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Evidence for a Mono-electron Transfer Process in the BF_3-Promoted Reaction of 4'-Nitrobenzenesulphenanilide (NBSA).

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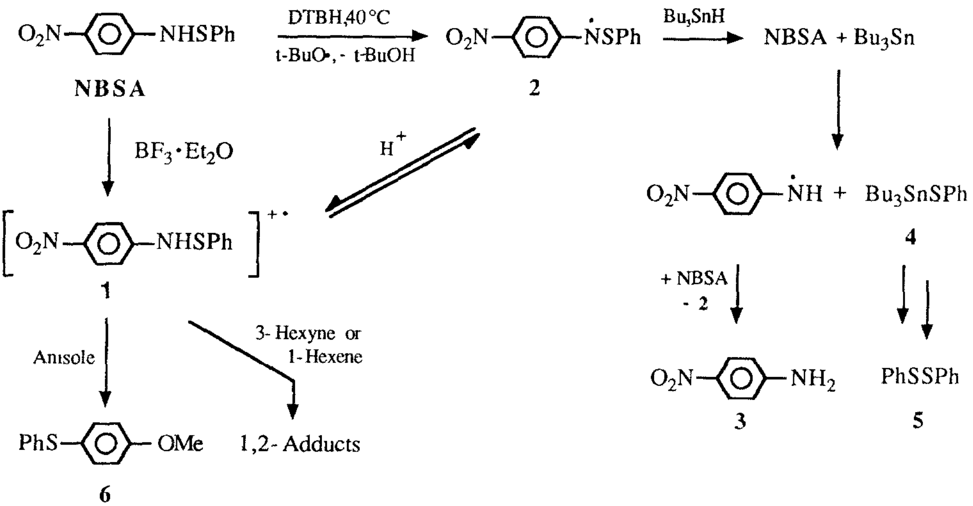
Abstract : ESR spectroscopy shows the formation of a radical species in the BF_3-promoted reaction of NBSA, an acid/base Lewis-type reaction

In the recent years attention has been devoted to the chemistry of benzenesulphenanilides, which have been considered from both synthetic and speculative point of view. In particular, we have reported that BF_3 transforms these sluggish compounds into reactive species which can undergo fast displacement at the sulphur atom by suitable nucleoplhiles[1]. Under these conditions 4'-nitrobenzenesulphenanilide (NBSA) was found to be a powerful sulphenyl transfer agent, usefully employed as synthetic intermediate in the 1,2-difunctionalization of alkenes and alkynes[1,2]. However, in spite of our efforts, no evidence for the actual nature of the sulphenylating agent was provided, although the tetracoordinate acid/base complex, $4\text{-}O_2NC_6H_4N^+(SPh)BF_3^-$, was tentatively suggested.

We wish now to report evidence obtained from both chemical and ESR spectroscopy studies of BF_3-promoted reaction of NBSA, which suggest that a radical cation, $(O_2NC_6H_4NHSPh)^{\dot{+}}$, could be the sulphenylating agent (**1**).

When a degassed benzene or methylene chloride solution of NBSA was allowed to react with $BF_3.Et_2O$ (ca. 47% BF_3) (1.5 molar equiv.) directly in the ESR cavity, a quite persistent radical[3] was immediately detected and its structure, N-(4-nitrophenyl)-N-(phenylthio)aminyl radical (**2**), was easily assigned by comparison of its spectroscopic parameters with those reported in the literature[4]. When to such a solution a slight excess of a nucleophile, i.e. anisole, 1-hexene, or 3-hexyne, was added the ESR signal of the radical species (**2**) was istantaneously quenched. Actually, these compounds are known to undergo efficiently the sulphenyl transfer in the promoted reaction of NBSA[2,5], therefore the radical (**2**) itself might be the sulphenylating agent. However, independent experiments ruled out this hypothesis. In fact, producing the radical (**2**) by hydrogen abstraction with ButO·, obtained by thermal decomposition of di-ter-butyl hyponitrire (DTBH) at 40°C, in anisole as well in benzene in the presence of 3-hexyne or 1-hexene, we found that the reaction products were substantially identical to those reported for the same reaction carried out in benzene in the absence of nucleophilic species[6]. The lack of any product deriving from the sulphenylation of these nucleophiles leads to conclude that the radical (2) is not capable to act as sulphenyl transfer agent. In agreement with these chemical evidence, when the radical (2) was produced from NBSA and DTBH under the same conditions directly in the ESR cavity, it was not quenched by adding an excess of anisole, 3-hexyne, or 1-hexene Then, these findings might suggest that the thioaminyl radical (**2**) could be in rapid equilibrium with the sulphenylating agent (**1**), so that the disappearance of (2) can be achieved when the species (**1**) is trapped by nucleophiles. This suggestion was compelled by independent experiments. In fact, when the BF_3-promoted reaction of NBSA was carried out in anisole in the presence of 2 molar equiv of tributyltin hydride, a strong hydrogen donor, column chromatography led to the separation in nearly quantitative yield of 4-nitroaniline (**3**) and of an inseparable mixture of tributyltin phenyl sulphide (**4**) and diphenyl disulphide (**5**) in ca. 4.1 ratio. No formation of 4-methoxyphenyl phenyl sulphide (**6**) was evidenced: this compound was exclusively formed when this reaction was carried out in the absence of tributyltin hydride through electrophilic sulphenylation of the nucleophilic aromatic solvent [2c,5]. Therefore, it may be inferred that the presence of a radical trap as Bu_3SnH can be capable to suppress the sulphenylating agent (**1**) by quenching the radical (**2**). The formation of the product (**3**) and (**4**) can be attributed to a chain reaction involving an S_H2 displacement at the sulphur atom of NBSA by stannyl radicals (see Scheme), and the minor amount of disulphide (**5**) probably arose from the sulphide (**4**), which was found to be unstable under the reaction conditions and work-up.

Scheme

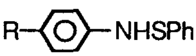


On these bases it seem unlikely that a tetracoordinate complex might be claimed as possible sulphenylating agent and, although we do not have definitive evidence, it seems more sensible that the sulphenylating agent (**1**) could be the radical cation $(O_2NC_6H_4NHSPh)^{\dot{+}}$, a species that actually could exist in equilibrium with radical (**2**) through a protonation/deprotonation reaction[7].

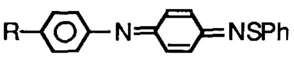
Such a radical cation $(O_2NC_6H_4NHSPh)^{\dot{+}}$ might arise from a single electron transfer process from NBSA to the Lewis acid BF_3, but unfortunately we were not able to detect it directly by ESR spectroscopy. However, we found that a SET process involving NBSA can actually lead to the radical (**2**). In fact, when a benzene solution of NBSA was allowed to react in a ESR spectrometer cavity with an N-methyl-4-cyanopyridinium salt, an easy electron acceptor substrate[8], the signal due to radical (**2**) was istantaneously detected; its formation came undoubtedly from intermediacy of the radical cation $(O_2NC_6H_4NHSPh)^{\dot{+}}$ through a deprotonation reaction.

It has been noted that a SET process was claimed to occur in several reactions involving electron reach substrates[9] but, at the best of our knowledge, no examples are reported in which a Lewis acid can act as electron acceptor. On the other hand the formation of the radical (**2**) from the reaction of NBSA with Lewis acid appears to be not confined to the reaction with the BF_3 only. Treatment of a benzene solution of NBSA with $AlCl_3$ produced the same radical (**2**) as BF_3 and also in this case the radical was quenched indirectly by nucleophilic substrates, i.e. anisole, 3-hexyne, and 1-hexene, and directly by tributyltin hydride. Moreover, the reaction products distribution followed the same pattern as evidenced for the related BF_3-promoted reaction carried out in anisole solution, both in the absence and in the presence of tributyltin hydride.

Attempts to detect related aminyl radicals in the BF_3-promoted reaction of 4'-substituted benzenesulphenanilides (BSA) other than NBSA, failed. In fact, no paramagnetic species were found by treatment of a degassed benzene solution of 4'-methylbenzenesulphenanilide (BSA, R=Me) with 1.5 molar equiv. of $BF_3 \cdot Et_2O$ directly in the cavity of the ESR spectrometer, whereas under the same conditions 4'-chloro (BSA, R=Cl) and 4'-methoxybenzenesulphenanilide (BSA, R=OMe) gave radical species that were attributed to some reaction of BF_3 with respectively N-(4-chlorophenyl)-(7, R=Cl) and N-(4--methoxyphenyl)-N'-(phenylthio)-p-quinonedi-imine (7, R=OMe)[10], ultimate reaction products[11].



BSA



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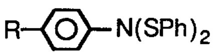

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In this light the single electron transfer process between a Lewis acid and benzenesulphenanilides seems to be confined to NBSA only. On the other hand it has been reported that in the BF_3-promoted reactions of BSA (other than NBSA), these compounds can themselves act as nucleophiles towards the sulphenylating agent, initially leading to the corresponding N,N-bis(phenylthio)aniline (**8**)[11]. Therefore, the failure in the detection of thioaminiy radical as $(4\text{-}RC_6H_4NSPh)\cdot$ (R=Cl, Me, OMe) does not reject *a priori* that an electron transfer process might be involved with BSA too; in fact, the resulting radical cations might be immediately quenched by the nucleophilic BSA.

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