Fluorescence and Predissociation of Sulfur Dioxide

Sir:

Much work[1-5] has been devoted to elucidating the nature of two excited states of SO_2 produced by light of wavelength above 2500 Å, where no photochemical dissociation takes place. The third excited state, generated by light absorption at about 2100 Å, was found by Lotmar[6] to fluoresce strongly in the spectral region from 2100 Å to the violet.

In the present work the fluorescence intensity was measured as a function of incident wavelength in the region 2000 to 2300 Å, where photochemical dissociation is expected to compete with fluorescence. The absorption and the undispersed fluorescence intensity of SO_2 were measured as before[7] as a function of incident wavelength. In brief, a hydrogen continuum was used as a light source. A fluorescence cell, 6.95 cm in length, was placed behind the exit slit of a 1-m near-normal incidence vacuum monochromator with a 600-line/mm grating. A slit width of 0.2 mm corresponding to a 3-Å resolution was used for measuring both absorption and fluorescence. The fluorescence intensity, I_f, was measured at right angles to the incident beam by a 13-stage photomultiplier with a cathode of "S" (Q) spectral sensitivity. A color filter transmitting light of wavelength from 2300 to 4200 Å was placed in front of the multiplier to eliminate the scattered light. I_f was normalized to the incident light intensity, I_0, to obtain the relative fluorescence intensity, I_f/I_0.

Figure 1a shows the absorption spectrum of 0.3 Torr of SO_2 in the region 2000–2300 Å. In accordance with previous measurements,[8,9] 18 main bands were observed. According to Duchesne and Rosen,[10] bands 1 and 3 belong to excited state α_1 and bands 4–18 to the α_2 state. Figure 1b shows the I_f/I_0 *vs.* incident wavelength (2000–2370 Å) curve of 0.3 Torr of SO_2 obtained with a scanning speed of 10 Å/min and a time constant of 5 sec. Intensity peaks corresponding to the 18 absorption bands appear. The peak intensity increases from band 1 to 6 in accordance with an increase in absorption. While the absorption still continues to increase further after 6, the fluorescence peaks show a sudden decrease after 6, indicating the occurrence of another process. The threshold energy of incident photons, $h\nu$, responsible for this process, lies in the range 5.66 eV (2189 Å) > $h\nu$ > 5.62 eV (2208 Å).

The bond dissociation energy, $D_0(\text{OS–O})$, may be calculated from

$$D_0(\text{OS–O}) = (1/2)D_0(S_2) + (1/2)\Delta H_f{}^\circ{}_0(S_2) + D_0(O_2) - \Delta H_f{}^\circ{}_0(SO_2) - D_0(SO) \quad \text{(I)}$$

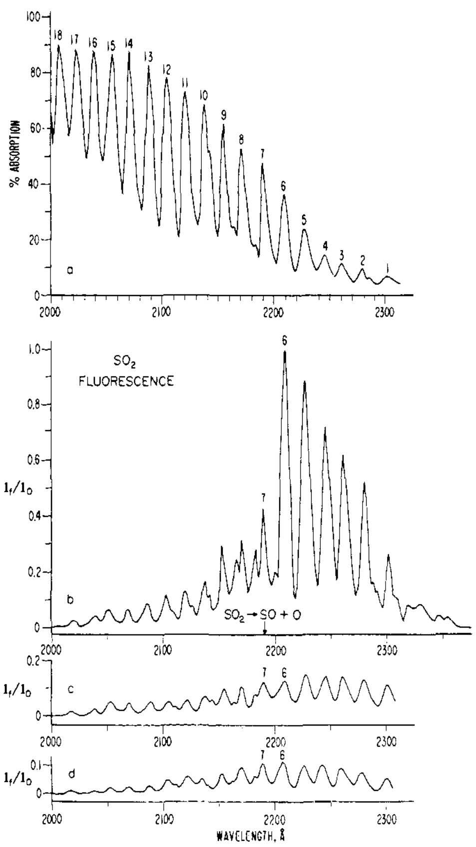

Figure 1. (a) Absorption of 0.3 Torr of SO_2, path length 6.95 cm, in the region from 2000 to 2300 Å, resolution 3 Å. (b) Fluorescence intensity (undispersed) of 0.3 Torr of SO_2 as a function of incident wavelength, resolution 3 Å, scanning speed 10 Å/min, time constant 5 sec. An arrow shows the thermochemical threshold of dissociation, corresponding to 2192 Å. (c) Fluorescence intensity as a function of incident wavelength of a mixture of 0.3 Torr of SO_2 and 400 Torr of Ar. (d) Fluorescence intensity as a function of incident wavelength of 0.3 Torr of SO_2 in ambient air.

Using the following thermochemical values for $D_0(S_2) = 4.366$ eV,[11] $\Delta H_f{}^\circ{}_0(S_2) = 1.33 \pm 0.01$ eV,[12] $D_0(O_2) = 5.116$ eV,[12] $\Delta H_f{}^\circ{}_0(SO_2) = 3.050$ eV, and $D_0(SO) = 5.358$ eV,[13] $D_0(\text{OS–O}) = 5.65 \pm 0.01$ eV is obtained. This value corresponds almost exactly with the threshold energy found for the nonfluorescence process. Figure 1c shows the quenching effect of the addition of 400 Torr of Ar to 0.3 Torr of SO_2. An estimate of the quenching rate k_3 by Ar may be made from the following equations

$$SO_2 \longrightarrow SO_2{}^* \qquad (1)$$

$$SO_2{}^* + SO_2 \longrightarrow 2SO_2 \qquad k_2 \qquad (2)$$

$$SO_2{}^* + Ar \longrightarrow SO_2 + Ar \qquad k_3 \qquad (3)$$

$$SO_2{}^* \longrightarrow SO + O \qquad k_d \qquad (4)$$

$$SO_2{}^* \longrightarrow SO_2 + h\nu \qquad k_f \qquad (5)$$

$$I_f{}^0/I_f = 1 + k_3[Ar]/(k_f + k_d + k_2[SO_2]) \qquad \text{(II)}$$

where $I_f{}^0$ is the fluorescence intensity of pure SO_2 and I_f that of a mixture of SO_2 and Ar. For simplicity, the internal conversion process was not included.

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Apparently the fluorescence lifetime, $\tau = 1/k_f$, has not been directly measured. Integrating the absorption coefficient measured previously,[8,9] in the region 1650–2300 Å, the oscillator strength of 0.067 is obtained which gives a lifetime of 9 nsec. If this value is adopted, eq II may be reduced to

$$I_f^0/I_f = 1 + k_3[\mathrm{Ar}]/(k_f + k_d) \qquad \text{(III)}$$

because $k_2[\mathrm{SO_2}]$ can be neglected with respect to $k_f + k_d$.

Using $I_f^0/I_f = 7.7$, $k_d = 0$ (Figures 1b and c, band 6), $[\mathrm{Ar}] = 1.4 \times 10^{19}$ molecules cm^{-3} and 1.1×10^8 sec^{-1} for k_f, the quenching rate k_3 of the excited state at band 6 is 5×10^{-11} cm^3 molecule^{-1} sec^{-1}. This value is in reasonable agreement with the quenching rate by Ar of 5.2×10^{-11} for the first excited singlet state produced by light of wavelength 2750–3020 Å.[14] Assuming the same quenching rate for the excited state produced at band 7 and from the measured I_f^0/I_f, the lifetime can be calculated to be 3.2 nsec. This reduced lifetime must be due to predissociation; *i.e.*, k_d is no longer zero in band 7. The change in the width of an absorption band introduced by predissociation would be too small to provide evidence for predissociation.

Finally, Figure 1d shows the fluorescence intensity curve of a mixture of 0.3 Torr of SO_2 and 1 atm of air. The fluorescence is still detectable, the radiative life being sufficiently short relative to the quenching rate. The result suggests that a small amount of SO_2 in ambient air can be detected without interference from other pollutants by using an intense light source of appropriate wavelength.

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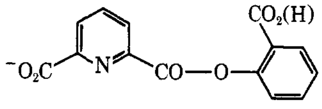
Intramolecular Bifunctional Catalysis of Ester Hydrolysis by Metal Ion and Carboxylate in a Carboxypeptidase Model

Sir:

Extensive work has clarified the nature of the active site in the enzyme carboxypeptidase A and the functional groups involved in catalysis.[1] In the hydrolysis of peptides there is participation by a zinc ion, a carboxylate ion, and a tyrosine hydroxyl. The enzyme will also hydrolyze esters, but in the latter case apparently only the metal ion and the carboxylate play a role,[2] the former as a Lewis acid coordinated to carbonyl oxygen and the latter as either a general base or nucleophile. This situation naturally raises the question as to how effective such a combination can be in simple chemical models.

Of course, there are many examples[3] of metal-promoted hydrolysis of carboxylic acid derivatives, and the effects of metal ions can in some cases be quite high, comparable to enzymatic accelerations.[4] Similarly, neighboring group participation by carboxylate ion in the hydrolysis of compounds such as acetylsalicylic acid has been extensively studied,[5] although in this system catalysis is rather modest. We wish to report the study of a case in which simultaneous catalysis by internally bound metal ion and neighboring carboxylate operates on the hydrolysis of an ester.[6]



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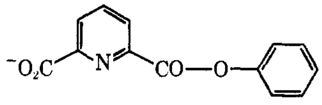

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We have studied the hydrolysis of the salicylic acid ester of pyridine-2,6-dicarboxylic acid (**1**) and the corresponding phenyl ester of pyridine-2,6-dicarboxylic acid (**2**) as a function of pH with and without metal ion. For most of the work the metal ion chosen was Ni^{2+} (Ni^{2+} can replace Zn^{2+} in the enzyme[7]) although Zn^{2+} was also examined in two cases. The pyridinecarboxylate group is a good metal ligand[8] and there is no difficulty in binding a metal ion to it in a position to activate the ester group. Kinetic studies as a function of metal concentration showed that under the conditions reported below the substrate was present entirely as a 1:1 metal complex (*i.e.*, the metal concentration is so high that the kinetics are zero order in metal). All hydrolysis studies were carried out at 25.0° in H_2O with $\mu = 0.5\ M$ (NaCl). Substrate concentrations were $5 \times 10^{-4}\ M$ and metal concentrations were 0.2 *M;* buffers were used at three different concentrations and rates were extrapolated to zero buffer concentration. Runs were monitored at 298 (**1**) or 276 nm (**2**) with a Gilford spectrophotometer, and the computer-processed (least-squares and Guggenheim treatment) kinetic data of at least three runs were averaged (average deviation 3–5%) for each datum point. The results of this study are displayed in Figure 1 and the kinetic constants extracted from these studies are listed in Table I.

These data show fairly large metal ion catalysis in the hydrolysis of either **1** or **2**. Thus, the rate of attack

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[1] W. N. Lipscomb, J. A. Hartsuck, F. A. Quiocho, and G. N. Reeke, *Proc. Nat. Acad. Sci. U. S.*, **64**, 28 (1969); for a recent review, see J. E. Coleman, *Progr. Bioorg. Chem.*, **1**, 159 (1971).

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[3] Reviewed by A. E. Martell, *Pure Appl. Chem.*, **17**, 129 (1968).

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[5] *Cf.* W. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969.

[6] Although many apparent examples of intramolecular bifunctional catalysis have been reported, these have been critically examined by T. Maugh II and T. C. Bruice, *J. Amer. Chem. Soc.*, **93**, 3237 (1971), who conclude that there is no authentic case of bifunctional catalysis, as contrasted with monofunctional catalysis accompanied by electrostatic effects associated with protonation. A recent report by T. Higuchi, H. Takechi, I. H. Pitman, and H. L. Fung (*J. Amer. Chem. Soc.*, **93**, 539 (1971)) describes what seems to be an authentic case of bifunctional catalysis of ester hydrolysis. Thus ours may be the second authentic case of intramolecular bifunctional catalysis, and the first involving a metal ion.

[7] J. E. Coleman, P. Pulido and B. L. Vallee, *Biochemistry*, **5**, 2019 (1966).

[8] For Ni^{2+}, $\log K_1 = 6.4$ and for Zn^{2+}, $\log K_1 = 5.12$, according to L. G. Sillen and A. E. Martell, Ed., *Chem. Soc. Spec. Publ.*, **No. 17** (1964).