

Preliminary communication

AZOLE ANIONS AS ONE-ELECTRON REDUCERS OF FERRICINIUM SALTS

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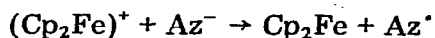
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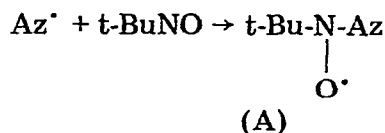
Summary

Azole anions are capable of reducing ferricinium cation to ferrocene in solution at room temperature. The formation of azolyl radicals under these conditions is detected.

As we have shown earlier [1, 2], azole anions act as one-electron reducers of carbonyl derivatives of low-valent iron ($\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$, $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{I}$). It should be noted that azole anions also reduce Fe^{II} in cyclopentadienyldicarbonyliron halides; as a result $[\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}]_2$ is formed [3]. These anions (pyrazolide, imidazolide, benzotriazolide) turned out to be capable of reducing Fe^{III} compounds, viz. ferricinium cations:



This reaction proceeds in tetrahydrofuran or dimethylsulfoxide and leads to ferrocene and short-lived azolyl radicals, identified by a spin trap (tert-nitrosobutane). Azolyl-tert-butylnitroxide radicals (A) are formed as a result of the reaction:



As has been discussed previously [1], tert-nitrosobutane may oxidise azole anions. This reaction, however, results mainly in di-tert-butylnitroxide radicals, and only significant amounts of azolyl-tert-butylnitroxide radicals are formed as the reaction proceeds further. In contrast, the reaction of azole anions with

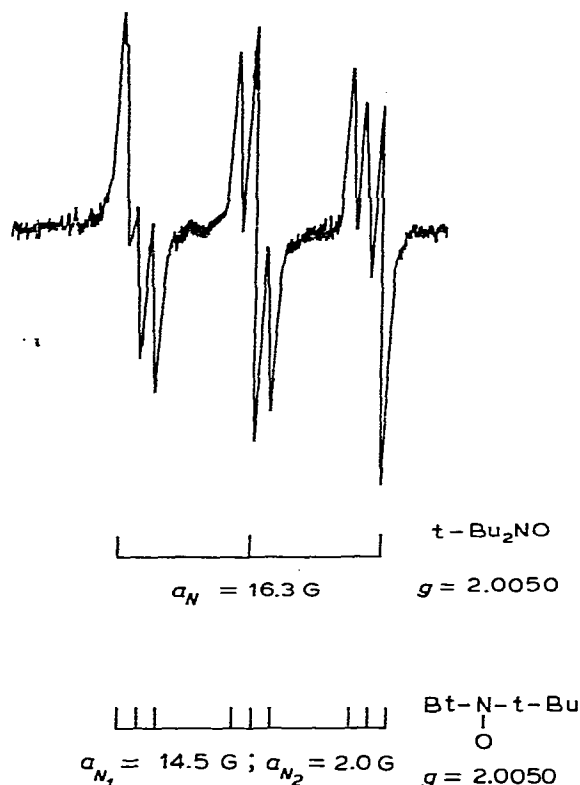


Fig. 1. ESR spectrum of benzotriazolyl-tert-butyl nitroxide radical (Bt-N(O[•])-t-Bu) generated in the reaction of ferricinium hexafluorophosphate ($10^{-1} M$) with sodium benzotriazolide ($10^{-1} M$) in the presence of tert-nitrosobutane ($10^{-3} M$). The spectrum was recorded within 3 min after mixing the reagents (THF, 20°C).

ferricinium salts gives radicals of the type A mainly, di-tert-butyl nitroxide radicals being present in insignificant amounts (see Fig. 1). In the case when a sodium salt of 2,4,5-triphenylimidazole is introduced into the reaction, stable radicals of this heterocycle may be identified without use of a spin trap.

References

- 1 V.N. Babin, V.V. Gumenyuk, S.P. Solodovnikov and Yu.A. Belousov, *Z. Naturforsch. B*, **36** (1981) 400.
- 2 Yu.A. Belousov, V.V. Gumenyuk, V.N. Babin, S.P. Solodovnikov and N.S. Kochetkova, *Koord. Khim.*, in press (in Russian).
- 3 A.N. Nesmeyanov, V.N. Babin, N.S. Kochetkova, E.I. Mysov, Yu.A. Belousov and L.A. Fedorov, *Dokl. Akad. Nauk SSSR*, **200** (1971) 1112.