Molecular Dissociation of 3-Cyclopenten-1-one Photosensitized by Excited Mercury ($^3P_1$)

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The mercury photosensitized decomposition of 3-cyclopenten-1-one produced carbon monoxide and 1,3-butadiene in equal quantum yields as the exclusive products, independent on the absence or presence of nitrogen oxide. Thus the process was a molecular dissociation. The quantum yield was dependent on the pressure of argon added as a third body and revealed a maximum at the pressure of about 100 mmHg. A possible reaction scheme was proposed to explain the above kinetic behavior. It was suggested that the vibrationally excited state of 3-cyclopenten-1-one was a main precursor to decompose to carbon monoxide and 1,3-butadiene. An energy about 20 kcal·mol^{-1} was estimated to be lost before its production from the original triplet state 3-cyclopenten-1-one according to the proposed reaction scheme. This result is compared with the behaviors of excited 3-cyclopenten-1-ones produced by different excitation procedures.

Mechanisms of pyrolyses, photolyses and photosensitized reactions of saturated cyclic ketones and cyclic unsaturated hydrocarbons have been well elucidated in recent years.[1] But those of unsaturated cyclic ketones are rarely investigated. Among them is 3-cyclopenten-1-one (abbreviated as CP). Dolbier and Frey[2] studied the thermal decomposition of this ketone. Hess and Pitts[3] reported the direct photolysis at 313 nm briefly. In both cases, carbon monoxide (CO) and 1,3-butadiene (BD) were exclusive products. To our knowledge, however, there is no report on the mercury photosensitization of this ketone.

During our study of the atomic oxygen reaction with 1,3-cyclopentadiene,[4] CP was proposed as an important intermediate to decompose to CO and BD. The spin state of the intermediate cyclopentenone could be either singlet or triplet. Apart from the oxygen atom reaction, a triplet state CP is expected to be prepared through mercury photosensitization of the ketone itself. Moreover, the energy which is transferred from the excited mercury atom to the ketone should be 113 kcal·mol^{-1} or less, which is relatively close to the possible excess energy possessed by the intermediate CP of the atomic oxygen reaction with cyclopentadiene; that is about 105 kcal·mol^{-1}.[5]

Thus we are interested in the possible difference in the mechanism of decomposition of CP excited by mercury photosensitization from those of cyclopentenones excited thermally or by direct photon absorption, or prepared through the reaction of oxygen atoms with 1,3-cyclopentadiene. This matter will be discussed after the photosensitized decomposition of CP is described.

Experimental

Materials. The preparative method of 3- and 2-cyclopenten-1-one were described by Hess and Brown.[6] The crude pentenones were purified by repeated distillations. Gas-chromatographic analyses showed that the CP and the 2-cyclopenten-1-one were more than 99 and 97% pure, respectively.

Commercially obtained argon (pure grade; the purity is more than 99.99%; from Takachiho Shoji Co., Ltd.), nitrogen, CO, BD, and 1-butyne (the four gases are of research grade from Takachiho Shoji Co., Ltd.) were used without further purification. Commercially obtained dinitrogen oxide, nitrogen oxide and ethane (all, research grade; from Takachiho Shoji Co., Ltd.) were distilled several times *in vacuo* before use.

Cyclobutene (CB) was synthesized through the photoisomerization of BD according to the method described by Sriniuasan[7] and purified gas-chromatographically.

Apparatus. The cyclindrical quartz photochemical cell was 5 cm in diameter and 10 cm long, equipped with a gas circulation line with a glass-made circulation pump having Teflon bearings, mercury store, a U-type trap, and a reservoir. The total volume of the reaction system mentioned above was 650 ml. A conventional vacuum system was used for gas handling.

The 253.7 nm light source was a flat-spiral low pressure mercury resonance lamp (Ushio Electric Inc., type UTL-7SQ). The light from the lamp passed through a glass filter (Toshiba Kasei Co., Ltd., UV-D25) to get rid of the radiation below 200 nm, an iris (diameter 10 mm), a quartz lens (f=10 cm) and a quartz beam splitter. The transmitted light reached the cell. The reflected light at right angles from the beam splitter reached a phototube (Hamamatsu TV Co., Ltd., R765). Thus the relative intensity of this radiation could be monitored to be corrected for any fluctuation of the radiation all through the experimental runs.

Experimental Procedure. A measured amount of CP (and nitrogen oxide, if necessary) was introduced into the reaction system. Then argon, if necessary, was added through a slightly opened stopcock until the desired total pressure was reached. The gas mixture was circulated all through the total reaction system by means of the circulation pump for at least an hour before photolysis. Within an hour, mercury vapor evaporated from the mercury store into the gas mixture until the equilibrium pressure at the temperature was reached. Irradiation was carried out for a desired period, while the gas mixture was being circulated.

After the irradiation, the gas mixture was treated as follows. In the experiments without argon, the mixture was divided to three portions. The first portion, non-condensable at liquid nitrogen temperature, was collected by a Toepler pump. The other two portions, one of which was not condensable at Dry Ice–methanol temperature (−78 °C) and the other of which, condensable at that temperature, were sampled in gas samplers cooled at the adequate temperatures, respectively. In the experiments with argon, a part of the mixture was expanded into a gas sampler. The remaining part was pumped out very slowly through several spiral traps immersed in a Dry

Table 1. Estimation of the percentage absorption of light in various gas mixtures

Run	$P_{C_2H_6}$ (mmHg)	P_{N_2O} (mmHg)	$P_{C_5H_6O}$ (mmHg)	P_{NO} (mmHg)	P_{Ar} (mmHg)	a ($\times 10^{-8}$ A)	b ($\times 10^{-10}$ A)	c ($\times 10^{-2}$)	d (%)
1[a]	0.0	0.0				5.40	299.6	55.5	0.0
2	99.8	104.2				5.49	14.7	2.68	95.2
3	99.3	101.4				5.16	14.0	2.71	95.1
4	103.6	107.8				5.26	15.9	3.02	94.6
5			10.3	0.0	0.0	5.39	17.3	3.14	94.3
6			10.9	0.0	0.0	4.63	15.5	3.38	93.9
7			9.2	10.9	456.9	5.14	11.1	2.16	96.1
8			10.1	4.3	469.2	5.14	12.1	2.36	95.8
9			10.2	21.7	461.6	6.00	14.1	2.43	95.6
10			10.1	26.7	444.7	5.29	12.2	2.30	96.8

Reaction temperature; 25±3 °C. a) Without any mercury. a: The reflected light (phototube current) from the beam splitter. b: The leaking light (phototube current). c: b/a. d: The percentage of absorption $((1-(c_i/c_1))\times 100)$.

Iice–methanol bath. The collection efficiency of the traps was checked for BD and was found to be at least 95%.

Analyses of Products. The products were identified and analysed quantitatively by means of gas-chromatography (Yanagimoto Seisakusho Co., Ltd., G80-PT(TCD), G80-FTP (FID)) with several appropriate columns. The columns used were 3,4-dimethylsulfolane (4.5 m, 0 °C) and Squalane (3 m, 30 or 90 °C) for BD and also for lower hydrocarbons, Molecular Sieve 5A (2.25 m, 60 °C) for nitrogen and CO, bis(2-ethylhexyl)phthalate (2.25 m, 70 °C) and Polyethylene Glycol 20M (2.25 m, 100 °C) for searching for other possible products of a larger molecular weight. Usually a thermal conductivity detector was used for nitrogen and CO and a flame ionization detector for hydrocarbons.

In the experiments with argon, the product CO could not be separated from the large amount of argon by a conventional method. Thus the part which represented the total photolysed mixture correctly, and had been expanded into a gas sampler, was introduced into the gas-chromatograph after being got rid of the condensable products at Dry Ice–methanol temperature. The product CO was then separated from argon through the Molecular Sieve 5A column in the gas-chromatograph, converted to methane by the reduction with the carrier gas hydrogen at 320 °C through the nickel catalyst column (from Gasukuro Kogyo Co., Ltd.) connected to the Molecular Sieve 5A column directly, and then detected with a flame ionization detector. Carbon monoxide of more than 30 ppm in argon could be analysed quantitatively by the above procedure, provided that the total mixture of 3000 mmHg·cm^3 was introduced to the gas-chromatograph.

Measurements of the Intensity of Light Which Leaks out from the Cell. The intensity of the light coming out from the inside of the cell (transmitted light and re-emitted light from the excited mercury) was measured with a phototube at various positions around the cell. The total amount of the leaking light could be then estimated by summing the measured intensity values with taking into account the geometry of the cell.

Estimation of the Amount of Absorbed Light in the Cell. The amount of the light which leaked out from the cell was measured by the above procedure under several different experimental conditions as shown in Table 1. Thus the percentage of the absorption was always about 95%, in various experimental runs including the case of the photolysis of the mixture of dinitrogen oxide and ethane. Then the amount of absorbed light in the cell could be calculated based on the experimental nitrogen yield from the photolysis of dinitrogen oxide–ethane; the quantum yield of the nitrogen production is unity according to Ref. 8.

Results

The main products were CO and BD. Trace amounts of C_2 and C_3 hydrocarbons, 1,2-butadiene and 1-butyne were detected in some experiments, especially when the conversion was high. But they were always produced in negligibly small quantum yields. No other C_4H_6 isomers such as CB and 3-methylcyclopropene could be detected. Their quantum yields should be less than 0.002, considering from the detection limit of our analysis. Small amount of 2-cyclopenten-1-one, one of the isomers of cyclopentenones, were detected in some experiments. But quantitative analyses gave relatively poor reproducibility for this product, possibly because of its easiness to adsorb on the wall of the reaction and/or analysis systems. Thus quantitative analyses were confined to CO and BD.

The quantum yield of carbon monoxide was independent on the irradiation time as shown in Fig. 1, which guaranteed that no secondary photolysis of the products proceeded to appreciable extents under the

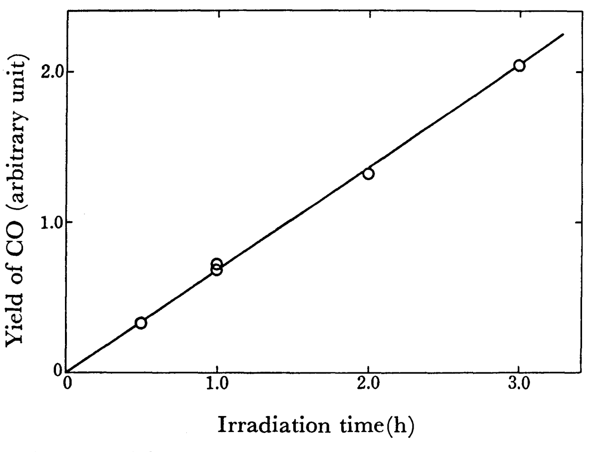

Fig. 1. Yield of carbon monoxide *versus* irradiation time Pure CP (10.0—12.4 mmHg) was photosensitized, at 20—25 °C. The yield of CO is corrected for the variation of the light intensity.

Table 2. The quantum yields of carbon monoxide and 1,3-butadiene

Run	$P_{C_5H_6O}$ (mmHg)	P_{Ar} (mmHg)	P_{NO} (mmHg)	ϕ_{CO}	ϕ_{BD}	ϕ_{BD}/ϕ_{CO}
5	10.3	0.0		0.874	n.d.	n.d.
6	10.9	0.0		0.849	0.876	1.03
7	9.2	456.9	10.9	0.568	0.590	1.04
8	10.1	469.2	4.3	0.685	0.701	1.04
9	10.2	461.6	21.7	0.399	0.410	1.03
10	10.1	444.7	26.7	0.427	0.412	0.97
11	10.1	316.3		0.814	0.847	1.04
12	10.8	88.1		0.954	0.901	0.94
13	11.3	0.0		0.854	0.828	0.97
14	10.5	0.0		0.855	0.876	1.02
15	10.3	492.3		0.678	0.740	1.09
16	10.5	275.8		0.877	0.860	0.98
17	10.5	45.5		0.914	0.947	1.04
18	10.5	647.2		0.606	0.618	1.02
19	9.8	137.7		0.913	0.904	0.99
				average		1.01±0.04

n.d.=not determined. Reaction conditions; irradiation time, 1.0 or 2.0 h, reaction temperature, 25±3 °C.

present conditions.

Table 2 shows the quantum yields of CO and BD. In some experiments, argon was added in order to know its effect as a third body. Argon is known not to quench excited mercuries in any appreciable extent. In several experiments, nitrogen oxide as a radical scavenger[9)] was added. The ratio of the quantum yield of CO versus that of BD was found to be always very close to unity under various conditions, as shown in the last column of the table.

We carried out one special experimental run where the mixture of methane (656 mmHg) and CP (10 mmHg) was photolysed. No C_4H_6 isomers other than BD could be detected. The yield of CB, if it were produced, should be less than 0.03% of that of BD produced, judging from the gas-chromatographic sensitivity.

Discussion

Molecular Dissociation. As shown in Table 2, the ratio of the quantum yield of CO to that of BD was about unity in any experiment under various conditions. Even in the experiments where nitrogen oxide was added, the ratio did not change. The decrease of the yield of CO and BD with the addition of NO should be attributed to the quenching effect of NO for the excited mercuries. These observations show that CO and BD are produced *via* a common intermediate, and no radical species seems to contribute to the production of CO and BD. Therefore, the main reaction is considered to be a molecular dissociation of a certain excited CP to produce CO and BD, under the present conditions.

Absence of Excited Cyclobutene as an Intermediate. BD is considered to be produced through a molecular dissociation as stated in the previous section. One possibility is that BD is, in fact, produced as a secondary product through isomerization from some other vibrationally excited C_4H_6 isomers which might be produced primarily. Among C_4H_6 isomers other than BD, CB seems to be the most plausible primary species, because CB could be produced as a molecular dissociation product from excited CP without any serious rearrangements of molecular structures and also because it is known to isomerize thermally to BD exclusively.[10)] Thus we must determine whether BD is produced *via* the excited CB intermediate, $CB^{\neq}$, or is produced directly. Because some part of $CB^{\neq}$ should be collisionally stabilized and analysed as CB, we can estimate the fraction of the process *via* $CB^{\neq}$, X, based on the fraction of CB among product C_4H_6 isomers (CB+BD), β, which is experimentally obtainable. Here, the following scheme is assumed.

$$\mathrm{Intermediate\,(C_5H_6O)} \longrightarrow \mathrm{CO} + \mathrm{CB}^{\neq} \qquad k_a \qquad (1)$$

$$\longrightarrow \mathrm{CO} + \mathrm{BD} \qquad k_b \qquad (2)$$

$$\mathrm{CB}^{\neq} \longrightarrow \mathrm{BD} \qquad k_{iso} \qquad (3)$$

$$\mathrm{CB}^{\neq} + \mathrm{M} \longrightarrow \mathrm{CB} + \mathrm{M} \qquad \alpha k_\omega \qquad (4)$$

(α=collisional deactivation efficiency,
k_ω=kinetic collision frequency at the pressure)

X and β are equated to the rate constants, as follows.

$$X = \frac{k_a}{k_a+k_b} \qquad (5)$$

$$\beta = \frac{k_a}{k_a+k_b} \times Y \qquad (6)$$

Here, $Y=\alpha k_\omega/(\alpha k_\omega+k_{iso})$. Therefore, X can be calculated from β and Y.

$$X = \beta Y^{-1} \qquad (7)$$

The value β is determined experimentally. The value Y can not be obtained experimentally, but may be approximately estimated by simple statistical considerations as described below. At first, the rate constant k_{iso} is calculated by the following equation when the excess energy of $CB^{\neq}$ is E.

$$k_{iso} = A(1-E_a/E)^{s-1} \qquad (8)$$

By use of $s=10$, $E_a=32.9$ kcal·mol^{-1}, $A=10^{13.3}$ s^{-1} and $E=66$ kcal·mol,$^{-1}$ k_{iso} is calculated to be 1×10^{10} s^{-1}. Here, the value $s=10$ is claimed to be optimum to explain the experimental results of the thermal isomerization of CB,[10,11)] and then rate parameters E_a and A are taken from the data of the thermal isomerization.[10)] The excess energy E is estimated as follows. It is likely that about 105 kcal·mol^{-1} energy is transferred to CP from the $^3P_1$ mercury, referred to the experimental results of Montague and Rowland.[12)] According to the simple statistical consideration, $CB^{\neq}$ possesses the excess energy which is equivalent to the available energy multiplied by the ratio of the number of internal degrees of freedom of CB(24) to that of CP(30). The available energy is equal to the transferred energy (105 kcal·mol^{-1})+ the heat of reaction of the dissociation of CP to CO and CB (−23 kcal·mol^{-1}). Its twenty four-thirtieth is 66 kcal·mol^{-1}. Secondly, the term αk_ω is estimated by adopting 1×10^7 s^{-1} as the kinetic collision frequency at 1 mmHg and by use of appropriate α values. α is 0.24 for methane[13] and unity deactivation efficiency is assumed for CP.

Thus, the value of Y is estimated to be 0.14 in the experiment with 656 mmHg of methane (CP, 10 mmHg) and to be 0.0099 in the experiments without additive gases (CP, 10 mmHg). As described in the result section, CB could not be found both in the experiment with 656 mmHg of methane and in the experiments without additive gases. Correspondingly, the possible maximum of β is 3×10^{-4} in both cases. According to Eq. 7, the possible maximum of X should be then 2×10^{-3} in the experiment with 656 mmHg of methane and 3×10^{-2} in the experiments without additive gases.

The above discussions show that the process *via* the excited CB contributes to a very small extent, if at any. BD must be produced as the primary dissociation product from the molecular dissociation.

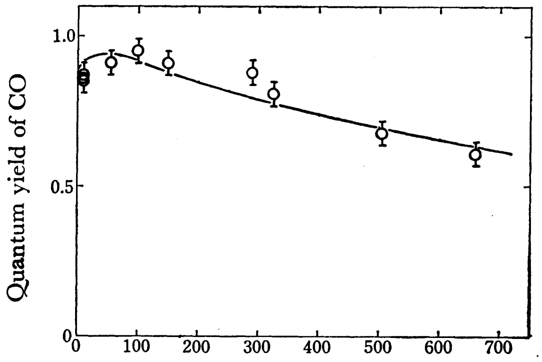

Fig. 2. Quantum yield of carbon monoxide versus total pressure.
Data are from Table 2. total pressure=Ar pressure+CP pressure (9.8—11.3 mmHg)

Reaction Scheme. Figure 2 shows the relationship between the quantum yield of CO, ϕ_{CO}, and the total pressure. Here, the total pressure is the sum of the pressure of CP which was about 10 mmHg all through the experimental runs and the pressure of argon which was varied.

The fact that the extrapolation value of the plots to zero pressure is not unity suggests the existence of a channel through which products other than CO and BD are produced. Those products could not be clearly identified, but the isomer 2-cyclopenten-1-one is one possibility. The complex dependence of ϕ_{CO} on the pressure indicates the existence of several consecutive competitions between stabilization and dissociation to produce CO and BD. At least two independent processes which are affected by collisions are required in order to explain the positive and then negative pressure dependence of ϕ_{CO}. It is very plausible that the vibrationally excited state of CP is the immediate precursor to decompose to CO and BD, taking into account the facts that the products of pyrolysis of CP is exclusively CO and BD,[2] and that the Woodward-Hoffmann rule indicates the possibility of the production of CB from electronically excited CP's, against our observation.

As a simple model which satisfy the above considerations, we propose the following reaction scheme.

$$C_5H_6O(S_0) + Hg(^3P_1) \longrightarrow C_5H_6O(T) + Hg(^1S_0) \tag{9}$$

$$C_5H_6O(T) \longrightarrow CO + BD \tag{10}$$

$$C_5H_6O(T) \longrightarrow \text{other products except CO and BD} \tag{11}$$

$$C_5H_6O(T) + M \longrightarrow C_5H_6O(T') + M \tag{12}$$

$$C_5H_6O(T') \longrightarrow C_5H_6O(S_0^*) \tag{13}$$

$$C_5H_6O(S_0^*) \longrightarrow CO + BD \tag{14}$$

$$C_5H_6O(S_0^*) + M \longrightarrow C_5H_6O(S_0) + M \tag{15}$$

Here, M means a third body. Argon and CP are not differentiated from each other, though they may have different quenching ability. We did not vary the pressure of CP to reveal its different quenching ability from argon, because of its low vapor pressure at room temperature, which is 13 mmHg.

The reaction 10 may be a single process as described above or more plausibly a consecutive process (Eqs. 10a and 10b),

$$C_5H_6O(T) \longrightarrow C_5H_6O(S_0^+), \tag{10a}$$

$$C_5H_6O(S_0^+) \longrightarrow CO + BD, \tag{10b}$$

where S_0^+ means a vibrationally excited ground state of CP with a larger excess energy than S_0^*. The process (Eq. 10a) is a collision free intersystem crossing. Because of the very large amount of excess energy of S_0^+, its subsequent process is almost confined to the dissociation (Eq. 10b) under the present pressures. The T′ state is either the vibrationally relaxed T state or any other different triplet state with a lower triplet energy. S_0^* means a vibrationally excited S_0 state, and is assumed to possess less energy than is originally transferred from the excited mercury because of the collisional deactivation (Eq. 12).

According to the above scheme, we can derive.

$$\phi_{CO} = \frac{1}{1+(k_{11}/k_{10})+(k_{12}M/k_{10})} + \frac{k_{12}M/k_{10}}{1+(k_{11}/k_{10})+(k_{12}M/k_{10})}\,\frac{1}{1+k_{15}M/k_{14}}. \tag{16}$$

Adoptation of appropriate values for the ratios of the rate constants is found to result in coincidence between the experimentall values and calculated values according to Eq. 16 within experimental errors. When the optimum values, $k_{11}/k_{10}=0.15$, $k_{12}/k_{10}=5\times10^{-2}$ mmHg^{-1}, $k_{15}/k_{14}=9\times10^{-4}$ mmHg^{-1} are adopted, the calculated values of ϕ_{CO} are shown as a bold line in Fig. 2. Though these rate ratios could not be determined unequivocally, the allowable range of k_{15}/k_{14} to satisfy the experimental results was found to be between 1×10^{-3} and 7×10^{-4} mmHg^{-1}. This range could be rather unequivocally determined, because the relationship between ϕ_{CO} and the pressure is determined by this ratio almost exclusively, when the pressure is above 150 mmHg.

Adoptation of a multi-step deactivation process in place of Eqs. 14 and 15 was found to result in a little better coincidence, but the improvement was minor. Thus we consider that the scheme (Eqs. 9—15) is enough to explain the experimental results. This scheme is also compatible with the considerations of the excess energy of the intermediate S_0^* state, as will be described in the next section.

Excess Energy of the Excited Ground State 3-Cyclopenten-1-one. The experimental value of k_{15}/k_{14} gives the value of k_{14} as $1.1 \times 10^9\ s^{-1}$ on the basis of the assumption, $k_{15} = 1 \times 10^6\ mmHg^{-1} \cdot s^{-1}$. Here, the k_{15} value of one-tenth (which is the collisional deactivation efficiency) of the gas kinetic collision frequency is used.[13) The excess energy of S_0^* can be estimated by use of

$$k(E) = A(1-E_a/E)^{s-1}. \tag{17}$$

Here, $k(E)$ is a rate constant of decomposition when an excess energy is E. We get $E = 86.6$ kcal·mol^{-1} by using the values of A ($10^{14.5}\ s^{-1}$) and E_a (51.3 kcal·mol^{-1}) taken from the experiment of Dolbier and Frey,[2) and assuming $s = 15$. The possible range of the ratio k_{15}/k_{14} between 1×10^{-3} and 7×10^{-4} mmHg^{-1} corresponds to the range of the excess energy E between 86.2 and 87.1 kcal·mol^{-1}. The estimation of the excess energy is also dependent on the assumed value of the collisional deactivation efficiency. For example, unit efficiency, which is an unlikely large efficiency, result in the increase of the excess energy about 10 kcal·mol^{-1}. But even in this case, the excess energy is still smaller by about 10 kcal·mol^{-1} than the energy, about 105 kcal·mol^{-1}, which is originally transferred to CP from the excited mercury. Thus the dissociating intermediate S_0^*, and also T′ seem to be deactivated by 20 kcal·mol^{-1} or so before the dissociation. The energy loss should be due to the vibrational deactivation process (Eq. 12) in the triplet state.

Triplet State of 3-Cyclopenten-1-one. CP possesses two active chromophores which are relatively independent on each other; they are C=O and C=C double bond. Then two kinds of triplet states of low energy are expected to exist; one is $^3(n\text{–}\pi^*)$ mainly excited in the C=O chromophore (T_a) and the other is $^3(\pi\text{–}\pi^*)$ mainly excited in the C=C chromophore (T_b).

The absorption spectrum of CP measured by Hess and Pitts[3) clearly shows two different absorption systems, one of which is relatively weak ($\varepsilon \approx 10$ l·mol^{-1}·cm^{-1}) and in the region from 250 to 320 nm, and the other is strong ($\varepsilon \approx 10^3$ l·mol^{-1}·cm^{-1}) and in the region from 180 to 230 nm. The upper state of the first system is safely assigned to $^1(n\text{–}\pi^*)$ of the C=O chromophore. The upper state of the second system is not clear enough, but might be $^1(\pi\text{–}\pi^*)$ of the C=C chromophore. The 0–0 energies of the two systems are apparently 86 kcal·mol^{-1} and 114 kcal·mol^{-1}, respectively, judging from their absorption spectra. Considering that the difference between a $^1(n\text{–}\pi^*)$ state and the corresponding $^3(n\text{–}\pi^*)$ is usually about 5 kcal·mol^{-1} or so,[14) the T_a state may be above the ground state by about 80 kcal·mol^{-1}. The difference between a $^1(\pi\text{–}\pi^*)$ and the corresponding $^3(\pi\text{–}\pi^*)$ is usually large and also varies very much from molecule to molecule. The fact that the rotation around the C–C axis is restricted due to the ring structure in the case of CP, makes it more difficult to presume the energy of T_b.[15) It is thus difficult to decide which is the lowest triplet state. Anyhow, at least one triplet state whose triplet energy is around the same as the excess energy of the assumed T′ state seems to exist. Thus our assumption of the two-step consecutive deactivation process ((Eqs. 12, 15); the first step in the triplet vibrational manifold and the second step in the ground state vibrational maifold) is self-consistent.

Comparison among the Excited 3-Cyclopenten-1-ones from Different Excitation Methods. Hess and Pitts[3) obtained CO and BD with the quantum yield of 0.87 in the direct photolysis of CP by using 313 nm light (91.3 kcal·mol^{-1}) at 35 mmHg of total pressure. A singlet ($^1(n\text{–}\pi^*)$) CP is considered to be produced as a primary product through the direct photon absorption. Provided that the dissociation is from the vibrationally excited ground state molecule which has been prepared from the singlet excited state through internal conversion, the excess energy of the decomposing molecule is calculated to be about 90 kcal·mol^{-1} by the similar procedure as described in the fourth section, based on the above quantum yield (0.87 at 35 mmHg). The excess energy is then very near the initial excitation energy. Thus it is plausible that the singlet $^1(n\text{–}\pi^*)$ state CP changes before any appreciable collisions to a vibrationally excited ground state molecule, which then decomposes unimolecularly.

In the reaction of atomic oxygen with 1,3-cyclopentadiene, we assumed the existence of an excited CP as the intermediate to decompose to CO and BD (the corresponding process is expressed by Eq. IV in the previous paper[4)). Provided that the intermediate is a vibrationally excited ground state CP, its excess energy is estimated to be 104 kcal·mol^{-1}, by the similar calculation procedure based on the data presented in Fig. 7 of the paper. On the other hand, the heat of reaction of the process, O(^{3}P) + 1,3-cyclopentadiene → 3-cyclopenten-1-one, is 102 kcal·mol^{-1}, which is near the above estimated excess energy.

Thus in the above two excitation procedures, the collisional events do not seem to affect the processes preceding the decomposition, which should be attributed to the rapid conversion of the primary products to the corresponding vibrationally excited ground state CP's. We found a moderate pressure effect of the quantum yield of the products in the case of the mercury photosensitization, and attributed it to the collisional deactivation in the triplet state, as described before. A relatively long triplet lifetime is expected because of the possibly slow intersystem crossing.

Our reaction scheme is based on a very simple kinetic treatment of the CO quantum yield, and might be modified with future additional informations. We wish to stress, however, that the pressure dependence of ϕ_{CO} in the mercury photosensitization is somewhat different from those in the other two excitation systems even though the products are CO and BD in every case. The existence of this difference is independent on the assumption of reaction schemes.

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