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SHORT COMMUNICATION

PHOTOCHEMICAL AND RADIOLYTIC CLEAVAGE OF 10-METHYLACRIDINE DIMER IN SOLUTIONS AND CRYOGENIC GLASSES

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10-Methylacridine dimer [$(AcrH)_2$] dissociates into a pair of 10-methylacridyl radicals ($AcrH^{\cdot}$) on laser excitation (308 nm) in solvents of various polarities. Exposure of $(AcrH)_2$ in methylcyclohexane glass at 77 K to γ-rays of ^{60}Co generates the radical cation $(AcrH)_2^{+\cdot}$. Thermal annealing of the matrix to 90 K results in dissociation of $(AcrH)_2^{+\cdot}$ into $AcrH^{\cdot}$ and 10-methylacridinium cation ($AcrH^+$).

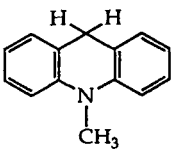
It has recently been shown that photolysis of 10-methylacridane ($AcrH_2$) in acetonitrile results in the formation of 10-methylacridane radical cation ($AcrH_2^{+\cdot}$).[1,2] The subsequent deprotonation of $AcrH_2^{+\cdot}$ generates 10-methylacridyl radical ($AcrH^{\cdot}$), which is oxidized in the presence of molecular oxygen to give the 10-methylacridinium cation ($AcrH^+$). Much less information is available concerning 10-methylacridine dimer [$(AcrH)_2$].

It was previously discovered that $(AcrH)_2$ may act as a unique net two-electron donor in the stepwise one-electron reduction of triphenylmethyl cation.[3] The 10-methylacridine dimer radical cation $(AcrH)_2^{+\cdot}$ formed in the first step of this oxidation process was found to be dissociative [reaction (1)] and its lifetime was estimated to be shorter than 10 ms.

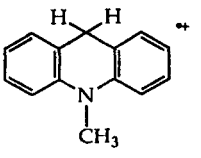
$$(AcrH)_2^{+\cdot} \rightarrow AcrH^{\cdot} + AcrH^+ \qquad (1)$$

In this paper we describe the homolysis of the central C—C bond of the dimer $(AcrH)_2$ on exposure to UV or ionizing radiation. The elusive behavior of excited or ionized $(AcrH)_2$ will be compared with that observed for $AcrH_2$.

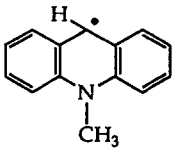
Laser excitation (308 nm)[4] of a deaerated solution of $(AcrH)_2$ in solvents of various polarity (pentane,



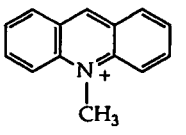
$AcrH_2$



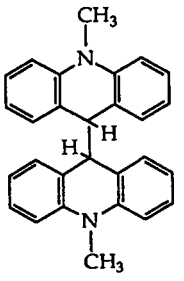
$AcrH_2^{\cdot+}$



$AcrH^{\cdot}$



$AcrH^+$



$(AcrH)_2$

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3-methylpentane, dichloromethane, 2-methyltetrahydrofuran, methanol, acetonitrile, acetonitrile–water (5 : 1) and dimethyl sulfoxide) generates species that absorb at 360 and 510 nm (Figure 1). Both of these absorption bands decayed in all solvents at the same rate and are therefore probably due to a common species which is assigned to the 10-methylacridyl radical (AcrH$^{\cdot}$). AcrH$^{\cdot}$ has been observed previously and it is characterized by its long-wavelength absorption band,[5,6] whose shape and wavelength at the absorption maximum match our observations well. The yield of AcrH$^{\cdot}$ formation decreased sharply when the temperature was lowered. Radical AcrH$^{\cdot}$ was also generated on laser flash photolysis of $AcrH_2$ in pentane.

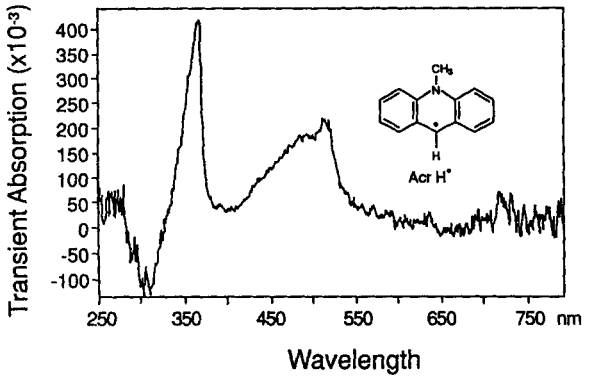

Figure 1. Transient absorption spectrum measured 0·5 μs after 308 nm laser excitation of $(AcrH)_2$ in pentane at room temperature

In contrast to $AcrH_2$, where $AcrH_2^{+\cdot}$ was effectively generated in polar solvents by laser excitation, we were not able to detect $(AcrH)_2^{+\cdot}$ under similar conditions. Further, the addition of an electron scavenger (CH_2Cl_2 or CH_2Br_2) to polar solvents did not result in appreciable formation of $(AcrH)_2^{+\cdot}$ on UV excitation. Electron transfer sensitization with anthraquinone again led to 10-methylacridyl radical (AcrH$^{\cdot}$) and not to $(AcrH)_2^{+\cdot}$ as desired. Apparently the dissociation of excited $(AcrH)_2$ into a pair of AcrH$^{\cdot}$ radicals is a much more rapid process than the generation of $(AcrH)_2^{+\cdot}$ by electron transfer. This observation is not surprising as PM3 (MOPAC version 5·01) calculations[7] predict that the heat of formation of a pair of AcrH$^{\cdot}$ radicals is only 28·3 kcal mol^{-1} higher in energy than that of $(AcrH)_2$ but that $(AcrH)_2^{+\cdot}$ lies 172·7 kcal mol^{-1} above $(AcrH)_2$ in the gas phase (1 kcal = 4·184 kJ).

Exposure of $(AcrH)_2$ in methylcyclohexane glass at 77 K (containing *n*-butyl chloride as an electron scavenger) to ^{60}Co γ-rays leads to the formation of $(AcrH)_2^{+\cdot}$ with absorption maxima at 346, 393 and 675 nm (Figure 2). Under these conditions $AcrH_2^{+\cdot}$ can also be generated (336, 384 and 690 nm). The spectra of both ions were also recorded in pure *n*-butyl chloride at 77 K following γ-radiolysis and were similar to the spectra observed in methylcyclohexane.

It has been found that on thermal relaxation of the matrix to 90 K $(AcrH)_2^{+\cdot}$ dissociates to form $AcrH^+$ (356, 398, 420 and 448 nm) and AcrH$^{\cdot}$ (480 nm; note that the short-wavelength transition is masked by the absorption of $AcrH^+$) . As translational diffusion in methylcyclohexane glass occurs above 100 K,[8] we believe that the dissociation products are in close prox-

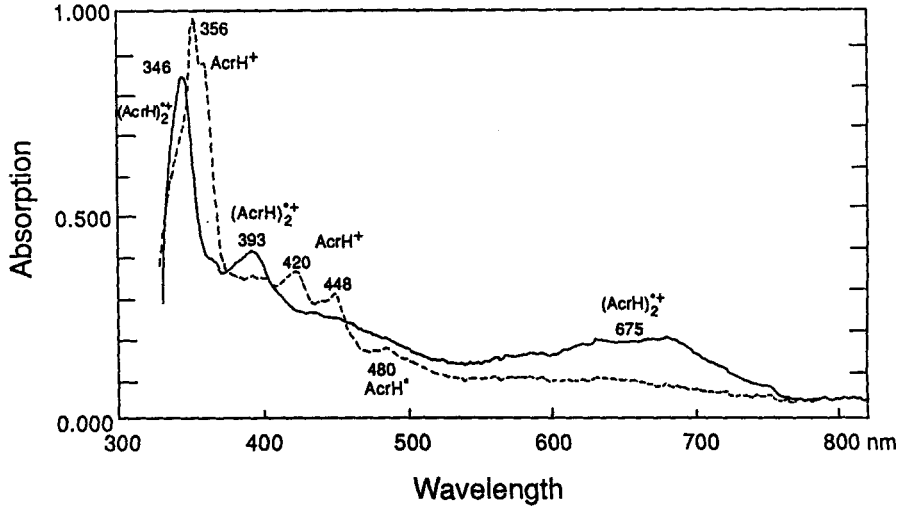

Figure 2. Absorption spectrum of γ-irradiated (^{60}Co) $(AcrH)_2$ (0·0015 M) in a glassy matrix of methylcyclohexane containing *n*-butyl chloride (1 M) at 77 K (solid line). The sample was 2 mm thick and received a radiation dose of 10^4 Gy. The spectrum was obtained after the irradiated sample had been warmed to 90 K (2 min) and cooled back to 77 K (dashed line)

imity and are locked together in a solvent cage. Since the isolated radical $AcrH^{\cdot}$ absorbs at 518 nm in methylcylohexane glass, the shift of its absorption maximum to 480 nm when $AcrH^{\cdot}$ is generated from $(AcrH)_2^{+\cdot}$ points toward specific interactions between $AcrH^{\cdot}$ and $AcrH^{+}$.

It was found that the dissociation reaction of $(AcrH)_2^{+\cdot}$ takes place abruptly when the matrix is heated to 82 K. We believe that the stabilization of $(AcrH)_2^{+\cdot}$ is mostly due to the rigidity of the matrix at 77 K. At temperatures above 82 K, rotational diffusion is possible, thereby facilitating dissociation of $(AcrH)_2^{+\cdot}$. The intrinsic dissociation of $(AcrH)_2^{+\cdot}$ may even take place at temperatures lower than 82 K, as PM3 calculations predict that the dissociation of $(AcrH)_2^{+\cdot}$ is slightly exothermic (0·7 kcal mol^{-1}) with an activation barrier of only 2 kcal mol^{-1}. If these predictions are correct, the dissociation process should take place even at 77 K in the absence of matrix friction.

The spectroscopy and kinetics of radicals and radical cations and their dimeric forms generated from other NADH analogues are currently under investigation.

ACKNOWLEDGMENTS

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