to $H = -\log C_{H^+} = +1.00$, and pK_a's were calculated. The results (Table I) show that the two acetamides have basic strengths which are identical within the (rather small) experimental error and that the acidity constants of the p-nitrobenzamides differ by less than a factor of 2. These effects are clearly incompatible with N protonation, but they are just what is expected for O protonation.

The two cyclic acetamides were also used to determine the effect of ring size upon the rate of acid-catalyzed amide hydrolysis. The reactions were monitored by nmr spectroscopy, using the change in acetyl group proton signal which occurs as the amides are converted into acetic acid. The results are summarized in Table I.

These rate measurements were made in 20% aqueous $HClO_4$ where both amides are essentially completely protonated; the initial states of the reactions are therefore the O-protonated conjugate acids with fully sp^2 hybridized nitrogen atoms. The fact that the five-membered ring substrate reacts more slowly than its six-membered homolog indicates that a change in hybridization occurs as hydrolysis takes place. The rate factor, however, is only 5, which is much less than the approximately thousandfold difference shown by the N-(p-nitrophenyl)amines for the full hybridization change, $sp^2 \rightarrow sp^3$,[11] and that suggests that the change in hybridization is only partly complete at the hydrolysis transition state. This is incompatible with either of the two reaction mechanisms commonly advanced for amide hydrolysis via N-protonated species: (1) rate-determining formation of a tetrahedral intermediate from the N-protonated cation or (2) direct displacement of nitrogen by water in this ion.[13] In both of these mechanisms, the N-protonated cation is formed, and the change to sp^3 hybridization is thus complete, before the rate-determining step. A small rate factor, on the other hand, is compatible with rate-determining formation of a tetrahedral intermediate from the O-protonated cation. In such a mechanism, conjugation between the nitrogen atom and the carbonyl group is being destroyed in the rate-determining step; this converts the nitrogen atom from an amide nitrogen into an amine nitrogen, which changes its hybridization from sp^2 to sp^3. This change, however, can be no more than partly accomplished at the rate-determining transition state, and that leads to a rate factor considerably less than the full hybridization change effect.

The results of this investigation thus favor O-protonated species, and discredit N-protonated conjugate acids, not only as the principal products of the equilibrium protonation of amides in dilute and moderately concentrated aqueous acids but also as essential intermediates in acid-catalyzed amide hydrolysis.

(13) For a particularly good recent discussion of the various mechanisms for acid-catalyzed amide hydrolysis, see C. R. Smith and K. Yates, *J. Amer. Chem. Soc.*, **94**, 8811 (1972).
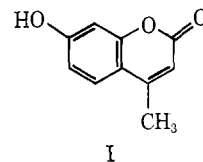
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Excited-State Reactions of a Laser Dye.
Evidence for a Two-Step Phototautomerism in
## 7-Hydroxy-4-methylcoumarin

Sir:

Previously[1] we have shown that 7-hydroxy-4-methylcoumarin (I) exhibits a variety of fluorescence spectra

I

depending on the acidity of the solution being tested. These observations led to the construction of a tunable dye laser in which laser action from the near uv (390 nm) to the yellow (600 nm) was obtained from a single solution of I which was pumped by a nitrogen laser. Three different fluorescent species were identified: the "neutral" form I* which has excitation and emission maxima at 320 and 387 nm, respectively; the "basic" form (anion) II*, λ_{max}^{excit} 364 nm, λ_{max}^{emiss} 445 nm; and the "acid" form III*, λ_{max}^{excit} 320 nm, λ_{max}^{emiss} 485 nm. The formation of the "acid" form originally was attributed to an excited state protonation reaction in which the product appeared to have no corresponding stable ground state.[1,2]

$$I \xrightarrow{h\nu} I^*$$

$$I^* + H^+ \longrightarrow (I \cdots H^+)^*$$

$$(I \cdots H^+)^* \longrightarrow I + H^+ + h\nu \text{ (485 nm)}$$
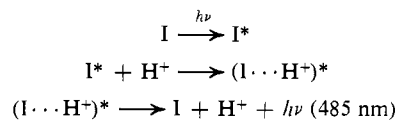
Subsequent experiments[3] on the time-resolved spectroscopy of stimulated fluorescence from the "acid" form III* furnished additional evidence that an excited state reaction was occurring. Independently, Nakashima, et al.,[4] and Yakatan, et al.,[5] have suggested that the "acid" form III is a phototautomer of I.

III
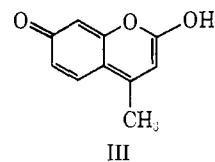
We have now further elucidated the nature and formation of the excited states, I*, II*, and III*, by the use of gain spectroscopy.[6] (The gain spectrum of a fluorescent molecule differs from the fluorescence spectrum which would be measured in an ordinary spectrophotofluorometer, in that it represents the efficiency of *stimulated* fluorescence rather than spontaneous fluorescence over the wavelength range.) In addition to supporting the assignment of III as a phototautomer,[4,5] we have been able to demonstrate that the phototautomerization

(1) C. V. Shank, A. Dienes, A. M. Trozzolo, and J. Myer, *Appl. Phys. Lett.*, **16**, 405 (1970).
(2) The instability of the ground state which is meant to be conveyed here is that the "equilibrium" concentration of the ground state is smaller than can be detected by absorption measurements.
(3) A. Dienes, C. V. Shank, and A. M. Trozzolo, *Appl. Phys. Lett.*, **17**, 189 (1970).
(4) M. Nakashima, J. A. Sousa, and R. C. Clapp, *Nature (London)*, **235**, 16 (1972).
(5) G. J. Yakatan, R. J. Juneau, and S. G. Schulman, *Anal. Chem.*, **44**, 1044 (1972).
(6) A. Dienes, C. V. Shank, and R. L. Kohn, *IEEE J. Quantum Electron.*, **9**, 833 (1973).
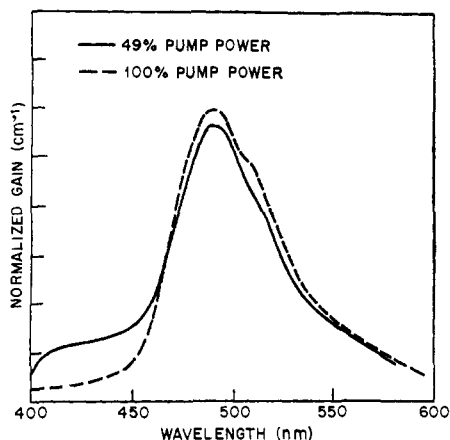
Figure 1. Gain spectrum of 7-hydroxy-4-methylcoumarin (5 × 10⁻³ M in ethanol); HCl concentration ≈ 0.15 N.
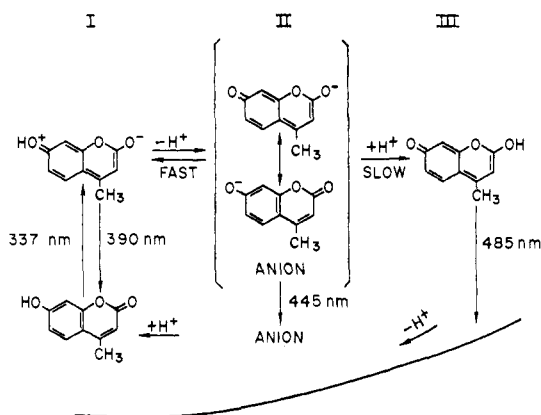

Figure 2. Excited state reactions of 7-hydroxy-4-methylcoumarin.

occurs in two distinct consecutive steps, each of which is an excited-state reaction in which the *products* are also in excited states.

It was found, somewhat unexpectedly, that the shape of the gain spectrum[7] of an acidified solution of I depended on the pump power of the nitrogen laser (Figure 1). There was relatively less gain at high pump power in the region near 400 nm. This observation suggests that an absorbing species is being produced which could account for the decrease in gain in the 400-nm region. Since one would expect I to become both a stronger acid (at the hydroxyl group) and a stronger base (at the carbonyl group) in the excited state I*[8] (see Figure 2), the first excited-state reaction would be a rapid reversible loss of a proton to form the excited anion II* (this is a unimolecular reaction and would be expected to be relatively independent of hydrogen ion concentration). This rapid step is then followed by a proton transfer from the solvent to the excited anion II* to form the phototautomer, III*. (Previous studies[3] showed that the rate of producing III* is dependent on the acid concentration.) The fluorescence of III* at 485 nm leads to the ground state, III, which is "unstable" in this solvent environment. The ground state of the anion, II, is also "unstable" in this solution (no absorption due to II

(7) The apparatus and procedure for obtaining gain spectra are described by C. V. Shank, A. Dienes, and W. T. Silfvast, *Appl. Phys. Lett.*, **17**, 307 (1970).

(8) A. Weller, *Progr. React. Kinet.*, **1**, 188 (1961); E. Vander Donckt, *ibid.*, **5**, 273 (1970).
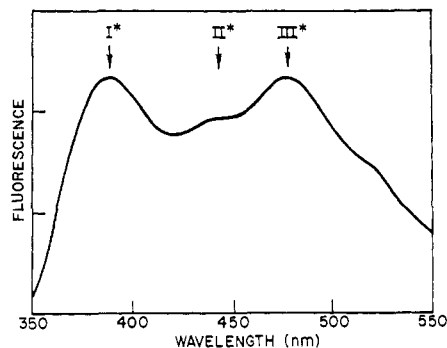

Figure 3. Spontaneous fluorescence spectrum of I (2.5 × 10⁻⁵ M) in slightly acidified (2.0 × 10⁻⁵ M HClO₄) aqueous 95% methanol.

could be detected by spectrophotometry). However, the reaction II + H⁺ → I should proceed more slowly than the ionization of III (the former reaction is bimolecular, the latter is unimolecular), and, at higher pump power, there would be a transient accumulation of ground state anions II which absorb beyond 400 nm and thus the gain would be decreased in that region.

Further evidence for this scheme was obtained from the spontaneous fluorescence spectrum of I in very weakly acidic media (see Figure 3) where it was found that I*, II*, and III* all emit from the same solution. In this case, presumably, the water and acid concentrations are sufficiently low so that the fluorescence from I* and II* compete successfully with the deprotonation and protonation reactions, respectively.

It should be noted that this example of a two-step phototautomerism is to be distinguished from the cooperative one- or two-proton transfers found in the prototropy of the excited state of salicylic acid derivatives[8] and 7-azaindole,[9] respectively. The utility of gain spectroscopy in probing other adiabatic photoreactions[10] is currently being investigated in related systems.

(9) C. A. Taylor, M. A. El-Bayoumi, and M. Kasha, *Proc. Nat. Acad. Sci. U. S.*, **63**, 253 (1969).
(10) Th. Forster, *Pure Appl. Chem.*, **24**, 443 (1970).
(11) University of California, Davis, Calif. 95616.

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One-Step and Two-Step Displacements at Silicon

Sir:

The hydrolysis of aryloxytriphenylsilanes in 60% acetonitrile–40% water is second order in hydroxide ion at low base concentrations but becomes first order at high base concentrations. This shows that the rate-determining step changes as a function of hydroxide ion concentration. The reaction therefore involves at least two steps and passes through an intermediate, presumably the "expanded octet" adduct.[1,2]

(1) C. G. Swain, R. M. Esteve, and R. H. Jones, *J. Amer. Chem. Soc.*, **71**, 965 (1949).