

greatly indebted to Dr. R. Ryhage for the mass spectro-metric analyses.

Bengt Samuelsson

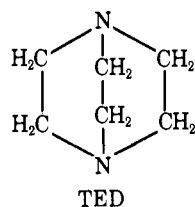
Department of Chemistry, Karolinska Institute  
Stockholm, Sweden

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### The Triethylenediamine Cation Radical

Sir:

A recent study of the crystal structure of 1,4-diaza-bicyclo[2.2.2]octane<sup>1</sup> (or triethylenediamine, TED) showed that the nitrogen atoms are only 2.5 Å. apart.



This fact, along with the spatial disposition of the nitrogen unshared electron pairs in orbitals whose axes coincide with the C<sub>3v</sub> symmetry axis, led us to consider the possibility of observing the electron spin resonance (e.s.r.) spectrum of the cation radical, TED<sup>+</sup>; this possibility has now been realized.

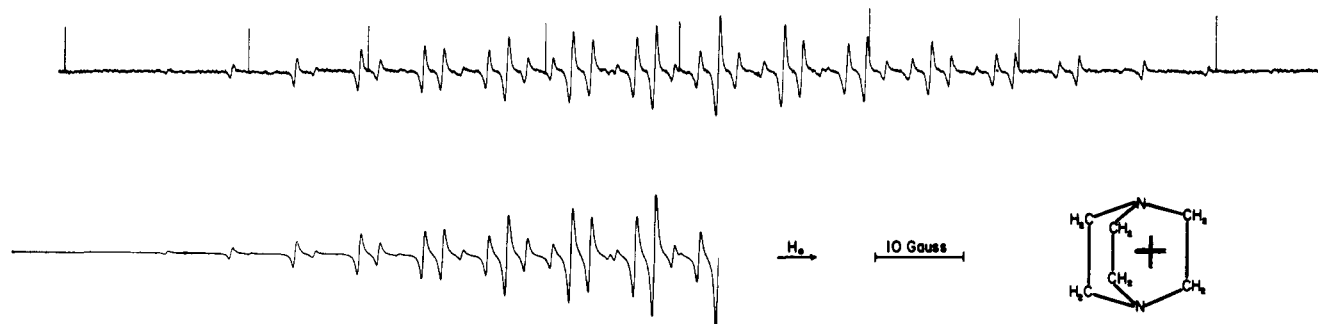


Figure 1. First-derivative electron spin resonance spectrum of the cation radical of triethylenediamine; experimental spectrum given in upper portion and computed spectrum given in lower portion.

A preliminary investigation of the electrochemistry<sup>2</sup> of TED provided the basis for electrochemical generation of TED<sup>+</sup>. The half-wave potential for electro-oxidation of TED on a rotating platinum electrode in acetonitrile solution is +0.68 v. vs. aqueous s.c.e. This electrode process is established as involving one electron by comparison of the limiting current constant of  $4.5 \pm 0.3 \mu\text{a. mM}^{-1}$  for TED with the value of  $4.9 \mu\text{a. mM}^{-1}$  for the known one-electron oxidation of iodide ion on the same electrode under identical stirring conditions. Cyclic voltammetry using a platinum electrode in an unstirred solution established that the life-time of the cation radical is limited to several seconds.

The e.s.r. spectrum of TED<sup>+</sup> shown in the upper portion of Figure 1 was obtained by electrooxidation of a 4 mM solution of TED in acetonitrile which was

(1) G. S. Weiss, A. S. Parker, E. R. Nixon, and R. E. Hughes, *J. Chem. Phys.*, **41**, 3759 (1964).

(2) The electrochemistry of TED was briefly studied in aqueous solution by A. Juliard, *J. Electroanal. Chem.*, **1**, 10 (1959).

allowed to flow slowly (ca. 0.2 ml. min.<sup>-1</sup>) over a platinum gauze electrode in a flat quartz cell which was placed directly in the microwave cavity. The potential of the platinum electrode was +1 v. vs. aqueous s.c.e. and the steady-state current was ca. 100  $\mu\text{a.}$

The spectrum has been assigned on the basis of a coupling constant of  $16.96 \pm 0.08$  gauss for two equivalent <sup>14</sup>N nuclei and a coupling constant of  $7.34 \pm 0.08$  gauss for twelve equivalent protons. A computed spectrum using these constants, a line width of 0.4 gauss, and a Lorentzian line shape is shown below the experimental spectrum in Figure 1.

The observation of equivalent nitrogen atoms establishes that electron transfer between the nitrogen atoms occurs at a rate greater than the observed hyperfine splitting, i.e.,  $>4 \times 10^7$  c.p.s. While electron transfer may occur through spatial overlap of nitrogen orbitals, the possibility of participation of the ethylene bridge carbon atoms cannot be ignored. In this context, previous observation of the anion radicals of paracyclophanes<sup>3</sup> and adamantane and hexamethylene-tetramine<sup>4</sup> is noteworthy.

Whereas the nitrogen atom in most nitrogenous cation radicals is located in a plane with the three atoms bonded to it, this is not the case for TED<sup>+</sup> where a pyramidal distortion exists.<sup>5</sup> Recent theoretical calculations<sup>6</sup> of  $a_N$  for the NH<sub>3</sub><sup>+</sup> cation yielded values of 20.9 gauss and 66 gauss for planar and

pyramidal models, respectively. Since the experimental<sup>7</sup> value for the nitrogen coupling constant for NH<sub>3</sub><sup>+</sup> is 19.5 gauss, the calculated value supports the suggestion that the radical is planar. The fact that  $a_N$  for two nitrogen nuclei in TED<sup>+</sup> is almost 17 gauss probably reflects enhancement of the nitrogen coupling constant by the pyramidal configuration about the nitrogen atom.

Examination of the ultraviolet spectrum of gaseous TED showed an intense line,  $\epsilon = 1000$  l./mole cm., at 2510 Å. with rich vibronic structure decreasing to shorter wave lengths. The emission spectrum, obtained by electron impact in a high-power radiofrequency field, showed 19 discrete lines between 2730

(3) S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 6462 (1958). Details of electron transfer in the paracyclophane anion radicals have been examined by H. M. McConnell, *J. Chem. Phys.*, **35**, 508 (1961).

(4) K. W. Bowers, G. J. Nolfi, Jr., and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 3707 (1963).

(5) Since the C-N-C bond angle in TED is 108.9°, it is reasonable to assume approximately the same bond angle in TED<sup>+</sup>.

(6) G. Giacometti and P. L. Nordio, *Mol. Phys.*, **6**, 301 (1963).

(7) T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961).

and 3475 Å. with the most intense line at 3050 Å.<sup>8</sup> The remarkable intensity of the emission spectrum indicates unusual stability of the excited species.

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(8) We are indebted to Dr. F. J. Dinan for securing these data.

Ted M. McKinney, David H. Geske  
Department of Chemistry, Cornell University  
Ithaca, New York  
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## An Unusual Solvent Effect on the Air Oxidation of a Stable Carbanion

Sir:

The rate constants for the air oxidation of the carbanion ( $R^-$ )<sup>1</sup> related to Koelsch's radical ( $R\cdot$ , 2-phenylbis(biphenylene)allyl)<sup>2</sup> vary through a series of aprotic solvents by a factor of at least  $10^5$  (Table I<sup>3</sup>).

Table I.<sup>3</sup> Solvent Effects on Rates of Anion Oxidation<sup>a</sup>

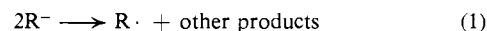
Metal ion	Solvent <sup>b</sup>					<i>(n</i> -Bu) <sub>2</sub> O, Et <sub>2</sub> O, Et <sub>3</sub> N, Benzene
	DMSO, DMF	Pyridine	1,2-DME	THF	2-MeTHF	
Na <sup>+</sup>	$<3 \times 10^{-4c}$		0.34	0.65	$>25^d$	$>25$
K <sup>+</sup>	$<3 \times 10^{-4}$	0.015	0.19	0.63	$\sim 15^e$	$>25$
Cs <sup>+</sup>			0.20	0.61	2.1	

<sup>a</sup> Values tabulated are pseudo-first-order rate constants (sec.<sup>-1</sup>) at 1 atm. of oxygen. Initial concentrations of  $R^-$  were *ca.*  $3 \times 10^{-5} M$  in each case. <sup>b</sup> A rate constant about 0.1 of that found in 1,2-DME was obtained in 12% (by volume) DMF in 1,2-DME. <sup>c</sup> The limiting figure here was estimated on the conservative assumption that a 5% extent of reaction could have been detected, but was not, in a span of 50 hr. It is conceivable that equilibrium considerations may favor reactants in these solvents, but no evidence of lack of complete reaction was found in other solvents. <sup>d</sup> The limit here was calculated from our belief that we could have estimated the rate of any reaction with a half-life greater than about 25 sec., but that these had shorter half-lives at 1 atm. of oxygen. <sup>e</sup> Estimated from two points assuming pseudo-first-order kinetics.

This effect is novel both in the kind of reaction involved and in that more polar solvents *inhibit*, rather than enhance, the rate of a carbanion reaction.<sup>4,5</sup>

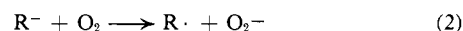
Since the visible spectra of  $R^-$  and  $R\cdot$  contain well-separated bands, both the disappearance of  $R^-$  and the

appearance of  $R\cdot$  could be followed, with the result that good first-order plots (at constant partial pressures of oxygen) gave the same rate constants for each kind of measurement. Equation 1 gives the partial stoichiometry of the reaction in pyridine, 1,2-dimethoxyethane (1,2-DME), tetrahydrofuran (THF), diethyl ether, di-*n*-butyl ether, and 12% *N,N*-dimethylformamide (DMF) in 1,2-DME. For a typical run (1,2-DME; potassium; 1 atm. of oxygen) a plot (eight points, including the



origin) of concentration of  $R\cdot$  produced vs. that of  $R^-$  consumed gives a straight line of slope  $0.50 \pm 0.03$ . It is evident that the reaction is exceptionally clean.

The extensive data of Russell and co-workers, on the base-catalyzed air oxidation of many organic compounds, has been interpreted in terms of reaction sequences in which a one-electron transfer from a carbanion to an oxygen molecule is a key step,<sup>6</sup> one which is presumed to be kinetically isolated in the present study, consistent with over-all second-order kinetics.<sup>7</sup>



The direction of the solvent effect in less polar ethers

and the presence of a distinct metal ion effect in 2-methyltetrahydrofuran suggest that the transition state tends to be more highly aggregated than the reactant ions. In turn, this is consistent with a more concentrated negative charge in the anionic portion of the transition state than in the reactant anion.<sup>8</sup>

At the concentrations employed in these experiments, ionic association appears to be unimportant in THF and 1,2-DME and is presumed to be absent in the more polar solvents pyridine, DMF, and dimethyl sulfoxide (DMSO). It follows that the difference between reactant and transition state anion solvation energies is similar for the two ethers of this group, but that this is not true among all five of these solvents. It is apparent

(1) R. Kuhn and F. A. Neugebauer, *Monatsh.*, **95**, 1 (1964).

(2) C. F. Koelsch, *J. Am. Chem. Soc.*, **79**, 4439 (1957).

(3) Vacuum manifold techniques and manometric devices were used to prepare closed reaction vessels containing reactants at the desired concentrations and pressures. Purified solvents were distilled from storage over sodium benzophenone ketyl (except for DMF and DMSO), ensuring the absence of peroxides. Periodic violent agitation ensured a sustained saturation of the solutions with oxygen, although this was unnecessary, since the solubility of oxygen in all these solvents is probably greater than  $10^{-3} M$  (at 1 atm.: water,  $10^{-3} M$ ; pyridine,  $4 \times 10^{-3} M$ ; diethyl ether,  $5 \times 10^{-3} M$ ; so that initial concentrations of dissolved oxygen constituted a constant excess.

Since in every solvent gaseous oxygen was in equilibrium with the activated complexes, the variations in rate constants reflect *entirely* changes in the activity coefficient ratio  $\gamma_{R^-}/\gamma_{R\cdot}$ , where these activity coefficients are referenced to the fact that the concentrations of  $R^-$  and activated complexes are considered to include all of their ionic aggregates. Where various aggregates are involved, it may be possible later to separate their contributions to the above rates through the dependence of the latter on the initial concentrations of  $R^-$ .

(4) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962), has reviewed solvation influences in dipolar aprotic solvents with many references to the rate-enhancing effects of these solvents as compared to protic ones.

(5) (a) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965); (b) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *ibid.*, **69**, 624 (1965). Rate enhancements of carbanion polymerization propagations in more polar ethers are evaluated.

(6) G. A. Russell, with A. J. Moye, E. G. Janzen, E. J. Geels, E. T. Strom, E. R. Talaty, S. Mak, A. G. Bemis, and S. A. Weiner, Preprints, Division of Petroleum Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 5-9, 1965, p. A7, and works cited therein, including G. A. Russell, A. J. Moye, and K. Nagpal, *J. Am. Chem. Soc.*, **84**, 4154 (1962).

(7) Variation of the partial pressure of oxygen over 1,2-DME and THF gives pseudo-first-order rate constants which appear to vary linearly with the partial pressure, although a sufficiently wide range of pressures to rigorously exclude a one-half-order pressure dependence of the rates has not yet been examined.

(8) Details of solvation- and aggregation-based arguments of the type which generate these conclusions are given in ref. 4 and 9.

(9) J. F. Garst and E. R. Zabolotny, *J. Am. Chem. Soc.*, **87**, 495 (1965), and earlier papers cited therein.