Inorganica Chimica Acta, 32 (1979) L1–L2

Spin Trapping of Azide Radicals in Photolysis of Azido Cobalt(III) Complexes*

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Received September 22, 1978

Azide radicals ($\cdot N_3$) are believed to be the primary products in the photolysis of many transition metal azido complexes [1, 2]. Although the formation of azide radicals in the photolysis of azido cobalt(III) complexes is very likely, until now there is no direct evidence for it. Thus Endicott *et al.* [3–5] on the basis of scavenging experiments with iodide ions have proposed the formation of azide radicals during the photolysis of $[Co(CN)_5N_3]^{3-}$ and $[Co(NH_3)_5N_3]^{2+}$ but no ESR evidence for the formation of azide radicals has been found by Balashev and Shagisultanova [6] in the low-temperature photolysis of $[Co(CN)_5N_3]^{3-}$.

In this paper we wish to show that azide radicals formed by photolysis of $K_3[Co(CN)_5N_3]$ and $[Co(NH_3)_5N_3]Cl_2$ in aqueous or methanolic solutions could be detected by ESR spin trapping at room temperature.

Using phenyl-N-tert.butyl nitrone (*PBN*) as a spin trap the ESR spectrum of a short-lived spin adduct consisting of a triplet of a 1:2:2:1 quadruplet (Fig. 1) could be observed. The hyperfine splitting is due to the interaction of the unpaired electron with the nuclear spins of two nitrogens (one from the nitrone and the other from the trapped azide; $a_N^1 = 1.501 \pm 0.008$ mT, $a_N^2 = 0.201 \pm 0.005$ mT) and one β-hydrogen atom ($a_H = 0.201 \pm 0.005$ mT). The hyperfine splitting due to the two remaining nitrogen atoms of the trapped azide radical could not be resolved.

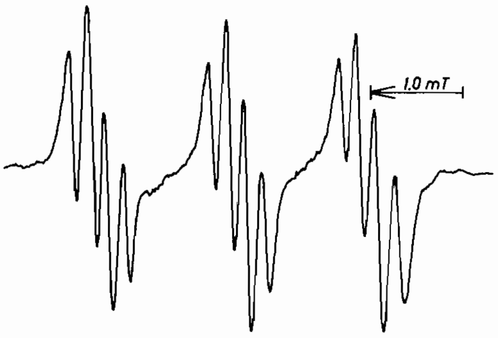

Figure 1. ESR spectrum of azide spin adduct to *PBN*, produced by photolysis of 0.05 *M* aqueous solution of $K_3[Co(CN)_5N_3]$ in the presence of *PBN* (saturated solution) at room temperature.

The azide spin adduct with *PBN* detected here has a half-life time of about 20 seconds.

The addition of methanol or even the reaction of $K_3[Co(CN)_5N_3]$ in pure methanol led to the formation of only traces of hydroxymethyl ($\cdot CH_2OH$) spin adducts ($a_N = 1.540$ mT, $a_H = 0.377$ mT [7]). Therefore, the hydrogen abstraction by azide radicals seems to be a rather slow process compared with the trapping by *PBN*.

Surprisingly, the use of nitrosodurene (2,3,5,6-tetramethylnitroso benzene, *ND*) as a spin trap gave stable spin adducts of the azide radical too. Strong ESR signals (Fig. 2) could be obtained during photolysis of methanolic solution of $K_3[Co(CN)_5N_3]$ at room temperature. The hyperfine splitting due to three nitrogen atoms ($a_N^1 = a_N^2 = 0.734 \pm 0.008$ mT, $a_N^3 = 0.229 \pm 0.005$ mT) could be observed readily. Since it may be very likely that the splitting caused by the other nitrogen is too small to be resolved, the nitroxide observed may be assigned to the azide spin adduct.

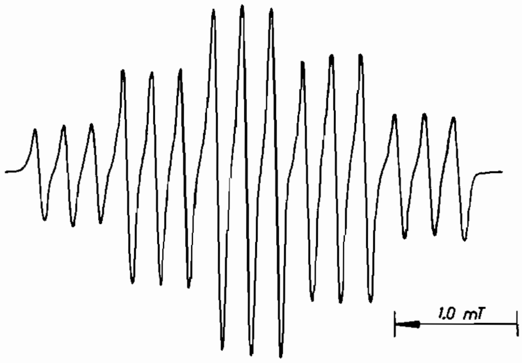

Figure 2. ESR spectrum produced by photolysis of $K_3[Co(CN)_5N_3]$ in methanol in the presence of nitrosodurene.

The alternative assumption, according to which the nitroxide corresponds to the $[Co(CN)_5]^{3-}$ adduct to *ND* may be rejected for the following reasons: $[Co(CN)_5]^{3-}$ synthesized by another method [8] does not form a stable adduct with *ND*. Secondly, photolysis of a CBr_4/NaN_3 mixture in methanol also produced the spectra of the radicals described above. Therefrom it follows that spin trapping by the nitroxide method provides a reliable possibility for detection of azide radicals produced photolytically in both aqueous and organic media.

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*Photocatalytic Systems, XXV. Part XXIV: D. Rehorek, *Radiochem. Radioanalyt. Lett.*, in press.

Experimental

$K_3[Co(CN)_5N_3]$ [9], $[Co(NH_3)_5N_3]Cl_2$ [10], *PBN* [11] and *ND* [12] have been prepared according to literature methods. 0.05 *M* aqueous solution of $K_3[Co(CN)_5N_3]$ and $[Co(NH_3)_5N_3]Cl_2$, respectively, saturated with *PBN* and bubbled with nitrogen before used were irradiated by a high pressure mercury lamp HBO-200 (VEB Narva Berlin) within a cavity of a JES-3BQ (Jeol) spectrometer. Similar experiments were carried out with $K_3[Co(CN)_5N_3]$ or CBr_4/NaN_3 in methanol using *ND* as a spin trap. All spectra were recorded at room temperature. The g-values of the spin adducts have been estimated to be 2.0059 ± 0.0005 using DPPH ($g = 2.0036$) as reference standard.

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