195. *Unstable Intermediates. Part VII.* Nuclear Magnetic Resonance Studies of Solutions of Iodine in Oleum.*

By T. M. Connor and M. C. R. Symons.

The proton nuclear resonance absorption band for solutions of iodine in oleum is much broader than that for oleum alone, and is shifted to higher fields. The shift and broadening are approximately proportional to the molar concentration of iodine from 0·1 to 0·4M. These changes are interpreted in terms of the formation of a paramagnetic species for which a magnetic moment of about 1·5 B.M. is estimated on the arbitrary assumption that all the iodine is converted into this species. The results are discussed in terms of the postulate that the paramagnetic species is the iodine cation.

Iodine reacts with concentrated oleum to give blue solutions in which iodine is largely in the +1 valency state and which are powerful iodinating agents.[1] It was tentatively suggested that iodine cations are present in these solutions and, since the ground state for these ions is considered to be $^3P_2$, that these ions are responsible for the paramagnetism. Since there was no way of estimating the concentration of these ions, a magnetic moment was calculated on the arbitrary basis of complete conversion. A mean value of 1·9 B.M. was estimated for 0·1M-solutions.

Spectrophotometry showed that these solutions had four bands in the 200—1000 mμ region. Since the $^3P_2 \rightarrow {}^1D_2$ transition for iodine cations should be found in the 700 mμ region,[2] the 640 mμ band was assigned to the iodine cation and the remaining bands to other species containing iodine.[2] These results showed that a considerable quantity of the iodine was present in one or more forms other than as the bare cation, and hence that the real magnetic moment for this ion should be considerably greater than 1·9 B.M. Unfortunately, there seems to be no way of predicting accurately the magnitude of the magnetic moment for I^+ in solution: the " spin-only " value would be 2·83 B.M. but there is no compelling reason for assuming this value.

Nuclear resonance studies were undertaken to provide independent proof of the presence of a paramagnetic species, in view of the very small changes in weight upon which earlier calculations were based,[1] and because a consideration of the results in detail might provide further evidence about the presence of iodine cations.

All attempts to observe electron spin resonance spectra for these solutions have failed, although solid solutions covering a wide concentration range have been studied at 20° K. If the paramagnetic species is indeed the iodine cation, this result is reasonable, since one would expect considerable zero-field splitting of the energy levels in addition to marked spin–orbit coupling for a ^3P ground state. Hence a single magnetically diluted crystal would be a minimum requirement for a successful study and all attempts to prepare such crystals have failed.

Nuclear resonance is not usually considered as a technique suitable for the detection of paramagnetic species in small concentration. However, in cases of this sort, when electron spin resonance fails, nuclear resonance may often be used, although the sensitivity is far smaller. When proton resonance absorption bands are studied in solutions containing various concentrations of paramagnetic ions there is generally a marked shift in addition to an increased intensity and broadening.[3,4] These phenomena are characteristic, and the data can be used to estimate a value for the magnetic moment which is generally very close to the static magnetic moment of the ion.

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* Part VI, preceding paper.

[1] Symons, *J.*, 1957, 387.

[2] Symons, *J.*, 1957, 2186.

[3] Wertz, *Chem. Rev.*, 1955, **55**, 829.

[4] Dickinson, *Phys. Rev.*, 1951, **81**, 717.

EXPERIMENTAL

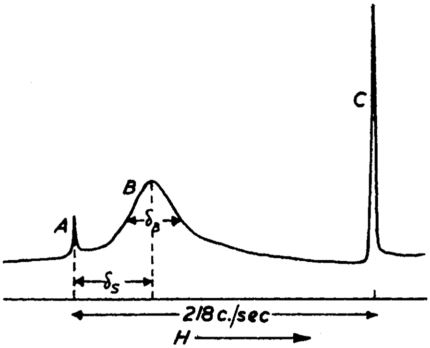
The proton nuclear resonance spectra of solutions of iodine in 65% oleum were measured at 40 Mc./sec. by using a Varian 4300 high-resolution spectrometer. The samples were contained in tubes of 5 mm. outside diameter which were spun to reduce effective field inhomogeneities. Two external reference capillaries were included with each sample, one containing pure 65% oleum and the other distilled water, enabling the shifts and broadening of the oleum resonances to be found by interpolation. Owing to the width of some of the oleum signals this was a more convenient method of measuring shifts than the usual side-band technique which was however used to measure the distance between the two reference capillaries. This was found to be 218 c./sec., the oleum lying on the low-field side.

The oleum was not specially purified.[2] The line-width of the signal obtained was about 2 c./sec., indicating the absence of any appreciable quantity of paramagnetic impurities. The iodine was " AnalaR."

TABLE 1. *Broadening and chemical shift due to the presence of* I_2.

Concn. (mole/l.)	Line-width at ½ height (c./sec.)	Broadening (c./sec.)	Shift from 65% oleum (c./sec.)	Concn. (mole/l.)	Line-width at ½ height (c./sec.)	Broadening (c./sec.)	Shift from 65% oleum (c./sec.)
Pure oleum	2	0	0	0·2003	24	22	29
0·00985	4	2	0	0·3136	34	32	43
0·0197	4	2	0	0·401	41	39	56
0·0281	7	5	2	Saturated	75	73	104
0·0985	14	12	14·5				

A typical spectrum for a 0·401M-solution of iodine in 65% oleum is shown in the Figure. The widths of the oleum resonances at half-height and their shifts to higher field with respect to the pure oleum reference signal are tabulated as a function of iodine concentration (Table 1).



Proton nuclear resonance spectrum of iodine (0·401M) *in oleum* (65%).
A, 65% Oleum reference.
B, Iodine solution.
C, Water reference.

The proton resonance spectra of brown solutions obtained by dissolving iodine in 20% oleum were also examined and showed no appreciable broadening or shift. It is therefore concluded that these solutions do not contain paramagnetic species, a result in accord with previous findings.[1,2] The broadening was determined by subtracting the line-width due to pure oleum (2 c./sec.) from the line-width at half-height found for the solutions. The shift and broadening are approximately proportional to the iodine concentration (Table 1) although the broadening falls off at high iodine concentrations.

DISCUSSION

Shift.—Dickinson [4] showed that the variation of chemical shift with concentration is given by

$$d\delta_s/dc = -2\pi\chi H_0/3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where δ_s is the chemical shift, c the concentration, and χ the susceptibility of a particular solution. H_0 is the field in the magnet gap, 9·4 kilogauss. This expression requires that: (*a*) the sample shape approximates to an " infinite cylinder "; (*b*) the field due to the remaining ions in the Lorentz cavity is zero. The approximation (*a*) is good in this case (dimensions 60 mm. × 3·5 mm.). Dickinson [4] found deviations from eqn. (1) which he interpreted in terms of a non-zero Lorentz cavity field. In this case the field will be assumed to be zero. Since

$$\chi = N\beta^2\mu^2/3kT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where β is the Bohr magneton and μ is the effective magnetic moment of I^+, the slope, $d\delta_s/dc$, can be expressed in terms of μ.

The data of Table 1 give -72 cycles/mole/l. for $d\delta_s/dc$. This gives $\mu = 1{\cdot}5$ B.M. on the arbitrary assumption that all the iodine is present as I^+, *i.e.*, that the reaction $I_2 \longrightarrow 2I^+ + 2e$ goes to completion. This result may be compared with the value of 1·9 B.M. found previously for 0·1M-solutions by using a conventional Gouy balance.

Although this result qualitatively confirms the earlier measurements independently, there is not quantitative agreement. Deviations from equation (1) are often found and have been explained in two ways. Bloembergen and Dickinson [5] developed an expression which takes into account possible magnetic anisotropy. Since spin–orbit coupling is expected for the iodine cation, this could cause the discrepancy. On the other hand, marked deviations from eqn. (1) can occur if covalent bonding between the paramagnetic species and the compound containing the resonating nucleus gives rise to a finite density of unpaired electrons at the nucleus.[6,7] The latter effect may be so important that the direction of shift is reversed. The deviation described here is relatively small and this mechanism can hardly play an important rôle. This conclusion is in agreement with the postulate that iodine cations are present, and eliminates certain protonated paramagnetic species such as HI^+ or HI_2^{2+}.

Broadening.—For a Lorentzian line shape, the line-width at half-height in cycles/sec., δ_B, is related to the spin–spin relaxation time, T_2, by the expression

$$\delta_B = 1/\pi T_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

For solutions, T_2 and T_1, the spin–lattice relaxation-time, can normally be assumed to be equal. To test this assumption, T_1 for a 0·4M-solution of iodine in oleum (65%) was measured directly, using spin-echo techniques,[8] to be 7 ± 1·5 μsec., which is very close to the value of 8·15 μsec. calculated from the line-width at this concentration, thus showing that the above assumption is valid in this case.

Bloembergen, Purcell, and Pound's [9] original expression relating T_1 to the magnetic moment of the paramagnetic ions was modified by Abragam [10] to

$$1/T_1 = 16\pi^2 N_{\text{ion}}\mu^2\gamma^2\eta\beta^2/15kT \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where N_{ion} is the concentration of paramagnetic ions in moles/c.c., γ is the magnetogyric ratio for the proton, and η is the viscosity.

TABLE 2. *Viscosity of* I_2–65% *oleum solutions.*

Solution	Average flow time (sec.) (of 4 readings)	Viscosity (centipoises)
65% Oleum	238·6	44·5
0·208M-I_2	244·8	45·6
0·402M-I_2	259·6	48·4

The viscosity was measured at 25° (Table 2), a value of 44·5 centipoises being taken for 65% oleum.[11] There is a small increase in viscosity which would slightly accentuate the deviation from linearity of the graph of broadening against concentration of iodine found at high concentrations (Table 1).

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[5] Bloembergen and Dickinson, *ibid.*, 1950, **79**, 179.
[6] McConnell and Holm, *J. Chem. Phys.*, 1958, **28**, 749.
[7] Phillips, Looney, and Ikeda, *ibid.*, 1957, **27**, 1435.
[8] Hahn, *Phys. Rev.*, 1950, **80**, 580.
[9] Bloembergen, Purcell, and Pound, *ibid.*, 1948, **73**, 679.
[10] Abragam, personal communication.
[11] Bright, Hutchison, and Smith, *J. Soc. Chem. Ind.*, 1946, **65**, 385.

Using equation (4) and the previously calculated value of $\mu = 1{\cdot}5$ B.M., we find the inverse relaxation time to be $7{\cdot}35 \times 10^3$ sec.$^{-1}$ for a 0·4M-solution. The experimental value of $1{\cdot}2 \times 10^2$ sec.$^{-1}$ is far smaller, and the broadening is a factor of 60 less than predicted by eqn. (4). We conclude that this equation is not a satisfactory representation in this case.

An alternative approach is simply to compare the results with similar data for other systems. This can be done by interpolation of the data given by Morgan *et al.*,[12] who measured T_1 for protons in aqueous solutions of chromic ions bonded to a variety of ligands. The viscosity of these solutions was varied over a wide range by addition of glycerol. From the data for $Cr(en)_3{}^{3+}$ we estimate $T_1 = 0{\cdot}53$ μsec. for a solution 0·4M in chromic ions and having a viscosity of 0·48 poise. Using 3·9 B.M. for the magnetic moment of chromic ions in the ethylenediamine complex, one can then estimate the moment of the paramagnetic species in oleum from

$$T_1(\mathrm{I})/T_1(\mathrm{Cr}) = \mu^2(\mathrm{Cr})/\mu^2(\mathrm{I}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The result, 1·1 B.M., is comparable with the results previously obtained, and suggests that the paramagnetic species are affecting the protons of the solvent in similar ways in these solutions. The main conclusion drawn by Morgan *et al.*[12] is that direct proton exchange between the complex ion and the solvent is not occurring. When applied to the iodine solution, this means that species such as HI^+ can again be rejected, but that the postulate that iodine cations are present is in accord with the results.

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UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER, CANADA.
THE UNIVERSITY, SOUTHAMPTON (*present address*, M. C. R. S.) [*Received, November 3rd*, 1958.]

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[12] Morgan, Nolle, Hull, and Murphy, *J. Chem. Phys.*, 1956, **24**, 906.