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INCREASE AND APERIODIC OSCILLATION IN FLUORESCENCE INTENSITY FROM IRRADIATED SOLUTION OF N-METHYLANTHRANILOHYDROXAMIC ACID IN METHANOL 1)

Ewa LIPCZYNSKA-KOCHANY 2) and Hiizu IWAMURA*
Division of Applied Molecular Science, The Institute for Molecular Science,
Myodaiji, Okazaki 444

A methanol solution of N-methylanthranilohydroxamic acid showed a reversible increase and an eventual oscillation of fluorescence intensity during continued excitation at 370 nm in a spectrofluorometer.

Whereas hydroxamic acids play important roles in many facets of chemistry and biochemistry,3) they still remain one of the less well characterized compounds. For example, a long-standing puzzle concerning the tautomeric and resonance structures of hydroxamate anions was solved only recently.1) As an extension of our structural studies, we became interested in their pK_a values in photoexcited states to find an unexpected fluorescence behavior of a methanol solution of N-methylanthranilohydroxamic acid.4)

Absorption, emission and excitation spectra of the hydroxamic acid in methanol are shown in Figure 1.5) The excitation band maximum exhibits a red shift from the absorption maximum, indicating that the fluorescence quantum yield (0.072 when excited at 345 nm) would be higher when excited at the longer-wavelength side of the absorption band. The presence of a species with different degree of solvation and/or hydrogen bonding or a tautomeric form of the hydroxamic acid is suggested. There appears to be a second much weaker emission at ca. 465 nm which becomes evident when excitation was made at 410 nm. The double emission could be explained in a manner similar to that of the benzoic acids carrying the hydroxyl or amino group at the ortho position.6) The long-wavelength emission is ascribed to phototautomeric forms generated by an intramolecular proton transfer from the hydroxyl or amino group to the adjacent carboxyl group in the excited state. The present situation may be more complicated, since there is an additional possibility of phototautomerism within the hydroxamic group. One of the candidates for such a form would be $Ar-C(OH)=N^{+}H-O^{-}$ or $Ar-C(OH)=NOH$.

When an unstirred methanol solution of N-methylanthranilohydroxamic acid (0.28 mM) in a stoppered but not degassed fluorescence cell was subjected to continued excitation at 370 ± 7 nm in a spectrofluorometer,5) the intensity of the emission bands increased gradually. In 6 hrs, the intensity at 430 nm increased ca. 14 times and that at 465 nm taken by excitation at 410 nm increased 22 times (Figure 1). In the meantime, at ca. 90 min after the start of the irradiation, an oscillation of emission intensity had started. An increase in the concentration

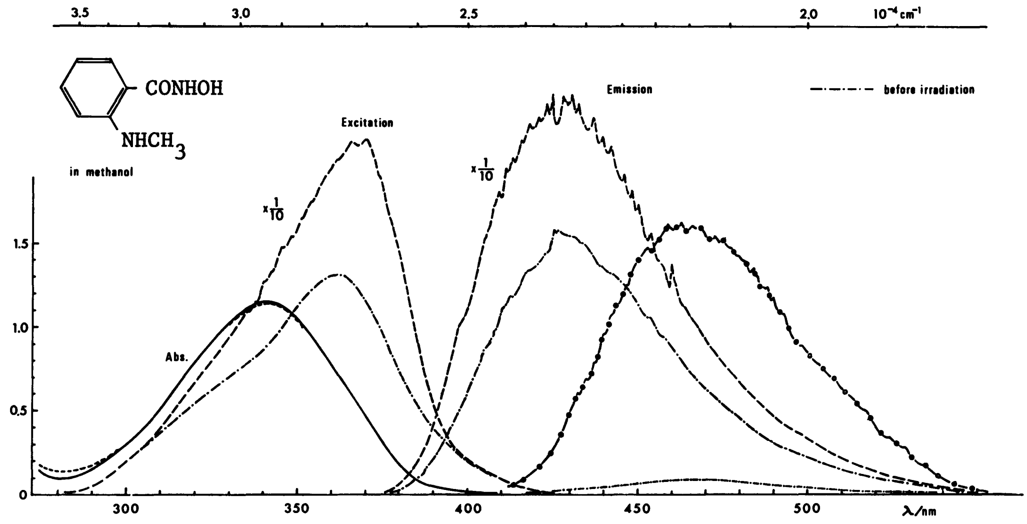

Figure 1. UV absorption (a full line), fluorescence and fluorescence excitation spectra of a 0.28 mM solution of N-methylanthranilohydroxamic acid in methanol at 25 °C. The excitation spectra (slit 3 nm) were taken at an emission wavelength of 425 nm (slit 7 nm). Broken lines show fluorescence and excitation bands after irradiation at 370 nm (slit 7 nm) for 6 hr.[5)]

of the sample appeared to shorten the induction period and increase the amplitude of the oscillation; an oscillation started with low amplitude (3 5 %) in ca. 30 min for a 0.6 mM solution, gradually increasing in intensity with excursion of the order of 25 % (Figure 2). The oscillation could be kept for several hrs. The periodicity was not found. After some time of relatively high oscillation, calmer periods often followed during which the amplitude of the oscillation became very low. It also happened that the oscillation was revitalized and the fluorescence intensity varied wildly.[5)]

The interruption of excitation of the sample solution resulted in rapid decrease in the emission band intensity. The original base level of the emission was nearly resumed. The absorption, excitation and fluorescence spectra became all superimposable to those obtained at the beginning of the experiment. When the excitation of the solution was started again, the sample followed the similar pattern as the freshly prepared solution. The overall pattern of the increase and aperiodic oscillation in fluorescence intensity observed for the hydroxamic acid is reliably reproducible. No net photochemical change was detected meaningfully after prolonged irradiation of the hydroxamic acid under these conditions.[7)]

Since Prigogine and others suggested the concept of an "open system" and developed the theory of fluctuations in 1940's, the phenomenon of chemical oscillations has aroused the interest of many theoreticians, biologists and inorganic chemists.[8)] There are, however, only few observations of oscillatory behavior of fluorescence intensity in purely organic systems. None of them has been fully understood mechanistically.[9)]

While we ourselves do not yet have a detailed interpretation of our findings, a working hypothesis based on photoprototropy may be proposed as follows.

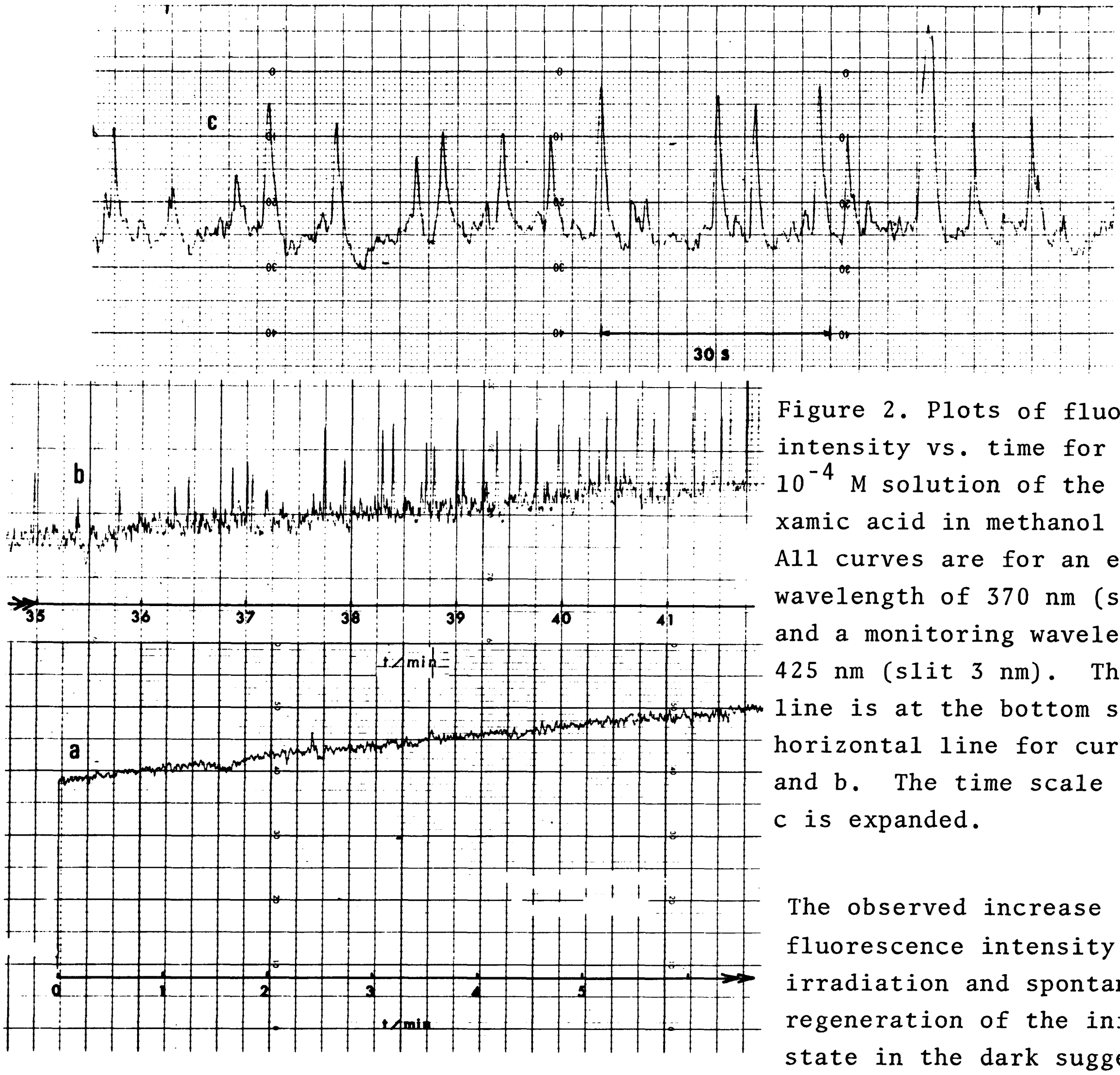

Figure 2. Plots of fluorescence intensity vs. time for a 6.0 × 10^{-4} M solution of the hydroxamic acid in methanol at 25 °C. All curves are for an excitation wavelength of 370 nm (slit 7 nm) and a monitoring wavelength of 425 nm (slit 3 nm). The baseline is at the bottom solid horizontal line for curves a and b. The time scale of curve c is expanded.

The observed increase in fluorescence intensity during irradiation and spontaneous regeneration of the initial state in the dark suggest the photochemical formation of one of the tautomeric forms of the hydroxamic acid which should have a similar chromophoric system but emit more efficiently than the original form.[10)] In the ground state the tautomeric form must be thermodynamically less stable and reverts to the initial form readily. Under extended excitation, the concentration of the tautomeric form would increase to reach the photostationary state. According to the current theory of chemical oscillation, we are dealing with the system of photoinduced chemical instability.[11)] The oscillation in the fluorescence intensity is considered to correspond to fluctuation of the concentration of the more strongly emitting phototautomer. Since the hydroxamic acid constitutes a complicated prototropic system, it could easily be led to the state far from equilibrium by slight change in the boundary conditions, e.g., local temperature, pH and so on of the irradiated zone of the sample solution. The amphoteric character of the N-methylanthranilohydroxamic acid may be serving as a good feedback mechanism of autocatalysis.

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5) Spectra were taken on a Hitachi 340 Recording Spectrophotometer equipped with a keyboard attachment and a Shimadzu RF-502 Spectrofluorometer. The wavelength dependence of the exciting light intensity was eliminated by the attached compensator. A Haake G temperature-controlled (25 ± 0.1 °C) cell holder was used in both cases. No variation of fluorescence intensities of a solution of anthracene in cyclohexane was observed under these conditions.

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