259. *Nuclear Magnetic Resonance of the Methyl Esters of Some Inorganic Oxyacids.*

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The spectra of the hydrogen nuclei of the methyl esters of 9 inorganic oxyacids at 26° in carbon tetrachloride are reported, and the values, extrapolated to infinite dilution, are compared. Plots of the resonance frequencies of (*a*) the borate, carbonate, nitrate and (*b*) the silicate, phosphate, sulphate, perchlorate against electronegativity of the heteroatom approximate to two parallel straight lines with the nitrate and perchlorate at lowest values of applied field. Resonances for the phosphite and sulphite occur at more shielded positions than for the phosphate and sulphate. Splitting of the trimethyl phosphite and trimethyl phosphate spectra, attributed to ^{31}P–H spin–spin coupling, are the same within experimental error (J 11·6 c./sec.). The methyl nitrate signal is broad.

KNOWLEDGE of the π-bonding between the oxygen and the heteroatom in inorganic oxyacids and their anions and esters may be expected to be of value in interpreting the acid strength and alkylating properties [1] of these compounds. This bonding has been proposed to explain the weak Lewis acidity of the borate esters [2] in comparison with the trialkylborons and many aspects of boron [3] and silicon chemistry.[4]

Measurements of bond distances in the ions have been variously interpreted.[5] Changes in other physical properties have been attributed in part to changes in π-bonding. Thus variations have been observed in the basicity of the alkoxysilanes as demonstrated by hydrogen-bonding studies,[6] in the force constants of the oxygen–heteroatom bonds,[7] and in the ultraviolet absorption spectra of a limited number of phenyl esters.[8]

A systematic study of the physical properties of the esters may provide an answer to the problem and one such series of measurements, namely, that of the nuclear magnetic resonance of hydrogen nuclei of the methyl esters, is reported here.

The resonance frequency of a methyl proton in a given external magnetic field depends on the perturbation caused by the magnetic shielding due to the electron environment, and on the net bulk magnetic susceptibility of the sample. The last effect may be eliminated [9] by comparing infinitely dilute solutions in inert, magnetically isotropic (spherical) solvents: we used carbon tetrachloride.

EXPERIMENTAL

Measurements were made in a spinning, cylindrical tube, of 5 mm. outside diameter, by means of a Varian spectrometer operating at 60 megacycles/sec. A fine capillary tube (0·5 mm.) containing water was supported symmetrically in the sample by a Plasticine seal at the top of the tube, and the resonance frequencies from water were determined with respect to a 60 c./sec. side-band imposed on the spectra by an audio-oscillator. The same capillary and tube were used throughout the experiments.

Solutions were prepared in distilled, reagent-grade carbon tetrachloride through which helium had been bubbled overnight. Commercial samples of all esters except methyl nitrate, nitrite, and perchlorate were fractionally distilled. Methyl nitrate was prepared by the

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[1] Anbar, Dostrovsky, Samuel, and Yoffe, *J.*, 1954, 3603.

[2] Brown and Fletcher, *J. Amer. Chem. Soc.*, 1951, **73**, 2808.

[3] Coyle, Stafford, and Stone, *J.*, 1961, 3103.

[4] Stone and Seyferth, *J. Inorg. Nuclear Chem.*, 1955, **1**, 112.

[5] Phillips, Hunter, and Sutton, *J.*, 1945, 146; Wells, *J.*, 1949, 55.

[6] West, Whatley, and Lake, *J. Amer. Chem. Soc.*, 1961, **83**, 761.

[7] Kriegsmann, *Z. anorg. Chem.*, 1959, **299**, 138; Goubeau, *Angew. Chem.*, 1957, **69**, 77; Siebert, *Z. anorg. Chem.*, 1954, **275**, 225.

[8] Hammond, University of California Radiation Laboratory Report, UCRL 9519, Jan. 31st, 1961.

[9] Allred and Rochow, *J. Amer. Chem. Soc.*, 1957, **79**, 5361; Bothner-By and Naar-Colin, *ibid.*, 1958, **80**, 1728.

method of Black and Babers [10] and was used without further purification. No lines were seen in the nuclear magnetic resonance spectrum that could be attributed to proton-containing impurities. Methyl nitrite [11] was passed over glass wool at −15° and collected in carbon tetrachloride at this temperature, and the solution was slowly allowed to warm. When the change in weight showed that a predetermined concentration had been reached, standard samples were made immediately and were stored at −10°.

Methyl perchlorate solutions were prepared by reaction of silver perchlorate and a small, known excess of methyl iodide in carbon tetrachloride. The mixture was shaken overnight in the dark, filtered through fine, sintered-glass funnels, and diluted to standard concentrations. The spectra showed two peaks about 150 and 30 c./sec. from water. The ratio of these areas was approximately in the proportion of the excess of methyl iodide to silver perchlorate, indicating nearly quantitative conversion of the salt into the ester.

Similar attempts to prepare methyl chlorate and chlorite from the silver salts were not successful. The reactions were tried at −15° in the absence of light the night before the measurement, and the mixtures were allowed to warm to room temperature only in the spectrometer tube. The chlorate showed no new lines in the spectrum; the chlorite showed two faint ones. The colour of iodine was present in both the chlorate and the chlorite solution and weakly so in the perchlorate. An attempt to extract methyl hypochlorite [12] in cold carbon tetrachloride produced a solution having only a faint line in the spectrum.

Methyl phosphite solutions were prepared at room temperature (26°) an hour before the measurements and no products of chemical reaction were detected in the spectra. Solutions of concentration 2·0, 1·6, 0·8, 0·6, and 0·4 in methyl protium molarity were studied. Values quoted for resonance frequencies are means of at least five measurements.

RESULTS

Experimental values are shown in Table 1. The frequencies at infinite dilution, determined by linear graphical extrapolation, are shown in Table 2.

TABLE 1.

Resonance frequencies * of methyl esters in carbon tetrachloride.

Molarity:	2·0	1·6	0·8	0·6	0·4	τ
Borate	78·9	78·4	79·2	78·8	78·5	6·49
Carbonate	62·6	62·8	62·3	62·3	62·9	6·23
Nitrate	40·2	39·7	39·9	40·0	40·1	5·85
Nitrite	48·4	46·2	47·7	46·3	46·4	(5·94)
Silicate	75·5	75·3	75·7	75·6	75·5	6·44
Phosphate	59·2	59·1	57·5	58·3	58·1	6·24
	70·3	70·7	68·7	69·6	69·6	
Phosphite	72·7	74·9	74·0	74·6	74·8	6·53
	83·8	86·8	85·7	86·5	87·2	
Sulphate	51·0	52·0	52·2	51·7	51·3	6·04
Sulphite	75·4	75·3	74·0	74·3	74·1	6·41
Perchlorate............	31·0	31·1	30·5	31·1	31·1	5·70
Chlorate	—	—	—	—	—	—
Chlorite	69·5	73·2	—	—	—	(6·35
	96·4	95·8	—	—	—	3·76)
Hypochlorite	53·8	57·7	—	—	—	(6·10)

* Frequencies are in c./sec., except for the last column where the values are for infinite dilution. The value (5·18) for water was determined in an auxilliary experiment where tetramethylsilane in carbon tetrachloride was used as reference.

Standard deviations are usually ±0·5 c./sec.

Where these measurements and those of Allred and Rochow [9] overlap, close agreement is obtained except for the borate where our value is 3·0 c./sec. higher. Variations with concentration are small. The frequencies for methyl nitrate and methyl perchlorate are the lowest values for methyl–oxygen compounds yet recorded.

The spectra of trimethyl phosphate and phosphite show two sharp peaks, and the frequency separation between them does not vary on dilution. This is attributed to coupling between

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[10] Black and Babers, *Org. Synth.*, Coll. Vol. II, p. 412.

[11] Hartung and Crossley, *Org. Synth.*, Col. Vol. II, p. 363.

[12] Sandmeyer, *Ber.*, 1886, **19**, 857.

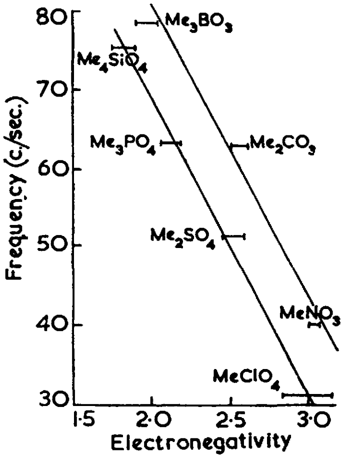
TABLE 2.

Resonance frequencies from water (c./sec.) of methyl esters in carbon tetrachloride at infinite dilution.

Borate	Carbonate	Nitrate	—	—
78·6	63·0	40·2		
—	—	Nitrite (45·6)	—	—
—	Silicate	Phosphate	Sulphate	Perchlorate
	75·6	57·6 } 63·3 69·0 } *J* 11·4	51·6	31·2
—	—	Phosphite	Sulphite	Chlorate
		75·0 } 80·9 86·8 } *J* 11·8	73·8	—
—	—	—	—	Chlorite (70, 95)
—	—	—	—	Hypochlorite (55)

^{31}P and the proton nuclei. The coupling constants for the phosphate and phosphite are the same (see Table 2).

For increasing electronegativity of the heteroatom, methyl resonance appears at decreasing values of the applied field. Plots of the frequencies for borate, carbonate, nitrate, and for silicate, phosphate, sulphate, perchlorate against electronegativity of the heteroatom (see Figure) approximate to parallel straight lines. For sulphur and phosphorus, the resonance for an oxyacid of lower oxidation state occurs at a higher value of the applied field. Variations in line width occur. In particular, methyl nitrate produces a broad line, broader, for example, than that for methyl nitrite (line half-widths 4·8 compared with 2·2 c./sec.).



Plots of the resonance frequency for the methyl esters of inorganic oxyacids against electronegativity of the heteroatom. (Range of electronegativity values comes from ref. 15, also Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1960, p. 93; Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745; Allred and Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 264; Allred, *ibid.*, 1961, **17**, 215.)

DISCUSSION

The variations in resonance frequency may be considered to correspond to changes in a nuclear magnetic resonance parameter that closely resembles classical group electronegativity. Several authors [9,13,14] have drawn attention to linear relations between the electronegativity of an element and the frequency of protium resonance of similar methyl compounds, yet the interpretation in some cases is not simple [13] and a scale of values of this parameter may have limited application. However, Table 3 shows values estimated

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[13] Bothner-By and Naar-Colin, *Ann. N.Y. Acad. Sci.*, 1958, **70**, 833.

[14] Allred and Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269.

from Table 2 and the work of Allred and Rochow[9] on the methyl halides, with Huggins's electronegativity values for the halogens.[15]

TABLE 3.

Group electronegativity for the oxyacids from the information in Table 2 and the work of Allred and Rochow[9] on the methyl halides.

Borate	Carbonate	Nitrate	—	—
3·42	3·58	3·81		
—	Silicate	Phosphate	Sulphate	Perchlorate
	3·45	3·58	3·70	3·90
—	—	Phosphite	Sulphite	—
		3·40	3·47	

If the main influences on the resonance frequency are considered to be those affecting electron density on the methyl hydrogen atoms, shielding constants can be ascribed to contributions from (*a*) structures of the type $C-\overset{+}{O}=X$ and (*b*) electronegativity differences between oxygen and the group containing the heteroatom. Changes in molecular geometry may also alter the resonance frequency. Thus alteration in the C–O–X bond angle, which will reflect changes in the π-bond character, and alteration in the number of electronegative oxygen atoms that are neighbours to the methyl groups, can contribute to the shifts observed. The result involving electronegativity shown in the Figure refers to molecules of similar geometry. Discrepancies may be introduced by anisotropy effects,[13] and these limit the interpretation at present, although the linear relations suggest that these are small.

Effect (*b*) will contribute for acids of different oxidation state. It is also noteworthy that there is no simple correspondence between acid strength and resonance frequency.

Geometrical isomerism has been observed for methyl nitrite.[16,17] At low temperatures this produces two lines in the nuclear magnetic resonance spectrum, and at room temperature the single line obtained represents an averaging effect for the two. The ratio of isomers[17] at room temperature is about 1 : 1 although it is not known in carbon tetrachloride to the accuracy of the other measurements in the Table. The separation of the doublet at low temperature is of the order of a chemical shift and this is comparable with the total spread of the values in Table 2. The broad line of the nitrate is probably associated with the quadrupole moment of the ^{14}N nucleus. The sharper line for the nitrite implies that quadrupole relaxation occurs at a different rate owing to the difference in electron environment of the nitrogen atom.

If there is a change of π-bonding in the phosphate and phosphite esters this will require a redistribution of *d*-orbital electrons. That the hydrogen–phosphorus coupling constants are the same requires the bonding to be unaltered or the coupling to be insensitive to *d*-orbital bonding.

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[15] Huggins, *J. Amer. Chem. Soc.*, 1953, **75**, 4123.

[16] Tarte, *J. Chem. Phys.*, 1952, **20**, 1570; Haszeldine and Jander, *J.*, 1954, 691; Gray and Reeves, *J. Chem. Phys.*, 1960, **32**, 1878.

[17] Piette, Ray, and Ogg, *J. Chem. Phys.*, 1957, **26**, 1341.