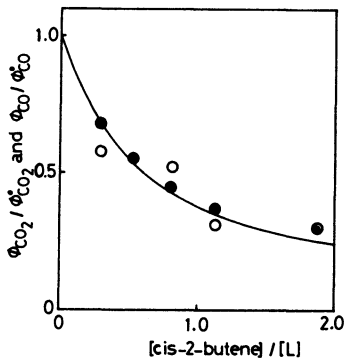


Fig. 2. Quantum yields of CO_2 (●) and CO (○) in the mercury-photosensitized reaction of PL in the presence of *cis*-2-butene.

lactone pressure and reached zero at about 5000 Pa)

When *cis*-2-butene was added to lactone, the quantum yields of carbon dioxide and carbon monoxide decreased as the quantum yield of *trans*-2-butene formation increased with the increase in the *cis*-2-butene pressure. From the slope of the reciprocal plot of the quantum yield of *trans*-2-butene vs. the lactone/*cis*-2-butene ratio, the quenching efficiency of lactone relative to that of *cis*-2-butene was estimated to be 0.62. Figure 2 shows the effect of *cis*-2-butene on the yields of carbon dioxide and carbon monoxide. The solid line shows the relative quantum yields calculated using the relative quenching efficiency of lactone obtained above. As Fig. 2 shows, the decrease in the quantum yields observed in the presence of *cis*-2-butene can be explained by the competitive quenching of the triplet mercury atom by lactone and *cis*-2-butene.

When oxygen was added to lactone, the quantum yields of the products decreased. For example, when 1333.3 Pa of oxygen was added to 4000 Pa of lactone, the following ratios of yields were obtained:

ϕ/ϕ°=0.87 (carbon dioxide), 0.75 (ethylene), 0.82 (ethylene oxide), and 0.85 (acetaldehyde). Here, ϕ° is the quantum yield in the absence of oxygen. These values are in good agreement with the ratio (0.81) calculated using the following relative quanching efficiencies of lactone and oxygen:

$$\sigma(\text{lactone})/\sigma(\textit{cis}\text{-2-butene}) = 0.62$$
$$\sigma(\text{oxygen})/\sigma(\textit{cis}\text{-2-butene}) = 0.45^{4)}$$

The decrease in the quantum yields can again be explained by the Competitive quenching of the triplet mercury atoms by lactone and oxygen. These findings show that the nature of the formation of these products was not affected by the addition of *cis*-2-butene and oxygen.

In order to explain the experimental results, the following set of reactions is proposed:

$$Hg(^1S_0) + h\nu(253.7\text{ nm}) \longrightarrow Hg(^3P_1), \quad (1)$$
$$Hg(^3P_1) \longrightarrow Hg(^1S_0) + h\nu(253.7\text{ nm}), \quad (2)$$
$$Hg(^3P_1) + L \longrightarrow Hg(^1S_0) + {}^3L, \quad (3)$$
$${}^3L \longrightarrow CO_2 + C_2H_4, \quad (4)$$
$${}^3L \longrightarrow CO + C_2H_4O^*, \quad (5)$$
$$C_2H_4O^* \longrightarrow CH_4 + CO, \quad (6)$$
$$C_2H_4O^* + L \longrightarrow \triangle_O + L, \quad (7)$$
$$C_2H_4O^* + L \longrightarrow CH_3CHO + L, \quad (8)$$
$$C_2H_4O^* + L \longrightarrow \text{other products}. \quad (9)$$

Here, ^3L denotes triplet lactone, while $C_2H_2O^*$ is an energy-rich intermediate. From this mechanism, the following equations can be derived:

$$\frac{\phi C_2H_4}{\phi CO_2} = 1.0, \quad (10)$$
$$\frac{\phi\triangle_O}{\phi CO_2} = \frac{k_5}{k_4}\frac{k_7[L]}{k_6+(k_7+k_8+k_9)[L]}, \quad (11)$$
$$\frac{\phi CH_3CHO}{\phi CO_2} = \frac{k_5}{k_4}\frac{k_8[L]}{k_6+(k_7+k_8+k_9)[L]}, \quad (12)$$
$$\frac{\phi CO}{\phi CO_2} = \frac{k_5}{k_4}\left(1+\frac{k_6}{k_6+(k_7+k_8+k_9)[L]}\right). \quad (13)$$

These equations show that the yield of ethylene is equal to that of carbon dioxide, and that the relative yields of acetaldehyde and ethylene oxide increase with the increase in the lactone pressure and reach a constant value at higher pressures, while the relative yield of carbon monoxide decreases with the increase in the lactone pressure and becomes constant (k_5/k_4) at higher pressures. These pressure dependences are consistent with those observed (Fig. 1). The decrease in the yield of methane observed (Fig. 1) is parallel to that of carbon monoxide at lower pressures, as was predicted by the above reaction mechanism. From the constant values of the relative yields at higher pressures, some ratios of

Table 1. Ratios of Rate Constants

$k_5/k_4=0.38$
$k_7/(k_7+k_8+k_9)=k_8/(k_7+k_8+k_9)=0.33$
$k_7:k_8:k_9=1:1:1$

rate constants are obtained; they are listed in Table 1.

The fate of the $C_2H_4O^*$ formed in Reaction (5) at high pressures requires some comment. Reactions (7) and (8), simple rearrangements (or stabilizations) to acetaldehyde and ethylene oxide, are suggested as the sources of these products, and because the sum of ethylene oxide and acetaldehyde was always less than carbon monoxide, Reaction (9) is suggested.

One possibility for Reaction (9) is a reaction with lactone to give higher products which were not observed.

Another possibility is the formation of vinyl alcohol, CH_2=CHOH, which would probably have been lost by polymerization before or during analysis. Although vinyl alcohol is about 84 kJ mol^{-1} less stable thermodynamically than acetaldehyde, the formation of either compound through the biradical($\cdot CH_2CH_2O\cdot$) which is considered to be formed from $C_2H_4O^*$ before formation of acetaldehyde in the thermal decomposition of ethylene oxide[5] should be quite exothermic; both would require hydrogen transfer through three-membered transition states, which might be about equally probable:

$$\overset{\cdot\cdot}{C}H_2CH\text{-}O \longrightarrow CH_3CHO, \quad (14)$$
$$\cdot\cdot H\cdot\cdot$$

$$CH_2\text{-}\overset{\cdot\cdot}{C}H\text{—}O \longrightarrow CH_2\text{=}CHOH. \quad (15)$$
$$\cdot\cdot H\cdot\cdot$$

As Table 1 shows, the rate of Reaction (9) is equal to that of Reaction (8). This seems to show that the second case is more possible, although the existence of vinyl alcohol has not been reported in the reaction of ethylene with the oxygen atom,[6] the mercury-photosensitized reaction of ethylene oxide,[7] etc.[8,9]

From the above mechanism, the following relationship can be derived:

$$\frac{\phi CO}{\phi\Delta_O+\phi CH_3CHO}=\frac{k_7+k_8+k_9}{k_7+k_8}+\frac{2k_6}{k_7+k_8}\frac{1}{[L]}. \quad (16)$$

From the slope of the line shown in Fig. 3, $2k_6/(k_7+k_8)$=906 Pa was obtained. As is shown in Table 1, $k_7=k_8$. Therefore, $k_6/k_7=k_6/k_8$=906 Pa. The experimental value of k_6/k_7 gives $k_6=7.14\times10^7$ s^{-1} when 7.9×10^4 s^{-1} is adopted as the kinetic collision frequency at 1 Pa snd 100° C and when a collision deactivation efficiency of unity is assumed for lactone.

The excess energy of energized intermediate ($C_2H_4O^*$) can be estimated using

$$k_6(E)=A\left(1-\frac{E_a}{E}\right)^{s-1}, \quad (17)$$

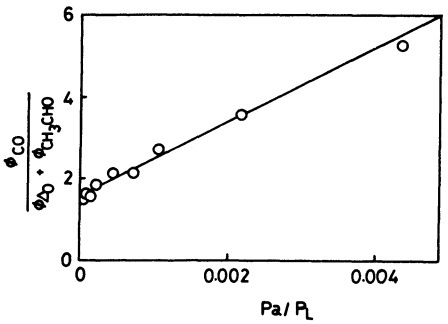


Fig. 3. Plots of $\phi_{CO}/(\phi_{\Delta_O}+\phi_{CH_3CHO})$ against the reciprocal of lactone pressure.

Here, k (E) is the rate constant for the decomposition of $C_2H_4O^*$ when the excess energy is E; A is the frequency factor, E_a is the critical energy, and s is the number of effective oscillators in the molecule. Using the experimental value of k_6 and substituting $A=10^{14.34}$ S^{-1} and E_a=240.2 kJ mol^{-1} (taken from the experiment of Mueller and Walters[8]) and s=8 (about half of the number of the modes of vibration of ethylene oxide), the value of E was found to be 272 kJ mol^{-1}. This excess energy corresponds to about 78% of the enthalpy change for the following reaction, which is estimated to be 351 kJ mol^{-1} by using the standard enthalpies of formation (ΔH_f°=−282.8 (propiolactone), −52.7 (CO), and −110.0 kJ mol^{-1} (ethylene oxide) and the excitation energy of mercury (E_T=469 kJ mol^{-1});

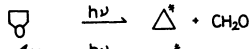
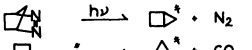
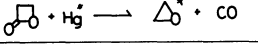
(18)

A comparison of the vibrational energy distribution in different systems is given in Table 2. It is evident that the major portion of the excess energy goes to the product with the most vibrational degree of freedom.

The reactions of oxygen atoms with ethylene in the gas phase[6] and in a liquid nitrogen solution[10] have been reported, and it was concluded that the primary step of the reactions involves the direct addition of an oxygen atom to the double bond to form an energy-rich intermediate ($C_2H_4O^*$) which then undergoes further reactions.

Cvetanovic pointed out[6] that there is a significant similarity among the following different modes of the decomposition of ethylene oxide: The thermal,[8] photolitic,[9] mercury-photosensitized decompositions,[7] and the decomposition of the energy-rich molecule formed in the reaction of oxygen atoms with ethylene in the gas phase.[6] As Table 3 shows, the product distribution in the present case is much simpler than those in the other cases mentioned above, and it is rather similar to that for the reaction of oxygen atoms with ethylene in a liquid nitrogen solution. It seems to be interesting that the fate of $C_2H_4O^*$ in the present case is very similar to that in the reaction of oxygen atoms with ethylene in the liquid phase.[10]

Table 2. Comparison of Excess Energy in Primary Products

Reaction	Energy carried over from primary process (kJ)	% of Energy entering complex product	Ref.
	481	75	a
	418	77	b
	351	78	This work

a) B. C. Roquitte, *J. Am. Chem. Soc.*, **91**, 7664 (1969). b) T. F. Thomas, C. I. Suita, and C. Steel, *J. Am. Chem. Soc.*, **89**, 5107 (1967).

Table 3. Comparison of Product Distribution in the Reactions of Energy-rich Molecule, $C_2H_4O^*$

Reaction	Ref.	Products
Reaction of oxygen atoms with ethylene in the gas phase	6	CO, H_2, CH_4, C_2H_6, C_3H_8, Ethylene oxide, CH_2O, Aldehydes
Mercury-photosensitized reaction of ethylene oxide	7	CO, H_2, CH_4, C_2H_6, C_3H_8, CH_2CO, C_2H_4, Aldehydes
Thermal decomposition of ethylene oxide at 400°C	8	CO, H_2, CH_4, CH_3CHO, CH_2O, CH_2CO
Photolysis of ethylene oxide at wavelengths below 200 nm	9	CO, H_2, CH_4, C_2H_6, CH_2O, CH_3CHO
Reaction of oxygen atoms with ethylene in liquid nitrogen solution	10	Ethylene oxide, CH_3CHO (CH_2O, cyclopropane)
Mercury-photosensitized reaction of β-propiolactone	This work	Ethylene oxide, CH_3CHO (CO, CH_4)

The Cadmium-Photosensitized Reaction. The cadmium-photosensitized reaction was carried out at 235°C to get a sufficient vapor pressure of cadmium. The thermal decomposition of PL occurred at this temperature and gave carbon dioxide and ethylene. Under the irradiation of the cadmium-resonance line, we obtained carbon monoxide, ethylene oxide, and acetaldehyde besides carbon dioxide and ethylene. The amounts of carbon dioxide and ethylene were almost the same as those obtained from the thermal decomposition. We checked the influence of carbon dioxide and/or ethylene on the cadmium-photosensitized reaction, and found that the quantum yields of carbon monoxide, ethylene oxide, and acetaldehyde are independent of the pressure of the carbon dioxide (and/or ethylene) added, if the competitive quenching of the triplet cadmium atoms by lactone and carbon dioxide (and/or ethylene) is taken into account. Therefore, the influence of the thermal decomposition on the results of the cadmium-photosensitized reaction was regarded as negligible. The rate of the cadmium-photosensitized reaction decreases more rapidly than that of the thermal decomposition with a decrease in the reaction temperature. Therefore, the cadmium-photosensitized reaction was difficult to study at temperature lower than 235°C.

The major products obtained in the cadmium-photosensitized reaction of PL were carbon monoxide, ethylene oxide, and acetaldehyde. The yields of these products increased linearly with the reaction time,

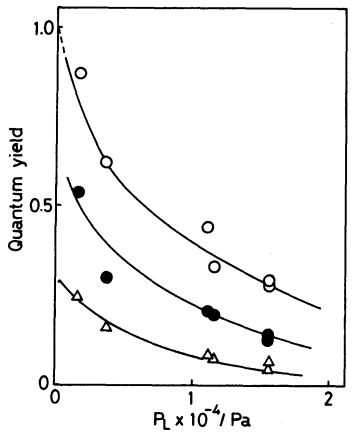


Fig. 4. Pressure dependence of quantum yields of CO (○), ethylene oxide (△), and acetaldehyde (●) in the cadmium-photosensitized reaction of PL.

showing that these are primary products. The quantum yields of these products are shown in Fig. 4 as a function of the lactone pressure. All of them decrease with an increase in the lactone pressure, showing the operation of the collisional deactivation process. This pressure dependence is quite different from that in the mercury-photosensitized reaction. Furthermore, in contrast with the mercury-photosensitized reaction, carbon dioxide and ethylene were not obtained, and the sum of ethylene oxide and acetaldehyde yields almost equals the carbon monoxide yield at low pressures (methane was not obtained even at low pressures).

These findings indicate that the cadmium-photosensitized reaction of PL proceeds through a different intermediate from that in the mercury-photosensitized reaction.

As has been mentioned previously,[1] the triplet state of BL seems to lie at about 440 kJ mol^{-1} above the ground state. If the energy of the triplet state of PL is similar to that of BL, the triplet state of PL is formed in the mercury-photosensitized reaction, as has been mentioned above ($Hg(^3P_1)$ has an energy of 469 kJ mol^{-1}), but it can not be formed by reaction with $Cd(^3P_1)$, which has an energy of only 367 kJ mol^{-1}. This probably accounts for the difference between the mercury- and cadmium-photosensitized reactions of PL.

In order to explain the experimental results, the following set of reactions is proposed:

$$Cd(^1S_0) + h\nu(326.1\ nm) \longrightarrow Cd(^3P_1), \quad (19)$$

$$Cd(^3P_1) \longrightarrow Cd(^1S_0) + h\nu(326.1\ nm), \quad (20)$$

$$Cd(^3P_1) + L \longrightarrow CdL^*, \quad (21)$$

$$CdL^* \longrightarrow Cd(^1S_0) + CO + C_2H_4O^*, \quad (22)$$

$$CdL^* + L \longrightarrow Cd(^1S_0) + 2L, \quad (23)$$

$$C_2H_4O^* \longrightarrow \triangle O, \quad (24)$$

$$C_2H_4O^* \longrightarrow CH_3CHO, \quad (25)$$

$$C_2H_4O^* + L \longrightarrow \text{other products}. \quad (26)$$

Here, CdL* stands for a transient complex between an excited cadmium atom and a lactone molecule, and $C_2H_4O^*$ is an energy-rich intermediate. The large pressure dependence of the quantum yields for the product formation is explained by Reaction (23). This mechanism is almost the same as that proposed for the cadmium-photosensitized reaction of γ-butyrolactone,[1] and of γ-valerolactone and α-methyl-γ-butyrolactone.[11]

From the above mechanism, the following equations can be derived:

$$\frac{\phi CO}{\phi\triangle_O} = \left(1+\frac{k_{25}}{k_{24}}\right) + \frac{k_{26}}{k_{24}}[L], \quad (27)$$

$$\frac{\phi CO}{\phi CH_3CHO} = \left(1+\frac{k_{24}}{k_{25}}\right) + \frac{k_{26}}{k_{25}}[L]. \quad (28)$$

Plots of $\phi_{CO}/\phi_{\triangle O}$ and ϕ_{CO}/ϕ_{CH_3CHO} vs. the lactone pressure are presented in Fig. 5. The values of k_{25}/k_{24} obtained from the intercepts and the slopes of the straight lines in Fig. 5 are in good agreement with one another within the limits of experimental error

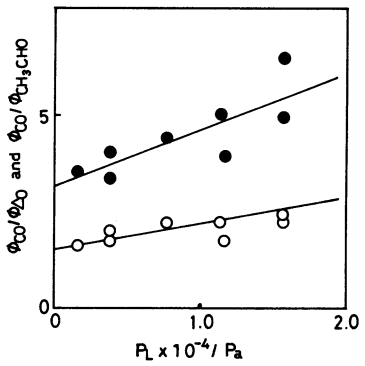


Fig. 5. Plots of $\phi_{CO}/\phi\triangle_O$ (●) and ϕ_{CO}/ϕ_{CH_3CHO} (○) against lactone pressure.

(2.1±0.1). This demonstrates that the above scheme is reasonable.

The intermediate, $C_2H_4O^*$, is similar to that in the mercury-photosensitized reaction. Since methane was not found even at low pressures, as has been mentioned above, the excess energy of $C_2H_4O^*$ in the cadmium-photosensitized reaction seems to be considerably smaller than that in the mercury-photosensitized reaction. As has been described above, the cadmium-photosensitized reaction are always accompanied by a rapid thermal decomposition at 235°C. Therefore, we could not obtain more detailed data, and further quantitative discussion of the cadmium-photosensitized reaction does not seem to be justified.

References

1) S. Yamamoto, S. Matsuda, C. Ozaki, H. Takahoso, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **57**, 3408 (1984).

2) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

3) S. Tsunashima and S. Sato, *Bull. Chem. Soc. Jpn.*, **41**, 284 (1968).

4) R. J. Cvetanovic, "Mercury Photosensitized Reactions," Progress in Reaction Kinertics, Vol. 2, ed. by G. Porter, The Macmillan Co., New York (1964), p. 39.

5) S. W. Benson, *J. Chem. Phys.*, **40**, 105 (1964).

6) R. J. Cvetanovic, *J. Chem. Phys.*, **23**, 1375 (1955).

7) R. J. Cvetanovic, *Can. J. Chem.*, **33**, 1684 (1955).

8) K. H. Mueller and W. D. Walters, *J. Am. Chem. Soc.*, **73**, 1485 (1951); **76**, 330 (1954).

9) R. Gomer and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **72**, 101 (1950).

10) S. Hirokami and R. J. Cvetanovic, *Can. J. Chem.*, **51**, 373 (1973).

11) S. Yamamoto, H. Takahoso, Y. Sueishi, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **58**, 2038 (1985).