Use of Stable 2,2,6,6-Tetramethylpiperidine N-Oxyl Radical for the Measurements of Lewis Acidity of Solvents

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The use of the stable 2,2,6,6-tetramethylpiperidine N-oxyl (TMPNO) radical as a standard base made it possible to introduce a new scale of Lewis acidity for solvents. The parameter E_B is defined as the energy (in kJ mol^{-1}) of n–π^* transition in the TMPNO spectrum measured in different solvents; it correlates very well with other scales of Lewis acidity such as E_T, AN, and Z. Interaction of TMPNO with inorganic acids (H^+ and Li^+) in water is different as evidenced by changes in the absorption spectra.

Grunwald and Winstein were first to introduce[1] a solvent parameter Y, the 'ionizing power'. This parameter used the linear free energy relationship postulate[2] in the field of solvent effects. Since then many other solvent parameters have been proposed.[3] The best known are those of Kosower,[4] Gutmann and Mayer,[5] and Dimroth and Reichardt,[6] the Z, AN, and E_T scales respectively. These parameters describe properties which may be called the solvent electrophilicity,[7] Lewis acidity,[8] or electron-pair-accepting activity.[5] On the other hand, a description of the solvent properties in terms of the Lewis basicity resulted in the introduction of basicity parameters (BPs).[3] The most popular BPs are those given by Gutmann[9] and Kamlet and Taft.[10]

Two important problems arise when one tries to apply all these parameters in correlation analysis:[2,3] (1) the problem of specific and non-specific contributions thoroughly discussed by Koppel and Palm[7] and (2) the choice of the 'proper' acidity or basicity parameter.

In this paper we discuss the second problem. A general analysis of both problems will be a subject of a separate paper.[11]

Among acidity parameters the most extensive list is obtained[6] for E_T. However E_T for some highly 'inactive' solvents or for water cannot be estimated directly due to the limited solubility of the betaine.

The aim of this paper is to present a new scale of solvent Lewis acidity by using the stable 2,2,6,6-tetramethylpiperidine N-oxyl (TMPNO) free radical as a probe and to discuss the problem of the choice of the 'proper' acidity parameter. Our choice of TMPNO is mostly based on the good solubility of this compound in all the solvents studied. The considerable solvatochromism of piperidine nitrogen oxides is known.[12,13]

Experimental

2,2,6,6-Tetramethylpiperidine N-oxyl (TMPNO) was prepared by a three-stage synthesis.[14-16] The free radical was purified by three-fold sublimation. The TMPNO solutions in 56 solvents and in 6 H$_2$O–organic solvent mixtures were prepared a few hours before measurement. The solutions were stable for several months. TMPNO concentrations in all the solvents were of the order of 10^{-2} and 10^{-4} mol dm^{-3} for measurements in the visible and u.v. region, respectively.

Apparatus.—Absorption spectra were recorded on a mini-computer-controlled Zeiss Specord-M-40 spectrophotometer, with wavelengths accurate to ± 3—10 cm^{-1} and absorbances ± 0.005.

Results

(a) *Absorption Spectra of* TMPNO *in Pure Solvents.*—The absorption spectra of N-oxides show two bands, one in the region 410—460 nm, having molar absorptivity ε *ca.* 10 dm^3

(1)
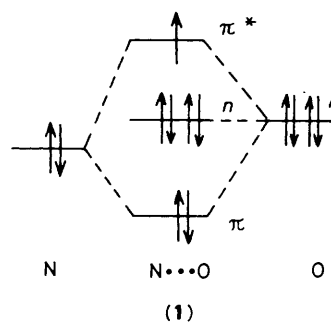
mol^{-1} cm^{-1}, and the other at *ca.* 240 nm, with molar absorptivity ε *ca.* 2 000 dm^3 mol^{-1} cm^{-1}. The maximum of the former band is very sensitive to change in the solvent.[12,13]

In dialkyl N-oxides the >N–O· group is responsible for the absorption in both u.v. and visible regions. The isolated >N–O· group can be described by analogy to the isoelectronic ketyl group, *i.e.* a carbonyl group with one electron on the anti-bonding π^* orbital.[12,13,17] The electron structure of the TMPNO chromophore can be represented[13,18,19] schematically as (1). The bonding and anti-bonding π orbitals are formed from the $2p_z$ atomic orbitals of nitrogen and oxygen whereas the non-bonding n orbital is formed from the $2p_x$ and $2p_y$ atomic orbitals of oxygen. The unpaired electron is present on the π^* orbital. The u.v. and visible bands in the spectra of N-oxides are, therefore, attributed[12] to $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ transitions, respectively. In agreement with theoretical considerations, the u.v. ($\pi \longrightarrow \pi^*$) band in the TMPNO spectrum is not sensitive to solvent changes. On the other hand, the absorption maximum of the visible ($n \longrightarrow \pi^*$) band depends on the Lewis acidity of the solvents: the corresponding wavenumber increases with increasing acidity and is highest in water ($\bar{v}_{max.}$ 23 560 cm^{-1}) and lowest in n-hexane ($\bar{v}_{max.}$ 20 960 cm^{-1}).

The results of the measurements are listed in Table 1.

The parameter E_B is defined as the energy (in kJ mol^{-1}) of the $n \longrightarrow \pi^*$ transition in the TMPNO spectrum measured in different solvents. The standardized values of the parameter E_B^N can be calculated from equation (1). Water and n-hexane

$$E_B^N = \frac{E_B(\text{solvent}) - E_B(\text{n-hexane})}{E_B(H_2O) - E_B(\text{n-hexane})} \quad (1)$$

were used as reference solvents as they are of highest and lowest acidity. The values of E_B form a new scale of Lewis acidity of solvents.

(b) *Mixed Solvents.*—The spectra of TMPNO were also recorded in six mixtures of water with non-aqueous solvents: MeOH, EtOH, Pr^{i}OH, acetone, dioxane, and pyridine. The

Table 1. $\bar{v}_{max.}$ of TMPNO, and E_B and E_B^N for pure solvents. The solvents are numbered according to Kappel and Palm[7]

No.	Solvent	$\bar{v}_{max.}/$ kK	$E_B/$ kJ mol^{-1}	E_B^N
3	Pentane	20.96	250.9	0.00
4	Hexane (Hex)	20.96	250.9	0.00
12	Cyclohexane	20.96	250.9	0.00
13	Decalin	20.96	250.9	0.00
18	Mesitylene	21.16	253.3	0.08
19	Benzene (BE)	21.20	253.8	0.09
21	Toluene	21.24	254.3	0.11
30	Carbon tetrachloride	21.20	253.8	0.09
31	Chloroform	21.72	260.0	0.29
32	Dichloromethane	21.68	259.5	0.28
33	1,2-Dichloroethane	21.56	258.1	0.23
78	Diethyl ether	21.16	253.3	0.08
79	Di-n-propyl ether	21.12	252.8	0.07
80	Di-n-butyl ether	21.08	252.4	0.05
87	Anisole	21.40	256.2	0.17
95	Tetrahydrofuran (THF)	21.24	254.3	0.11
97	1,4-Dioxane (Diox)	21.36	255.7	0.16
100	Acetic anhydride	21.84	261.4	0.33
105	Ethyl acetate	21.40	256.2	0.17
118a	Trimethyl phosphate (TMP)	21.48	257.1	0.20
122a	Propylene carbonate (PC)	21.64	259.1	0.27
124	Formamide (FA)	22.48	269.1	0.59
128	NN-Dimethylformamide (DMF)	21.52	252.6	0.21
128a	NN-Diethylformamide (DEF)	21.36	255.7	0.16
129	NN-Dimethylacetamide (DMA)	21.44	256.7	0.19
130	Tetramethylurea (TMU)	21.40	256.2	0.17
133	Acetic acid (AcA)	22.88	273.9	0.73
131	Hexamethylphosphoramide (HMPA)	21.28	254.8	0.12
145	Acetone (AC)	21.44	256.7	0.19
146	Butan-2-one	21.36	255.7	0.16
149	Heptan-4-one	21.32	255.2	0.15
151a	Cycloheptanone	20.96	250.9	0.00
152	Acetophenone	21.44	216.1	0.19
160	Acetonitrile (AN)	21.68	259.5	0.28
168	Benzonitrile (BN)	21.48	257.1	0.20
170	Acetonitrile	21.72	260.0	0.29
171	Water (W)	23.56	282.0	1.00
173	Methanol (MeOH)	22.40	268.2	0.55
174	Ethanol (EtOH)	22.28	266.7	0.51
175	n-Propanol (Pr^{n}OH)	22.16	265.3	0.47
176	n-Butanol (Bu^{n}OH)	22.16	265.3	0.47
177	n-Pentanol	22.12	264.8	0.44
178	n-Hexanol	22.20	265.8	0.48
179	n-Heptanol	22.00	263.4	0.40
183	Isopropyl alcohol (Pr^{i}OH)	22.16	265.3	0.47
184	Isobutyl$_2$ alcohol (Bu^{i}OH)	22.12	264.8	0.44
185	Pentan-2-ol	22.12	264.8	0.44
188	Butan-2-ol	22.08	264.3	0.43
214	t-Butylamine	21.24	254.3	0.11
215a	Ethylenediamine (EDA)	21.60	258.6	0.25
225	Pyridine (Py)	21.48	257.1	0.20
229	Nitromethane (NM)	21.88	201.9	0.36
234	Dimethyl sulphoxide (DMSO)	21.56	258.1	0.23

results obtained are given in Table 2. Generally these results show a similar behaviour to those observed[20] by Reichardt, *i.e.* with an increase of water content in the mixture one observes a gradual increase in the acidity parameter.

(c) *Behaviour of* TMPNO *in Aqueous Solutions of* HCl, H_2SO_4, *and* LiCl.—It was interesting to compare interactions of TMPNO with inorganic cations in aqueous solutions. Two cations were chosen, H^+ and Li^+. The results obtained are given in Supplementary Publication No. SUP 56189 (4 pp.)* and in Figure 1 in the form of a plot of $\bar{v}_{max.}$ against log C_N, where C_N is the normal concentration of the acid.
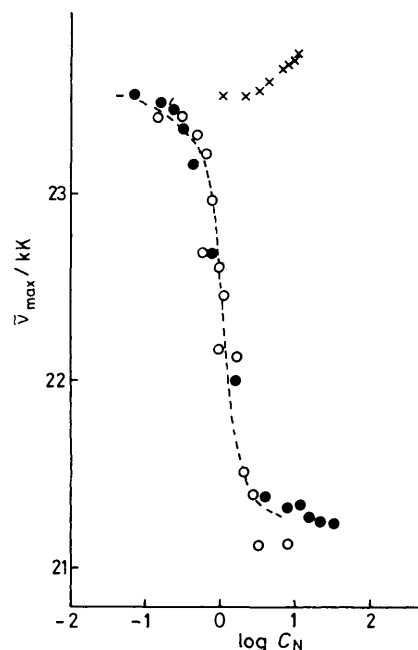

Figure 1. Dependence of $\bar{v}_{max.}$ of TMPNO on log C_N (C_N = normal concentration) of H_2SO_4 (●), HCl (○), and LiCl (×)
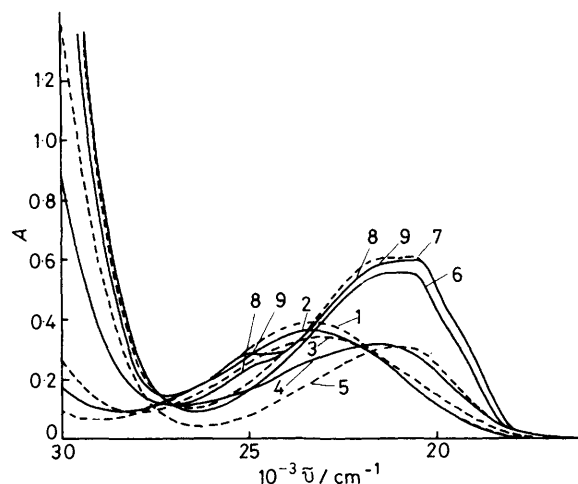

Figure 2. Visible spectra of TMPNO in solutions of various H_2SO_4 concentrations: 1, 0.14; 2, 0.44; 3, 0.88; 4, 1.47; 5, 7.36; 6, 30; 7, 54; 8, 80; 9, 98 vol.%

Figure 2 shows the spectra of TMPNO obtained in aqueous H_2SO_4 solutions. From the results in this Figure, at higher concentrations of H_2SO_4 (C_M > *ca*. 3M) the spectra of TMPNO became more complicated. Analysis of these spectra suggests that at least three different forms of TMPNO are present at higher H_2SO_4 concentrations. Our analysis was, however, limited to lower concentrations of H_2SO_4 (C_M < *ca*. 3M).

It was found that interaction of TMPNO with Li^+ is very weak ($\Delta\bar{v}_{max.}$ *ca*. 0.3 kK) and it resembled the interaction of TMPNO with solvents as the Lewis acids. We neglected interactions of TMPNO with Cl^- ions. It is not clear whether such an assumption is fully justified, but comparison of the results

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* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

Table 2. Values of E_B and E_B^N for water–non-aqueous solvent mixtures

Mol% H$_2$O	MeOH		EtOH		Pr^{i}OH		AC		Diox		Py	
	E_B	E_B^N	E_B	E_B^N	E_B	E_B^N	E_B	E_B^N	E_B	E_B^N	E_B	E_B^N
100	282.2	1.00	282.2	1.00	282.2	1.00	282.2	1.00	282.2	1.00	282.2	1.00
90	281.4	0.97	280.9	0.96	280.5	0.95	280.1	0.93	280.5	0.95	279.3	0.91
80	279.7	0.92	279.7	0.92	279.3	0.91	278.8	0.89	278.8	0.89	276.8	0.83
70	278.8	0.89	278.0	0.87	275.9	0.80	276.3	0.81	276.8	0.83	274.6	0.76
60	277.2	0.84	276.3	0.81	272.6	0.69	273.6	0.73	274.2	0.75	273.4	0.72
50	275.9	0.80	274.2	0.75	270.9	0.64	272.1	0.68	272.6	0.69	271.3	0.65
40	274.2	0.75	272.6	0.69	270.0	0.61	270.0	0.61	269.9	0.60	270.0	0.61
30	272.6	0.69	270.5	0.63	268.8	0.57	267.1	0.52	266.7	0.51	267.5	0.53
20	270.9	0.64	269.2	0.59	267.5	0.53	261.2	0.43	263.8	0.41	264.6	0.44
10	270.0	0.61	268.0	0.55	266.7	0.51	262.1	0.36	260.4	0.31	261.3	0.33
0	268.0	0.55	266.7	0.51	265.4	0.47	256.6	0.19	255.8	0.16	252.1	0.20

obtained in aqueous solutions of HCl and H$_2$SO$_4$ suggests that the influence of anions is not great. Nevertheless, the results obtained for HCl and H$_2$SO$_4$ solutions clearly indicate that the interactions of TMPNO with H$^+$ and Li$^+$ ions are markedly different.

Discussion

Comparison of Parameters of Lewis Acidity of Solvents.—(a) *Pure solvents.* It seems advisable to discuss the relationship between Kosower, Dimroth–Reichardt, and Gutmann parameters prior to comparing E_B with the other Lewis acidity scales. There exists[6b] a very good correlation between E_T and $Z: Z = 1.337E_T + 9.80$ (r 0.978; n 54). A reduction of the number of solvents to 15 leads to the relationship[3,6b] $Z = 1.330E_T + 10.47$ (r 0.998). Also, a good correlation is found between E_T and AN;[6b] AN $= 1.598E_T - 50.69$ (r 0.956; n 38). These relationships indicate the similarity of these scales.

The correlation between E_B^N and AN^N is given by the formula $E_B^N = -0.026 + 0.855$ AN^N (r 0.979, n 24). The largest deviations from linearity are observed for water and nitromethane. Omission of these two solvents leads to the formula $E_B^N = -0.006 + 0.767$AN^N (r 0.995; n 22). These correlations indicate that the standard processes and substances which take place are similar to each other. In both cases the solvent interacts with the standard base (2) or (3) with the participation of the non-bonding electron pairs of the oxygen atom.

For the parameters Z and E_B the formula $E_B^N = 0.035 + 0.863Z^N$ (r 0.980; n 21) has been found. In this case water was included, but the largest deviations are observed for acetic acid, CHCl$_3$, and CH$_2$Cl$_2$. For all these solvents the relationship is $E_B^N = 0.063 + 0.847Z^N$ (r 0.945; n 24).

The mechanism of interactions between the standard substances pyridinium-*N*-phenoxide betaine dye and TMPNO is also similar and involves participation of the non-bonding electron pairs of the oxygen atom. The steric hindrance around the oxygen atom seems to be approximately the same. The relationship between E_B and E_T is as follows: $E_B^N = -0.032 + 0.809E_T^N$ (r 0.946; n 42). The largest deviations are observed for water, acetic acid, and ethylenediamine. For all solvents the relationship is $E_B^N = -0.067 + 0.945E_T^N$ (r 0.930; n 46).

These four parameters were analysed[11] with the use of characteristic vector analysis (c.v.a.).[21–23] For 20 solvents each parameter gives an independent vector. The solvents used were water, MeOH, EtOH, AcA, Pr^{i}OH, NM, AN, DMSO, DMF, DMA, AC, BN, CH$_2$Cl$_2$, HMPA, Py, CHCl$_3$, THF, BE, and Hex. It was found that these four vectors are mutually correlated with the correlation coefficient r_4^1 0.9561 (first characteristic vector). Addition of the second characteristic vector resulted in the correlation coefficient r_4^2 0.9829. Table 3
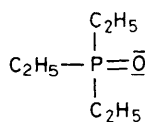
(2)
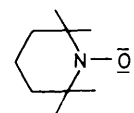
(3)

gives the parameters of the linear regression analysis of all four vectors with the first characteristic vector. From the results in Table 3 it follows that for 20 solvents all analysed vectors may be used interchangeably. Details of these calculations and other related problems will be presented in a separate paper.[11]

However, in our opinion TMPNO as a reference for Lewis acidity is superior from the experimental point of view to other standard bases. The compound can be readily prepared from cheap raw materials, purified by sublimation, and is very stable. Also TMPNO is very soluble in both polar and nonpolar organic solvents and water. The excellent solubility of TMPNO does not impose any restrictions in the choice of solvents whose Lewis acidity is to be measured. The parameter E_B can be determined, therefore, from direct measurements and no correlations are needed. Moreover, the $n \longrightarrow \pi^*$ band of TMPNO is not masked by any other bands over the whole range of solvents investigated. Also no extrapolation of the measurements to zero concentration of TMPNO is needed.

A disadvantage of the E_B scale is its low sensitivity to solvent properties compared with E_T. Thus, E_B ranges over 282.0—250.9 kJ mol^{-1} (Δ 31.1 kJ mol^{-1}) relative to E_T 264.2—129.4 kJ mol^{-1} (Δ 134.8 kJ mol^{-1}). However, the accuracy of the absorbance measurements with modern, computer-controlled spectrophotometers makes it possible to use the E_B scale successfully. It is possible that the introduction of some substituents in the 4-position may expand the E_B scale. TMPNO can be also used as a standard base for mixtures of solvents.

(b) *Mixed solvents.* As far as the results obtained in previous section suggest that the behaviour of all analysed acidity parameters in different solvents is similar, the results for mixed solvents indicate that the whole picture is more complicated. Figure 3 shows the dependence of E_B^N on the values of E_T^N, given[20] by Reichardt, for six mixtures of water with non-aqueous solvents. From the results in Figure 3 for all analysed mixtures, one observes negative deviations from ideal behaviour. One should observe such behaviour if the mechanisms of interaction of both basic probes were identical. The explanation of these deviations is rather difficult. We suspect that at least two explanations can be offered. (i) These deviations result from different specific solvations of both basic probes. However, since the points for pure solvents lie outside the ideal line the problem is more complicated. (ii) The

Table 3. Results of correlations of the first vector of c.v.a. (Y_1) with four acidity parameters. $Y_1 = a + b$ AP^N, were AP stands for normalized acidity parameter, $n = 20$

Acidity parameter	a	b	r
E_T^N	-0.404	0.923	0.9736
AN^N	-0.338	0.805	0.9716
Z^N	-0.208	0.756	0.9532
E_B^N	-0.282	0.915	0.9802
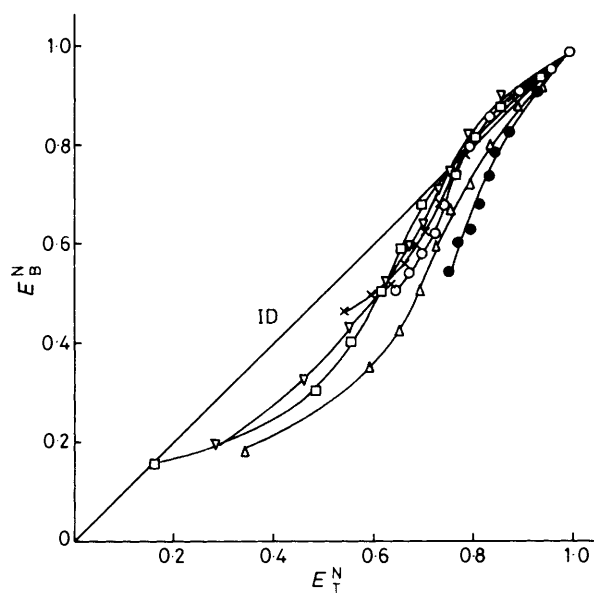
Figure 3. Dependence of E_B^N on E_B^N for water–organic solvent mixtures: ●, MeOH; ○, EtOH; ×, Pr^{i}OH; △, AC; □, Diox; △, Py (ID = ideal line)

mechanism of interactions of TMPNO and betaine with solvents is slightly different. Since at present a precise model of solvation is not known, it is difficult to give a detailed description of these differences. The best known is the model given by Buckingham[24] (for ions) and developed[25] later by Alfenaar and co-workers. We suggest that one may look at this problem from a different point of view, which follows from Drago's papers.[26] Drago proposed,[27] empirically, to describe the free enthalpy of adduct formation in the gas phase (and poor solvating solvents) by following equation (2) where E and C are

$$-\Delta H = E_A E_B + C_A C_B \qquad (2)$$

the empirical parameters of donors (B) and acceptors (A). For TMPNO it was found that $C_B = 6.21$ and $E_B = 0.915$. Going from the gas phase to strongly solvating solvents one may expect that the description of the solute–solvent interactions (ΔG instead of ΔH) become more complicated. However, the final picture should result in the formulation of more or less quantitative principles for different solvents and solutes similar to the HSAB principle known for water.

It is, however, too early at present to discuss this problem in more detail.

(c) *Absorption spectra of* TMPNO *in aqueous solutions of inorganic acids.* In aqueous H_2SO_4 and HCl solutions, contrary to what might be expected, the maximum of the


(4)   (5)
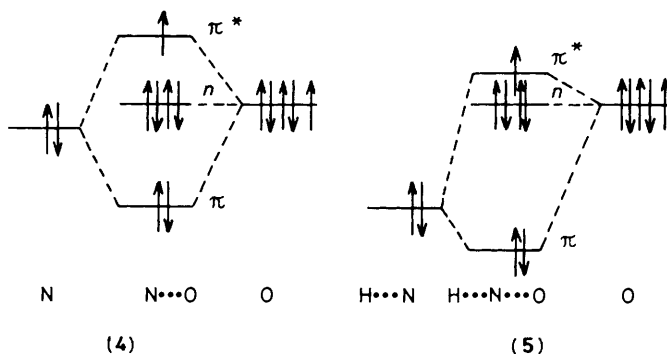
$n \longrightarrow \pi^*$ band of TMPNO is shifted towards lower wavenumbers compared with that in H_2O solution. Also, the values of molar absorptivity of the $n \longrightarrow \pi^*$ band decreased with increasing acid concentration. On the other band, as described above, in TMPNO solutions of organic solvents the wavenumbers corresponding to the maximum of the $n \longrightarrow \pi^*$ band increase with increasing Lewis acidity of the solvents. This indicates that the mechanism of interaction between TMPNO and strong inorganic acids and between TMPNO and solvents–Lewis acids is different.

The increase in wavenumber corresponding to the maximum of $n \longrightarrow \pi^*$ band with increasing Lewis acidity is due to interactions between the solvent and a lone electron pair of the oxygen atom of TMPNO. The opposite shift in the spectra of TMPNO in H_2SO_4 and HCl solutions indicates, in our opinion, that the site of interaction with proton is not a lone electron pair on the oxygen atom but the nitrogen atom, on which large spin density is present. All the experimental data can be explained on the basis of diagrams (4) and (5) of the energy levels of the $>$N–O⁺ chromophore.

The proton interacting with the nitrogen atom causes a decrease in the energy of both molecular orbitals, formed from the atomic orbitals of oxygen and nitrogen atoms, *i.e.* the bonding π and anti-bonding π^*, in comparison with that in aqueous solution. However, no covalent bond is formed between proton and nitrogen since π and π^* orbitals remain (molar absorptivities do not fall down to zero even at very high acid concentrations). Moreover, plots of $\bar{v}_{max}$ *versus* log acid (normal) concentration have the form of titration curves and it indicates that an equilibrium is established [equation (3)]. A

$$\text{TMPNO} + \text{H}^+ \rightleftharpoons [\text{TMPNO} \cdots \text{H}]^+ \qquad (3)$$

rapid increase in molar absorptivity on neutralization of TMPNO solution in H_2SO_4 reveals that the reaction is reversible. This indicates that the TMPNO $\cdots$ H interaction has the character of a weak, labile ionic bond. The pK of reaction has been estimated to be of the order of 0.0 ± 0.5 from the 'titration' curves. The behaviour of TMPNO in aqueous acid solutions was investigated by Ingold and Malesta[28] by the e.s.r. method. These authors have found that TMPNO is protonated in very strong acids only. In aqueous sulphuric acid solutions up to 40% H_2SO_4 the TMPNO spectrum is a triplet, which indicates that the radical is not protonated. In the concentration range above 40% the spectrum become diffuse and at 54% disappears completely due to rapid proton exchange. Only at concentrations above 80% TMPNO does protonation take place which is evidenced by the appearance of a weak signal. In 98% H_2SO_4 the signal is a distinct sextet. The proton interacts with TMPNO through the oxygen atom as indicated by an increase of the coupling constant and a decrease of the g factor. Two bonding π electrons are attracted by the
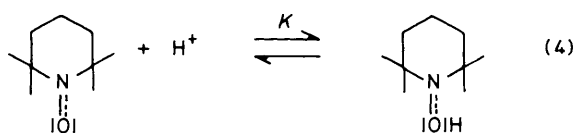
proton towards the oxygen atom whereas the anti-bonding π^* electron is shifted towards the nitrogen atom and, as a consequence, the spin density at the nitrogen atom and the coupling constant increase. Lowering of the g factor results from a reduction of the spin density at the oxygen atom and a decrease of the energy of non-bonding electrons at the oxygen atom. The negative log of the protonation constant at room temperature is equal to 5.5 ± 0.1

The results of Ingold and Malesta (protonation of the oxygen atom) and those obtained in this paper only seemingly contradict each other. Ingold and Malesta have studied TMPNO in sulphuric acid solutions by the e.s.r. method. The use of this method made it possible to observe changes in electron density distribution due to the interaction of the proton and the oxygen atom which took place in very concentrated solutions only. In less concentrated solutions no protonation was found. Actually, in this concentration region the proton does not interact with the oxygen atom. However, it does not indicate a lack of any interaction with the TMPNO molecule in another place. The use of absorption spectrophotometry reveals that in less concentrated aqueous solutions of sulphuric acid the proton does interact with TMPNO through the nitrogen atom. Thus, reaction (4) observed by Ingold and Malesta and the calculated pK correspond to the bonding of a second proton to TMPNO. The bonding of the first proton could not be observed by using the e.s.r. method probably because the proton is linked to the nitrogen atom by a weak ionic bond, as mentioned above. On the other hand, the Li^+ ion, much larger than proton, cannot interact with the nitrogen atom of the radical shielded by four methyl groups.

From the results presented here it seems clear that the interaction of H^+ and Li^+ ions with TMPNO is different. Whether it is a problem of the dimensions of the cations (both are solvated) or some specific Lewis acid–base interactions or special geometry is, however, not clear.

Conclusions.—It is proposed to use the stable 2,2,6,6-tetramethylpiperidine N-oxyl (TMPNO) radical as a standard base for the determination of an empirical Lewis acidity parameter of solvents. From a comparison of TMPNO behaviour with other standard bases one may conclude that all the bases behave similarly in pure solvents. In mixed solvents the situation is more complicated.

In water solutions interaction of TMPNO with H^+ and Li^+ is markedly different. The interaction with Li^+ cation resembled that of other non-aqueous solvents, whereas H^+ ions showed different behaviour. The reasons for this dualism are, however, not clear.

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