Paramagnetic Intermediates in Oxidative Coupling Reactions of Tertiary Aromatic Amines in Liquid Sulphur Dioxide

M. Donbavand and H. Möckel
Hahn-Meitner-Institut für Kernforschung, Berlin

Introduction

Paramagnetism in solutions of tertiary aliphatic amines in liquid sulphur dioxide has been reported recently and it was shown that the paramagnetic species is probably in the triplet electronic state. The present work extends this study to solutions of a number of aromatic tertiary amines where in certain cases similar donor-acceptor intermediates are observed, and in particular to oxidation reactions which take place in such solutions, on addition of a highly competitive electron acceptor and oxidising agent such as molecular iodine.

Solutions of the tertiary aromatic amines in liquid SO₂ seem to have received relatively little attention in the literature in comparison to their aliphatic homologues and little information is available. Vapour pressure measurements however, have indicated that the amine-SO₂ ratio is in most cases 1:1, and a recent patent has described the preparation of a number of such addition compounds. Three aromatic tertiary amines were selected for study here, triphenylamine, N,N-dimethylaniline and N,N-diethylaniline; they are considered separately below.

Experimental

The techniques used for drying, degassing and handling of the solvent as well as the ESR spectro-meter have been described. The amines were analytical materials of the best available grade and were used without further purification. The iodine was triply sublimed material.

Sample tubes were essentially of the types already described fitted with side arms containing the reactants sealed from the main cell until required with "teflon" valves ("Rotaflo").

Results and Discussion

Triphenylamine (TPA)

Solutions of triphenylamine in liquid SO₂ of the order of 0.3 M exhibit a deep flame-red colour, darkening perceptibly in shade on lowering the temperature. The absorption spectrum of a dilute solution after some 30 min standing at room temperature shows a broad absorption band starting in the visible at about 600 nm and moving uniformly to a maximum near the edge of the UV at 398.5 nm. In contrast to triethylamine solutions the spectrum undergoes no observable change with time. Evaporation of the solution in air yields a pale yellow solid with no detectable odour of SO₂ in contrast to the dark red oil obtained from triethylamine solutions.

The ESR spectrum of solutions of triphenylamine in liquid SO₂ (~0.1 M) presents a number of interesting features: The presence of a single sharp line, comparable to that found in solutions of tertiary aliphatic amines, attributable to the triplet state[TPA+SO₂] donor-acceptor pair, has only been observed fleetingly after rapid warming of fresh
solutions from about —60 °C to room temperature; the reproducibility of this experiment is poor, owing probably to the short lifetime of this entity under the experimental conditions used here. Attempts are in progress to improve the stability of this species by varying the experimental conditions such as temperature and concentration. Concurrent with the disappearance of the single line is observed the appearance of a five-line spectrum at lower field centred on \( g = 2.0025 \pm 10^{-4} \). The spectrum is reproduced in Fig. 1. The five principle lines (line-width 3.5 G) have an intensity ratio closely approximating to 1:2:3:2:1 and a mean separation of 6.3 G. Reduction of modulation amplitude to near the limit of detection of the spectrum (0.5 G for a \( 10^{-2} \) m solution) affects partial resolution of the main hyperfine group into a large number of closely spaced lines (insert Fig. 1), full resolution of which has however not been possible. The species responsible for this spectrum appears to be stable and a spectrum recorded several days later showed no appreciable change. The addition of molecular iodine to this solution (equimolar or excess) either as solid or in saturated \( \text{SO}_2 \) solution effects darkening to a deep brown and a massive increase in the concentration of the paramagnetic species present (at least 100 fold), but otherwise the spectrum remains unchanged. Increasing the microwave power to the system effected a steady increase of signal intensity and no evidence of saturation was noted within the available range of the 2 K 25 klystron, further no marked temperature dependence was noted for the five line spectrum indicating that the paramagnetic species is a normal monoradical \( (S = 1/2) \) and not a triplet state as reported for aliphatic amines.

Inspection of the ESR spectrum indicates that the five principle lines arise almost certainly from interaction of the unpaired electron with two equivalent nitrogen nuclei. Earlier studies by STAMIRE and TURKEVICH\(^4\) of the interaction between TPA and iodine and a number of other acceptors in a variety of organic solvents revealed a very similar five line spectrum with a hyperfine splitting of 6.0 G to which the structure \( [\text{TPA}^- : : \cdot N \cdot \text{TPA}^+] \) was assigned. The paramagnetic species formed apparently spontaneously in liquid sulphur dioxide is without doubt one and the same as the above but for reasons discussed below a different structure is preferred.

Later studies by a number of workers\(^5,6\) using a variety of techniques, including electrochemical and iodine oxidations revealed a similar five-line spectrum (although the reported N-splitting was somewhat smaller) and convincing evidence was presented that the free radical responsible for the spectrum is in fact a typical “Wurster’s salt”\(^7\) type radical with the structure \( i.e. \) the \( \text{N,N,N',N'}-\text{tetraphenylbenzidine cation radical.} \)

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The overall process of the reaction in liquid \( \text{SO}_2 \) may be represented by the following scheme:

1. Formation of transient TPA/\( \text{SO}_2 \) donor-acceptor complex

\[
\text{[TPA]} + \text{SO}_2 \rightarrow \text{[TPA}\text{-SO}_2^+] = \text{TPA}^+ + \text{SO}_2^-
\]
2. Attack of an uncomplexed amine molecule on the positively charged residue of the complex, i.e. coupling between resonance form I of the amine and resonance form II of the complex. This is clearly supported by steric considerations, direct attack by the nitrogen lone-pair would be hindered by the bulky phenyl groups.

\[
\begin{align*}
\text{[SO}_2\text{]} & \quad \text{[SO}_2\text{]} \\
\alpha_2^+ & \quad \alpha_2^+ \\
\alpha_2^+ & \quad \alpha_2^+ \\
\alpha_2^+ & \quad \alpha_2^+ \\
\end{align*}
\]

Alternatively the oxidation may proceed via a mechanism similar to that proposed in ref.\textsuperscript{5} where two TPA radicals react with one another to form the diamagnetic TPB which then undergoes further stepwise oxidation via the paramagnetic TPB\textsuperscript{+} to the final diamagnetic product. This mechanism would seem intuitively less likely in the present system but without further experimental evidence no firm decision can be made in favour of either model.

3. Further oxidation to the quinoid form of the product, the quinone diimine doubly charged cation, which is the usual product of complete oxidation of a paradiamine.

\[
[\alpha_2^+\text{N} \quad \text{N} \quad \text{N} \quad \text{N}^+\text{N}^+\phi_2]
\]

The nature of the counter ion formed in the absence of an oxidising agent is unclear, the situation where iodine is present is discussed presently. Analysis of the very fine structure seen under suitable conditions is probably not feasible owing to the large number of small ring proton splittings expected for this radical.

It has been suggested\textsuperscript{9} that poisoning by traces of oxygen in the solvent could be responsible for the apparently spontaneous formation of the TPB\textsuperscript{+} ion in the absence of iodine and although no effort was spared to rigorously exclude oxygen, which is reported as exceptionally difficult to remove\textsuperscript{10}, this possibility cannot be entirely dismissed. The TPB\textsuperscript{+} radical also seems to be stable in the solid state, and if the solvent is removed by evaporation in air a pale brown solid remains, characterized by a single, sharp Lorenzian ESR absorption with \( g = 2.0032 \) and a linewidth of 8 G.

\( N,N\text{-Dimethylaniline (DMAn)} \)

Dimethylaniline solutions in liquid \( \text{SO}_2 \) show a deep orange-red colour similar to that obtained in TPA solutions. In contrast to the above however no ESR signal has been detected in these solutions, either single line or multiplet.

On addition of a slight excess of iodine however, the solution darkens considerably (similar to the TPA case) and the growth of a complex ESR signal is observed (Fig. 2). The spectrum attains maximum intensity after a period of an hour or so (for a solution containing \( 6 \times 10^{-1} \text{ M DMAn} \)). It will be noted that although apparently well resolved there is considerable overlap and an assignment on cursory inspection in terms of a chemically "reasonable" radical is not obvious.

A number of studies of the oxidation of DMAn have been discussed in the literature, biochemically\textsuperscript{12}, chemically\textsuperscript{13} and, notably the work of Mizoguchi and Adams\textsuperscript{14} and Galus and Adams\textsuperscript{15} in anodic oxidation processes. In all cases the oxidation was postulated to proceed via initial production of DMAn\textsuperscript{+} radical cations (which were not however directly observed) to yield \( N,N,N',N'-\text{tetramethylbenzidine} \) (TMB) or its oxidation product the.
In other words a coupling process similar to that discussed for triphenylamine above was suggested. In ref.14 a weak ESR absorption was observed during in situ electrolysis of DMAn solutions in the microwave cavity, which was assigned to the TMB\(^+\) radical ion by comparison with the ESR spectrum produced by exhaustive anodic oxidation of TMB itself. An apparently unequivocal analysis\(^{16,17}\) of this complex spectrum in terms of TMB\(^+\) was later achieved by selective deuteration and computer simulation techniques in spite of the rather low yield and poor resolution of the experimental spectra in acetonitrile. The experimental spectra of the present study in contrast show a high degree of resolution in both the extreme wings where the theoretically expected first and fifteenth group of lines are clearly observable, and in the fine splitting of each of the 93 lines visible under lower resolution (inset Fig. 2).

**N,N-Diethylaniline (DEAn)**

Cold solutions of DEAn in liquid SO\(_2\) here studied in the range 0.025–0.3 \(\text{m}\) show a darkish yellow colour when freshly prepared which deepens to orange on warming to room temperature and then slowly to a reddish-brown on standing. Such solutions, in common with the aliphatic amines discussed in ref.\(^{1}\) show a strong narrow ESR line centred on \(g = 2.00673 \pm 2 \cdot 10^{-5}\) whose intensity exhibits a similar temperature and time dependence to that reported for triethylamine\(^{18}\). The absorption is assigned therefore to the triplet state donor-acceptor pair

\[
\begin{align*}
\Phi \text{NEt}_2 \rightarrow S \rightarrow O \rightarrow O^- \\
\Delta g = 2.00673 \pm 2 \cdot 10^{-5}
\end{align*}
\]

Addition of an excess of solid iodine yields a very dark brown solution similar to other amine-iodine solutions and a complex ESR absorption, the first derivative of which is illustrated in Fig. 3.

On cursory inspection, the spectrum appears as a major triplet of lines with an overlaying fine structure. In view of this and the apparent intensity ratio of the fine structure of the outer lines attempts were made initially to correlate the spectrum with donor-acceptor intermediates containing iodine, \(\text{e.g.} \)

\[\text{Et} \rightleftharpoons \Phi - N - I_2 \rightarrow \text{Et}\]

similar to that assigned by Stamiros and Turkevich\(^4\) to the spectrum observed in solid state studies of triphenylamine-iodine complexes. Closer inspection, however, reveals that apart from the apparent 1:3:1 intensity ratio of the three major groups, which is not in accord with that expected for a single N-atom (1:1:1), the nature of the overlap in the regions between the major lines and the intensity ratio within the central group is inconsistent with this assignment. This led to the conclusion that in common with the other systems studied there are in fact 5 major lines but the degree of overlap is such that the 2nd and 4th are effectively “cancelled”. This would also make the found 1:3:1 intensity ratio correct. On the basis of this, together with the findings and arguments of the analogous TPA and DMAn systems the spectrum is assigned with some reservation to the \(\text{N,N,N',N'-tetraethylbenzidine (TEB)}\) radical cation.

Attempts to obtain better resolution by reducing the radical concentration and working with small modulation-amplitudes and slow sweeps have so far only revealed that the linewidth is in fact due to very fine poorly-resolved splittings as expected.

It is clearly impossible in a spectrum where line interference is so manifest to make even a reasonable guess as to the assignment of the couplings present, especially when the proposed structure contains as many protons as the above, and this must await further study, possibly with the \(^{15}\text{N}\) substituted amine. It is of interest to note that DEAn solutions containing iodine develop a deep green colour concurrent with the formation of the radical species, similar to that reported for DMAn\(^5\) solutions. This appears to offer further evidence that the assignment here is correct if it is assumed that the fundamentally similar radicals TMB\(^+\) and TEB\(^+\) would exhibit a similar optical absorption.
A number of curious colour reactions were noted for this dark green solution; if a portion is added to chloroform a brilliant green is at first observed in the chloroform layer which fades with a few minutes to a muddy brown. When a portion of this latter solution is shaken with a little water a bright sky-blue colour develops in the chloroform layer. Similar phenomena were observed with SO\(_2\) solutions of TPA and DMAn containing iodine though in the former case red colours were predominant. These observations are possibly connected with similar ones noted by GALUS and ADAMS\(^{11}\) in their oxidation studies of DMAn where further coupling reactions were proposed between unoxidised tertiary amine and the TMB\(^+\) radical ion.

**Yields and Stability of Radical Intermediates**

One of the most striking features of the iodine oxidation of TPA and its homologues DMAn and DEAn in liquid SO\(_2\) is the very high yield (in comparison to those obtained in other solvents) and stability of the intermediate radicals produced during the oxidations. It is suggested that this is a further demonstration of the remarkable "ionising power" of liquid SO\(_2\), dominated it would seem by charge-transfer rather than by dielectric forces\(^8\). There exist numerous examples in the literature of the complexing of halide ions by SO\(_2\), from simple alkali halides\(^{10}\) to triarylmethyl halides\(^9\) (a most useful summary of which is provided by LICHTIN\(^9\)). Thus the oxidation by iodine may be viewed as

\[
2\Phi_2N + \frac{1}{2} I_2 \rightarrow [TPB+I^-] \\
SO_2 \rightarrow TPB^+ + [I\rightarrow SO_2^-]
\]

*i.e.* the negative charge of the iodide ion produced during the oxidation is effectively spread or delocalised away from the immediate vicinity of the positive ion, perhaps "smeared" over a shell of solvent molecules forming a complex anion of the type shown below.

\[
\begin{align*}
[O_2S^+ & \cdot 1 \cdot SO_2^-] \\
[O_2S^- & \cdot 1 \cdot SO_2^-]
\end{align*}
\]

\(^{8}\) E. C. BAUGHAN, private discussion.  
\(^{13}\) J. MITCHELL and K. H. PAUSAKER, Austral. J. Chem. 10, 460 [1957].  
\(^{14}\) T. MIZOGUCHI and R. N. ADAMS, J. Amer. chem. Soc. 84, 2053 [1962].  
\(^{15}\) Z. GALUS and R. N. ADAMS, J. Amer. chem. Soc. 84, 2061 [1962].  
\(^{17}\) J. M. FRITSCHE and R. N. ADAMS, J. chem. Physics 43, 1887 [1965].  
\(^{18}\) Temperature dependence of this entity plus a number of others will be reported in a subsequent publication.