Optical Outer-Sphere Charge Transfer and Photoreactivity of the Ion Pair Tetrabutylammonium Tetrabutylborate

Horst Kunkely and Arnd Vogler*

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

* Reprint requests to Prof. Dr. A. Vogler.

Email: Arnd.Vogler@chemie.uni-regensburg.de

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The ion pair \([\text{NR}_4]^+ [\text{BR}_4^-] \) in \(\text{CCl}_4 \) shows a \(\text{BR}_4^- \rightarrow \text{NR}_4^+ \) outer-sphere charge transfer (OSCT) absorption at \(\lambda = 306 \text{ nm} \) (sh, \(\varepsilon = 420 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1} \)). OSCT excitation of the ion pair in \(\text{CH}_2\text{Cl}_2 \) \((\check{\text{\alpha}}_{\text{irr}} > 275 \text{ nm}) \) leads to a photolysis with \(\phi = 1.5 \times 10^{-3} \) at \(\lambda_{\text{irr}} = 280 \text{ nm} \). Octane is formed as photoproduct.

1. Introduction

Ion pairs which consist of oxidizing cations and reducing anions frequently show outer-sphere charge transfer (OSCT) absorptions in their electronic spectra \([1–3]\). OSCT excitation leads to the reduction of the cation and oxidation of the anion to the corresponding radicals which may undergo secondary reactions to stable photoproducts. Such ion pairs are not stable if the cations and anions are strong electrophiles and nucleophiles, respectively. For example, ion pairs of carbenium cations \(\text{R}^+ \) and carbanions \(\text{R}^- \) simply combine to \(\text{R}^- \text{R}^+ \). However, the electrophilicity of \(\text{R}^+ \) and the nucleophilicity of \(\text{R}^- \) can be attenuated if they are attached to suitable molecules. The resulting ions should preserve the oxidizing and reducing properties of \(\text{R}^+ \) and \(\text{R}^- \) at least partially. We explored this possibility and selected the salt \([\text{NR}_4]^+ [\text{BR}_4^-] \) (Aldrich) for the present study. It represents a protected form of the hypothetical ion pair \([\text{n-butyl}]^+ [\text{(n-butyl)}]^- \). \(\text{BR}_4^- \) anions which are formed by the reaction of \(\text{R}^- \) \((\text{e.g. LiR}) \) with \(\text{BR}_3 \) have been frequently used as OSCT donors in ion pairs \([1–5]\). Upon OSCT excitation they are oxidized. Subsequently, neutral \(\text{BR}_4 \) eliminates the radical \(\text{R} \) \([6, 7]\). Conversely, amines \(\text{NR}_3 \) add carbenium ions \(\text{R}^+ \) to yield the ammonium cations \(\text{NR}_4^+ \). Very little is known on \(\text{NR}_4^+ \) as an acceptor for OSCT \([8]\). However, as expected these cations can be reduced to neutral \(\text{NR}_4 \) which also releases a radical \(\text{R} \) \([9, 10]\).

2. Results and Discussion

The association of cations and anions to ion pairs is favored in less polar solvents while such ion pairs may dissociate in more polar solvents including acetoneitrile \([6]\). In this solvent the salt \([\text{NR}_4]^+ [\text{BR}_4^-] \) absorbs only below \(280 \text{ nm} \) (Fig. 1). This absorption spectrum is apparently composed of the spectra of the isolated ions. In chlorinated alkalanes such as \(\text{CH}_2\text{Cl}_2 \), \(\text{CHCl}_3 \) and \(\text{CCl}_4 \) which are much less polar the absorption of the salt \([\text{NR}_4]^+ [\text{BR}_4^-] \) is shifted to longer wavelength (Fig. 1). In solutions which consist mostly of \(\text{CCl}_4 \) \(\text{NR}_4^+ \) is almost insoluble \([11]\) the largest shift is observed (Fig. 1). Moreover, an inflection at \(\lambda = 306 \) \((\varepsilon = 420 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1} \)) indicates the appearance of a new band. It is attributed to a \(\text{BR}_4^- \rightarrow \text{NR}_4^+ \) OSCT transition within the ion pair. The red shift of this absorption with decreasing solvent polarity reflects the extent of ion pairing. The salt \([\text{NR}_4]^+ [\text{BR}(\text{C}_6\text{H}_5)_4] \) does not show this effect. Since aryl borates are less reducing than alkyl borates \([6]\) the OSCT band of the tetraphenylborate should be shifted to shorter wavelength where it is obscured by the absorptions of the phenyl substituents.

Solutions of \([\text{NR}_4]^+ [\text{BR}(\text{n-butyl})_4] \) in chlorinated alkalanes are light sensitive. However, light absorption by the solvent must be excluded in order to avoid its photocytosis which can lead to seri...
uous complications [11]. CH2Cl2 is a suitable solvent because it does not absorb above 240 nm but provides sufficient ion pairing [6]. OSCT excitation ($\lambda_{\text{irr}} > 275$ nm) of the ion pair $[N(n\text{-butyl})_4]^+ [B(n\text{-butyl})_4]^- \text{in CH}_2\text{Cl}_2$ leads to a photoreaction. The accompanying spectral changes (Fig. 2) indicate the loss of the ion pair. The disappearance quantum yield is $\phi = 1.5 \times 10^{-3}$ at $\lambda_{\text{irr}} = 280$ nm. All polar constituents were removed from the photolyzed solution by adsorption chromatography on SiO2. A $^1$H NMR analysis (250 MHz Bruker AC 250) of this solution shows the presence of octane. These observations can be explained by the following scheme:

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\begin{align*}
[N(n\text{-butyl})_4]^+ [B(n\text{-butyl})_4]^- \xrightarrow{\text{hv/OSCT}} &\quad [N(n\text{-butyl})_4] + [B(n\text{-butyl})_4]^- \\
N(n\text{-butyl})_4 &\rightarrow N(n\text{-butyl})_3 + n\text{-butyl radical} \\
B(n\text{-butyl})_4 &\rightarrow [B(n\text{-butyl})_3] + n\text{-butyl radical} \\
2 \times \text{butyl radical} &\rightarrow \text{octane}
\end{align*}
\]

This mechanism is consistent with the well-known redox properties of NR4$^+$ cations [9, 10] and BR4$^-$ anions [6, 7]. Moreover, the analogy between NR4$^+$BR4$^-$ and the hypothetical ion pair R$^+$R$^-$ is obvious. In the latter case OSCT excitation would immediately generate two radicals R which should couple to R2. Of course, the ion pair R$^+$R$^-$ is not stable but directly combines to R2.

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