Triplet State Donor-Acceptor Intermediates in Sulphur Dioxide Solutions

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Paramagnetism in solutions of tertiary aliphatic amines and related compounds in liquid sulphur dioxide is reported. Evidence is presented that the paramagnetic species in triethylamine solutions is a triplet electronic state lying some 0.32 eV (5.1×10^{-20} joules) above a diamagnetic ground-state of an $n-k\pi$ donor-acceptor complex. The time-dependence of paramagnetism, optical absorption, and electrical conductivity of such solutions has also been investigated and an attempt is made to correlate these phenomena in terms of charge-transfer mechanisms. Finally a few properties of solutions of some similar compounds in liquid SO_2 are noted and discussed briefly.

Introduction

The nature of the species present in solutions of tertiary amines in liquid sulphur dioxide has been the subject of speculation for a number of years [1–5]. Such solutions are usually strongly coloured from pale yellow to brilliant red with a broad absorption band in the near UV and blue end of the visible region (the opacity of liquid SO_2 beyond about 330 nm does not allow for measurements at lower wavelength). They further show an often appreciable electrical conductivity and as the present study reports, in some cases an intense paramagnetism.

The Species in Solution

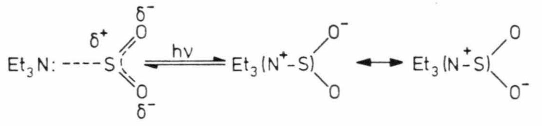
In the earlier investigations of solution of triethylamine (TEA) in liquid SO_2 [1, 2] Jander and his colleagues, in an attempt to categorise the SO_2 solvent system along with aqueous and similar systems, advanced the thionyl/sulphito theory which presupposes an autoionisation of SO_2 into SO^{2+} and $SO_3{}^{2-}$, and on the basis of this assigned the structure

$$[(Et_3N)_2SO]^{2+}SO_3{}^{2-}$$

to the species in solution analogous to the substituted ammonium ions which account for lower amine basicity in water.

The validity of Jander's interpretation was later convincingly challenged by Bateman et al. [3] who rejected the notion of salt formation and produced evidence that the species present was a simple adduct of formula Et_3N-SO_2, for which they proposed an ionised electron-transfer structure $(Et_3N)^+(SO_2)^-$.

In terms of the modern theory of charge-transfer processes, and in particular within the framework of Mullikan's thorough classification of donor acceptor interactions [6], the species in solution is probably best viewed as a typical $n-k\pi$ donor-acceptor pair with formation of a σ-bond between nitrogen and sulphur atoms and concurrent disruption of the sulphur-oxygen π-bonding system, i. e. schematically



I II III

with the possibility of resonance between ionised structures such as II and III (as well perhaps as others) which will be discussed later. (The formation of the isomer Et_3N-OSO seems unlikely in view of the dipolar properties of SO_2.)

The ESR Absorption

Solutions of triethylamine in liquid sulphur dioxide within the range of concentrations studied here (0.3 – 0.001 M) exhibit an intense, narrow and apparently structureless Lorenzian ESR line at room temperature with a g-value of 2.00667 ($\pm 2 \times 10^{-5}$) and linewidth of 0.66 G. The intensity of the absorption shows (a) anomalous temperature dependence, and (b) time dependence; these two phenomena are considered separately below.

(a) Temperature dependence

As the temperature of a solution of TEA in liquid SO_2 is lowered the ESR signal is found to display a temperature dependence inconsistent with that pre-

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dicted by the Curie-Weiss law for a free radical. A reversible loss instead of gain of intensity is seen.

Behaviour of this type has hitherto been observed in a number of charge transfer complexes in the solid state [7-10] and has been interpreted in terms of an even electron system where a triplet electronic state (spins unpaired) exists within range of thermal excitation from the lower lying diamagnetic singlet state (spins paired). In other words, where the energy separation J between singlet and triplet is of the same order of magnitude as kT at ambient temperatures the upper state will have a definite population in accordance with Maxwell-Bolzmann statistics. Thus although the spectrum of the triplet state would gain intensity in the normal way with decrease in temperature this is more than offset by the statistical redistribution of population between diamagnetic and paramagnetic states and a net intensity loss is observed.

A situation where similar temperature dependence would be observed from an odd electron system must also be considered, i. e. where a diamagnetic dimer (or polymer) exists in thermal equilibrium with a paramagnetic monomer – e. g. the NO_2/N_2O_4 system. This model seems to have little to recommend it in the present case, especially in view of a molecular weight determination of TEA in liquid SO_2 by Bateman et al. [3] where no evidence of dimerisation was found.

Interpretation of the temperature dependence in terms of the singlet/triplet concept appears to be logical in terms of the model proposed for the donor-acceptor complex. Indeed it is difficult to see how paramagnetism in such associative charge-transfer systems could be attributed to anything other than a triplet state even without the additional evidence of such marked temperature dependence. Following the transfer of charge from donor to acceptor, especially in a small molecule where no extensive π-systems are available to delocalise the newly acquired charge imbalance there must be strong interaction between the two centres of unpaired spin resulting in a splitting into two states [7, 11], singlet and triplet, the magnitude of the energy separation being a measure of this interaction in terms of overlap or exchange frequency [9, 10, 12]. In a complex where large π-systems were available, the formation of a true biradical would be possible with the unpaired electrons so well separated as to give two essentially independent spin-1/2 states.

The above ideas seem to be well supported by other investigations of donor-acceptor complexes where the presence of the triplet state has been irrefutably established by the identification of zero-field interactions [9, 10].

The energy separation J between singlet and thermally accessible triplet was determined from the temperature dependence of the ESR signal intensity in the range from 200 – 300 K by a procedure similar to those used previously [10, 13] from the relationship

$$I \propto (1/T\,(3 + e^{J/kT}))$$

where I is the intensity of the ESR absorption and T is absolute temperature. Whence neglecting the "3" term

$$\ln(IT) = -J/kT + \text{constant.}$$

The gradient of the asymptote to the linear part of expected curve yields the value of J as 0.32 eV or 5.1×10^{-20} joules; in the present case where J is fairly large only the linear part of the curve is seen within the experimental temperature range (Figure 1).

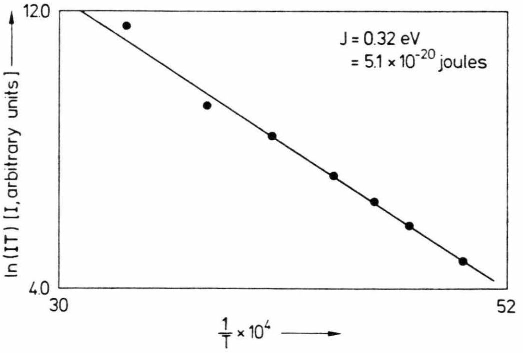


Fig. 1. Temperature dependence of paramagnetism in a solution of 0.05 M triethylamine in liquid sulphur dioxide.

In view of lineshape variations as the temperature was lowered, the simplification usually adopted by setting $I =$ (amplitude × square of linewidth) of the derivative curve was not used and a fully computerised (Trapezium Rule) numerical double integration of the derivative signal, including corrections for asymmetry and base-line drift, was carried out. The accuracy of the final values are estimated as within a few percent.

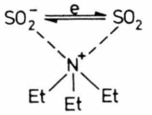
Corrections for changes in cavity Q and spectrometer performance during cooling were made by relating the measured intensity to the simultaneously measured amplitude of the resonance of a ruby crystal built into the cavity.

Checks were also made for possible saturation effects by recording spectra at various microwave power levels at different temperatures. No saturation was noted, even at relatively high powers.

The appearance of the ESR spectrum as a narrow structureless line may be accounted for in terms of a number of fast electron-exchange mechanisms.

1. Resonance between forms II and III of the $n-k\pi$ complex model involving rapid exchange of charge between oxygen atoms. This process together with rotation about the N – S bond and other molecular movement would be expected to average out dipolar interactions between the unpaired electrons and thus zero-field effects (although not so obviously N-hyperfine interaction).

2. A fast electron exchange between the complex and suitably oriented neighbouring SO_2 molecules resulting in strong exchange narrowing, collapse of hyperfine structure and effective suppression of zero-field interactions



Evidence that such an exchange takes place has been provided by isotopic labelling techniques with $^{35}SO_2$ [5].

3. A rapid exchange mechanism between the two unpaired electrons in the triplet state itself as has been proposed to explain the absence of zero field interactions in triplet states of crystalline charge-transfer complexes [7].

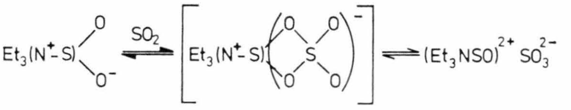
4. Averaging out as a result of rapid molecular tumbling which has been invoked in some cases to account for the absence of dipolar features in liquid solutions [14]. In view, however, of the expected large magnitude of the dipolar interaction if the model proposed for the complex is taken as essentially correct i. e. where the separation of the unpaired spins is of the order of 4 Å, and the persistent narrowness of the resonance line even near the freezing point of the solution (where the rate of tumbling as a function of the viscosity should be much smaller) it seems doubtful whether this mechanism is adequate to explain the observed phenomena.

It is difficult to say with certainty which of the above proposed mechanisms represents the most realistic situation, but in view of the lack of nitrogen hyperfine structure as well as zero-field interactions the second would appear to be most plausible. It seems, however, not unlikely that the others play a role as well.

(b) Time dependence

For the first short period of time after mixing solvent and solute (depending on temperature and concentration), solutions of TEA in SO_2 show little or no paramagnetism. When the signal appears it is observed to grow in intensity, the rate of growth being at first quite rapid then levelling off with time until after several hours a plateau is reached (temperature measurements were made on this plateau). The spin-concentration remains fairly constant for a further period of hours and then slowly fades again to zero over a period of days.

The observation of time dependent phenomena in charge-transfer complexes has been interpreted by Mullikan and others [6, 15] in terms of a transition from an "outer complex" to an "inner complex" for example in the pyridine iodine complex [16], $Py-I_2 \rightarrow (Py-I)^+I^-$. Although it is not at all easy to envisage such a process in the present system it is nevertheless guardedly submitted that such a process might at least account for the slow loss of paramagnetism according to an equilibrium similar to



IV V

where the "outer complex" such as V which is diamagnetic may be stabilised by solvent interaction (the cation) or perhaps by addition of a further TEA molecule (which would yield Jander's original model).

The initial strong increase in paramagnetism also presents problems, it is tentatively accounted for by the slow ionisation of the non-bonded form of the complex to the ionic form followed by the thermally induced excitation to the triplet state. Which of these two processes (if either) is the rate-determining step is a matter of conjecture.

The overall kinetics of the process, increase of spin-concentration from zero to a maximum followed by decline back to zero have not been subjected to a rigorous analysis to determine the rates of the processes involved (although this may be feasible), they nevertheless appear, at least in a general way, to fit a mechanism of the type proposed, i. e. consecutive first (or pseudo-first) order reactions $A \rightarrow B \rightarrow C$.

The Optical Absorption and Electrical Conductivity

Alongside the growth and decay of the paramagnetic species other time dependent changes take place in solutions of TEA in SO_2 in (a) optical absorption (b) electrical conductivity. Both of these processes have been examined and an attempt is made to correlate them with the results of the foregoing sections.

(a) The optical absorption

As mentioned earlier liquid sulphur dioxide is opaque to ultraviolet light below about 330 nm, nevertheless some information can be gleaned from a study of the optical absorption of solutions down to this wavelength. Solutions of TEA in liquid SO_2 exhibit a characteristic pale lemon colour when freshly prepared, corresponding to a broad absorption band starting in the visible region at about 500 nm and moving gently to a maximum in the UV at 340 nm. As the solution ages the colour passes through to a brownish tint (approaching the colour of weak tea), at which point the paramagnetism reaches a maximum and levels off. This colour change is reflected by the appearance of a number of strongly overlapping absorption bands in the visible region seen as a series of broad shoulders (of intensity increasing steadily with wave-number) on the main absorption band tailing off right down to the edge of the infrared at about 800 nm. With further ageing of the solutions, as the ESR signal wanes, the colour reverts back to a yellow shade and most of the absorption at higher wavelength disappears again leaving the final spectrum, although broader and more intense, essentially similar to the initial one. This spectrum persists without further observable change.

The time-dependent changes in colour and appearance of optical bands at higher wavelength parallel the changes in paramagnetism observed in these solutions and suggest that the paramagnetic intermediate species is responsible for the long wavelength absorption eventually decaying to produce an increase in concentration of the species responsible for the bands at short-wavelength.

(b) The electrical conductivitiy

A slight increase of electrical conductivity with time for solutions of TEA in SO_2 was noted earlier by Bateman et al.[3] who failed however to find an interpretation for the phenomenon and attributed it to the ingress of minute quantities of water and air into their conductivity cell.

In the present study the conductivity was measured as a function of time over a period of several days in order to establish or refute the possibility that the charge carriers be responsible for the paramagnetism, i. e. that an ionisation of the type $TEA - SO_2 \overset{\Delta T}{\rightleftharpoons} TEA^+ + SO_2^-$ takes place where the free ions (or at least the SO_2^- ion) are responsible for the ESR signal.

The specific conductivity of an 0.0257 M solution at 24 °C was found to be $2.339 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ (rather more than two orders of magnitude larger than that of the pure solvent) one minute after mixing, and was observed to increase at first relatively rapidly attaining a value of $2.950 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ after 3 hours and then more slowly, doubling the initial value in about 26 hours and trebling it in about 100 hours. Such behaviour clearly in no way reflects the growth and decay of the paramagnetism (or the optical absorption – the solution in the conductivity cell had reverted from brown back to yellow after some 40 hours) which after the first short induction period, where no signal is seen, increases at least tenfold within the first hour or so, levels off after several hours and then after a further period slowly declines.

These observations seem to show fairly definitely that no direct correlation exists between the paramagnetic species and the charge carriers and are consistent with the idea that the paramagnetic species itself bears no net charge. An explanation of the slow increase in conductivity possibly lies in the slow ionisation to an outer diamagnetic complex as suggested earlier to account for the loss of paramagnetism.

Experimental

1. Materials

Anhydrous sulphur dioxide of the highest available purity (J. T. Baker Chemical Co.) was transferred by high vacuum distillation from a precooled "lecture bottle" (cooled to 77 K immediately prior to distillation) into a greasefree high vacuum system. About 200 ml of the gas were stored in the liquid state at room-temperature (pressure about $3^1/_2$ atmospheres) over P_2O_5 in a glass bulb connected to the vacuum system by a metal bellows valve. Prior to use a 20 – 30 ml aliquot of SO_2 was distilled through a series of liquid nitrogen cooled glass traps under constant pumping at a pressure of 10^{-5} mm Hg or less to ensure total exclusion of oxygen. Triethylamine (Riedel-de Haen AG, Hannover, pure grade) was refluxed over sodium for two hours and then distilled twice from a fresh sample of the metal in a stream of pure nitrogen gas, the middle fraction being collected each time. The purified amine was stored over sodium in a tightly stoppered bottle.

2. *Preparation of ESR samples*

Sample tubes were of two types, either flat quartz cells of the type commonly used for aqueous solutions (thickness ca. 1.5 mm) in view of the relatively high dielectric constant of SO_2 (~ 14 at room-temperature) or thin-walled "spectrosil" (quartz) or "Duran" tubes of O. D. 3 mm.

A typical sample tube includes a) the section for insertion into the cavity, b) a graduated section, c) a "Teflon" high-vacuum stopcock, and d) a grease-free joint for attachment to the vacuum system.

Amine samples of the order of a few microliters were injected into the cell with the tap removed and then subjected to several freeze-pump-thaw degassing cycles before the appropriate volume of solvent was distilled in.

The ESR spectrometer used was the AEG X-band model 12X equipped with a 12 cm magnet, 125 kHz modulation and a rectangular reflectance cavity operating in the TE_{102} mode.

Supplementary Remarks

In addition to the study of triethylamine solutions in liquid sulphur dioxide a number of other similar systems have also been subjected to scrutiny including other aliphatic tertiary amines, aromatic tertiary amines, certain substituted phosphines, and a fairly new class of compounds, the phosphorines [17]. In general, the aliphatic amines, such as tri-n-propylamine and butylamine show comparable behaviour to triethylamine with the exception of the simplest member of the series, trimethylamine, where paramagnetism appears in some way to be catalysed by small concentrations of water, no signal being observable in its absence. Solutions of substituted phosphines such as triethylphosphine also show a single narrow ESR line though here the paramagnetic species are much less stable, having life-times of the order of minutes or at most a few hours at room temperature. Aromatic amines on the other hand such as triphenylamine (TPA) show rather different behaviour, in TPA solutions for example the presence of a strong single line has only been observed fleetingly and with poor reproducibility on warming up freshly prepared cold solutions, a spontaneous change to a further paramagnetic species then apparently taking place to yield a multiplet of lines. The phosphorines show yet another behaviour pattern, and seemingly undergo spontaneous oxidation to yield the known spectrum of the positive radical ion. These phenomena will be discussed in more detail in a further publication.

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