contaminant. Also, the molar extinction coefficients previously reported for $(Bu_4N)_2Re_2(NCS)_8(PPh_3)_2$ (see Table III of ref 11) should be increased by a factor of 2, since these values were calculated[11] for the monomeric formulation.
(15) A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, **17**, 231 (1975).
(16) W. R. Robinson, J. E. Hahn, T. Nimry, and R. A. Walton, unpublished observations. Upon completion of the structure refinement we will publish the full details of this structure determination.
(17) For a detailed discussion of this procedure see (a) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964), and (b) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).
(18) From plots of Λ_e (Ω^{-1} cm^2) against $c_e^{1/2}$, where c_e is the equivalent concentration, we obtained the following Λ_0 values (in Ω^{-1} cm^2): (I) $\Lambda_0 = 131$; (III) $\Lambda_0 = 136$; (VI) $\Lambda_0 = 90$; (X) $\Lambda_0 = 101$. The value for III is very close to that reported previously (140 Ω^{-1} cm^2).[11]
(19) F. A. Cotton, *Chem. Soc. Rev.*, 27 (1975).
(20) H. P. Gunz and G. J. Leigh, *J. Chem. Soc. A*, 2229 (1971).
(21) R. E. Myers and R. A. Walton, *Inorg. Chem.*, **15**, 3065 (1976).
(22) D. G. Tisley and R. A. Walton, *J. Chem. Soc., Dalton Trans.*, 1039 (1973).
(23) S. A. Best and R. A. Walton, *Isr. J. Chem.*, in press.
(24) R. R. Hendriksma, *Inorg. Nucl. Chem. Lett.*, **8**, 1035 (1974).
(25) The only mechanistic information currently available is that reported by Hynes[26] for substitution reactions of $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ with tri-*n*-butylphosphine in methanol.
(26) M. J. Hynes, *J. Inorg. Nucl. Chem.*, **34**, 366 (1972).
(27) F. A. Cotton, B. A. Frenz, B. R. Stults, and T. R. Webb, *J. Am. Chem. Soc.*, **98**, 2768 (1976).
(28) C. D. Cowman and H. B. Gray, *J. Am. Chem. Soc.*, **95**, 8177 (1973).
(29) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

Contribution from the Department of Chemistry, University of California,
and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

A Kinetic Study of the Hydrolysis of 2-Germaacetate in Neutral and Alkaline Solutions

DUCK J. YANG and WILLIAM L. JOLLY*

Received February 14, 1977 AIC70121X

In neutral and alkaline solutions, the 2-germaacetate ion decomposes to give germane and bicarbonate (or carbonate): $GeH_3CO_2^- + H_2O \rightarrow GeH_4 + HCO_3^-$. The rate of this decarboxylation is pH independent and is first order in the germaacetate ion. The rate constant at 60 °C and ionic strength 1.0 is 1.62×10^{-5} s^{-1}; the activation energy is 28.6 kcal/mol. In strongly alkaline solutions (especially at hydroxide concentrations above 1 M), a second decomposition reaction, producing hydrogen and the insoluble brown polymer $H_2Ge_2O_3{\cdot}xH_2O$, competes with the decarboxylation: $2GeH_3CO_2^- + 2OH^- + (3 + x)H_2O \rightarrow 6H_2 + H_2Ge_2O_3{\cdot}xH_2O + 2CO_3^{2-}$. The rate of the latter reaction is first order in germaacetate ion and is inversely proportional to the Hammett acidity function h_-, i.e., first order in hydroxide ion; $-d \ln (GeH_3CO_2^-)/dt = k(OH^-)$. At 60 °C, $k = 2.0 \times 10^{-5}$ M^{-1} s^{-1}; the activation energy is 20.8 kcal/mol. Probable mechanisms of the reactions are discussed.

Introduction

It has previously been shown that hot aqueous solutions of potassium 2-germaacetate decompose to give germane and bicarbonate.[1] In this study we investigated the kinetics of the reaction from pH 6 to pH ~15 in the temperature interval 45–75 °C to obtain information regarding the mechanism of the reaction and to allow comparison with similar data for the decarboxylation of organic carboxylates. We discovered that a second decomposition reaction (involving the formation of hydrogen and a brown precipitate) occurs concurrently in the strongly alkaline solutions. We identified the products, established the stoichiometry, and studied the kinetics of this reaction.

Experimental Section

General Information. Manipulations were carried out using a vacuum line or a nitrogen-filled glovebag. Commercial 1,2-dimethoxyethane was dried with potassium hydroxide, filtered, refluxed with sodium metal, and then distilled. Germane gas from the Matheson Co. (minimum purity 99.8%) was used without further purification. The identification of reaction products was aided by infrared spectrometry with a Perkin-Elmer Infracord spectrometer (Model 337) and by mass spectrometry with a Finnigan Instruments Corp. quadrupole mass spectrometer.

Preparation and Analysis of GeH_3CO_2K. A solution of potassium germyl in 1,2-dimethoxyethane was prepared by a method similar to that of Dreyfuss and Jolly.[2] The solution of $KGeH_3$ was stirred and shaken under approximately 1 atm pressure of carbon dioxide in an ice bath. After about 2 h, when the pressure in the closed system had become constant, the precipitated product was collected by suction filtration on a frit.

A 1.228-mmol sample of GeH_3CO_2K was heated in a sealed tube at 510 °C for 24 h. The pyrolysis products were analyzed as described by Kuznesof and Jolly.[1] Sample purity was calculated on the basis of the reaction $2GeH_3CO_2K \rightarrow 3H_2 + CO + 2Ge + K_2CO_3$. The purity was 97.0% based on the total amount of noncondensable gas (collected 2.382 mmol, theory 2.456 mmol), and 99.0% based on the carbon dioxide liberated upon acidification of the residue (collected 0.608 mmol, theory 0.614 mmol).

A 1.016-mmol sample of GeH_3CO_2K was treated with 100 mL of 1 M NaOH in a Teflon-lined reaction vessel at 60 °C for 100 h. Germane gas (0.368 mmol) was isolated from the volatile products. Germanium in the solution was analyzed by the mannitol method[3] after treatment with acid and peroxide to ensure that all the germanium was in the +4 oxidation state. The solution was found to contain 0.631 mmol of Ge. The total Ge found, 0.999 mmol, corresponds to a purity of 98.3%.

Chemical Analysis of the Dark Brown Compound. A dark brown precipitate was obtained by heating a solution of GeH_3CO_2K in 7 M NaOH at 75 °C for 1 h. The material was centrifuged and washed with degassed distilled water until the wash water was neutral. The sample was kept for several days at 0 °C in an evacuated system containing Drierite. The dehydrated sample was observed to be darker in color than the original wet sample. The reducing power per gram of sample was determined by treatment with a known excess of triiodide (under argon in the dark) followed by titration with standard thiosulfate solution, and the number of moles of germanium per gram of sample was measured by the mannitol method.[3] The reducing power per gram of sample was found to be 20.77 and 20.70 mequiv/g, average 20.74 mequiv/g. The number of millimoles of germanium per gram of sample was found to be 10.54, 10.86, and 10.84 mmol/g, average 10.75 mmol/g.

Alkali-digested germanous hydroxide was prepared by digestion of fresh germanous hydroxide[4] in 7 M NaOH at 75 °C for 1 h, followed by the same purification as described for the dark brown compound. Nujol mull infrared spectra of the dried dark brown compound and of alkali-digested germanous hydroxide are shown in Figure 1.

Procedure for Kinetic Study. A solution of GeH_3CO_2K (ca. 10^{-2} M in a buffer solution) was prepared at 0 °C. The ionic strength of the solutions in the pH range 6–14 was adjusted to $\mu = 1.0$ by appropriate addition of potassium chloride. The solution was placed in a flask with a magnetic stirring bar and connected to a vacuum line by means of a glass joint attached to a stopcock. The flask was evacuated while stirring the solution at 0 °C, and the solution was then warmed to the reaction temperature in a thermostated (±0.1 °C) oil bath. At measured intervals the volatile reaction products which formed in the 20-mL space over the solution in the reaction

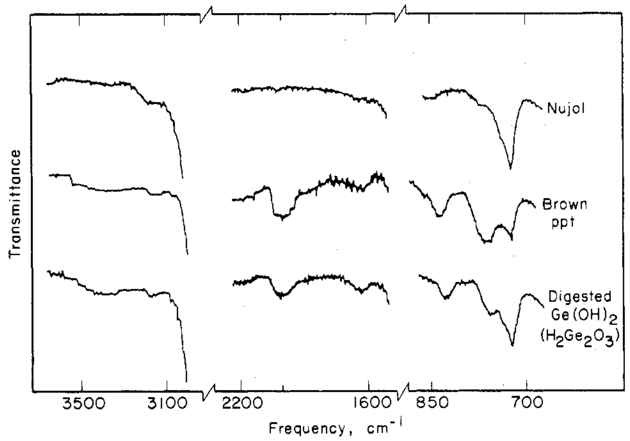


Figure 1. Comparison of the Nujol mull infrared spectra of the dark brown insoluble product of the hydrogen-producing reaction and alkali-digested germanous hydroxide ($H_2Ge_2O_3$).

Table I. First-Order Rate Constant, k_1, at 60 °C and Ionic Strength 1.0, $[GeH_3COO^-] \approx 10^{-2}$ M

pH	10^5k_1, s^{-1}	pH	10^5k_1, s^{-1}
6.0	1.63	9.9	1.58
7.3	1.60	11.4	1.60
8.3	1.67	13.0	1.61

vessel were allowed to expand into an evacuated 3-L bulb by momentarily opening the stopcock. By this procedure, more than 99% of the gaseous products were transferred. The germane in each batch of gas was isolated and measured. When the gaseous reaction products consisted only of germane or of germane and carbon dioxide (pH <13), the gases in the bulb were fractionated through two −78 °C traps, an Ascarite trap, another −78 °C trap, and a −196 °C trap. The germane collected in the −196 °C trap was transferred to a system of known volume and measured. When the volatile reaction products consisted only of germane and hydrogen (pH >13), the gases were fractionated through two −78 °C traps and a −196 °C trap into a calibrated gas collection system by means of a Toepler pump. In these cases both the germane and hydrogen were measured as a function of time.

Results

Kinetics in the pH Interval 6–13. It was confirmed that, in the pH interval 6–13, the principal reaction is decarboxylation with evolution of germane

$$GeH_3CO_2^- + H_2O \rightarrow GeH_4 + HCO_3^-$$

$$GeH_3CO_2^- + OH^- \rightarrow GeH_4 + CO_3^{2-}$$

Although some carbon dioxide was evolved along with the germane in the solutions of low pH, the yield of carbon dioxide was never quantitative. Therefore the rate of reaction was followed by measuring the germane gas as a function of time. The plots of log ($P_\infty - P$) of germane vs. time were straight lines (as shown by the typical plot in Figure 2), indicating that the hydrolysis of $GeH_3CO_2^-$ is first order in $GeH_3CO_2^-$. The first-order rate constant, k_1, was calculated from the slopes of such plots. The values of k_1 measured in different pH buffer solutions are summarized in Table I. The results show that the rate is pH independent. Thus, the rate can be expressed by $-d(GeH_3CO_2^-)/dt = k_1(GeH_3CO_2^-)$ where $k = (1.62 \pm 0.03) \times 10^{-5}\ s^{-1}$ at 60 °C.

Products and Stoichiometry of the Hydrogen-Producing Reaction. The decomposition of $GeH_3CO_2^-$ in solutions of pH greater than 13 involves the formation of hydrogen and a dark brown solid as well as germane and carbonate. A dried sample of the dark brown solid was found to contain 20.74 mequiv of reducing agent per gram and 10.75 mmol of germanium per gram. Thus 20.74/10.75 (or essentially 2) equiv of reducing agent is associated with each mole of germanium in the compound. This result, together with the color and amorphous character of the compound, suggests that the compound is germanous hydroxide, $Ge(OH)_2$.[5] However, the infrared spectra show that the compound is not ordinary germanous hydroxide, but rather the compound $H_2Ge_2O_3 \cdot xH_2O$ which forms when germanous hydroxide is digested with hot alkaline solutions.[6] This isomer of germanous hydroxide contains Ge–H bonds, as shown by the characteristic Ge–H stretching band at 2000 cm^{-1} and the Ge–H deformation band at 750 cm^{-1}. The measured equivalent weight of the dried sample, 48.2 g/equiv, is very close to the theoretical value 48.4 g/equiv, corresponding to the composition $H_2Ge_2O_3$.

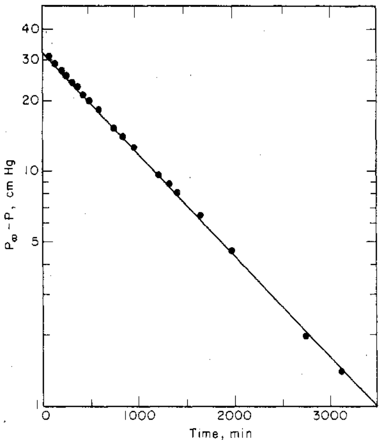


Figure 2. log $(P_\infty - P)_{GeH_4}$ vs. time for the hydrolysis of GeH_3COO^- at pH 9.9 at 60 °C (μ = 1.0).

Table II. Gaseous Products of the Decomposition in Strongly Alkaline Solutions

[NaOH], M	t, °C	Amt, mmol GeH_3-CO_2K	GeH_4	H_2	$[H_2]/([GeH_3$-$CO_2K] - [GeH_4])$
0.1	70	1.169	1.080	0.268	3.01
1.0	46	1.184	0.406	2.356	3.03
1.0	60	1.260	0.543	2.197	3.06
1.0	60	1.506	0.687	2.614	3.19
2.0	46	1.236	0.222	3.321	3.28
2.0	75	1.256	0.434	2.649	3.22
3.0	46	1.171	0.128	3.341	3.20

If $H_2Ge_2O_3 \cdot xH_2O$ and hydrogen are the only additional products of the decomposition of $GeH_3CO_2^-$ in strongly alkaline solutions, these products must be formed in accord with the equation

$$2GeH_3CO_2^- + 2OH^- + (3 + x)H_2O \rightarrow 6H_2 + H_2Ge_2O_3 \cdot xH_2O + 2CO_3^{2-}$$

That is, for each mole of $GeH_3CO_2^-$ which decomposes in this way instead of decomposing to give germane and carbonate, 3 mol of hydrogen should be formed. In some of the kinetic runs which were allowed to proceed to essentially 100% reaction, the total amounts of hydrogen and germane were measured. The data, presented in Table II, show that the moles of hydrogen divided by the moles of $GeH_3CO_2^-$ which did not decompose to germane was always close to the theoretical value of 3. Some of the values, particularly those for runs with hydroxide concentrations greater than 1 M, are significantly greater than 3. The extra hydrogen is probably due to the decomposition of a small amount of the $H_2Ge_2O_3 \cdot xH_2O$ as follows:[7]

$$H_2Ge_2O_3 \cdot xH_2O + 4OH^- \rightarrow 2GeO_3^{2-} + 2H_2 + (1 + x)H_2O$$

Kinetics in Strongly Alkaline Solutions. The overall decomposition of $GeH_3CO_2^-$ at pH values greater than 13 was

Table III. Rate Constants at Various Base Concentrations at 45.8 °C

			Rate constants			
			s^{-1}, $\times 10^6$			M s^{-1}, $\times 10^{20}$
[NaOH], M	H_-[a]	% yield of GeH_4	k_{obsd}	k_1	k_2'	$k_2 = k_2'h_-$
1.0	13.9	34	5.5	1.9	3.6	4.53
2.0	14.4	18	12.6	2.3	10.3	4.10
3.0	14.7	11	23.6	2.6	21.0	4.19
4.0	14.9	8	42.0	3.4	38.6	4.86
5.0	15.2	3	77.0	2.3	74.7	4.71

[a] From ref 8.

Table IV. Temperature Dependence of Rate Constants in 1.0 M NaOH

		$10^{-5} \times s^{-1}$		
Temp, °C	% yield of GeH_4	k_{obsd}	k_1	k_2'
45.8	34	0.55	0.19	0.36
54.4	42	1.76	0.74	1.02
60.0	45[a]	3.60	1.62[b]	1.98
65.0	52	5.25	2.73	2.52
70.1	55	8.43	4.64	3.79
74.4	59	14.44	8.57	5.87

[a] Average of three values, 45 ± 1.1%. [b] This value is close to the average value in Table I.

found to follow first-order kinetics at any given hydroxide concentration. From plots of log $(P_\infty - P)$ (for germane) vs. time, the overall first-order rate constant, k_{obsd}, was measured for various base concentrations. The overall first-order rate constant is the sum of two first-order rate constants, i.e., $k_{obsd} = k_1 + k_2'$ where k_1 is the first-order rate constant for the germane-producing reaction and k_2' is the pseudo-first-order rate constant for the hydrogen-producing reaction. The constants, k_1 and k_2', were calculated using the relation

$$\frac{k_1}{k_2'} = \frac{\%\text{ yield of GeH}_4}{100 - \%\text{ yield of GeH}_4}$$

The results are summarized in Table III. The values of k_1 are essentially constant, with an average value of $(2.5 \pm 0.5) \times 10^{-6}\ s^{-1}$, whereas the k_2' values increase with increasing basicity. It can be seen that the values of the product $k_2'h_-$ (where h_- is the effective hydrogen ion activity, or antilog $(-H_-)$)[8] are almost constant, with the average value $(4.48 \pm 0.30) \times 10^{-20}$ M s^{-1}. Hence we can define $k_2 = k_2'h_-$ and write, for the hydrogen-producing reaction

$$-\mathrm{d}\ln(\mathrm{GeH_3CO_2^-})/\mathrm{d}t = k_2/h_-$$

This result we interpret as evidence that the hydrogen-producing reaction is overall second order: first order in germaacetate and first order in hydroxide. Because of the unavailability of H_- values in the temperature region of our studies, we used H_- values determined at 20 °C in our calculations. For this reason the calculated value of k_2 lacks rigorous theoretical significance except in solutions of relatively low hydroxide concentration, where $k_w/h_- \approx (OH^-)$. The values of k_1 and k_2' for 1.0 M NaOH at various temperatures are summarized in Table IV. These k_2' values (evaluated at 1.0 M OH^-) may be taken as the second-order rate constants (with units of $M^{-1}\ s^{-1}$) for use in the rate law $-\mathrm{d}\ln(\mathrm{GeH_3CO_2^-})/\mathrm{d}t = k(\mathrm{OH^-})$, which is valid at low hydroxide ion concentrations. Plots of log k_1 and log k_2' vs. $1/T$ are shown in Figure 3; the calculated activation energy for the germane-producing reaction is 28.6 kcal/mol and that for the hydrogen-producing reaction is 20.8 kcal/mol.

Discussion of Mechanisms

The germane-producing reaction is analogous to the decarboxylation of an organic carboxylate ion, RCO_2^-. Such decarboxylation is facilitated when R contains electron-withdrawing groups, such as halogen atoms, which stabilize the carbanion R^-. It has been proposed that, in some decarboxylations of this type,[9,10] the reaction mechanism involves the formation of an intermediate R^- ion

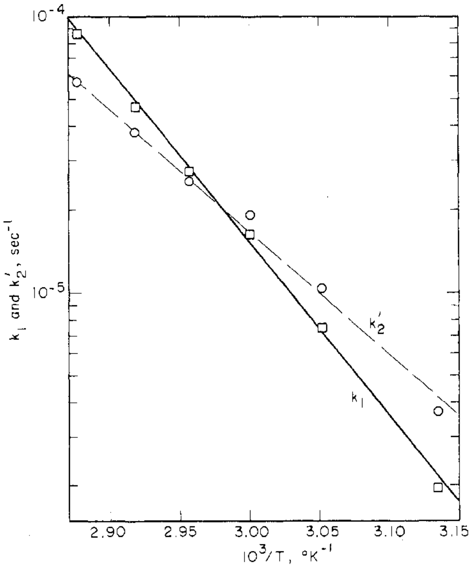
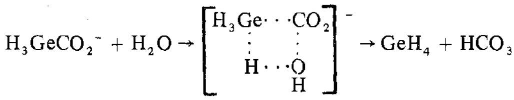


Figure 3. Semilogarithmic plot of k_1 and k_2' vs. $1/T$. Squares correspond to k_1; circles correspond to k_2'.

$$\mathrm{RCO_2^-} \xrightarrow{\text{slow}} \mathrm{R^-} + \mathrm{CO_2}$$

$$\mathrm{R^-} + \mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{RH} + \mathrm{OH^-}$$

One would expect the rate of the slow step to be closely correlated with the protonic acidity of RH. In fact such correlation can be seen in the fact that the 2-germaacetate and trichloroacetate ions undergo decarboxylation under comparable conditions.[11] The p*K* of germane (~25)[12] is close to that of chloroform (~24).[13] Although the above mechanism is reasonable for the germane-producing decomposition of 2-germaacetate, it should be pointed out that our data are also consistent with a four-center mechanism involving initial attack of a water molecule:



$$\mathrm{H_3GeCO_2^-} + \mathrm{H_2O} \rightarrow \left[\begin{array}{c} \mathrm{H_3Ge\cdots CO_2} \\ \vdots \qquad \vdots \\ \mathrm{H\cdots \underset{H}{O}} \end{array}\right]^- \rightarrow \mathrm{GeH_4} + \mathrm{HCO_3^-}$$

In fact the kinetic data for some decarboxylations of organic carboxylates are also consistent with this type of mechanism.[9-11]

The base-catalyzed hydrogen-producing reaction is somewhat analogous to the well-known base-catalyzed hydrolyses of silicon hydride derivatives.[14-17] The latter reactions involve the attack of hydroxide ion on the silicon atom, with displacement of hydride ion. These reactions may be S_N2 processes, or they may involve fleeting pentacoordinate intermediates. It seems reasonable to assume the same sort of process in the case of the 2-germaacetate ion, corresponding to the mechanism

$$\mathrm{GeH_3CO_2^-} + \mathrm{OH^-} \xrightarrow{\text{slow}} \mathrm{HOGeH_2CO_2^-} + \mathrm{H^-}$$

$$\mathrm{H^-} + \mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{H_2} + \mathrm{OH^-}$$

$$\mathrm{HOGeH_2CO_2^-} + \mathrm{OH^-} + 2\mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{(HO)_3GeH} + \mathrm{CO_3^{2-}} + 2\mathrm{H_2}$$

$$2\mathrm{(HO)_3GeH} + (x-3)\mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{H_2Ge_2O_3}\cdot x\mathrm{H_2O}$$

Complete hydrolysis to germanate(IV) does not immediately occur because of precipitation of the insoluble polymer $H_2Ge_2O_3 \cdot xH_2O$ after the evolution of 3 mol of hydrogen per germanium atom and the hydrolytic cleavage of the Ge–C bond.

Acknowledgment. This work was supported by the U.S. Energy Research and Development Administration.

Registry No. GeH_3CO_2K, 22054-96-2; $H_2Ge_2O_3$, 63937-01-9.

References and Notes

(1) P. M. Kuznesof and W. L. Jolly, *Inorg. Chem.*, **7**, 2574 (1968).
(2) R. M. Dreyfuss and W. L. Jolly, *Inorg. Chem.*, **10**, 2567 (1971).
(3) R. Belcher and C. L. Wilson, "New Methods in Analytical Chemistry", Reinhold, New York, N.Y., 1955, p 234.
(4) L. S. Foster, *Inorg. Synth.*, **2**, 102 (1946).
(5) W. L. Jolly and W. M. Latimer, *J. Am. Chem. Soc.*, **74**, 5751 (1952).
(6) D. J. Yang, A. O'Keefe, and W. L. Jolly, unpublished data.
(7) A. Tchakirian, *C.R. Hebd. Seances Acad. Sci.*, **199**, 886 (1934).
(8) G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Acta*, **27**, 348 (1944).
(9) See the many references in L. W. Clark in "The Chemistry of Carboxylic Acids and Esters", S. Patai, Ed., Interscience, New York, N.Y., 1969, p 589, Chapter 12.
(10) J. Hine and D. C. Duffey, *J. Am. Chem. Soc.*, **81**, 1129 (1959).
(11) F. H. Verhoek, *J. Am. Chem. Soc.*, **56**, 571 (1934).
(12) W. L. Jolly, "The Principles of Inorganic Chemistry", McGraw-Hill, New York, N.Y., 1976, pp 133–134.
(13) See footnote 23 in M. F. Semmelhack, R. J. DeFranco, Z. Margolin, and J. Stock, *J. Am. Chem. Soc.*, **95**, 426 (1973).
(14) N. V. Sidgwick, "The Electronic Theory of Valency", Oxford University Press, London, 1927, pp 155–160.
(15) F. P. Price, *J. Am. Chem. Soc.*, **69**, 2600 (1947).
(16) E. G. Rochow, "An Introduction to the Chemistry of the Silicones", 2nd ed, Wiley, New York, N.Y., 1951, pp 6 and 22.
(17) R. West, *J. Am. Chem. Soc.*, **76**, 6015 (1954).

Contribution from the Laboratoire de Chimie Physique Organique,
Equipe de Recherche Associée au CNRS, Université de Nancy I, C.O. 140, 54037 Nancy Cedex, France

Nuclear Magnetic Resonance Study of the Hexakis(trimethyl phosphate)gallium(III) and -indium(III) Complexes

LUDWIG RODEHÜSER,[1] PATRICE R. RUBINI, and JEAN-J. DELPUECH*

Received March 16, 1977 AIC702056

The complexes $Ga(TMPA)_6^{3+}$ and $In(TMPA)_6^{3+}$ were studied in deuterated nitromethane by ^1H, ^{31}P, and ^{71}Ga NMR and are compared to $Al(TMPA)_6^{3+}$. The coupling constants J between the phosphorus and cation nuclei and the quadrupolar relaxation rates T_{1Q}^{-1} of the cation nuclei computed for ^{31}P and ^{71}Ga spectra are $J = 19.9 \pm 0.2$, 33 ± 6, and 48 ± 3 Hz and $T_{1Q}^{-1} = 10$, 280 ± 90, and $850 \pm 150\ s^{-1}$ at 25 °C for ^{27}Al, ^{71}Ga, and ^{115}In nuclei, respectively. The sequence of T_{1Q}^{-1} values is shown to result from an increasing electric field gradient at the metallic nuclei. This effect is assumed to arise from a progressive release of the steric strain in the first solvation shell. The kinetics of the exchange of free and bound TMPA molecules are investigated. The substitution mechanism is shown to be S_N1 for $Ga(TMPA)_6^{3+}$ and S_N2 for $In(TMPA)_6^{3+}$, with the following kinetic parameters: $k(25\ °C) = 5.0\ s^{-1}$ and $7.2\ M^{-1}\ s^{-1}$; $\Delta H^{\ddagger} = 21.0$ and 8.5 kcal mol^{-1}; $\Delta S^{\ddagger} = 15.1$ and -26.1 cal K^{-1} mol^{-1}, respectively. This mechanistic change is again assigned to steric reasons.

Introduction

Nuclear magnetic resonance has been widely used to investigate a considerable number of labile solvation complexes of metallic cations. The most direct method uses systems in which the exchange of solvent molecules between the various species is sufficiently slow so that separate resonances are observed for the free and bound solvent.[2] In 1969, we proposed using ^{31}P spectroscopy of organophosphorus ligands, all containing the phosphoryl P=O solvating link.[3] Solvates of aluminum(III),[4] and more recently of beryllium(II),[5] with trialkyl phosphates, phosphonates, and phosphoramides revealed a variety of substitution mechanisms, either dissociative or associative, which were tentatively accounted for by a variable steric strain of the attached ligands. The present paper is devoted to the study of the complexes $[Ga(TMPA)_6](ClO_4)_3$ (**1**) and $[In(TMPA)_6](ClO_4)_3$ (**2**), dissolved in nitromethane containing variable amounts of free added trimethyl phosphate (TMPA). Very little is known about ligand exchange rates in complexes of gallium(III) and indium(III). The kinetics of ligand exchange is assumed to be dissociative for the system $Ga(H_2O)_6^{3+}$ in DMF[7] and $Ga(acac)_3$ in DMF or THF,[8] on the sole basis of larger or smaller values of activation parameters, especially of the positive or negative sign of the activation entropy. Our experiments allow us to measure for both systems the kinetic order with respect to the concentration of the free ligand. Therefore they constitute a firmer basis for comparisons between cations.

Experimental Section

Materials. Trimethyl phosphate was obtained from Aldrich Chemicals and was checked for purity before use. The solvent was 99.3% deuterated nitromethane (C.E.A., France) stored over molecular sieves. Complexes **1** and **2** were prepared in the solid state from the hydrated salts $Ga(ClO_4)_3 \cdot 6H_2O$ and $In(ClO_4)_3 \cdot 11H_2O$ (Alfa Inorganics).[9,10] These complexes are extremely hygroscopic and they were prepared in a glove box under purified argon. All of these compounds gave satisfactory elemental analyses. Anal. Calcd for $[Ga(TMPA)_6](ClO_4)_3$: Ga, 5.77; C, 17.89; H, 4.50; P, 15.38. Found: Ga, 5.89; C, 17.72; H, 4.53; P, 15.20. Calcd for $[In(TMPA)_6](ClO_4)_3$: In, 9.16; C, 17.23; H, 4.34; P, 14.82. Found: In, 9.38; C, 17.34; H, 4.48; P, 14.74.

NMR Spectroscopy. Proton spectra were taken on a Jeol C60-HL spectrometer operating at 60 MHz with TMS as an internal reference. Phosphorus-31 Fourier transform spectroscopy was performed with a Bruker HX-90 apparatus at 36.43 MHz (128–8192 scans of 4K/8K points over a frequency range of 3–6 kHz). Gallium-71 spectra were obtained from the same spectrometer at 22.63 MHz, using a standard ^{13}C probe and by decreasing the magnetic field from 2.114 to 1.743 T. No field-frequency lock could be used under these conditions. Satisfactory results, however, were obtained by fast accumulation. ^{71}Ga chemical shifts were measured with respect to the resonance of $Ga(H_2O)_6^{3+}$. This reference was a 0.2 M aqueous solution of $Ga(ClO_4)_3$ in a 5 mm o.d. tube immersed in a 10 mm o.d. tube filled with the solution being studied.

Line-Shape Measurements. Two types of exchange were examined in this paper: ^1H exchange between two doublets; ^{31}P exchange within a multiplet of ten lines (cf. infra). The corresponding line shapes are computed according to a matrix formulation due to Anderson,[11] Kubo,[12] and Sack.[13] All calculations were performed using the program TRECH[5] on a Texas Instruments 980 A minicomputer equipped with a digital plotter, Hewlett-Packard 7210 A.

Results and Discussion

Structure of the Solvates and Quadrupolar Relaxation Rates. Two ^1H doublets are obtained from 0.1–0.2 M solutions of