

CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY, UNIVERSITY OF ADELAIDE, ADELAIDE, SOUTH AUSTRALIA 5001

The First Coordination Sphere of Aluminum(III), Gallium(III), and Indium(III) in Trimethyl Phosphate. A Proton Magnetic Resonance Study

BY JOSEPH CREA AND STEPHEN F. LINCOLN*

Received June 7, 1971

Trialkyl phosphates have been widely investigated as solvents for metal ions, and the composition of the first coordination sphere of such metal ions has been the subject of considerable discussion.¹⁻⁴ In this work a direct pmr⁵⁻⁸ study of the first coordination sphere of aluminum(III), gallium(III), and indium(III) in trimethyl phosphate (TMP) and TMP-water mixtures is described.

Calcd: Al, 2.31. Found: Al, 2.30. Alpha (99.99%) Ga-(ClO₄)₃·6H₂O and G. F. Smith In(ClO₄)₃·11H₂O, respectively, were used in the preparations of previously unreported [Ga(TMP)₆](ClO₄)₃ and [In(TMP)₆](ClO₄)₃ by a method similar to that reported for the Al³⁺ analog. Analyses for Al³⁺, Ga³⁺, and In³⁺ were carried out by a cation-exchange method;¹⁰ C and H analyses were performed by the Australian Microanalytical Service, Melbourne, Victoria, Australia. Anal. Calcd for [Ga(TMP)₆](ClO₄)₃: Ga, 5.77; C, 17.87; H, 4.50. Found: Ga, 5.62; C, 17.34; H, 4.60. Calcd for [In(TMP)₆](ClO₄)₃: In, 9.16; C, 17.23; H, 4.34. Found: In, 8.99; C, 17.14; H, 4.33. Analytical grade acetone and redistilled TMP were dried over Linde 4A Molecular Sieves. Water was doubly distilled. All solutions were made up by weight under a dry nitrogen atmosphere and were sealed in standard pmr tubes. All spectra were run at least in triplicate on a Varian DP60 spectrometer. Integrations were carried out electronically and manually.

Results and Discussion

The pmr signal of TMP in the first coordination sphere of Al³⁺, Ga³⁺, and In³⁺ appeared as a doublet downfield from the doublet signal of bulk TMP as shown in Figure 1. Comparison of the integrated areas of the two signals gave a coordination number (*C*_{TMP})

TABLE I
COORDINATION NUMBERS OF Al³⁺, Ga³⁺, AND In³⁺ IN TMP-H₂O-ACETONE SOLVENTS

Mole ratio M ³⁺ :TMP:H ₂ O:acetone	Temp, °C	<i>C</i> _{TMP}	<i>C</i> _{H₂O}	$\Delta\nu(B_{TMP} - C_{TMP})$, Hz (± 0.5 Hz)	$\Delta\nu(B_{H_2O} - C_{H_2O})$, Hz (± 1 Hz)
M ³⁺ = Al ³⁺					
1.00:52.3:—:—	35	5.8 \pm 0.2	...	21.0 ^a	...
1.00:51.7:—:—	35	5.9 \pm 0.2	...	21.0 ^a	...
1.00:55.2:—:—	35	5.8 \pm 0.2	...	21.0 ^a	...
1.00:17.7:—:30.0	35	6.0 \pm 0.1	...	21.0 ^b	...
1.00:6.00:11.7:30.2	-10	1.0 \pm 0.2	5.0 \pm 0.2	15.2 ^{f,g}	297 ^{i,s}
1.00:6.00:5.60:30.5	-10	2.1 \pm 0.2	3.8 \pm 0.2	17.0 ^{g,s}	286 ^{m,s}
1.00:11.8:5.90:30.0	-10	2.3 \pm 0.2	3.5 \pm 0.2	18.5 ^h	291 ⁿ
1.00:29.1:7.20:30.3	-10	2.8 \pm 0.3	3.0 \pm 0.2	18.6 ^h	300 ^o
M ³⁺ = Ga ³⁺					
1.00:68.5:—:—	0	5.9 \pm 0.2	...	19.0 ^c	...
1.00:45.3:—:—	0	6.0 \pm 0.2	...	19.0 ^c	...
1.00:51.4:—:—	0	6.1 \pm 0.2	...	19.0 ^c	...
1.00:25.0:—:30.0	0	5.9 \pm 0.2	...	16.0 ^d	...
1.00:6.00:20.4:29.0	-40	<i>t</i>	5.1 \pm 0.3	13.0 ^f	297 ^p
1.00:6.00:12.1:29.0	-40	0.7 \pm 0.2	4.9 \pm 0.2	13.5 ^f	291 ^q
1.00:15.1:8.10:30.3	-40	2.2 \pm 0.2	3.8 \pm 0.2	16.4 ^h	286 ^r
M ³⁺ = In ³⁺					
1.00:47.0:—:—	-30	6.0 \pm 0.2	...	19.0 ^c	...
1.00:24.4:—:—	-30	6.1 \pm 0.2	...	19.0 ^c	...
1.00:21.4:—:20	-40	6.1 \pm 0.2	...	21.0 ^b	...

^{a-c} Chemical shifts of *C*_{TMP} downfield from the TMS capillary in the sample are 263, 259, 262, 260, and 261 Hz, respectively. ^{f-h} Chemical shifts of *C*_{TMP} downfield from internal acetone are 112, 114, 115, 108, 110, and 113 Hz, respectively. ^{i-r} Chemical shifts of *C*_{H₂O} downfield from internal acetone are 453, 443, 436, 429, 474, 472, and 461 Hz, respectively. Chemical shift of pure acetone from the TMS capillary is 143 Hz. ^s The coordinated signal exhibited fine structure; the chemical shift was measured from the most intense component. The values of *J*_{PM-H₁} are 11.2 \pm 0.1, 11.0 \pm 0.1, and 11.3 \pm 0.2 Hz for TMP coordinated to Al³⁺, Ga³⁺, and In³⁺, respectively. ^t A coordinated TMP signal was observed, but it was too small for meaningful integration.

Experimental Section

The salt Al(ClO₄)₃·9H₂O was prepared by dissolution of analytical grade Al wire in a stoichiometric amount of hot analytical grade perchloric acid. Anal. Calcd: Al, 5.54. Found: Al, 5.58. The colorless crystals obtained by evaporation of this solution were stored over P₂O₅. This product was used in the preparation⁹ of [Al(TMP)₆](ClO₄)₃. Anal.

(1) V. Gutman in "Coordination Chemistry in Non-Aqueous Solutions," Springer-Verlag, Vienna, 1968.

(2) I. L. Buerger, *Nucl. Sci. Eng.*, **16**, 428 (1963).

(3) P. Graham and M. Joesten, *J. Inorg. Nucl. Chem.*, **32**, 531 (1970).

(4) V. M. P. Forrest, D. Scargill, and D. R. Spickernell, *ibid.*, **31**, 187 (1969).

(5) N. A. Matwyoff and H. Taube, *J. Amer. Chem. Soc.*, **90**, 2796 (1968).

(6) R. E. Schuster and A. Fratiello, *J. Chem. Phys.*, **47**, 1554 (1967).

(7) L. D. Supran and N. Sheppard, *Chem. Commun.*, 832 (1967).

(8) S. F. Lincoln, *Coord. Chem. Rev.*, **6**, 309 (1971).

(9) N. M. Karayannis, E. E. Bradshaw, L. L. Pytlewski, and M. M. Labes, *J. Inorg. Nucl. Chem.*, **32**, 1079 (1970).

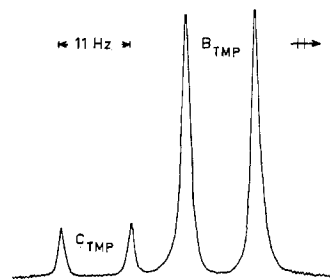


Figure 1.—Pmr spectrum of [Ga(TMP)₆](ClO₄)₃ in TMP at 10°. Coordinated and bulk doublets are labeled *C*_{TMP} and *B*_{TMP}, respectively. The Ga:TMP mole ratio of this solution was 1.00:50.4 and *C*_{TMP} = 6.1 \pm 0.2

(10) A. I. Vogel in "Quantitative Inorganic Analysis," 3rd ed, Longmans, Green and Co., London, 1961, p 702.

of 6, within experimental error, for all three metal ions as seen from some typical results in Table I. The majority of the Ga^{3+} and In^{3+} C_{TMP} determinations were made at 0 and -30° , respectively as broadening of the doublet components consistent with an increase in the rate of solvent exchange was observed at higher temperatures. Exchange broadening of the doublet signals from the Al^{3+} -TMP system was not marked at 35° . In acetone-TMP solvent the C_{TMP} remained close to 6 for the three metal ions, and no coordinated acetone signal was observed, which is consistent with acetone acting solely as an inert diluent as has been observed in acetone-water solvent.¹¹ This is an important observation as it was found that the use of acetone as a diluent for the TMP-water system first increased the miscibility of the solvents and second reduced the rate of proton exchange between coordinated and bulk water¹¹ thereby facilitating the observation of well-resolved coordinated and bulk water signals for the Al^{3+} and Ga^{3+} systems.

The data for a number of solutions, in which the mole ratios metal ion:TMP:water:acetone were varied, are listed in Table I. The total coordination number ($C_{\text{TMP}} + C_{\text{H}_2\text{O}}$) for both Al^{3+} and Ga^{3+} is seen to remain close to 6. The spectra were recorded at temperatures at which the best signal resolution was obtained, the upper temperature limit being determined by exchange broadening and the lower by viscosity broadening. A trend in which water competes more favorably than TMP for sites in the first coordination sphere is seen in both the Al^{3+} and Ga^{3+} data. Steric hindrance probably reduces the ability of TMP to compete with water as has been observed for other bulky solvent molecules.¹²

A spectrum of a solution of Al^{3+} in TMP-water-acetone solvent is shown in Figure 2. The coordinated

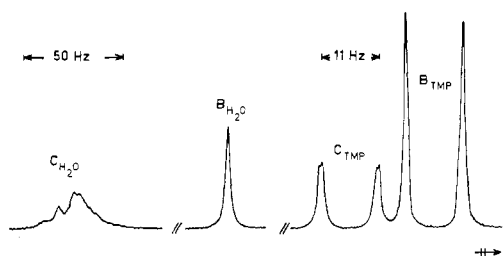


Figure 2.—Pmr spectrum of $\text{Al}(\text{ClO}_4)_3$ in TMP- H_2O -acetone solvent at -10° . Coordinated TMP and H_2O and bulk TMP and H_2O signals are labeled C_{TMP} , $C_{\text{H}_2\text{O}}$, B_{TMP} , and $B_{\text{H}_2\text{O}}$, respectively. Both H_2O signals were recorded at the same sweep width and at a gain 5 times that at which the TMP signals were recorded. The TMP signals were recorded over a smaller sweep width than were the H_2O signals. The acetone signal is not shown. The $\text{Al}:\text{TMP}:\text{H}_2\text{O}:\text{acetone}$ mole ratios were 1.00:6.00:5.60:30.5.

water signal has a multiplet character which is consistent with the superimposition of several singlets exhibiting different chemical shifts. Similarly the coordinated TMP signal consists of superimposed doublets. This spectrum suggests the existence of several species in equilibrium, possessing the formula $[\text{Al}(\text{TMP})_{6-n}(\text{H}_2\text{O})_n]^{3+}$, where n may vary from zero to 6, but it is not practicable to assign the various coordinated water and

TMP signals to specific species at this time. In some cases the coordinated signals, although broadened, did not exhibit a multiplet character, as indicated in Table I. At -80° , the lowest temperature studied, coalescence of coordinated and bulk TMP signals and coordinated and bulk water signals, consistent with rapid solvent exchange induced relaxation, precluded a determination of the composition of the first solvation sphere of In^{3+} .

Acknowledgment.—It is a pleasure to acknowledge the support of the Australian Research Grants Committee for this project.

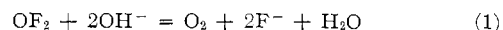
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON 98195

Kinetics of Hydrolysis of Oxygen Difluoride

BY SUDHINDRA N. MISRA AND GEORGE H. CADY*

Received June 15, 1971

The basic hydrolysis of oxygen difluoride has previously been studied, but under such conditions that the rate-controlling step was the rate of dissolving of the gas rather than the rate of hydrolysis when in solution.¹ In the present study, the rate of disappearance of dissolved OF_2 was measured. Substantially no gaseous phase was present in the system. The total reaction was



Oxygen difluoride does not behave as the anhydride of an acid. It has only a low solubility in water² or even in cold 40% KOH .³ None of its reactions are known to produce the recently discovered molecule HOF .⁴

Experimental Section

Oxygen difluoride used in this study was a commercial product obtained from the Allied Chemical Co. When a sample of that gas was taken directly from the cylinder, its infrared spectrum showed no evidence for impurities. Fractional codistillation of a sample also gave indication of the presence of only one substance. In spite of this evidence for purity, the gas, before use in studies of its hydrolysis, was bubbled through 0.1 M NaOH to remove SiF_4 and other acidic gases which might have been present. The base would have caused the introduction of some oxygen into the OF_2 . This oxygen impurity should not have been harmful. Before making a run, a solution of OF_2 was prepared by shaking a sample of the gas with water held in a 2-l. flask.

Apparatus.—The reactor was a vessel of polypropylene having a volume of 1245 ml. The vessel was 18 cm in diameter and had a tight but removable lid equipped with polypropylene fittings to hold the following items: (1) a fluoride ion sensitive electrode made by Orion Research, Inc., Model 94-09, (2) a reference electrode for use with the fluoride electrode, (3) and (4) a glass electrode and reference electrode for use in measuring pH, (5) a thermometer. A Teflon-covered magnetic stir bar was placed in the vessel and was rotated during a run by a magnetic stirrer placed under the thermostat bath. Measurement of pH was made with a Leeds and Northrup 7400 A2 series meter. The

(1) F. Ishikawa, T. Murooka, and H. Hagiwara, *Rikagaku Kenkyusho Iho*, **12**, 742 (1933).

(2) O. Ruff and W. Menzel, *Z. Anorg. Allg. Chem.*, **198**, 39 (1931).

(3) R. A. Rhein and G. H. Cady, *Inorg. Chem.*, **3**, 1644 (1964).

(4) M. H. Staudier and E. H. Appleman, *J. Amer. Chem. Soc.*, **93**, 2349 (1971).

(11) A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *Chem. Commun.*, 173 (1968).

(12) A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *Inorg. Chem.*, **8**, 69 (1969).