

## Proton-assisted Photoionization of Methoxynaphthalenes sensitized by Triplet Aromatic Ketones

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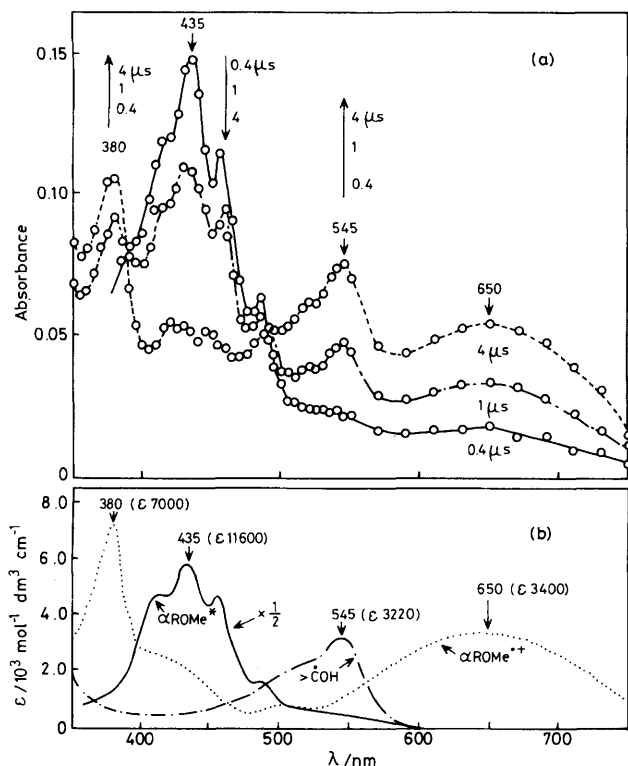
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Proton-assisted photoionization of methoxynaphthalenes sensitized by triplet aromatic ketones occurs effectively to give the cation radical and the ketyl radical.

The photochemical and photophysical properties of aromatic compounds in the presence of protons are currently of interest:<sup>1</sup> recent reports have included proton transfer reactions involving proton-induced quenching of aromatic compounds,<sup>2,3</sup> a one-way proton transfer reaction of the hydrogen-bonded complexes between naphthylammonium ions and 18-crown-6,<sup>4</sup> and hydrogen atom transfer reactions from triplet aromatic compounds (naphthylammonium ions<sup>5</sup> and 1-naphthol<sup>6</sup>) to aromatic ketones. We now report that the proton-assisted photoionization of methoxynaphthalenes (ROME) sensitized by triplet aromatic ketones (<sup>3</sup>>CO\*) occurs effectively to produce the methoxynaphthalene cation radical (ROME<sup>•+</sup>) plus the ketyl radical (>COH).

A degassed solution of benzophenone ([BP] = 6.7 × 10<sup>-3</sup> mol dm<sup>-3</sup>) and 1-methoxynaphthalene ([αROME] = 3 × 10<sup>-3</sup> mol dm<sup>-3</sup>) in MeCN-H<sub>2</sub>O (4:1 v/v) containing H<sub>2</sub>SO<sub>4</sub> (1 mol dm<sup>-3</sup>) was pulse irradiated by a nitrogen laser system at 337 nm and 290 K. The triplet BP (<sup>3</sup>BP\*) was produced effectively by fast intersystem crossing (I.S.C.) from the singlet BP [see equation (1)] and subsequently triplet energy transfer (*k*<sub>et</sub>) from <sup>3</sup>BP\* (*E*<sub>T</sub> 289.5 kJ mol<sup>-1</sup>)<sup>7</sup> to αROME (*E*<sub>T</sub> 249.8 kJ mol<sup>-1</sup>)<sup>7</sup> was expected [see equation (3)]. Figure 1(a) shows the transient absorption spectra of the above system in the

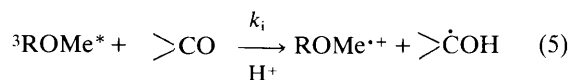
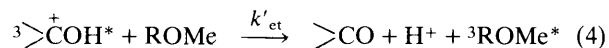
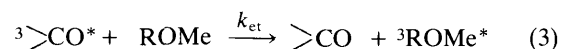
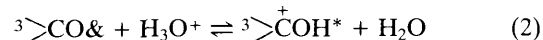
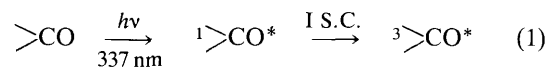
microsecond timescale. The T<sub>n</sub> ← T<sub>1</sub> absorption of BP at 525 nm disappears very rapidly within 0.1 μs after pulsing, resulting in fast build-up of the transient peak at 435 nm, which corresponds to the T<sub>n</sub> ← T<sub>1</sub> absorption of αROME.<sup>6</sup> New transient peaks at 380, 545, and 650 nm appear with a decrease in the 435 nm peak (<sup>3</sup>αROME\*) and an isosbestic point at 490 nm [Figure 1(a)]. The 545 nm transient is assigned to the benzophenone ketyl radical (>COH, ε 3220 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>).<sup>8</sup> Both transient peaks at 380 and 650 nm are assigned to the 1-methoxynaphthalene cation radical αROME<sup>•+</sup>.<sup>9</sup> The reference spectra of >COH and αROME<sup>•+</sup> are depicted in Figure 1(b). The increase rates of the new transient peaks at 545 nm (>COH) and at 650 nm (αROME<sup>•+</sup>) were the same as the decay rate [8.9 (±0.3) × 10<sup>5</sup> s<sup>-1</sup>] within experimental error. These results demonstrate that the ionization of <sup>3</sup>αROME\* is assisted by protons and ground state BP, leading to the production of αROME<sup>•+</sup> and >COH [see equation (5)]. This represents a new type of photoionization of aromatic compounds assisted by protons. There was no photoionization of αROME in the absence of protons, and the presence of acid ([H<sub>2</sub>SO<sub>4</sub>] > ~0.1 mol dm<sup>-3</sup>) was necessary for the photoionization. The ionization rate increased with increasing acid concentration, whereas the ionization yield decreased.



**Figure 1.** (a) Time-resolved transient absorption spectra of a degassed solution of benzophenone ( $[BP] = 6.7 \times 10^{-3} \text{ mol dm}^{-3}$ ) and 1-methoxynaphthalene ( $[\alpha\text{ROME}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ ) in MeCN-H<sub>2</sub>O (4:1) mixture containing H<sub>2</sub>SO<sub>4</sub> (1 mol dm<sup>-3</sup>) at 290 K, obtained by laser flash photolysis at 337 nm. Times refer to the delay after laser pulsing. (b) Reference spectra of  ${}^3\alpha\text{ROME}^*$ ,  $>\text{COH}$ , and  $\alpha\text{ROME}^{*+}$ . The extinction coefficients ( $\epsilon$ ) of  ${}^3\alpha\text{ROME}^*$  and  $\alpha\text{ROME}^{*+}$  were determined by using the  $\epsilon$  value of  $>\text{COH}$  (3220).<sup>8</sup> For details see text.

For the acetophenone ( $[AP] = 3.5 \times 10^{-2} \text{ mol dm}^{-3}$ ) and  $\alpha\text{ROME}$  ( $3 \times 10^{-3} \text{ mol dm}^{-3}$ ) system in the presence of H<sub>2</sub>SO<sub>4</sub> (1 mol dm<sup>-3</sup>), the decay rate of the  $T_n \leftarrow T_1$  absorption of  $\alpha\text{ROME}$  at 435 nm was  $2.8 (\pm 0.2) \times 10^6 \text{ s}^{-1}$ , which agreed with the rate of increase of the transient peak at 650 nm of  $\alpha\text{ROME}^{*+}$ .

The photoionization reaction of ROME assisted by protons can be accounted for by the equations (1)–(5). Prototropic reactions of  $>\text{CO}^*$  produced rapidly by equation (1) may take place as shown in equation (2).<sup>10,11</sup> Equation (3) or (4) shows the triplet energy transfer  $k_{\text{et}}$  (or  $k'_{\text{et}}$ ) from  ${}^3>\text{CO}^*$  (or



${}^3>\text{COH}^*$ ) to ROME, respectively. The new type of photoionization in equation (5) may be termed a 'proton-assisted photoionization.' It is noteworthy that, for example,  $\alpha\text{ROME}$ ,<sup>3</sup> with an ionization potential of 750.6 kJ mol<sup>-1</sup> can be ionized with the extremely low energy of 249.8 kJ mol<sup>-1</sup> ( $E_T$  of  ${}^3\alpha\text{ROME}^*$ ) in the present reaction.

Similar proton-assisted photoionizations occurred for the 2-methoxynaphthalene-aromatic ketone (BP and AP) systems in the presence of acid. Propiophenone and benzyl phenyl ketone could also be used for the photoionization of ROME. A mechanistic study is in progress.

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