October, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (10), 2841—2846 (1978)

Phosphorescence Emissions and Nonradiative Properties of Vapors of Aromatic Carbonyl Compounds at Low Pressure

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(Received April 17, 1978)

The phosphorescence quantum yields of benzaldehyde, acetophenone, *p*-fluorobenzaldehyde, *p*-chlorobenzaldehyde, and benzophenone vapors, measured at low pressure down to the order of 10^{-3} Torr as a function of excitation wavelength, are essentially constant in the region of excitation energy corresponding to the $S_1(n, \pi^*)$ state, whereas the yields decrease very sharply as the excitation energy is raised to the value corresponding to the $S_2(\pi, \pi^*)$ state. This indicates that the nonradiative pathway in the carbonyl compound varies according to the type of the singlet state to which the molecule is initially excited. When excited to the S_1 and S_2 states, the molecule passes to the phosphorescent triplet state and a decomposing state, respectively. Two mechanisms are suggested and examined for understanding the nonradiative properties of the carbonyl compound vapors: (I) The internal conversion $S_2 \rightarrow S_1$ is slow compared with the conversion from S_2 to the decomposing state; (II) the vibrational energy redistribution in S_1 between the vibrational mode populated through $S_2 \rightarrow S_1$ and the mode to be populated optically is slow compared with the conversion from the former mode to the decomposing state.

In the vapor phase at low pressure, organic molecules often show photochemical or photophysical properties that cannot be observed in the condensed phase.[1,2] The photochemical reactivity of benzaldehyde and acetophenone in the vapor phase is known to be very sensitive to the excitation energy or to the nature of the electronic state excited.[3,4] The vapor-phase phosphorescence yields of benzaldehyde and benzophenone also are known to be sensitive to the excitation energy.[5,6]

In a previous paper,[7] it was reported preliminarily that the phosphorescence quantum yield of benzaldehyde vapor varies, depending on the type of singlet state to which the benzaldehyde molecule is initially excited. That is, the quantum yield is essentially constant in the region of excitation energy corresponding to the $S_1(n,\pi^*)$ state, but it decreases very sharply as the energy is raised to the value corresponding to the $S_2(\pi,\pi^*)$. Since the excited-electronic-state dependence of the molecular emission property is of prime importance in connection with the mechanism of radiationless transition, we have extended this sort of study to various derivatives of benzaldehyde. The present paper reports the emission and excitation spectra of acetophenone, *p*-fluorobenzaldehyde, *p*-chlorobenzaldehyde, and benzophenone vapors at low pressure, down to the order of 10^{-3} Torr, in comparison with the corresponding spectral data on benzaldehyde. It is shown that, in all the molecules studied, the phosphorescence quantum yields decrease greatly on changing the excitation from $S_0 \rightarrow S_1$ to $S_0 \rightarrow S_2$.

Experimental

Benzaldehyde and acetophenone obtained from Nakarai Chemicals, Kyoto and *p*-fluorobenzaldehyde from Aldrich Chemical Company were purified by means of repeated vacuum distillations. *p*-Chlorobenzaldehyde obtained from Tokyo Chemical Industry was purified by repeated vacuum sublimations. Benzophenone from Nakarai Chemicals was vacuum sublimated and zone-refined. Carbon tetrachloride from Merck was used as a foreign gas without further purification. All the sample vapors were degassed in a mercury-free vacuum system, and their pressures were determined from the intensities of the $S_0 \rightarrow S_3$ absorption spectra. It was confirmed that no impurity emission was detected from the sample vapors.

Emission and excitation spectra were measured with a high-sensitivity spectrophotometer[8] equipped with a Hamamatsu TV R-585 photomultiplier, using the photon-counting method. Absorption spectra were measured with a Hitachi EPS-3, a Shimadzu MPS-5000, or a Cary-15 spectrophotometer. For most of the emission measurements, square 10-mm path length quartz cells were used. A spherical 160-mm path length cell with quartz windows was also used for benzaldehyde and *p*-fluorobenzaldehyde at very low pressure (<7 mTorr).

The excitation spectra were obtained with a 1- or 2-nm bandwidth for the excitation monochromator and a 19-nm bandwidth for the emission monochromator, and were corrected for the spectral intensity distribution of the exciting light by the use of an aqueous solution of rhodamine B as a quantum counter. The spectral measurements were conducted at 85 °C for benzophenone and at room temperature for the other compounds.

Results

The vapor-phase emission spectra of the carbonyl compounds studied are shown in Figs. 1 and 2. These

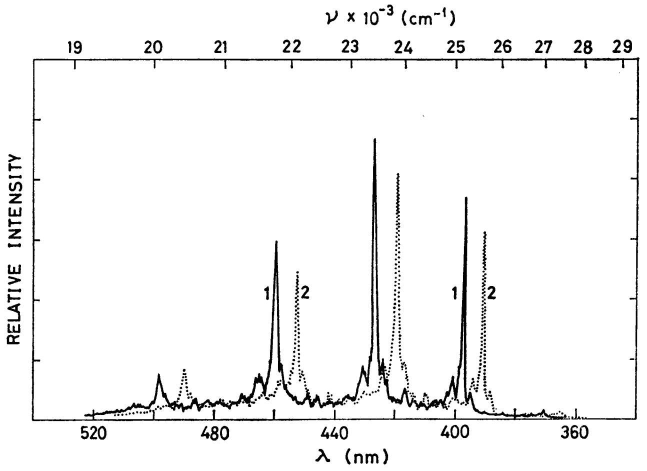

Fig. 1. Vapor-phase emission spectra of (1) benzaldehyde (bandwidth, 0.3 nm) and (2) *p*-fluorobenzaldehyde (bandwidth, 0.4 nm). The spectra are not corrected for the spectral response of the monochromator-photomultiplier system.

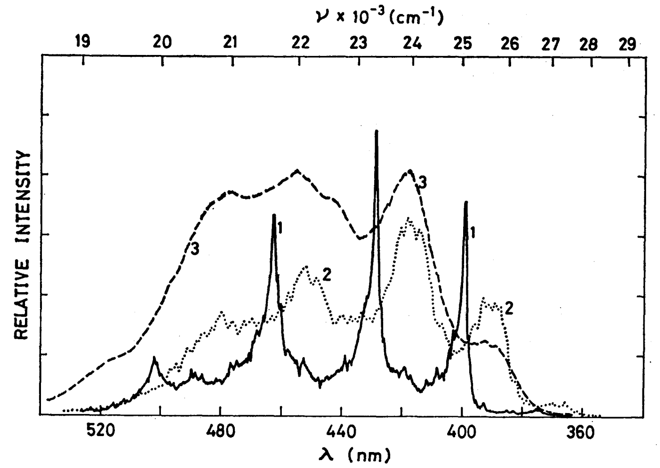

Fig. 2. Vapor-phase emission spectra of (1) *p*-chlorobenzaldehyde (bandwidth, 0.9 nm), (2) acetophenone (bandwidth, 1.2 nm), and (3) benzophenone (bandwidth, 1.0 nm). The spectra are not corrected for the spectral response of the monochromator-photomultiplier system.

spectra consist mainly of phosphorescence, accompanied by very weak E-type delayed fluorescence at shorter wavelengths. The spectral shapes were found to be independent of the pressure and excitation energy within the limit of experimental error.

Figures 3(a)—7(a) show corrected phosphorescence excitation spectra at different pressures of the vapors of the carbonyl compounds, together with the vapor-phase absorption spectra. In the presence of high-pressure carbon tetrachloride as a foreign gas, the excitation spectrum agrees well with the corresponding absorption spectrum for all the carbonyl compounds, except for benzophenone. The absorption spectrum of benzophenone in the long wavelength region is not known because of its low vapor pressure. However, its corrected excitation spectrum in the presence of high-pressure carbon tetrachloride resembles the absorption spectrum in isopentane solution. It is assumed, therefore, that the former excitation spectrum can be used as a substitute for the vapor-phase absorption spectrum. In the case of pure carbonyl compound vapors at low pressure, the intensities of the corrected excitation spectra are markedly low in the S_2 region, as compared with the absorption spectra.

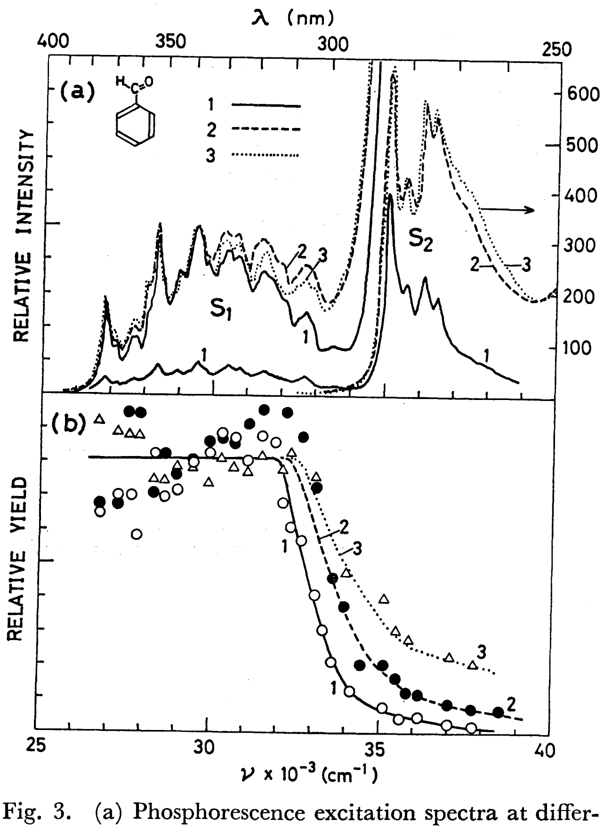

Fig. 3. (a) Phosphorescence excitation spectra at different pressures (1 and 2) and absorption spectrum (3) of benzaldehyde vapor. (1) 3 mTorr; (2) 500 mTorr of benzaldehyde in the presence of added CCl_4 ($\approx$100 Torr). Higher-intensity spectra are obtained by multiplying the ordinate values of the corresponding lower-intensity spectra by factors of 5 and 20, respectively, for curve 1 and for curves 2 and 3. (b) Plots of phosphorescence quantum yields of benzaldehyde vapor *vs.* excitation energy at different pressures. (1) 2 mTorr; (2) 4 mTorr; (3) 10 mTorr.

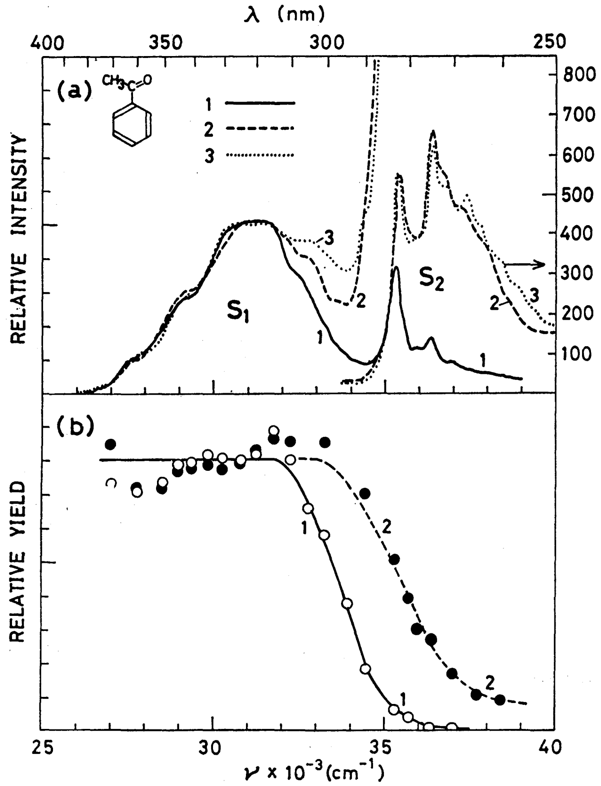

Fig. 4. (a) Phosphorescence excitation spectra at different pressures (1 and 2) and absorption spectrum (3) of acetophenone vapor. (1) 20 mTorr; (2) 30 mTorr of acetophenone in the presence of added CCl_4 ($\approx$200 Torr). Higher-intensity spectra are obtained by multiplying the ordinate values of the corresponding lower-intensity spectra by a factor of 10 for curves 2 and 3. (b) Plots of phosphorescence quantum yields of acetophenone vapor *vs.* excitation energy at different pressures. (1) 20 mTorr; (2) 220 mTorr.

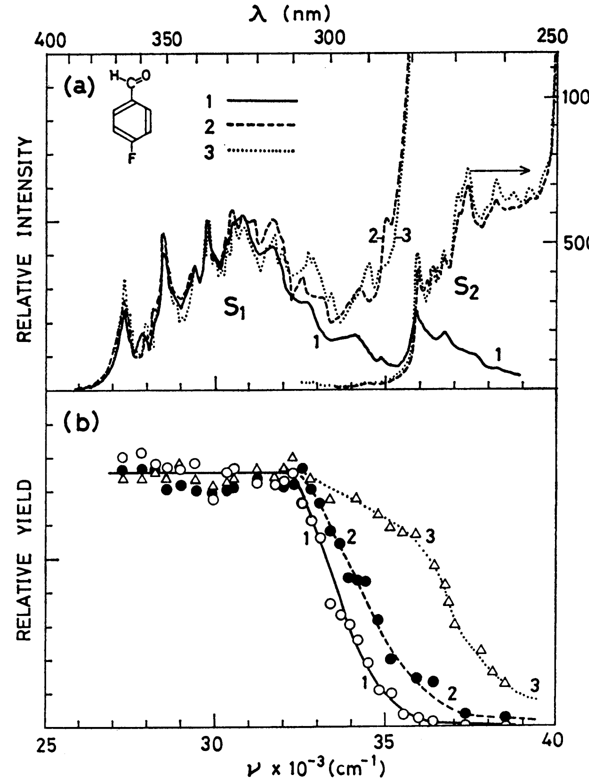

Fig. 5. (a) Phosphorescence excitation spectra at different pressures (1 and 2) and absorption spectrum (3) of *p*-fluorobenzaldehyde vapor. (1) 7 mTorr; (2) 300 mTorr of *p*-fluorobenzaldehyde in the presence of added CCl_4 (≈100 Torr). Higher-intensity spectra are obtained by multiplying the ordinate values of the corresponding lower-intensity spectra by a factor of 20 for curves 2 and 3. (b) Plots of phosphorescence quantum yields of *p*-fluorobenzaldehyde vapor *vs.* excitation energy at different pressures. (1) 7 mTorr; (2) 30 mTorr; (3) 100 mTorr.

Relative phosphorescence quantum yields are plotted against the excitation energy in Figs. 3(b)—7(b) for different pressures of the carbonyl compound vapors; in each of the figures the average values of the yields in the S_1 region are normalized to a common magnitude. These plots were obtained from comparison of the intensities of absorption and corrected excitation spectra. It should be emphasized that although the phosphorescence quantum yields, Φ_P, are essentially constant in the whole range of excitation energy corresponding to the S_1 state, they undergo an abrupt, step-like change when the excitation energy is raised to the value corresponding to S_2.

Figure 8 shows plots of $\Phi_P(S_2^0)/\Phi_P(S_1)$ against the pressure, *p*, for benzaldehyde, acetophenone, and *p*-fluorobenzaldehyde. Here, the Φ_P values obtained by excitation into the S_1 state and into the zero-point vibrational level of the S_2 state are denoted by $\Phi_P(S_1)$ and $\Phi_P(S_2^0)$, respectively; since in each of the carbonyl compounds $\Phi_P(S_1)$ is approximately constant regardless of the magnitude of the excess vibrational energy, the vibrational level excited is not specified in the case of $\Phi_P(S_1)$. As *p* is reduced to zero, the ratios $\Phi_P(S_2^0)/\Phi_P(S_1)$ appear to approach zero. This pressure dependence of the quantum yield ratios is consistent with the observation that the step-like changes of Φ_P, caused by changing the excitation from $S_0 \rightarrow S_1$ to $S_0 \rightarrow S_2$, become more pronounced as *p* is lowered (see Figs. 3(b)—7(b)).

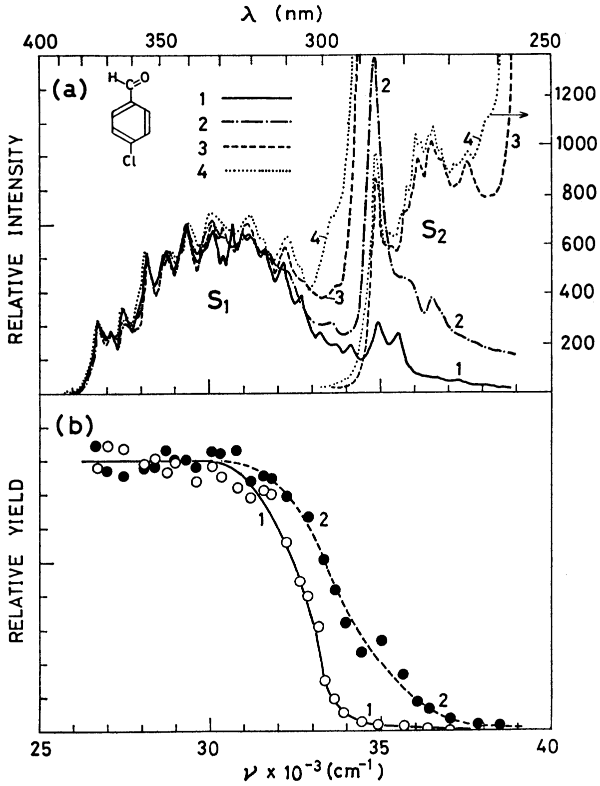

Fig. 6. (a) Phosphorescence excitation spectra at different pressures (1, 2, and 3) and absorption spectrum (4) of *p*-chlorobenzaldehyde vapor. (1) 9 mTorr; (2) 40 mTorr; (3) 50 mTorr of *p*-chlorobenzaldehyde in the presence of added CCl_4 (≈400 Torr). Higher-intensity spectra are obtained by multiplying the ordinate values of the corresponding lower-intensity spectra by a factor of 20 for curves 3 and 4. Since the molar extinction coefficients (ε) of this compound could not be determined directly because of its low vapor pressure, the ε values in the vapor phase were estimated from those in isopentane solution. (b) Plots of phosphorescence quantum yields of *p*-chlorobenzaldehyde vapor *vs.* excitation energy at different pressures. (1) 9 mTorr; (2) 60 mTorr.

The pressure dependence of $\Phi_P(S_1)$ and $\Phi_P(S_2^0)$ was already shown in the previous paper[7] for benzaldehyde; both $\Phi_P(S_1)$ and $\Phi_P(S_2^0)$ have a value of about 0.02 at 0.8 Torr. It was found that the phosphorescence quantum yields of other carbonyl compounds are comparable to that of benzaldehyde, when *p* is relatively large.

Discussion

We have measured the phosphorescence excitation spectra of carbonyl compounds at pressures lower than previous authors employed. The results show that Φ_P decreases very sharply as the excitation energy is raised

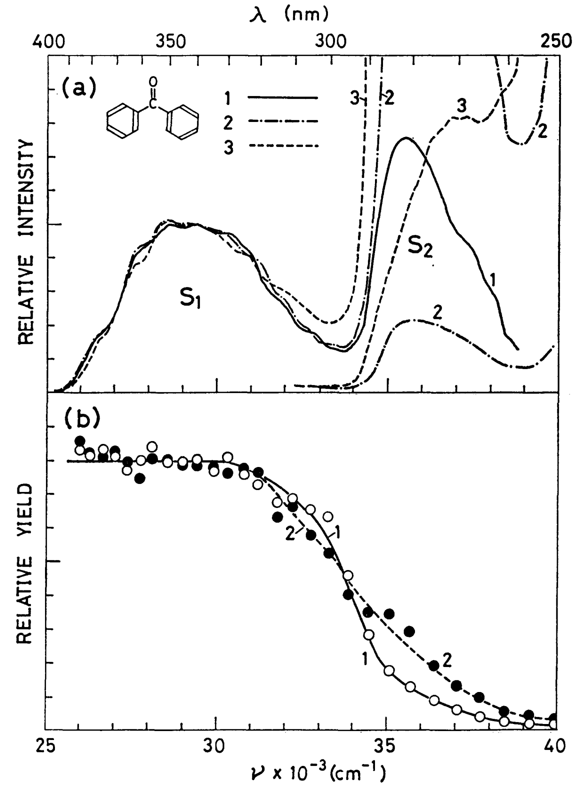

Fig. 7. (a) Phosphorescence excitation spectra at different pressures of benzophenone vapor. (1) 1 mTorr; (2) 110 mTorr; (3) 20 mTorr of benzophenone in the presence of added CCl_4 ($\approx$400 Torr). Higher-intensity spectra are obtained by multiplying the ordinate values of the corresponding lower-intensity spectra by a factor of 10 for curves 2 and 3. (b) Plots of phosphorescence quantum yields of benzophenone vapor *vs.* excitation energy at different pressures. (1) 1 mTorr; (2) 110 mTorr.

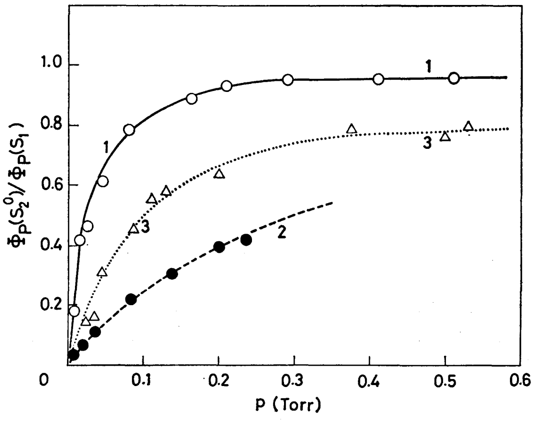

Fig. 8. Plots of $\Phi_P(S_2{}^0)/\Phi_P(S_1)$ *vs.* *p* for (1) benzaldehyde, (2) acetophenone, and (3) *p*-fluorobenzaldehyde.

to the value corresponding to the $S_2{}^0$ level, and that $\Phi_P(S_2{}^0)$ appears to approach zero as *p* is reduced to zero.

Berger *et al.*[3,4] studied the photochemistry of benzaldehyde and acetophenone vapors by determining the quantum yields of photoproducts as well as the lifetimes and quantum yields of phosphorescence emissions over a range of pressures and of excitation wavelengths. They reported that the molecules excited to the S_2 state decompose with unit probability at low pressure to produce carbon monoxide and benzene from benzaldehyde, and methyl and benzoyl radicals from acetophenone, but that excitation to the S_1 state does not result in such decomposition. They concluded also that the decomposition occurs from the excited vibrational levels of triplet states of these molecules.

It is possible that a decomposing level which leads to the step-like change of Φ_P may be situated accidentally near the $S_2{}^0$ level. For all the carbonyl compounds studied, however, Φ_P shows a sharp decrease when the excitation energy approaches the value corresponding to the $S_2{}^0$ level. This can be most clearly seen by comparing the excitation energy dependence of Φ_P of *p*-fluorobenzaldehyde ($S_2{}^0$, 35970 cm^{-1}) with that of *p*-chlorobenzaldehyde ($S_2{}^0$, 34970 cm^{-1}). In fact, on going from the former to the latter molecule, the starting point of the sharp decrease of Φ_P is red-shifted by about 1000 cm^{-1} (Figs. 5 and 6). It is, therefore, reasonable to consider that Φ_P varies according to the nature of the singlet electronic state to which the molecule is initially excited.

The pressure dependence of Φ_P suggests that the decomposition process occurs *via* a long-lived state such as a triplet, as will be explained in detail later. This decomposing state will hereafter be named an intermediate state, and will be denoted by Im. It is inferred that the state Im is relaxed to the phosphorescent state by collision.

Kinetic Considerations. The radiative and nonradiative properties of the vapors of the carbonyl compounds can be explained by the kinetic scheme illustrated in Fig. 9. For S_1 excitation,

$$S_1{}^v \xrightarrow{k_1} T_1{}^v, \tag{1}$$

$$T_1{}^v + S_0 \xrightarrow{k_2} T_1{}^0 + S_0, \tag{2}$$

and for S_2 excitation,

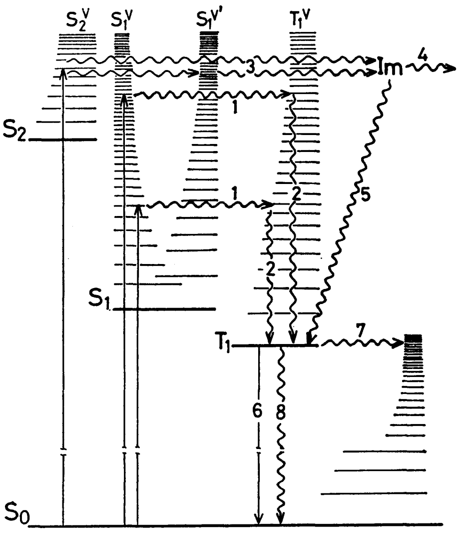

Fig. 9. A schematic diagram showing photophysical and photochemical processes in the carbonyl compound vapors.

$$S_2{}^v \xrightarrow{k_3} \mathrm{Im}, \tag{3}$$

$$\mathrm{Im} \xrightarrow{k_4} \text{Products}, \tag{4}$$

$$\mathrm{Im} + S_0 \xrightarrow{k_5} T_1{}^0 + S_0. \tag{5}$$

Processes 1 and 3 represent intersystem crossing from $S_1{}^v$ to $T_1{}^v$ and overall conversion from $S_2{}^v$ to Im, respectively. Here, $S_1{}^v$ and $S_2{}^v$ mean the optically populated vibrational levels in S_1 and S_2, respectively, and $T_1{}^v$ is the vibrational level in T_1 populated as a result of the crossing from $S_1{}^v$; $v=0$ corresponds to the zero-point vibrational level for each of the electronic states. Process 4 is the decomposition of the carbonyl compounds in the Im state. The resulting products in benzaldehyde and acetophenone have already been mentioned. No information is available as to the decomposition products in *p*-fluorobenzaldehyde, *p*-chlorobenzaldehyde, and benzophenone, but similar cleavage is expected to occur also in these compounds. Processes 2 and 5 represent, respectively, collisional deactivation of $T_1{}^v$ and Im to $T_1{}^0$; here, $T_1{}^0$ means lower vibrational levels of T_1, including the zero-point level. Since the shapes of the observed phosphorescence spectra are independent of the pressure, the emission originates only from the $T_1{}^0$ state.

The molecule in the $T_1{}^0$ state resulting from process 2 or 5 is deactivated in the following ways:

$$T_1{}^0 \xrightarrow{k_6} S_0 + h\nu, \tag{6}$$

$$T_1{}^0 \xrightarrow{k_7} S_0, \tag{7}$$

$$T_1{}^0 + S_0 \xrightarrow{k_8} 2S_0. \tag{8}$$

Process 7 represents the pressure-independent intersystem crossing from $T_1{}^0$ to the ground state, and process 8 the self-quenching. In this model, the quenching of the excited molecule by the cell wall is not taken into account for the sake of simplicity, although such a wall effect cannot be neglected in the measurement at very low pressure.

In the case of S_2 excitation, process 3 is followed exclusively by the decomposition process 4 when p is very small, but at large p values process 5 competes favorably with the decomposition. On the other hand, optical excitation to the S_1 state, *i.e.* excitation to $S_1{}^v$, does not lead to the decomposition.[3,4] These observations account for the fact that the quantum yield ratios $\Phi_P(S_2{}^0)/\Phi_P(S_1)$, which are zero at $p \simeq 0$, increase with increasing pressure (see Fig. 8).

In terms of the kinetic scheme mentioned above, $\Phi_P(S_1{}^v)$ and $\Phi_P(S_2{}^v)$ as functions of p are given by

$$\Phi_P(S_1{}^v) = \Phi_{ISC}(S_1{}^v \to T_1{}^v)\kappa, \tag{9}$$

$$\Phi_P(S_2{}^v) = \Phi(S_2{}^v \to \mathrm{Im})\frac{k_5 p}{k_4 + k_5 p}\kappa, \tag{10}$$

where

$$\kappa = \frac{k_6}{k_6 + k_7 + k_8 p},$$

and $\Phi_{ISC}(S_1{}^v \to T_1{}^v)$ and $\Phi(S_2{}^v \to \mathrm{Im})$ are the quantum yields of the intersystem crossing $S_1{}^v \to T_1{}^v$ and the overall conversion $S_2{}^v \to \mathrm{Im}$, respectively. It follows from Eqs. 9 and 10 that

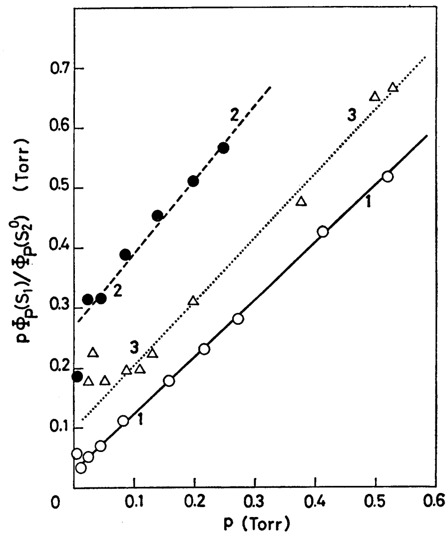

Fig. 10. Plots of $p\Phi_P(S_1)/\Phi_P(S_2{}^0)$ *vs.* p for (1) benzaldehyde, (2) acetophenone, and (3) *p*-fluorobenzaldehyde.

$$p\frac{\Phi_P(S_1{}^v)}{\Phi_P(S_2{}^v)} = \frac{\Phi_{ISC}(S_1{}^v \to T_1{}^v)}{\Phi(S_2{}^v \to \mathrm{Im})}\left(\frac{k_4}{k_5} + p\right). \tag{11}$$

The experimental data given in Fig. 8 are analyzed on the basis of Eq. 11 for benzaldehyde, acetophenone, and *p*-fluorobenzaldehyde, with the results shown in Fig. 10. Thus, the plots of $p\Phi_P(S_1)/\Phi_P(S_2{}^0)$ against p give straight lines, as may be expected from Eq. 11. From the intercepts and slopes of the straight lines, the values of k_4/k_5 and $\Phi_{ISC}(S_1 \to T_1{}^v)/\Phi(S_2{}^0 \to \mathrm{Im})$ are evaluated, respectively, to be 0.03 Torr and 0.95 for benzaldehyde, 0.23 Torr and 1.20 for acetophenone, and 0.10 Torr and 1.06 for *p*-fluorobenzaldehyde.

Berger *et al.*[3] pointed out that the decomposition of benzaldehyde occurs in two states with different lifetimes, but the linear plot in Fig. 10 appears to indicate that only a single state participates in the decomposition so far as the pressure region employed in Fig. 10 is concerned.

The Intermediate State and Nonradiative Processes. In terms of the kinetic model, the lifetime of the intermediate state is given by

$$\tau_{\mathrm{Im}} = \frac{1}{k_4 + k_5 p}. \tag{12}$$

The value of the collisional deactivation rate constant, k_5, may be assumed to be equal to or less than that of the bimolecular rate constant for collision, k_c. On the basis of the hard sphere model, the k_c values are estimated to be 1.07×10^7, 1.13×10^7, and 1.02×10^7 Torr^{-1} s^{-1}, respectively, for benzaldehyde (5.5 Å), acetophenone (5.8 Å), and *p*-fluorobenzaldehyde (5.6 Å), with the molecular diameters given in parentheses. If k_5 is assumed to be equal to k_c, the value of k_4 can immediately be obtained by using the k_4/k_5 values which have already been determined. In this way the lifetimes at zero pressure, $\tau_{\mathrm{Im}}(=1/k_4)$, are found to be 3.1×10^{-6}, 3.8×10^{-7}, and 9.8×10^{-7} s for benzaldehyde, acetophenone, and *p*-fluorobenzaldehyde, respectively.

The fact that fluorescence is not observed from S_1 and S_2 means that the lifetimes of these singlet states are very short ($<1\times10^{-9}$ s), and therefore Im cannot be the S_1 nor S_2 state. Taking this into account, Im should be one of the following states: (1) a dissociative vibrational mode in T_1, denoted by $T_1^{v'}$, which is different from T_1^v in nature; (2) a higher triplet state, $T_j(j>1)$; (3) a reaction intermediate which cannot be identified as any of the excited states of the initial carbonyl compound.

As has been shown, the phosphorescence quantum yield of the carbonyl compound vapor varies according to the nature of the singlet state (S_1 or S_2) to which the molecule is initially excited. This indicates that the molecule excited to S_2 takes a nonradiative pathway different from the one taken by the molecule excited to S_1. According to the kinetic scheme already mentioned, the excitation to S_2^v is followed by the overall $S_2^v \rightarrow$Im conversion, whereas the molecule excited to S_1^v converts to T_1^v.

Two mechanisms, (I) and (II), are conceivable for the overall $S_2^v \rightarrow$Im conversion. (I) S_2^v converts to Im without passing through S_1, *i.e.* $S_2^v \rightarrow$Im. (II) S_2^v converts to Im *via* $S_1^{v'}$, *i.e.* $S_2^v \rightarrow S_1^{v'} \rightarrow$Im, where $S_1^{v'}$ represents the vibrational mode in S_1 populated as a result of the $S_2 \rightarrow S_1$ internal conversion; $S_1^{v'}$ is in general different from S_1^v in nature (see Fig. 9). In the former mechanism the $S_2^v \rightarrow S_1^{v'}$ conversion should be slow compared with the $S_2^v \rightarrow$Im conversion, while in the latter the vibrational energy redistribution between $S_1^{v'}$ and S_1^v should be slow compared with the $S_1^{v'} \rightarrow$Im conversion.

We have mentioned three possible states (1)—(3) for Im and two mechanisms (I) and (II) for $S_2^v \rightarrow$Im. It is at present difficult to know which state is most probable and which mechanism is more important. If Im is $T_j(j>1)$ or a reaction intermediate, the mechanism (I) will be more important, because the $S_2 \rightarrow S_1$ internal conversion in the carbonyl compounds studied is expected to be relatively slow owing to the large energy separation ($\approx$8000 cm^{-1}) between S_2^0 and S_1^0. When Im is $T_1^{v'}$, the mechanism (I) corresponds to the process $S_2^v \rightarrow T_1^{v'}$. If this process occurs directly, its rate must be slow because of the large energy gap between S_2^0 and T_1^0, so that the mechanism (II) will become favorable compared with (I). It is possible, however, that the process $S_2^v \rightarrow T_1^{v'}$ may occur *via* a higher-energy triplet state. In any case, in order that $T_1^{v'}$ may be a candidate for Im, both the intersystem crossing $S_1^v \rightarrow T_1^{v'}$ and the vibrational energy redistribution between T_1^v and $T_1^{v'}$ should occur only slowly; otherwise the optical excitation to S_1^v would lead to the decomposition reaction.

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