Flash Photolysis of Aqueous Solutions of Azide and Nitrate Ions

By FRANÇOIS BARAT, BERNARD HICKEL, and JACK SUTTON*
(*Service de Chimie Physique, Centre d'Etudes Nucléaires de Saclay, B.P. No. 2, Gif-sur-Yvette, France*)

IN a study of the absorption spectrum of the azide ion in aqueous solution, Burak and Treinin[1] have shown the presence of three bands, designated A, B, and C, lying in the region 3000—1990 Å. Band A appears as a shoulder at 2400 Å (ϵ 400 M^{-1} cm.$^{-1}$) and is attributed to the transition $^1\Delta_u \rightarrow {}^1\Sigma_g{}^+$; band B has a maximum near 2000 Å (ϵ 4000 M^{-1} cm.$^{-1}$) and is considered to represent a charge transfer to solvent, whilst the band C, situated in the far u.v., is considered to involve excitation to a $^1\Sigma_u{}^+$ state.

In the flash photolysis of a deaerated solution of sodium azide, ([N_3^-] 4 × 10^{-4} M, flash energy 1000 J, duration at half intensity 4 μsec.) a transient absorption was observed in the region 4500—7000 Å. This band has maximum intensity immediately after the photolytic flash and disappears in 60 μsec. The similarity of the profile of this band and of the kinetics of its disappearance to the corresponding properties of the band observed in the flash photolysis of potassium iodide ([I^-] 5 × 10^{-4} M), and the fact that the band does not appear in aerated solutions, leads us to attribute it to the solvated electron.[2]

A second absorption (Figure 1), observed in both aerated and deaerated solutions, lies between 2500 and 3000 Å with a maximum at 2720 Å. This band also exhibits its maximum intensity immediately after the photolytic flash

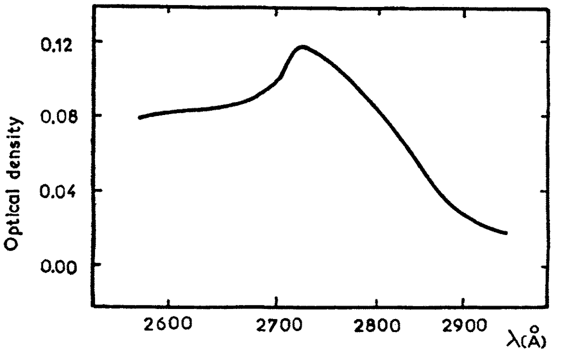

FIGURE 1. *Absorption spectrum attributed to the* N_3 *radical.*

and its lifetime is about 1 msec. In the flash photolysis of gaseous HN$_3$, Thrush[3] has shown the presence of a large number of absorption bands between 2600 and 2730 Å, the most intense lying near 2720 Å: these are attributed to the radical N$_3$. We believe that the spectrum observed in aqueous solution is also due to this species.

Since in our experiments the photolytic cells were transparent at 2000 Å, and in view of the concentration of N$_3^-$ employed, the absorption occurred principally in band B.[1] These preliminary results thus confirm the conclusions of these authors.

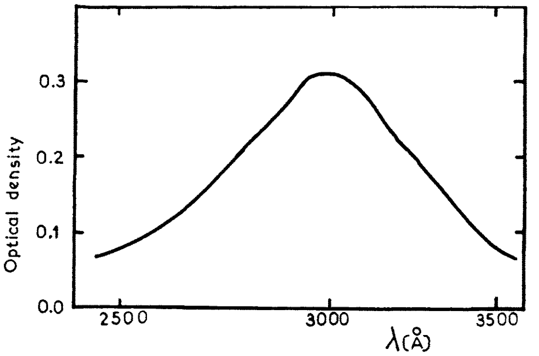

FIGURE 2. *Absorption spectrum attributed to the peroxynitrite ion.*

Meyerstein and Treinin[4] have studied the absorption spectrum of the nitrate ion in the range 1900—3400 Å. The first band in the region 2600—3200 Å (ϵ_{max} at 3020 Å 7·1 M^{-1} cm.$^{-1}$) is attributed to a forbidden transition, either $n \rightarrow \pi^*$ or $n \rightarrow \sigma^*$. Below 2600 Å another more intense band exists with a maximum at 2010 Å (ϵ 9900 M^{-1} cm.$^{-1}$); this is attributed to an allowed $\pi \rightarrow \pi^*$ transition.

The flash photolysis of dilute neutral solutions of potassium nitrate (10^{-4}—10^{-5}M, wavelength in the second absorption band, same flash characteristics as before) showed no absorption between 4000 and 7000 Å in deaerated solutions, immediately after the photolytic flash. In the region 4500—7000 Å this seems to show that the primary photolytic effect is not the dissociation of the ion into an NO$_3$ radical and a solvated electron as one might expect if the nitrate absorption spectrum were due to a change transfer to solvent as certain authors have supposed.[5] Since a reaction between NO$_3^-$ and the solvated electron has been observed[6] we have verified [by flash photolysis of aqueous 1·5 × 10^{-4}M-K$_4$Fe(CN)$_6$ in the presence of 1·1 × 10^{-5}M. nitrate] that the solvated electron has a sufficiently long half life at the lower nitrate concentrations employed to be observed.

In neutral aerated solutions a broad absorption band (Figure 2), extending from 2500 to 3600 Å with a maximum at 3000 Å grows with approximately first-order kinetics (Figure 3) after the photolytic flash, reaching a maximum intensity at 100 µsec., and thereafter disappears with zero-order kinetics (Figure 4) over about 3 sec. In alkaline solutions (pH = 11·3) this band persists for more than 10 min., but it does not appear in acid media. We attribute this absorption to the peroxynitrite ion O–N–O–O$^-$, of which the absorption spectrum, preparation, stability, and decomposition mechanism have been reported.[7]

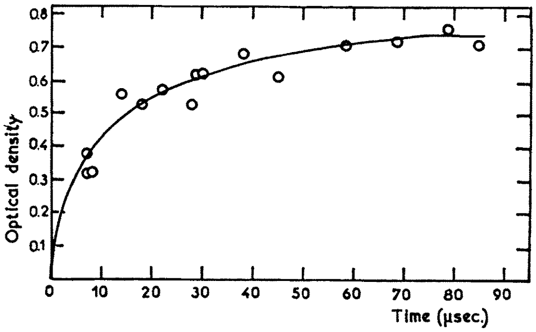

FIGURE 3. *Flash photolysis of neutral* NO$_3^-$ *solutions* (10^{-4}M): *first-order appearance of the 'peroxynitrite ion.'*

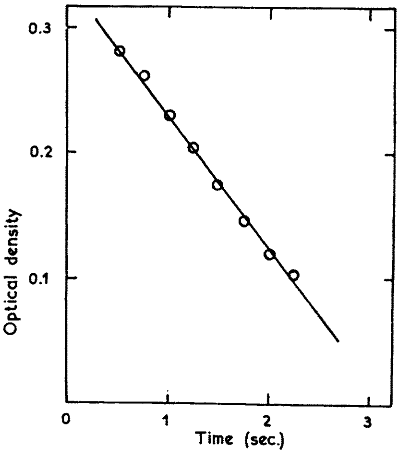

FIGURE 4. *Zero-order decay of the 'peroxynitrite ion.'*

The addition of O(^3P) oxygen-atom scavengers (propylene 2 × 10^{-2}M, allyl alcohol 1·1 × 10^{-3}M) and OH radical scavengers (methanol 6 × 10^{-1}M, formate 9 × 10^{-4}M) had no effect on the production of this absorption. It would therefore appear that oxygen atoms O(^3P) and O$^-$ radicals, if produced in the primary photolytic act[8] are not precursors of the peroxynitrite.

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