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NUCLEOPHILIC ADDITION OF PRIMARY ALCOHOLS TO N-METHYLACRIDINIUM CATION

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N-Methylacridinium chloride (MA) reacted with primary alcohols to yield corresponding N-methyl-9-alkoxyacridanes, which dissociated to MA and alcohols at 77 K upon UV-irradiation.

Acridinium salts have been known as metachromatic compounds. For example, both absorption and fluorescence spectra of Acridine Orange in water are varied by increasing its concentration[1] or by addition of anionic polyelectrolytes.[2] Such metachromatic behavior is ascribed to a strong tendency of Acridine Orange to aggregate spontaneously. In the present study, we found that the absorption and emission spectra of N-methylacridinium chloride (MA) in primary alcohols are quite different from those in water, which is ascribed to the formation of N-methyl-9-alkoxyacridanes.

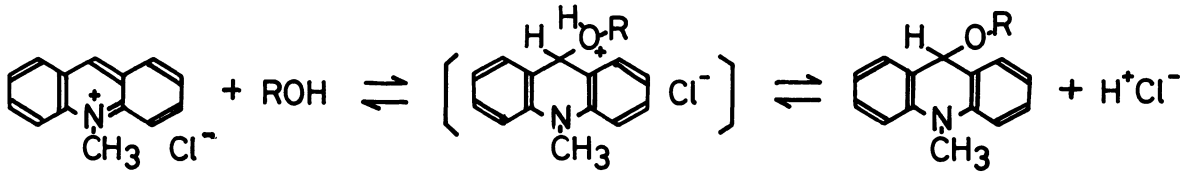

Figure 1 shows the absorption spectra of MA (1×10^{-5} M) in water and methanol at room temperature. In water, characteristic ^1L_a and ^1L_b bands were observed at 440 (ε = 2000 $M^{-1}cm^{-1}$), 415 (3800), and 395 nm (3700)

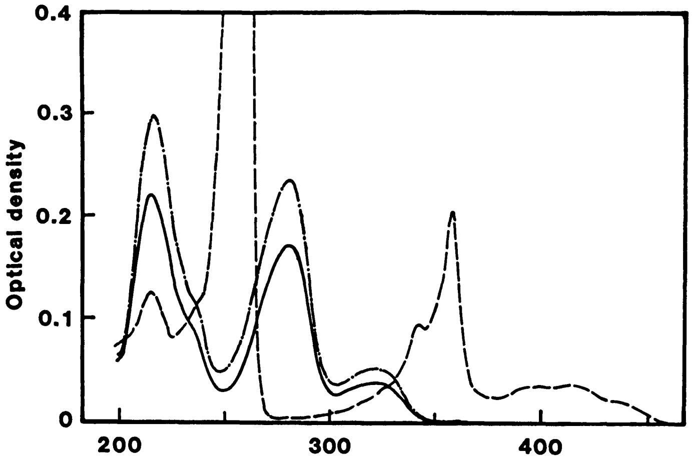

Fig. 1. Absorption spectra of MA (1×10^{-5} M) in water (– – – –) and methanol (——) and of N-methyl-9-methoxyacridane (1×10^{-5} M) in methanol (—·—) at room temperature.

and at 358 (21050) and 342 nm (10100), respectively.[3)] In methanol, however, the ^1L_a and ^1L_b bands of MA disappeared completely and new absorption bands were observed at 320 (ε = 3800 $M^{-1}cm^{-1}$) and 280 nm (19000). As shown in Fig. 1, the absorption spectrum of MA in methanol is in good agreement with that of an authentic sample of N-methyl-9-methoxyacridane,[4)] though a smaller extinction coefficient of MA in methanol at each wavelength. The intense fluorescence of MA was observed at around 480 nm (λ^F_{max} = ca. 510 (sh), 487, and 465 nm) in water while very weak fluorescence was measured at around 350 nm in methanol.

The absorption spectra of MA in ethanol, 1-propanol, 1-butanol, and 1-pentanol are essentially the same as that in methanol. In 2-propanol, very weak ^1L_a and ^1L_b bands (ε at 358 nm = 3000 $M^{-1}cm^{-1}$) were observed along with the N-methyl-9-methoxyacridane-type absorption bands (ε at 280 nm = 17000 $M^{-1}cm^{-1}$). The shape of the absorption spectra of MA in t-butyl alcohol, glycerol, acetonitrile, and acetic acid was virtually the same as that in water. These results indicate a strong interaction between MA and alcohols which is markedly inhibited by bulkiness of alcohols.

The absorption bands due to N-methyl-9-methoxyacridane appeared when the aqueous MA (1 x 10^{-5} M) solution contained over 50 %(v/v) methanol. The optical densities at 320 and 280 nm increased at the expense of the ^1L_a and ^1L_b bands with increasing the amounts of methanol. No progressive spectral change of MA was observed in water-methanol mixture, suggesting that no irreversible reaction occurs in this system.

MA did not fluoresce in methanol even if the solution was frozen at 77 K in the dark. The relatively intense fluorescence having maxima at 514 (sh), 486, and 457 nm, however, appeared when the frozen sample was irradiated at 77 K by UV light. The excitation spectrum at 77 K corresponded to the absorption spectrum of MA in water, the excitation maxima being observed at 444, 418, 398, 358, and 343 nm. This fluorescence disappeared when the sample was thawed. No irreversible reaction was detectable during this treatment.

On the basis of these results, we conclude that the nucleophilic addition of primary and secondary alcohols to MA occurs in dilute alcoholic MA solutions to form N-methyl-9-alkoxyacridanes, which dissociate easily into original MA and alcohol upon UV-irradiation in rigid alcohol matrix at 77 K. The formation of the alkoxyacridanes may be hindered sterically in the cases of glycerol and t-butyl alcohol.

References

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