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ELECTRON TRANSFER FROM AMINES TO LIQUID SULFUR DIOXIDE

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Epr spectra were obtained from solutions of amines in liq.SO_2 due to the radical cations of the amines which might be the first observation of the electron transfer from organic molecules to liq.SO_2.

In the present communication, we wish to report an experimental evidence of the electron transfer of amines by obtaining epr spectra of various amines in liquid sulfur dioxide, (liq. SO_2).

To purified and degassed amine in a sample tube with 2 mm i. d ., dry sulfur dioxide was introduced by distillation after repeated freeze-pump-thaw cycles. Amine concentration was ca. 5×10^{-2} mol. l^{-1}. Epr spectra were taken on a JES ME 2X-type spectrometer at room temperature.

Figure 1 shows a five-line epr spectrum obtained from a solution of triphenylamine (TPA) in liq.SO_2. The splitting pattern consists of five lines separated by about 6 gauss intervals, being ascribed to the hyperfine splitting from two equivalent nitrogens.

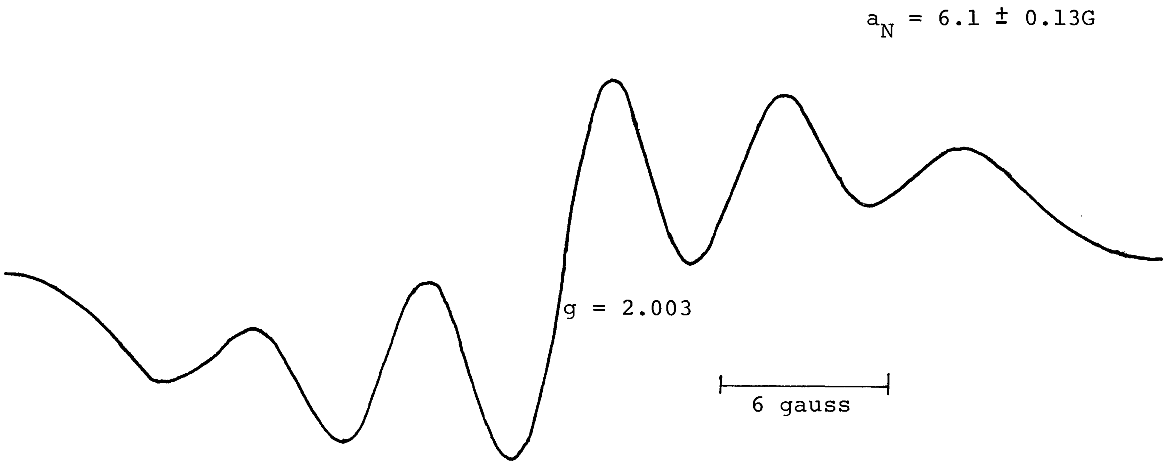


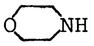
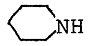
Fig. 1 EPR spectrum of triphenylamine in liq.SO_2

An earlier study[1)] of a paramagnetic C-T complex of TPA with iodine showed that this type of five-line spectrum results and tentatively will be attributed to a bimolecular TPA radical ion $[(C_6H_5)_3\overset{\cdots}{NN}(C_6H_5)_3]^+$. However, a recent electrochemical oxidation study by Bruning et al.[2)] indicated that the cation radical of N,N,N',N',-tetraphenylbenzidine (TPB) is responsible for the five-line spectrum, where TPA radical cation of transient existence couples rapidly to give the TPB.

The spectrum with a_N=6.1 ± 0.13 gauss, g=2.003 and the shape shown in Fig. 1 of the present system is essentially identical with those of the TPB radical cations observed by Bruning and by other investigators.[3)]

Table 1 summarizes the EPR results obtained from solutions of various amines in liq.SO_2.

Table 1 EPR results for the system of various amines in liq.SO_2

Amines	Intensity and number of line	Total width* of signal in gauss	Ionization potential IP ev
$NH_2CH_2CH_2NH_2$	no signal	—	
n-$C_4H_9NH_2$	no signal	—	8.71$^{5)}$
$C_6H_5CH(NH_2)CH_3$	no signal	—	
$C_6H_5NH_2$	no signal	—	
$(C_6H_5)_2NH$	Weak, one line	18	7.25$^{4)}$
	Weak, one line	2	
	Weak, one line	2	
C_5H_5N	Weak, one line	2	9.32$^{5)}$
$(C_6H_5)_3N$	Strong, 5 lines	38	6.86$^{4)}$
$(CH_3CH_2)_3N$	Strong, one line	1.7	7.50$^{5)}$

* Total width was measured between the points where the resonance signal could just be distinguished from the noise.

It should be noted from Table 1 that in the case of secondary amine and pyridine much lower radical concentrations were observed than in the tertiary one, while no signal was detected in the primary amines. The strength of the epr signal is not consistent with the inverse order of the ionization potentials of the amines.

Most of the spectra obtained have no hyperfine splitting and their widths in gauss are very small except in the cases of TPA and diphenylamine which have a sp^2-like nitrogen stabilized by resonance, suggesting a rapid electron exchange among the produced cation radicals or a complication by chemical reaction. The spectra have not been totally interpreted and thus these data are not unequivocal. However, the signals observed clearly indicate that the electron transfer occurred from the amines to liq.SO_2 molecule. This might be a first observation of the electron transfer of the organic molecule in liq.SO_2 as far as we know and the result is interesting in view of the role of liq.SO_2 as an electrophilic and good ionizing solvent.

The both values of the E_A (1ev)[6] and the dielectric constant, ε, (13.8) of liq. SO_2 are not so much higher than those of usual acceptors or polar solvents. So, it is difficult to account for the stabilization of the ion of the present system only by a physical solvation.[7]

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