Photochemical Cleavage of the Al–C Bond of Al(TPP)(Et) (TPP = tetraphenylporphyrinato). Spin Trapping of the ˙Al(TPP) Radical and Photolysis Quantum Yield

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The Al–C bond of Al(TPP)(Et) (TPP = tetraphenylporphyrinato) is homolytically cleaved upon visible light photolysis in benzene in the presence of an excess of 2,4,6-tri-t-butylnitrosobenzene, yielding spin adducts of Al(TPP) and ethyl radicals with a quantum yield of the order of 10^{-3}.

The study of metalloporphyrin π-cation and anion radicals has made fundamental contributions to our understanding of photosynthetic and metabolic processes, as well as contributing to our theoretical understanding of these systems.[1] Aluminium porphyrins occupy a unique place in porphyrin chemistry in view of their catalytic activity in CO_2 fixation.[2—4] The reactivity of Al(TPP)(Et) (TPP = 5,10,15,20-tetraphenylporphyrinato) towards CO_2 is known to be greatly affected by visible light, and it has been postulated that the Al–C bond is homolytically cleaved upon photolysis. The photoactivity of Al(TPP)(Et) itself, however, has not been described extensively. We now report the spin trapping of the

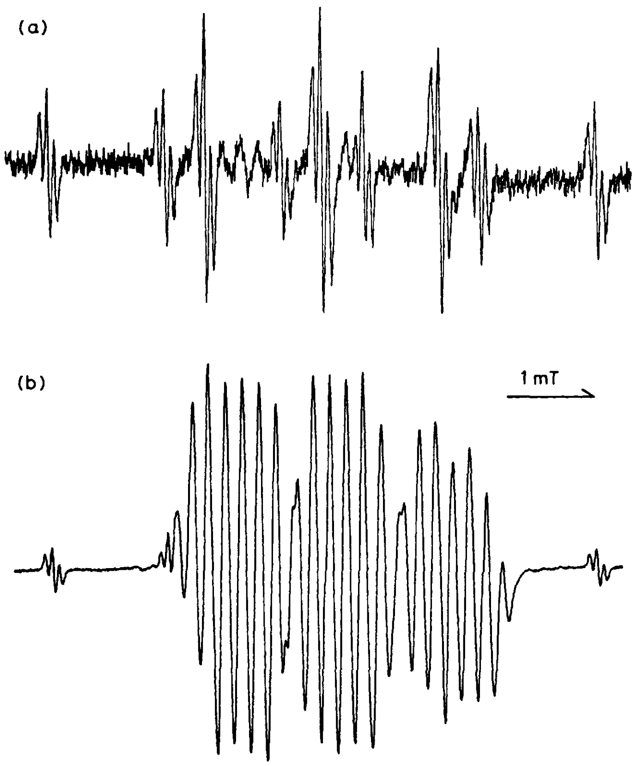

Figure 1. E.s.r. spectra of a benzene solution of Al(TPP)(Et) with added TBN: (a) before and (b) after photolysis.

photolysis products, $^{\cdot}$Al(TPP) and $^{\cdot}$Et, by 2,4,6-tri-t-butylnitrosobenzene (TBN) together with the photolysis quantum yields.

Figure 1(a) shows the weak e.s.r. signal generated upon addition of a 10-fold excess of TBN to a degassed benzene solution of Al(TPP)(Et) in the dark.† The hyperfine splitting constants $a^{N} = 1.34$, $a^{H}(2H) = 1.79$, and $a^{H}(2H) = 0.08$ mT and the g value of 2.0061 are consistent with the nitroxyl spin-adduct, TBN–Et [equation (1)].[5] The intensity of the signal gradually increases at room temperature and it appears that the dissociation of the ethyl radical proceeds thermally, though slowly, at room temperature even in the dark. It should be noted, however, that no e.s.r. signal is observed unless the spin trapping agent is present.

When the same solution was irradiated with visible light (ultra-high pressure Ushio 500 W mercury lamp and Toshiba O-55 glass filter; $\lambda > 550$ nm), a new e.s.r. signal is generated and the signal of the ethyl adduct intensifies (Figure 1b). The intense triplet of sextets is best interpreted in terms of hyperfine interaction by both ^{14}N ($I = 1$) and ^{27}Al ($I = 5/2$), and the e.s.r. parameters were determined as $a^{N} = 1.20$, $a^{Al} = 0.19$ mT, and $g = 2.0049$. This spin adduct is thus formulated as a TBN–Al(TPP) radical. It is most likely that the TBN is bound to the Al(TPP) through its oxygen atom to form the anilino radical [equation (1)], rather than a nitroxyl radical, owing to steric hindrance by the t-butyl substituents at the 2- and 6-positions. In fact, the a^{N} and g values obtained are smaller than normal values for nitroxides.[5]

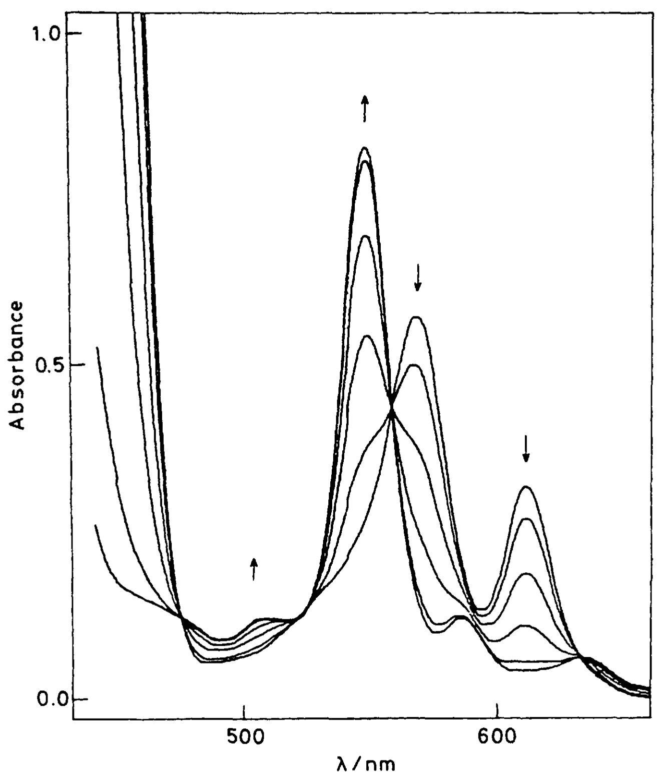

Figure 2. Absorption spectral change upon photolysis of a chloroform solution of Al(TPP)(Et) at 10 °C. Photolysis conditions: λ 430 nm, band width 10 nm, duration 5 × (2 min).

$$\mathrm{Al(TPP)(Et)} + \mathrm{Ar{-}NO} \xrightarrow[\text{heat}]{h\nu \text{ or}} \mathrm{Ar{-}N(-\dot{O}){-}Et} + \mathrm{Ar{-}\dot{N}O{-}Al(TPP)} \qquad (1)$$

$$\mathrm{Ar} = 2,4,6\text{-}\mathrm{Bu^{t}_{3}C_{6}H_{2}}$$

$$\mathrm{Al(TPP)(Et)} \xrightarrow[\mathrm{CHCl_3}]{h\nu} \mathrm{Al(TPP)Cl} \qquad (2)$$

In an attempt to define quantitatively the effect of light on the Al–C homolytic cleavage, the photolysis quantum yields were determined for three different wavelengths, which correspond to the absorption maxima of the Soret (435 nm), $Q_{0,1}$(568 nm), and $Q_{0,0}$(612 nm) bands, respectively, of the Al(TPP)(Et). Chloroform was used as solvent in order to study the pseudo-first-order reaction in equation (2).‡ The reaction can easily be followed spectrophotometrically and selected absorption spectra are shown in Figure 2. The Q bands (612 and 568 nm) of the starting Al(TPP)(Et) complex gradually diminish as a new intense band appears at 548 nm; the sharp isosbestic points persist.§ The spectrum obtained on complete photolysis is nearly identical to that reported for Al(TPP)Cl, prepared chemically, in methanol–carbon tetrachloride.[6]

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† E.s.r. spectra were recorded on a JEOL FE2XG spectrometer (100 kHz modulation) at room temperature. The Al(TPP)(Et) sample was freshly synthesized from chlorin-free H_2TPP (purified by the reported procedure (G. H. Barnett, M. F. Hudson, and K. M. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1401) and Al(Et)$_3$, and manipulated in a standard vacuum system throughout this work.

‡ It was also convenient that the extent of the dark (thermal) reaction was negligibly small in freshly purified chloroform. The other main product in this reaction is ethane.

§ Prolonged irradiation of the chloroform solution made the isosbestic points appear indistinct. We suggest that various radicals arising from the chloroform may cause undesirable side-reactions. A small shoulder at 634 nm in the 'Al(TPP)Cl' spectrum may be due to chlorin species produced in this manner. No such band was observed in the benzene–TBN system.

Photolysis quantum yields¶ were calculated using data collected during the initial $< 10\%$ of the total change.§ The results at 20 °C are as follows: $\Phi = (3.1 \pm 0.2) \times 10^{-3}$ (irradiation at 435 nm), $(8.7 \pm 0.5) \times 10^{-3}$ (568 nm), and $(4.9 \pm 0.3) \times 10^{-3}$ (612 nm). These values, which are not impressively large, suggest rapid recombination of photogenerated radicals but it is worth noting that the *Q* band illumination is definitely more efficient than the Soret excitation.

Quantum yield measurements were performed also in the benzene–TBN (100-fold excess of the complex) system. The overall absorption spectral change that accompanies reaction (1) was quite similar to that upon photolysis in neat chloroform§ and the quantum yield for the spin adduct formation was found to be of the same order of magnitude.

Presumably, the mechanism of bond scission involves energy transfer from the excited porphyrin π^* orbital to the σ^* orbital of the Al–C bond leading to homolytic Al–C dissociation, and we are currently studying the nature of the excited states responsible for the photodissociation process in Al(TPP)(Et).

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¶ For determination of the quantum yields, the sample solution (3 ml) was sealed in a glass tube, with a 1 cm quartz cell attached, on a vacuum line. The cell was placed in a thermostatted cell-holder before irradiation began. A 150 W Varian VIX-150UV xenon lamp was monochromatized by a Jobin-Yvon HL monochromator (band width 5 nm) and the light intensity was constantly monitored by a Scientech Model 36-0001 Power Meter, placed next to the cell, which was calibrated by ferric oxalate actinometry.

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