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Triplet-State Excitation of 1-Indanone by Electron Impact

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Electron-impact-induced phosphorescence of 1-indanone was observed for the first time at low pressure. The mechanism of triplet-state formation of this molecule by electron-impact excitation was studied by measuring excitation energy dependence of the phosphorescence intensity.

Electron impact excitation of triplet states in organic molecules has been the subject of interest in connection with electron-molecule interactions.[1] In the present paper, we chose 1-indanone and studied mechanism of triplet excitation under electron impact by measuring phosphorescence intensity as a function of electron energy (excitation function), the results being compared with those of other aromatic carbonyl compounds, i.e., benzaldehyde,[2] acetophenone,[3] and benzophenone.[4]

The apparatus for the measurements of electron-impact-induced phosphorescence have been described in detail elsewhere.[5] A thoria-coated tungsten filament was used for the electron gun, and the energy spread of the electron beam was less than 0.5 eV. The optical band-pass widths were about 1 nm for phosphorescence spectra and 2 nm for excitation functions. The pressure was monitored using an MKS Baratron pressure gauge. 1-Indanone was purified by distilling under reduced pressure.

Figure 1 depicts a time-resolved emission spectrum of 1-indanone at 0.2 Pa excited with 10 eV electron beam. The excitation duration and delay and aperture times were 100, 10, and 100 μs, respectively. This spectrum, exhibiting prominent peaks at 380.5, 407.2, and 438 nm, is assigned as that of 1-indanone

phosphorescence since the spectral features are very similar to that obtained in the condensed phase.[6] The prominent peaks were assigned as the 0-0 band and progressions in the C-O stretching mode. This is the first observation of electron-impact-induced phosphorescence of 1-indanone. In the cases of benzaldehyde,[2] acetophenone,[3] and benzophenone,[4] phosphorescence from vibrationally excited T_1 states (hereafter abbreviated as VET) has been observed at low pressures. The features of the excitation functions for the phosphorescence of thermalized T_1 state and those of VET's are different in acetophenone[3] and benzophenone.[4] In the present study we investigated whether phosphorescence from VET's can be observed in 1-indanone or not. Phosphorescence spectra were measured at pressures down to 0.1 Pa, but the feature of the spectrum did not change with decreasing pressure. A possible reason for the absence of VET phosphorescence in 1-indanone is that the rates of $T_1 \rightarrow S_0$ intersystem crossing from VET's are very rapid. Hirata and Lim[7] measured rates of $T_1 \rightarrow S_0$ intersystem crossings in acetophenone and 1-indanone as functions of excess vibrational energies in T_1. They have found that these rates become larger as excess vibrational energies increase and that the rate of increase is much more prominent in the latter molecule.

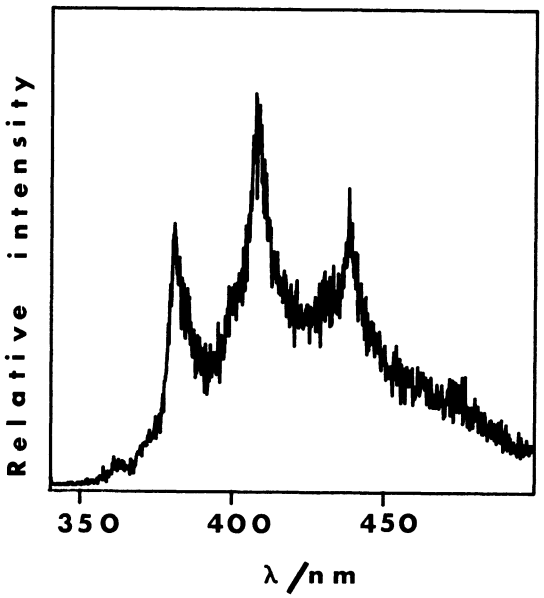

Fig.1. Electron-impact-induced phosphorescence of 1-indanone at 0.9 Pa.

1-Indanone has been found to phosphoresce both from $^3n\pi^*$ and $^3\pi\pi^*$ in condensed phases.[6] However, no phosphorescence which could be assigned as that from $^3\pi\pi^*$ state was observed in the present case. This may be due to the fact that the phosphorescence radiative decay rate of the latter state is very small and its phosphorescence is subject to efficient quenching by the wall at low pressures. Such phosphorescence could have been observed at much higher pressures, where the rate of diffusion of triplet molecules to the wall is smaller.

Unfortunately, it is very difficult to measure luminescence at pressures higher than 5 Pa using the present apparatus.

The phosphorescence decay curves were measured at 380.5 nm at pressures between 0.1-0.33 Pa, and were analyzed using Marquardt method.[8] At pressure as high as 0.33 Pa the decays were found to be single exponential with lifetimes of 670 μs. This lifetime is shorter than those obtained in the condensed phase at 77 K, probably due to the effect of temperature and/or collision with the wall. At 0.1 Pa the decays were biexponential with shorter and longer lifetimes of 146 and 506 μs, respectively. Since phosphorescence spectrum of 1-indanone did not change with decreasing pressure or by changing delay time, and since the decay characteristics do not depend on the wavelength of phosphorescence measurements, these non-exponential decays were not due to the occurrences of other emission than the phosphorescence from the thermalized T_1 state. These apparently non-exponential decays can be attributed to drifting of T_1 molecules out of the field of view during decay measurements. Such effect becomes unimportant at higher pressures.

Phosphorescence excitation function of the 0-0 emission band of 1-indanone was measured at 0.2 Pa with electron energy up to 80 eV. The excitation duration, delay, and aperture times were the same as those in the case of time-resolved spectrum. Thus obtained excitation function (Fig.2) exhibits a large peak located at energies around 10 eV, while much smaller band is observed at energies 60-80 eV. High energy band may be associated with pathways through singlet state excitation due to Coulombic interaction followed by $S_1 \rightarrow T_1$ intersystem crossing, since the cross sections of such processes are large at higher electron energies.[9] On the other hand, the

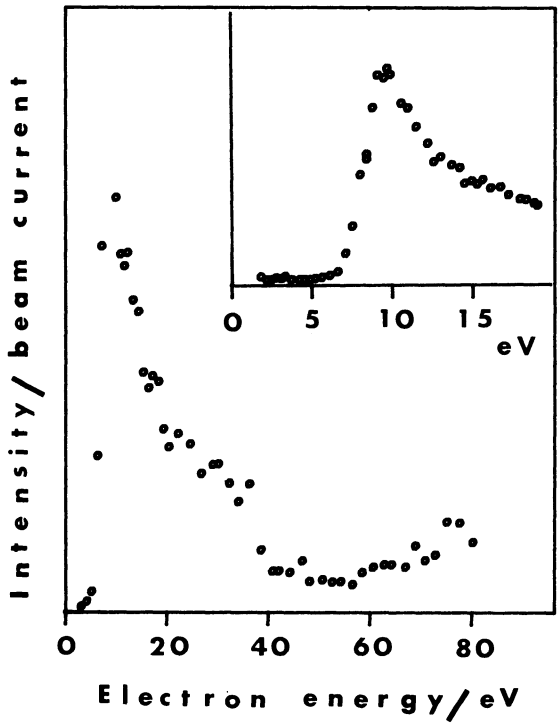

Fig.2. Electron impact excitation functions of phosphorescence of 1-indanone at 0.2 Pa.

band at 10 eV can be ascribed to the mechanisms due to electron exchange or to core-excited shape resonances. Detailed measurements were made at energies 2-18 eV in order to see fine structure of the band at around 10 eV, the results being shown in the insert of Fig.2. The slope of the initial rise is relatively slow, and the maximum occurs at about 4 eV higher than the threshold, not having any sharp structure. These features are very different from those of benzaldehyde,[2] acetophenone,[3] and benzophenone[4] where the initial rises are very steep with sharp structures. The present excitation function of 1-indanone indicates that excitations are mainly due to exchange mechanism and that core-excited shape resonances do not play important roles in this molecule.[9,10]

Although 1-indanone has the same electronic configuration with acetophenone and benzaldehyde with respect to π and n electron systems, its triplet state properties have been considered to differ greatly from those of acetophenone and benzaldehyde, probably due to rigid framework at the carbonyl group.[7,11] The difference of excitation mechanism may be due to the differences of triplet properties.

References

1) L.G.Christophorou and M.W.Grant, Adv. Chem. Phys., 36, 413 (1977).
2) A.Inoue and N.Ebara, Chem. Phys. Lett., 109, 27 (1984).
3) A.Inoue, M.Ushiyama, and N.Ebara, Chem. Phys. Lett., 117, 18 (1985).
4) A.Inoue, Chem. Lett., 1986, 2085.
5) A.Inoue and N.Ebara, Appl. Spectrosc., 40, 410 (1986).
6) N.C.Yang and S.Murov, J. Chem. Phys., 45, 4358 (1966).
7) Y.Hirata and E.C.Lim, Chem. Phys. Lett., 71, 167 (1980).
8) J.N.Demas, "Excited State Lifetime Measurements," Academic Press, New York (1983), pp.89-99.
9) A.Kuppermann, W.M.Flicker, and O.A.Mosher, Chem. Rev.,79, 77 (1979).
10) G.J.Verhaart and H.H.Brongersma, Chem. Phys. Lett., 71, 345 (1980).
11) S.Niizuma and N.Hirota, J. Phys. Chem., 82, 453 (1978).

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