Disappearance of the Sodium—Electron Pair Formed upon Photolysis of Sodium Pyrenide

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A reply is given to a suggestion by Giling *et al.* that benzene can trap electrons from immediately formed e^-, Na^+ in the photolysis of sodium pyrenide at room temperature. The present investigations do not confirm that hypothesis. An alternative possible reaction path for the disappearance of e^-, Na^+ , not earlier considered by us, is presented.

Flash photolysis of sodium pyrenide (π^-, Na^+) in tetrahydrofuran (THF) leads to photoejection of electrons, which form e^-, Na^+ ion pairs. The reactions following the flash can be monitored spectrophotometrically at 493 nm for π^-, Na^+ and at 650 nm for e^-, Na^+ . Fisher *et al.*^{1,2} reported that the e^-, Na^+ pairs disappeared more rapidly than π^-, Na^+ was reformed and that the concentration of the latter species continued to increase even when e^-, Na^+ was no longer detectable. Analysis of the kinetics led to the conclusion that the decay of the 650 nm transient is due to two reactions:

The species X, assumed to have no absorption at 650 nm, must further react with pyrene (π) yielding π^-, Na^+ in order to ensure the observed complete reversibility of the system.

As a possible identification of the species X, a relatively slow collapse of the e^-, Na^+ pair into a Na-atom was suggested, the corresponding rate constant being $4 \times 10^8 \text{ s}^{-1}$. This value seems plausible because the desolvation of the e^-, Na^+ pairs should slow down the collapse process.

The interpretation of these results was questioned by Giling *et al.*³ They pointed out that benzene is probably present in the experiments as an unavoidable impurity, presumably in the solvent THF, and proposed that the reaction

is responsible for the decay of the 650 nm transient (due to the disappearance of e^-, Na^+). The latter process is faster than the reappearance of π^-, Na^+ (measured by the decrease of bleaching at 493 nm). In view of the lower electron affinity of benzene as compared to that of pyrene, the $C_6H_6^{\cdot-}, Na^+$ radical anions react with pyrene and form π^-, Na^+ .

The proposal by Giling *et al.* is kinetically equivalent to the scheme suggested by Fisher *et al.*, but the pseudo-first order rate constant, k_{obs} , governing the decay of the 650 nm transient and given in the treatment by Fisher as

$$k_{\text{obs}} = k_3[\pi] + k_4$$

should acquire the form

$$k_{\text{obs}} = k_3[\pi] + k_7[C_6H_6]$$

To test the validity of this proposal we initially determined the benzene content in THF both spectrophotometrically and by gas chromatography and found it to be $\sim 10^{-5} \text{ M}$. Thereafter, we performed a new series of flash photolysis experiments with the $\pi^-, Na^+ + \pi$ system to which increasing amounts of benzene were added. If we consider the last equation above and choose $k_7 = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (available literature data for the capture of the electron

Fig. 1. Logarithmic plot of the change in absorbance as a function of time for the photolysis of $\pi^{\cdot-}, \text{Na}^+$ in THF at room temperature in the absence and presence of added benzene as monitored at 493 nm (Δ , $\blacktriangle$) and 650 nm ($\circ$, $\bullet$). The solutions were photolyzed in a 60 cm cell and surrounded by a CuCl_2 filter solution. $\circ, \Delta$: no benzene added, $[\pi^{\cdot-}, \text{Na}^+] = 4.1 \times 10^{-7} \text{ M}$, $[\pi]_{\text{av}} \approx 5 \times 10^{-7} \text{ M}$. $\bullet, \blacktriangle$: $[\text{C}_6\text{H}_6] \approx 10^{-2} \text{ M}$, $[\pi^{\cdot-}, \text{Na}^+] = 3.0 \times 10^{-7} \text{ M}$, $[\pi]_{\text{av}} \approx 4 \times 10^{-7} \text{ M}$.

by benzene in water⁴), $k_3 = 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $[\pi] = 5 \times 10^{-7} \text{ M}$ (a representative value of the pyrene concentration in the previous experiments), a significant increase in k_{obs} can be predicted upon increasing the benzene concentration from 10^{-5} to 10^{-2} M . If we use a value $k_7 = 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ calculated from $k_6 = 4 \times 10^8 \text{ s}^{-1}$ and $[\text{C}_6\text{H}_6] = 10^{-5} \text{ M}$, we would expect an even more drastic increase in k_{obs} .

The present experimental results demonstrate that neither the decay of the 650 nm transient nor the reappearance of $\pi^{\cdot-}, \text{Na}^+$ monitored at 493 nm is affected by the increase in the concentration of benzene from 10^{-5} to 10^{-2} M , provided the concentration of pyrene is kept constant. This is evident from an inspection of Fig. 1 depicting plots of the logarithm of the change in absorbance at 650 nm and 493 nm as a function of time in two series of experiments in which the concentration of benzene was 10^{-5} and 10^{-2} M , respectively. Moreover, the presence of 10^{-2} M benzene had no effect on the difference spectra recorded at various times after a flash. In particular we found no transient absorption, which could be attributed to the benzene radical anion. Absorption from this species has been reported in the 435 nm region both from its preparation in dimethoxy-

ethane at -70°C ⁵ and recently through the use of crown ethers at room temperature in nonpolar solvents in contact with alkali mirrors.⁶

Obviously the presence of benzene even at concentrations of 10^{-2} M do not lead to a faster decay of the 650 nm transient. This is not surprising since the low electron affinity of benzene should make the equilibrium constant of the reaction

extremely small at room temperature. The equilibrium is shifted to the right at low temperatures and therefore Giling *et al.*, working under such conditions, did observe the formation of $\text{C}_6\text{H}_6^{\cdot-}, \text{Na}^+$ in their photolytic experiments with relatively high concentrations of benzene (10^{-2} to 10^{-1} M). However, even at these low temperatures they found benzene ineffective at concentrations 10^{-4} to 10^{-5} M .

In conclusion, the e^-, Na^+ pair is evidently not trapped by impurity benzene. We can still consider the collapse of the sodium-electron pair as the most feasible reaction path for e^-, Na^+ of the various alternatives discussed in Refs. 1,2 although it has not been experimentally confirmed to date. Thus we can look for further reactions for the disappearance of e^-, Na^+ through routes other than $\pi + e^-, \text{Na}^+ \rightarrow \pi^{\cdot-}, \text{Na}^+$. Recent findings by us in the photolysis of cesium pyrenide⁷ and by Levin *et al.* in the photolysis of tetracene⁸ have shown that the photolysis of aromatic radical anions is followed, at least partially, by the formation of the corresponding dianions, *i.e.*

Electron transfer from the dianion to the hydrocarbon ultimately regenerates radical anions and reverts the system to its initial state.

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