SPECTROSCOPIC EVIDENCE FOR THE FORMATION OF 2-QUINOLONE METHIDE BY FLASH PHOTOLYSIS OF 2-(2-HYDROXYETHYL)QUINOLINE, 2-(2-DEUTERIOXYETHYL)QUINOLINE, AND 2-BUTYLQUINOLINE <sup>1</sup>

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Abstract. Flash photolysis of the title compounds in cyclohexane gave rise to transient absorptions around 400 nm from a species assigned as 2-quinolone methide.

Studies on the photochemistry of aza aromatic compounds have shown that reactions analogous to the hydrogen abstractions of excited carbonyl compounds may take place.<sup>2</sup> Thus 2-(2-hydroxyethyl)quinoline (<u>1</u>), 2-methoxymethylquinoline, and 2-butylquinoline (<u>2</u>) all undergo photoelimination in a similar manner to the Norrish type II cleavage of carbonyl compounds with  $\gamma$  hydrogens.<sup>3</sup> When irradiated in benzene all three compounds are quantitatively converted to 2-methylquinoline.



The elimination products formaldehyde and propene were identified as well. When 2-(2-deuterioxyethyl)quinoline is photolysed, deuterium is incorporated in the methyl group only. It was suggested, that product formation took place <u>via</u> 2-quinolone methide, 4.<sup>3</sup>

By flash photolysis ( $\lambda_{excit.} > 300 \text{ nm}$ ) of compound <u>1</u> (3 x 10<sup>-5</sup> M in dry cyclohexane) a transient absorption (Fig.) was observed. It decayed in a first order reaction with <u>k</u> = 70 s<sup>-1</sup> at 25 °C. The magnitude of this rate constant was independent on the presence of oxygen, independent on the concentration of starting material (1.2 x 10<sup>-5</sup> - 1.2 x 10<sup>-4</sup> M), and on the intensity of the flash exciting light.<sup>4</sup>

Flash photolysis ( $\lambda_{excit.} > 230 \text{ nm}$ ) of compound  $\underline{2}$  (10<sup>-4</sup> M in dry cyclohexane) gave rise to a transient absorption which decayed with  $\underline{k} = 72 \text{ s}^{-1}$  (25 °C).



Spectra obtained by flash photolysis of compounds <u>1</u> and <u>2</u> in cyclohexane. \_\_\_\_\_, Compound <u>1</u>, 3 x  $10^{-5}$ M, in aerated solution, ..., compound <u>1</u>, 3 x  $10^{-5}$ M, in degassed solution, ---, compound <u>2</u>,  $10^{-4}$  M, in aerated solution. The optical density of absorptions is approximately 0.01.

The spectrum of this species was identical with the spectrum obtained by flash photolysis of compound  $\underline{1}$  (Fig.).

In order to obtain further information about the properties of this common transient species 2-(2-deuterioxyethyl)quinoline was flash photolysed in exactly the same manner as the 2-hydroxy compound. The first order rate constant of decay was now measured as 34 s<sup>-1</sup> (25 °C). This shows that the position of the hydrogen initially bonded to oxygen is changed during the thermal reaction of the observed intermediate.

On the basis of these experiments the transient species is assigned as 2-quinolone methide, <u>4</u>. Its absorption spectrum may be compared with the spectrum of <u>N</u>-methyl-2-quinolone methide, prepared according to Ref. 5. The spectrum of this compound in cyclohexane has  $\lambda_{max}$  at 398 nm ( $\varepsilon_{max} = 3800 \text{ M}^{-1} \text{ cm}^{-1}$ ).

Measurements of  $\underline{pK}_{a}$  values have shown that the equilibrium constant associated with the equilibrium between 2-quinolone methide and 2-methylquinoline in water is  $10^{9.9}$  (Ref. 6).

## REFERENCES AND NOTES

- 1. This work was supported by the Danish Natural Science Research Council.
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- 3. F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, <u>J. Amer. Chem. Soc</u>. <u>92</u> 2745 (1970).
- 4. First order to at least 90% of conversion. Identical transient absorptions were observed in benzene.
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(Received in UK 3 February 1982)