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SIMULTANEOUS PARTICIPATION OF SEVERAL EXCITED STATES IN PHOTOCHEMICAL METHOXYLATION AND METHYLATION OF 3-PYRIDINECARBOXAMIDE IN METHANOL

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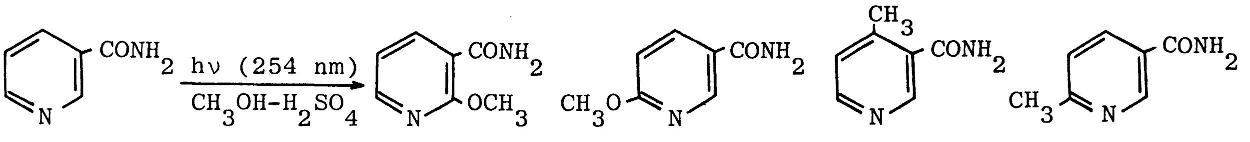
The UV-irradiation of 3-pyridinecarboxamide in methanol in the presence of sulfuric acid brings about methoxylation (ionic reaction) at the 2- and 6-position and methylation (radical reaction) at the 4- and 6-position. The effects of quenchers indicate that two methylation products originate from one excited triplet state which is quenched by energy transfer mechanism and that two methoxylation products originate from two different excited singlet states which are quenched by electron transfer mechanism.

In the preceding papers$^{1-5)}$ we have reported the remarkable photoreactivities of pyridinecarboxylic esters: parallel occurrence of ionic and radical reactions and simultaneous participation of several kinds of excited states. The most characteristic example is the photoreaction of methyl 3-pyridinecarboxylate in methanol in the presence of sulfuric acid.$^{1)}$ It has been concluded that an excited singlet state, n-π* triplet state, and π-π* triplet state coexist and that the excited singlet state gives the products methoxylated at the 2- and 6-position, whereas π-π* and n-π* triplet states give the methylation products at the 4- and 6-position, respectively.

In the present paper, we report that 3-pyridinecarboxamide shows another remarkable photoreactivity: There participate two excited singlet states which undergo methoxylation and one excited triplet state which gives two methylation products. Another important conclusion of the study is that the excited triplet state is quenched by an energy transfer mechanism and two excited singlet states are quenched by electron transfer mechanism.

The irradiation of 3-pyridinecarboxamide(1)(1.0×10^{-2} mol dm^{-3}) in methanol in the presence of sulfuric acid (5×10^{-2} mol dm^{-3}) with a low pressure mercury lamp under nitrogen brings about both methoxylation and methylation.$^{6)}$



1 2 12% 3 3% 4 17% 5 23%

With respect to the reaction type, the photoreaction of **1** is similar to that of 3-pyridinecarboxylic ester.$^{1)}$

In order to identify the excited states which participate in the photoreactions, the effects of additives (1,3-pentadiene (triplet energy E_T= 248 kJ mol^{-1} ;$^{7)}$ ionization potential I_p = 8.42 eV $^{8)}$), naphthalene (E_T = 255 kJ mol^{-1} ;$^{7)}$ I_p = 8.12 eV $^{8)}$), anthracene (E_T = 176 kJ mol^{-1} ;$^{7)}$ I_p = 7.43 eV$^{8)}$), and fluorene (E_T = 285 kJ mol^{-1} ;$^{7)}$ I_p = 7.78 eV $^{8)}$)) were investigated. Typical examples are shown in Fig. 1a (Stern-Volmer plots for the quenching by 1,3-pentadiene) and in Fig. 1b (Stern-Volmer plots for the quenching by fluorene$^{9)}$).

The quenching by 1,3-pentadiene has a feature which is different from that by fluorene. 1,3-Pentadiene inhibits the two photo-methylation reactions in the same manner, while it does not affect the photo-methoxylation at the 2- and 6-position. Though there was no effect of 1,3-pentadiene on the photo-methoxylation, fluorene inhibits the photo-methoxylation even more than photo-methylation. Furthermore, methoxylation at the 2-position is much more influenced by fluorene than methoxylation at the 6-position.

These facts suggest that there participate at least three kinds of excited states: one triplet state and two singlet states. The conclusion is more clearly demonstrated by the dependences of $k_q\tau$ values obtained from the Stern-Volmer plots on the ionization potentials and on the triplet energies of the quenchers (Figs. 2a and 2b).

The $k_q\tau$ values for the quenching of photo-methylation are correlated with the triplet energy values of the quenchers: The quenchers whose triplet energies are less than 250 kJ mol^{-1} inhibit the photochemical methylation efficiently,

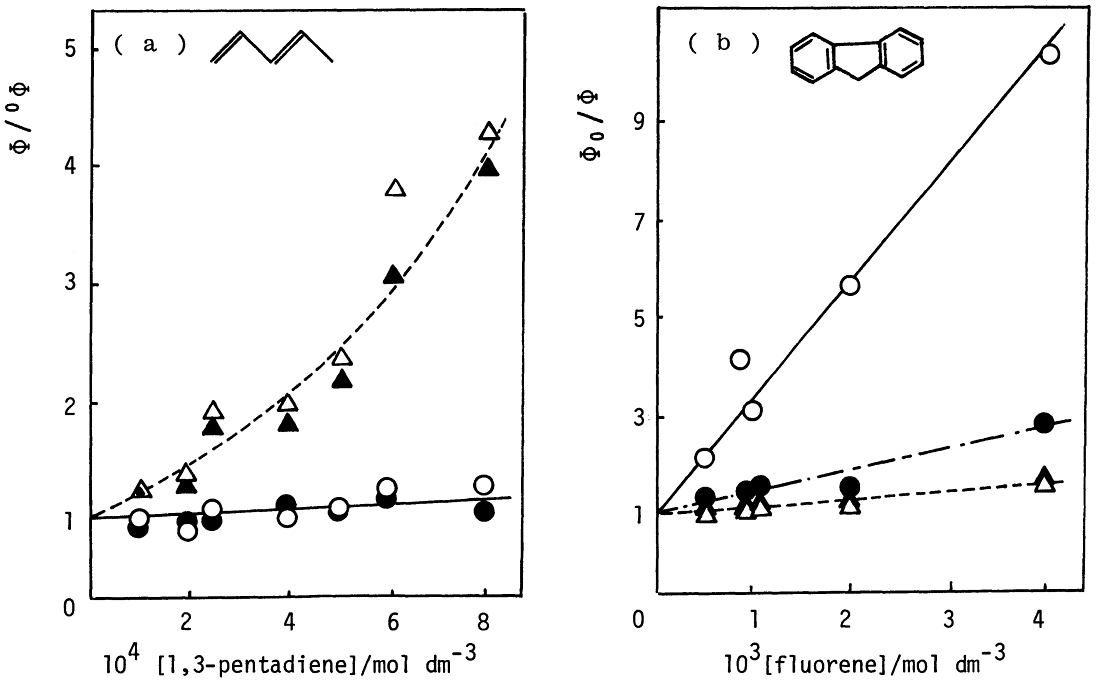


Fig. 1. Stern-Volmer plots for quenching of photoreactions of **1** by 1,3-pentadiene (a) and by fluorene (b).

—○—,Methoxylation at the 2-position; —·—●—·—,Methoxylation at the 6-position;
--△--,Methylation at the 4-position; ---▲---,Methylation at the 6-position.

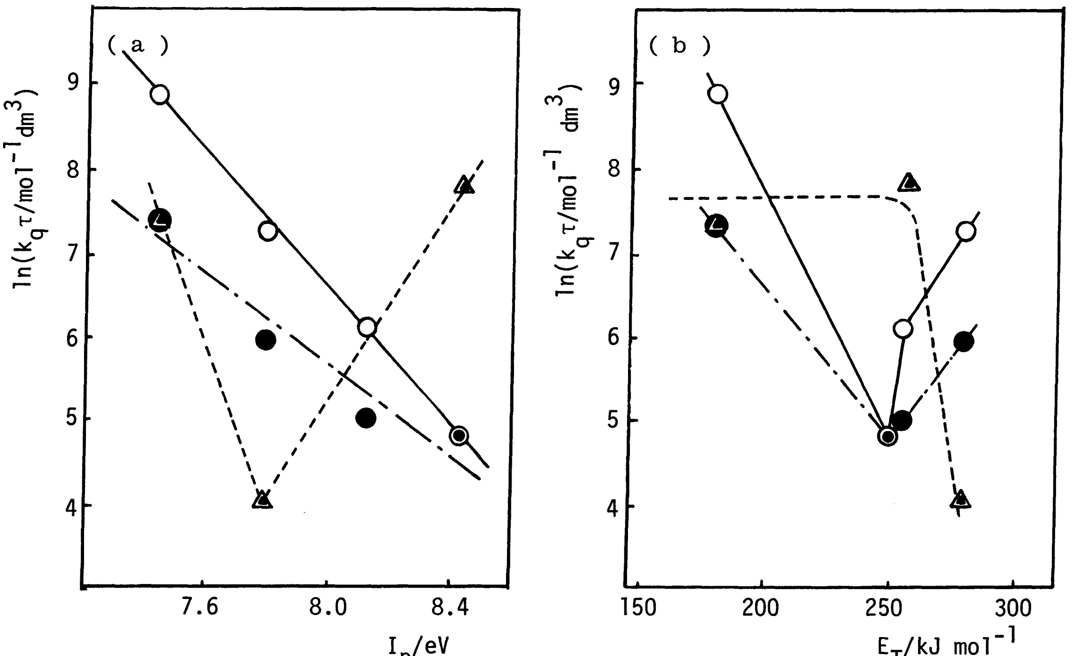


Fig. 2. Relations between $k_q\tau$ and ionization potential (a) and between $k_q\tau$ and triplet energy (b) of additive.
—○—, Methoxylation at the 2-position; —·—●—·—, Methoxylation at the 6-position;
- - △ - -, Methylation at the 4-position; - - ▲ - -, Methylation at the 6-position.

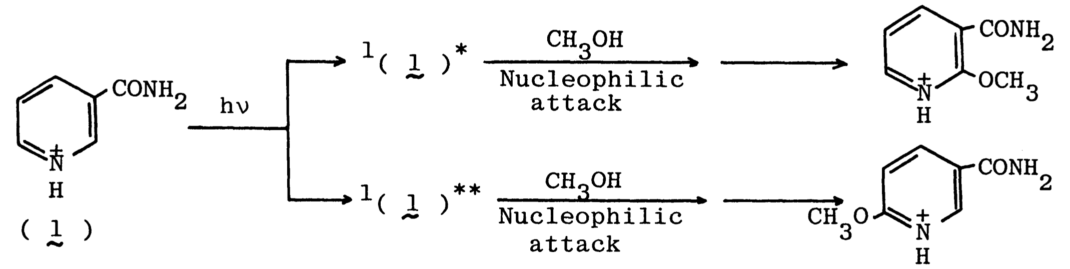
while the additives with higher triplet energies do not inhibit the photochemical methylation. On the other hand, $k_q\tau$ values for photo-methoxylation do not correlate with the triplet energies of the quenchers.

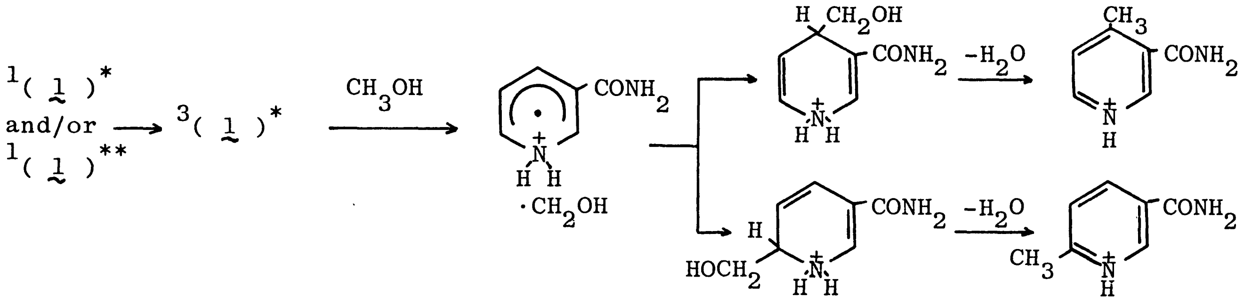
In contrast, ionization potentials do not correlate with the $k_q\tau$ values for the quenching of photo-methylation, but correlate well with the $k_q\tau$ values for the quenching of photo-methoxylation. The dependence of $k_q\tau$ for the quenching of the photo-methoxylation at the 2-position on the ionization potential is different from that at the 6-position.

This indicates that the excited state to give methylation products is quenched by the triplet energy transfer and the excited states to give methoxylation products are quenched by the electron transfer from the electron-rich aromatic hydrocarbons to the excited **1** (in protonated form).

3-Pyridinecarboxamide is not fluorescent under the conditions for the photoreaction and no information could be obtained from the emission concerning the nature of the excited states which are responsible for the photoreaction.

The fact that the photoreaction of 3-pyridinecarboxamide occurs via several kinds of excited states is similar to the photoreactions of 3-pyridinecarboxylic ester. However, there exists an important difference: In the photoreaction of 3-pyridinecarboxamide one excited triplet state and two excited singlet states contribute at the same time, while in the photoreaction of methyl 3-pyridinecarboxylate two excited triplet states and one excited singlet state contribute simultaneously. The photoreactions of **1** should proceed in the following Scheme.





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6) The dependence of UV-spectra of **1** on the concentration of H_2SO_4 indicates that under the conditions for irradiation **1** is completely protonated. Compound **1** shows the same photoreactivity in the region $[H_2SO_4] > 2 \times 10^{-2}$ mol dm^{-3}. The photoproducts **2**, **4**, and **5** were identified by IR and ^1H NMR spectra. Their melting poits agreed with those in the literature. Photoproduct **3** : mp 167-168 °C; IR(KBr disk) 3420, 3170, 1670, and 1620 cm^{-1}; ^1H NMR(D_2O) δ = 4.03(3H, s, OCH_3), 7.01(1H, d, J=9.4 Hz), 8.16(1H, dd, J = 9.4 and 3.0 Hz), and 8.60(1H, d, J=3.0 Hz); Found: C, 54.6; H, 5.3; N, 18.1%. Calcd for $C_7H_8N_2O_2$: C, 55.2; H, 5.3; N, 18.4%.

7) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, NY(1973), pp. 3-7.

8) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, NY(1973), pp.198-9.

9) Because fluorene, anthracene and naphthalene absorb the light of 254 nm competitively with **1** , the quantum yields were corrected on the basis of the light absorbed by **1** , according to the formula described in reference 1.

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