

and iodide, respectively, and, thus, show the same order of stability ( $\Delta H^\circ$ ) as seen above for the reaction of the gaseous halide and mercuric ions.

The effect of temperature on  $-\Delta H_1^\circ$  and  $-\Delta H_2^\circ$  in the case of I can be explained by analysis of the heats of hydration of the products and reactants. The fact that  $-\Delta H_1^\circ$  increases as temperature decreases indicates that the heat of hydration of the final product,  $\text{HgI}^+(\text{aq})$ , is more temperature dependent than is that of the reactants.  $-\Delta H_2^\circ$  decreases as temperature decreases because  $\text{HgI}^+$  is now a reactant rather than a product in the reaction. Heats of hydration of  $\text{HgBr}^+$  and  $\text{HgCl}^+$  are affected to a lesser extent by temperature and consequently  $\Delta H_1^\circ$  and  $\Delta H_2^\circ$  for Br and Cl are not as temperature dependent. This trend is also apparent in  $\Delta S_1^\circ$  and  $\Delta S_2^\circ$  for the corresponding reactions.  $\Delta H_{12}^\circ$  shows little variation with temperature since the effects of the intermediate species are subtracted out in each case.

The following trends in  $\Delta S^\circ$  values are observed from the data in Table II. (a) At a given temperature, values of  $\Delta S^\circ$  decrease in the order Cl, Br, I. This trend parallels the solvent ordering effect of the halide ions. (b)  $\Delta S_2^\circ$  values are more negative at each temperature than are corresponding  $\Delta S_1^\circ$  values in the cases of Cl and Br. The  $\Delta S_2^\circ$  value in the case of I is more positive at 8°, but less positive at 25 and 40°, than is the  $\Delta S_1^\circ$  value. (c) The effect of temperature on  $-\Delta S_1^\circ$  and  $-\Delta S_2^\circ$  is more noticeable in the case of I than in that of either Cl or Br, and the effect on  $-\Delta S_1^\circ$  is opposite to that on  $-\Delta S_2^\circ$ , especially in the case of I.

The  $\Delta S^\circ$  values for the stepwise and over-all formation of  $\text{HgX}_2(\text{aq})$  from  $\text{Hg}^{+2}(\text{aq})$  and  $\text{X}^-(\text{aq})$  may be

divided into two quantities.<sup>11</sup> These are (a) the cratic portion, *i.e.*, that which deals with the number of particles involved in the reaction and is negative for the reactions under consideration since two particles combine to form one and (b) the unitary portion, *i.e.*, that which depends on the ordering ability that the products and reactants have toward the solvent. The unitary portion is positive in the reactions considered here since the reactants carry greater charge than do the products. The  $\Delta S^\circ$  values in Table II become more positive in the order I, Br, Cl as a result of the relative solvent ordering abilities of these halide ions, indicating an increasing importance of the unitary term in the above order.

At 25° the absolute ionic entropies ( $S_{\text{H}^+}^\circ = 0$ ) of  $\text{HgI}^+$ ,  $\text{HgBr}^+$ , and  $\text{HgCl}^+$  calculated from data in Table II and the literature<sup>9</sup> are approximately the same, *i.e.*, 19, 21, and 20 e.u., respectively. Absolute entropies at 25° of  $\text{HgI}_2(\text{aq})$ ,  $\text{HgBr}_2(\text{aq})$ , and  $\text{HgCl}_2(\text{aq})$  calculated in a similar manner are 41, 41, and 39 e.u., respectively.

From the trends observed in  $\Delta H^\circ$  and  $\Delta S^\circ$  it is apparent why  $\Delta G^\circ$  values are constant with temperature.  $\Delta H^\circ$  and  $\Delta S^\circ$  values are affected in the same manner by similar temperature dependent factors. Since  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , increases in  $\Delta H^\circ$  and  $\Delta S^\circ$  cancel the effect of each other.

**Acknowledgments.**—The authors gratefully acknowledge the assistance of Miss Judy Gates, Mr. Don Wrathall, and Mrs. Arlene Hill in solution preparation and analysis and in performing the thermometric titrations.

(11) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953.

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## The Mechanism of Substitution Reactions at Octahedral Sites. III.<sup>1</sup> Deuterium Isotope Effects in the Acid and Base Hydrolysis of Anionopentaamminechromium(III) Ions

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The hydrolysis of  $\text{Cr}(\text{NH}_3)_5\text{X}^{+2}$ , where  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{SCN}^-$ , has been examined in solvents containing varying proportions of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . For  $\text{X} = \text{SCN}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ,  $k_{\text{D}}/k_{\text{H}}$  takes on the values 0.43, 0.60, 0.95, and 1.51, respectively. The interpretation of these effects suggests a transition state which intimately involves one or more water molecules and is strongly polar but does not involve separated ions. In basic solution, the corresponding ratio of rate constants for the chloro complex is 1.37. The interpretation of these data suggests that the transition state for the base hydrolysis involves direct interaction and charge transfer between the hydroxide ion and the metal ion. The exchange of hydrogen between the solvent and the ammonia molecules of the solute has also been measured.

It has been shown previously<sup>3</sup> that the acid and base

(1) Previous paper in this series is T. P. Jones, W. E. Harris, and W. J. Wallace, *Can. J. Chem.*, **39**, 2371 (1961).

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(3) M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961).

hydrolyses of halopentaamminechromium(III) ions follow essentially the same pattern as the cobalt(III) compounds with respect to their dependence on pH. Distinct regions are found in both systems. At low pH (<10 for Cr(III), <5 for Co(III)) the hydrolysis

is independent of pH and at high pH the hydrolysis is inversely dependent upon the first power of the hydrogen ion concentration. The rate follows a relation

$$-\frac{d[\text{complex}]}{dt} = k_a[\text{complex}] + k_b[\text{complex}][\text{OH}^-]$$

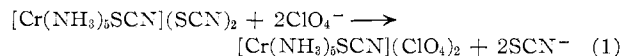
Since base hydrolysis contributes significantly to the over-all reaction at a much lower pH for the cobalt complexes than for the chromium complexes, the  $k_b$  for cobalt must be relatively much greater than for chromium. The reason for this difference is not obvious if the two reactions proceed *via* a common mechanism. In the case of the halopentaamminechromium(III) ions, the variation in the rates of hydrolysis as the halogen is changed has been shown to be due principally to the pre-exponential factor rather than to the activation energy factor.<sup>3</sup> Consequently, in this case at least, the energy expended in bond rupture must be at least partially offset by a compensating solvation of the incipient halide ion, and there is a consequent decrease in the entropy of the solvents. Ultimately this concept treats the solvent as an electrophile competing with the metal ion for the halide ion.

In an attempt to gain greater insight into the nature of solvent participation in the hydrolysis of the halopentaamminechromium(III) ions, the solvent isotope effect upon these reactions has been examined. Since the rate of exchange of the ammine hydrogen atoms is so much slower than the rate of aquation at low pH, the properties of both the light and heavy amines may be examined in a solvent of independent isotope composition. The hydroxide ion catalyzed exchange, on the other hand, is of such magnitude that, in the high pH region, only the ammine of isotope content predetermined by the solvent composition can be investigated.<sup>4</sup> The effect of isotopic content upon the nucleophilicity of water has been extensively examined.<sup>5-9</sup> Reactions in which the solvent develops charge while participating in the transition state produce, relative to the bulk solvent, proton donors or acceptors. The appearance of these centers of acidity or basicity has been thermodynamically correlated with the calculatable lyoxide ion activity in the solvent.<sup>9</sup> Participation of the solvent as an electrophile, particularly in halide ion solvation, was treated by a statistical mechanical method based upon the hindering of the librational modes of the solvating lyons.<sup>10</sup> Such calculations suggested that a reaction which involves hydrogen donation by the solvent in the transition state will proceed more slowly in heavy water than in light water. This is due principally to the lower basicity of D<sub>2</sub>O. Similarly it was shown that a reaction producing a highly solvated anion proceeds more slowly in heavy water than in light water. This effect is attributed to the greater loss of structure from the "free"

D<sub>2</sub>O than from the "free" H<sub>2</sub>O. Conversely, a reaction involving diminution of charge and consequent liberation of solvent must proceed more slowly in light than in heavy water.

### Experimental

**Preparation of Compounds.**—The compounds used were prepared by conventional methods.<sup>3,11,12</sup> The perchlorate salts used throughout were obtained by crystallization from aqueous 2 M perchloric acid solutions of the appropriate intermediates, e.g.



The aquation of Cr(NH<sub>3</sub>)<sub>5</sub>I<sup>2+</sup> proved too rapid for the application of this procedure and the complex was used in the form [Cr(NH<sub>3</sub>)<sub>5</sub>I]<sub>2</sub>.

[Cr(ND<sub>3</sub>)<sub>5</sub>Cl](ClO<sub>4</sub>)<sub>2</sub> was prepared by mixing anhydrous chromic chloride with liquid ND<sub>3</sub>, produced by the action of D<sub>2</sub>O upon Li<sub>3</sub>N,<sup>11b</sup> and dried by freezing out excess D<sub>2</sub>O. The chloropentaammine-*d*<sub>15</sub>-chromium(III) chloride was converted to the perchlorate by crystallization from a 2 M solution of DClO<sub>4</sub> in D<sub>2</sub>O. Separation of the trace of hexaammine was effected by a second crystallization from 2 M DClO<sub>4</sub>. The infrared spectrum of the resultant compound, taken in a Nujol mull, showed effective absence of NH and OH bands. This indicated virtually complete deuteration.

DClO<sub>4</sub> was prepared by the reaction of deuteriosulfuric acid<sup>11c</sup> with sodium chloride; the liberated DCl was distilled into a D<sub>2</sub>O solution of AgClO<sub>4</sub>; AgCl was filtered off and excess DCl was removed by distillation.

NaOD was prepared by the reaction between distilled sodium and D<sub>2</sub>O in a vacuum system. It proved convenient to add NaOD solutions by means of a Burroughs Wellcome "Agl<sub>1</sub>" microsyringe rather than by weighing.

**Heavy water** of deuterium content 99.7% (Merck) was redistilled in a baked Pyrex apparatus under dry nitrogen. The solutions in D<sub>2</sub>O and in mixtures of D<sub>2</sub>O and H<sub>2</sub>O were prepared and standardized by weight.

**Determination of the Hydrogen Exchange Rate.**—The rate of exchange of the ammine hydrogens was determined only for the chloropentaammine complex. The infrared method described by Basolo, Palmer, and Pearson<sup>4</sup> was used. The appearance of the 1.65 μ OH band in an acetate-D<sub>2</sub>O buffer saturated with the light complex (approximately 0.2 M) was followed on a thermostated Cary Model 14 spectrophotometer.

The pH of a light water buffer 0.1 M in sodium acetate and 0.05 M in acetic anhydride was observed to change from 4.7 to 4.5 upon addition of the appropriate amount of the pentaammine salt. This decrease of 0.2 pH unit was used to correct empirically the calculated pD of the corresponding heavy water buffer from 5.26 to 5.06 and derive a second-order rate constant for hydrogen exchange at 25° for Cr(NH<sub>3</sub>)<sub>5</sub>Cl(ClO<sub>4</sub>)<sub>2</sub> as 9.5 (±2) × 10<sup>5</sup> M<sup>-1</sup> sec.<sup>-1</sup>,<sup>13</sup>

(11) (a) G. Schlessinger, *Inorg. Syn.*, **6**, 138 (1960); (b) E. Masdupuy and F. Gallais, *ibid.*, **4**, 1 (1953); (c) N. N. Greenwood and A. Thompson, *ibid.*, **6**, 121 (1960).

(12) A. W. Adamson and R. G. Wilkins, *J. Am. Chem. Soc.*, **76**, 3379 (1954).

(13) The pH of the light water buffer and of the light water buffer containing the complex ion are, respectively

$$\text{pH} = \text{p}K^1_{\text{HA}} + \log \left( \frac{f_{\text{A}}}{f_{\text{HA}}} \right)_{\text{H}_2\text{O}}, \quad \text{pHc} = \text{p}K^1_{\text{HA}} + \log \left( \frac{f_{\text{A}}}{f_{\text{HA}}} \right)_{\text{C,H}_2\text{O}}$$

For the corresponding heavy water solutions

$$\text{pD} = \text{p}K^1_{\text{DA}} + \log \left( \frac{f_{\text{A}}}{f_{\text{DA}}} \right)_{\text{D}_2\text{O}}, \quad \text{pDc} = \text{p}K^1_{\text{DA}} + \log \left( \frac{f_{\text{A}}}{f_{\text{DA}}} \right)_{\text{C,D}_2\text{O}}$$

Hence

$$\text{pDc} = \text{p}K^1_{\text{DA}} + (\text{pHc} - \text{pH}) + \log \left( \frac{f_{\text{A}}}{f_{\text{HA}}} \right)_{\text{H}_2\text{O}} \times \left( \frac{f_{\text{DA}}}{f_{\text{A}}} \right)_{\text{D}_2\text{O}} \cdot \left( \frac{f_{\text{HA}}}{f_{\text{A}}} \right)_{\text{C,H}_2\text{O}} \left( \frac{f_{\text{A}}}{f_{\text{DA}}} \right)_{\text{C,D}_2\text{O}}$$

(4) F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 1073 (1960).

(5) E. L. Purlee, *ibid.*, **81**, 263 (1959).

(6) C. A. Bunton and V. J. Shiner, *ibid.*, **83**, 42 (1961).

(7) E. A. Halevi, F. A. Long, and M. A. Paul, *ibid.*, **83**, 305 (1961).

(8) C. G. Swain, R. F. W. Bader, and E. R. Thornton, *Tetrahedron*, **10**, 200 (1960).

(9) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 3584 (1961).

(10) C. G. Swain and R. F. W. Bader, *Tetrahedron*, **10**, 182 (1960).

TABLE I  
 RATE PARAMETERS FOR THE ACID HYDROLYSIS OF  $\text{Cr}(\text{NH}_3)_5\text{X}^{+2}$  AT 25°

Parameter	SCN	Cl	Br	I <sup>b</sup>
$\Delta S^*_{\text{H}_2\text{O}}$ , <sup>a</sup> e.u.	-7.9	-9.2	-6.1	-1.9
$\Delta E^*_{\text{H}_2\text{O}}$ , kcal. mole <sup>-1</sup>	24.9	22.4	21.5	21.4
$\Delta S^*_{\text{D}_2\text{O}}$ , <sup>a</sup> e.u.	-9.4	-8.2	-2.3	+4.2
$\Delta E^*_{\text{D}_2\text{O}}$ , kcal. mole <sup>-1</sup>	25.2	23.0	22.9	23.0
$k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$	0.43	0.60	0.95	1.51
Solubility in $\text{H}_2\text{O}$ , mole l. <sup>-1</sup>	$5.88 \times 10^{-3}$	$1.20 \times 10^{-2}$	$8.71 \times 10^{-2}$	$1.1 \times 10^{-1}$ c
Solubility in $\text{D}_2\text{O}$ Solubility in $\text{H}_2\text{O}$	0.610	0.744	0.996	1.1
$k_{\text{D}_2\text{O}} \times \text{sol. in } \text{D}_2\text{O}$ $k_{\text{H}_2\text{O}} \times \text{sol. in } \text{H}_2\text{O}$	0.26	0.45	0.92	1.66

<sup>a</sup>  $\Delta S^*$  calculated on the basis of pre-exponential factor  $\nu = 10^{13}$  sec.<sup>-1</sup> and  $k = \nu e^{\Delta S^*/R} e^{-\Delta E^*/RT}$ . We can in practice identify  $\Delta H^*$  with  $\Delta E^*$ , the Arrhenius activation energy for the reaction over the limited temperature range studied (ca. 50°). <sup>b</sup>  $[\text{Cr}(\text{NH}_3)_5\text{I}]_2$ , all other salts were perchlorates  $[\text{Cr}(\text{NH}_3)_5\text{X}](\text{ClO}_4)_2$ . <sup>c</sup> 0°.

This result demonstrates that at pH 1-2, at which the acid hydrolysis reactions were normally carried out, the exchange rate does not exceed 1% of the aquation rate. In order to ensure that the rate of exchange was negligible compared with the rate of acid hydrolysis in other cases also, portions of the heavy water solutions of the light ammine were removed upon completion of the hydrolysis study; the solvent was completely distilled off under vacuum and the infrared spectrum examined in a thin film (0.015 mm.) between KRS5 plates. In the case of the iodo complex 1-5% exchange had occurred, but OH bands were not observed for the remaining pentaammines.

**Acid Hydrolysis Reactions.**—Solutions, in appropriate solvents, of the perchlorate salts of the complexes ( $10^{-3}$  M) with requisite amounts of NaOH or NaOD were adjusted to constant ionic strength ( $\mu = 0.2$ ) with anhydrous sodium perchlorate. Aliquots were quenched by addition of sufficient perchloric or sulfuric acid to bring the pH to approximately unity, and the course of the reaction was followed polarographically as described previously.<sup>3</sup>

A sulfate medium enabled better separation to be obtained between the polarographic waves for  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{+2}$  and  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$ , but in the cases of  $\text{Cr}(\text{NH}_3)_5\text{Br}^{+2}$  and  $\text{Cr}(\text{NH}_3)_5\text{I}^{+2}$  sufficient separation is obtained in a perchlorate medium. For  $\text{Cr}(\text{NH}_3)_5\text{Br}^{+2}$  and  $\text{Cr}(\text{NH}_3)_5\text{I}^{+2}$  it generally proved convenient to use only the reactant polarographic waves. It was also feasible to use the  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$  anodic waves, using a potassium nitrate salt bridge to avoid contamination.

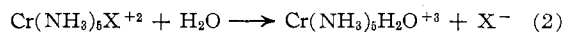
Plots of  $\log(i_d, \infty - i_d, t)$  vs.  $t$  yielded straight lines with values of  $i_d$  for  $\text{Cr}(\text{NH}_3)_5\text{X}^{+2}$ ,  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$ , or  $\text{X}^-$  waves in acid solutions. In basic solutions,  $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{+3}$  is removed by subsequent hydrolysis and its polarographic wave cannot be used here.

**Solubility Measurements.**—The solubilities of the perchlorate salts of the complex cations were determined by shaking excess solid with the solvent for not less than 15 min. at 25° and filtering. The chromium content in a weighed portion of the saturated solution was determined by oxidation with perchloric acid, dilution, addition of potassium iodide, and titration of the liberated

iodine with thiosulfate solution. In the case of the iodopentaamminechromium(III) iodide the solubilities were determined at 0° with a 5-min. shaking period, but aquation was rapid enough that the results are of doubtful value.

## Results and Discussion

Table I gives the ratios  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$  of the first-order acid hydrolysis rate constants at 25° for some reactions of the type



The constants  $k_{\text{H}_2\text{O}}$  have been determined previously<sup>3</sup> and the values here tabulated are in reasonable agreement.

The solubility ratios are listed in order that initial-state isotope effects may be adjudged. The final row of Table I contains values of the rate ratios corrected to a comparable initial state of solvation. The arbitrarily selected reference state was that exhibited by the chloroammine- $h_{15}$  in  $\text{H}_2\text{O}$  solvent.

The conclusions drawn previously<sup>3</sup> with respect to the effect of halide solvation upon the rate of acid hydrolysis are strengthened by the data for the  $\text{D}_2\text{O}$  solutions. A slight increase in the enthalpy of activation is attended by a much greater decrease in the entropy of activation. The significant observation here is that  $\text{Cl}^-$  (the most solvated halide) is being released relatively more slowly in  $\text{D}_2\text{O}$  compared to  $\text{H}_2\text{O}$  than  $\text{I}^-$  (the least solvated halide). The force of this argument is somewhat lessened by the observation that the effect of solvent  $\text{D}_2\text{O}$  upon the rate is more pronounced for the thiocyanate complex than for the chloro complex. This, despite the fact that the thiocyanate ion is reported to be less solvated than the iodide ion.<sup>15</sup> It is, of course, possible that an attached thiocyanate ion is modified through  $\pi$ -interaction with the  $t_{2g}$  orbitals of chromium and the resulting intensification of charge density on the ion causes it to interact to a greater than normal extent with the solvent.

Table II presents the acid hydrolysis rate ratios for the chloropentaammine- $h_{15}$ -chromium(III) and chloropentaammine- $d_{15}$ -chromium(III) ions in both light and heavy water. For comparison, the values for the

It is assumed that:  $(f_{\text{HA}}/f_{\text{A}})_{\text{C.H}_2\text{O}} \approx (f_{\text{A}}/f_{\text{DA}})_{\text{C.D}_2\text{O}}$  when the solutions in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are identical in formal concentration, and that  $(f_{\text{A}}/f_{\text{HA}})_{\text{H}_2\text{O}} \approx 1$ . This is true to a first approximation for the light buffer since  $\text{pH} = \text{p}K_{\text{HA}} = 4.7$ , and may be presumed to be true for the heavy buffer. Hence  $\text{pDC} = \text{p}K_{\text{DA}} + (\text{pHC} - \text{pH})$ .  $\text{p}K_{\text{DA}} = 5.26$ ,<sup>14</sup> and on this basis  $\text{pDC}$  is calculated to be 5.06. When this value is combined with  $K_{\text{D}_2\text{O}} = 1.5 \times 10^{-15}$ ,  $[\text{OD}^-]$  is found to be  $1.7 \times 10^{-10}$ .

The rate law for hydrogen exchange is

$$\text{rate} = k_2[\text{OH}^-][\text{Cr}(\text{NH}_3)_5\text{X}^{+2}]$$

However, the observations made in a buffered solution yield a pseudo-first-order rate constant  $k_1 = k_2[\text{OH}^-]$ . The value of this constant in  $\text{D}_2\text{O}$ -acetate buffer at  $[\text{OD}^-] = 1.1 \times 10^{-10}$  (see above) was  $1.6 \pm 0.3 \times 10^{-4}$  sec.<sup>-1</sup>. The value of  $k_2$  is then  $9.5 \pm 2 \times 10^8$  M<sup>-1</sup> sec.<sup>-1</sup>.

(14) S. Kormann and V. K. La Mer, *J. Am. Chem. Soc.*, **58**, 1396 (1936); R. Kingerley and V. K. La Mer, *ibid.*, **63**, 3260 (1941).

(15) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).

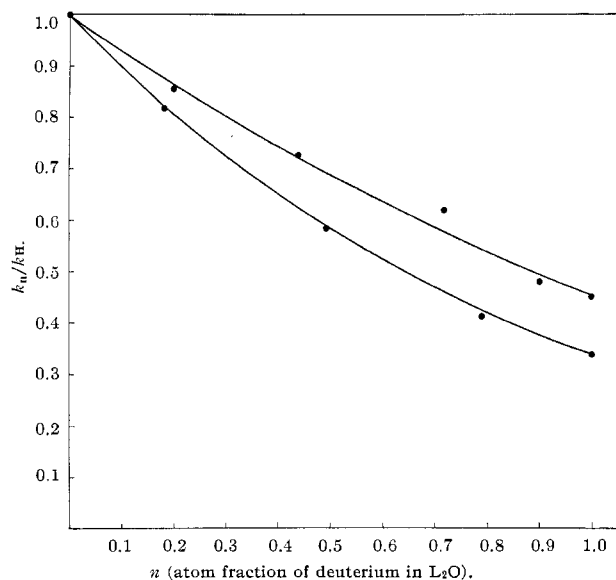


Figure 1.

TABLE II  
RELATIVE RATES OF HYDROLYSIS AND SOLUBILITIES OF COMPLEX  
SALTS IN H<sub>2</sub>O AND D<sub>2</sub>O

Complex ion	Solvent	Relative rates		Relative solubilities	
		Cr <sup>b</sup>	Co <sup>a</sup>	Cr <sup>b</sup>	Co <sup>a</sup>
M(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>+2</sup>	H <sub>2</sub> O	1.00	1.00	1.00	1.00
M(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>+2</sup>	D <sub>2</sub> O	0.60	0.70	0.74	0.74
M(ND <sub>3</sub> ) <sub>5</sub> Cl <sup>+2</sup>	H <sub>2</sub> O	0.96	0.76 <sup>c</sup>	1.20	1.14 <sup>c</sup>
M(ND <sub>3</sub> ) <sub>5</sub> Cl <sup>+2</sup>	D <sub>2</sub> O	0.43	0.60 <sup>c</sup>	0.90	0.86 <sup>c</sup>

<sup>a</sup> Chloride salts. <sup>b</sup> Perchlorate salts. <sup>c</sup> 96.2% deuteration in complex.

chlorides of the corresponding cobalt(III) complex at 49.4°<sup>16</sup> are also listed.

The similarities in behavior of the chromium(III) and cobalt(III) complex ions are striking. The differences in relative rates of the deuterioammines may be attributable to a small residual hydrogen content of the cobalt compounds. Certainly comparison with the data, corresponding to different degrees of isotopic substitution, in ref. 16 indicates that the trend is in this direction. The solubility of the ammine-*h*<sub>15</sub> perchlorate was found to decrease along with its rate of hydrolysis as the solvent became progressively higher in deuterium. The end members of these two series of measurements are shown in Table I, and the actual values for the composite of these two measurements are displayed in Fig. 1. By contrast, the effect of increasing the deuterium content of the complex while maintaining the solvent constant is to increase the solubility but to decrease the rate. These observations may be explained in terms of the influence of the dissolved complex upon the structure of the solvent. Figure 2 illustrates, schematically, the trends expected in the free energy of solution of the complex ions in H<sub>2</sub>O and D<sub>2</sub>O. The basis for the diagram is the assumption that since D<sub>2</sub>O has more structure than H<sub>2</sub>O in the pure liquid<sup>8</sup> it has more to lose through the disruptive influence of a dissolved cation. This would

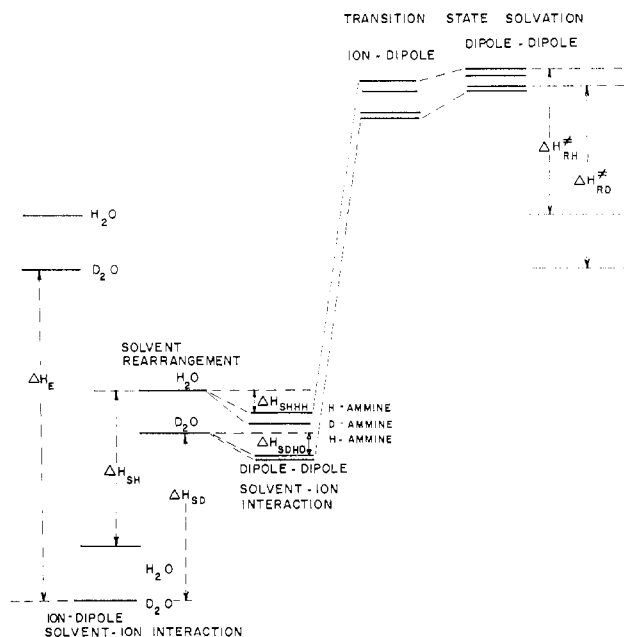


Fig. 2.—Schematic representation of enthalpy changes in dissolution and activation of Cr(NH<sub>3</sub>)<sub>5</sub>X<sup>+2</sup> ions.

mean that the energy required to rearrange the solvent is greater for D<sub>2</sub>O than for H<sub>2</sub>O. On this basis a particular complex is expected to be more soluble in H<sub>2</sub>O than in D<sub>2</sub>O. In a similar way, in the same solvent, the ammine-*h*<sub>15</sub> is expected to be more soluble than the ammine-*d*<sub>15</sub>. The data presented in Table I are in good agreement with these predictions.

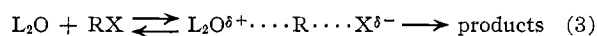
The observation in connection with solubility data which remains to be explained is the change of relative solubility as the labile group is varied. Of the factors affecting the relative solubility, the only one that should be a function of the labile group in a complex involves the direct interaction of the solvent with this group. The greater the charge localization on a species the greater should be the association of the solvent with that species. However, the only part of this increased solvation which will be solvent dependent is that part which reflects upon the structure of the solvent. Hence, the quantity labeled  $\Delta H_{SL}$  should be a direct function of this charge separation. Furthermore, the difference between  $\Delta H_{SH}$  and  $\Delta H_{SD}$  should increase as the total value of this parameter increases. This suggests that ligands which form highly polar bonds with chromium should cause the solubility of the complex in H<sub>2</sub>O to increase relative to D<sub>2</sub>O. Certainly the trend in relative solubility shown in Table I is in this direction. The actual solubility is, of course, also affected by the lattice energy and need not show the same simple dependence upon the charge separation in the complex.

These considerations suggest that initial state interaction with the solvent produces a set of four energy levels each characteristic of a particular solvent-ammine pair as shown in Fig. 2. These initial-state energy levels represent a sufficient condition for a difference in activation energy and a consequent variation in rate for different conditions of deuteration in the

(16) R. G. Pearson, N. C. Stellwagen, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 1077 (1960).

amine and in the solvent for a particular complex. If, as seems likely, the transition state is characterized by an increased charge separation between the leaving group and the residual complex, then the transition-state energy levels which correspond to the initial-state energy levels should lie closer together. In fact, it would appear that as the degree of separation increases the energy levels corresponding to the D<sub>2</sub>O solvent should move up relative to the H<sub>2</sub>O solvent levels. In this way, the activation energy for the reaction would be expected to vary in the direction  $\Delta H^*_{h-H} < \Delta H^*_{d-H} < \Delta H^*_{h-D} < \Delta H^*_{d-D}$  where h and d refer to the complex and H and D to the solvent. It is seen here that on this basis the reaction of a particular ammine is expected to proceed more slowly in D<sub>2</sub>O than in H<sub>2</sub>O. In a particular solvent the deuterioammine reacts more slowly than the hydrogenoammine.

In this fashion the observations of Table I are rationalized provided only that the governing factor in solvent isotope effects is the interruption of the solvent structure produced by the reactants. If this rationale is correct the interaction of the solvent with the dipole produced at the leaving group is required. The argument will be pursued in a somewhat more quantitative fashion on the basis of a model which involves solvent interaction in the activated complex, as illustrated by equation 3.



The treatment of Swain and Thornton<sup>9</sup> indicates a relation between solvent deuterium atom fraction  $n$  and the rate ratio  $k_n/k_H$  given by eq. 4 for the model of the reactive system suggested

$$k_n/k_H = \xi^y (1 - 0.293n)^2 \quad (4)$$

where basicity of L<sub>2</sub>O is taken into account by the  $(1 - 0.293n)^2$  term and the halide solvation is described by the  $\xi^y$  term. The parameter  $y$  is a measure of the increase in X-solvation and thus, indirectly, of S-X bond breaking in forming the transition state. The relation between  $k_n/k_H$  and  $n$  is then uniquely determined by the value of  $k_D/k_H$ . The upper line in Fig. 1 shows calculated values of  $k_n/k_H$  for Cr(NH<sub>3</sub>)<sub>5</sub>Cl<sup>+</sup> aquation using a  $y$  value of 0.36. The  $k_n/k_H$  values for Cr(ND<sub>3</sub>)<sub>5</sub>Cl<sup>+</sup> are closely approached by using  $y = 1.5$  in eq. 4. This great difference in  $y$  is difficult to reconcile with a common mechanism. However, the difference may not be real since it is assumed in the theoretical treatment that only X-solvation is a factor in the determination of the relative activation energies. If the foregoing discussion is valid then there should be initial state and transition state specific interactions with the solvent which are different for the hydrogeno- and -deuterioammines. These specific interactions should act to introduce a spread in activation energies such that  $\Delta E^*_{H_2O-\text{ammine-}h_{15}} < \Delta E^*_{H_2O-\text{ammine-}d_{15}} < \Delta E^*_{D_2O-\text{ammine-}h_{15}} < \Delta E^*_{D_2O-\text{ammine-}d_{15}}$ . This, of course, is the observed order of the reaction rates as shown in Table II. Such changes as these

ought to be reflected in the parameter  $\xi$ , which is related to the free energy of activation for the process concerned. An effort was made to estimate the change in  $\xi$  which might be necessitated by the initial state solvation differences as reflected in the difference in solubility of the hydrogeno and deuterioammines in a common solvent. On the basis of the data presented in Table II this effect was estimated to reduce  $\xi$  from 0.744 for the ammine- $h_{15}$  and  $\alpha = 1.00$  to 0.432 for the ammine- $d_{15}$  and  $\alpha = 1.00$ . Using this value of  $\xi$  and the observed ratio  $k_D/k_H$  for the ammine- $d_{15}$  of 0.336, the value of  $y$  is calculated to be 0.478. The corresponding variation of  $k_n/k_H$  is given by the lower curve in Fig. 1 for the deuterioammine. The agreement with experiment is seen to be reasonable. There is no doubt that additional modification of the  $\xi$  parameter would be necessitated by transition-state effects but there is no straightforward method for the experimental estimation of such changes.

TABLE III  
RATE CONSTANTS FOR THE BASE HYDROLYSIS OF  
CHLOROPENTAAMMINECHROMIUM(III)

Complex ion	Solvent	— $k_{\text{OL}}, M^{-1} \text{sec.}^{-1}$ —	
		Cr (25°)	Co (18°)
M(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>+</sup>	H <sub>2</sub> O	$1.9 \times 10^{-3}$	$2.53 \times 10^{-1}$
M(ND <sub>3</sub> ) <sub>5</sub> Cl <sup>+</sup>	D <sub>2</sub> O	$2.6 \times 10^{-3}$	$1.43 \times 10^{-1}$

The observations on the solvent deuterium isotope effects suggest that reactions of the type represented by eq. 2 proceed through a reaction intermediate which involves a water molecule intimately and which probably does not consist of separated ions. The present observations suggest that the leaving group is replaced by a water molecule which is held, in the transition state, at a position adjacent to the leaving group. The model proposed for the aquation of *trans*-chloroamminobis(ethylenediamine)cobalt(III) by Tobe<sup>17</sup> and for the halopentaamminechromium(III) ions<sup>1</sup> seems to be a satisfactory representation. The present work indicates that the entering water molecule is hydrogen bonded to both the leaving group and the adjacent ammine nitrogen, but there seems no reason to suggest specific interaction between the incoming water molecule and the metal ion prior to the transition state.

Turning now to the hydroxide ion catalyzed hydrolysis of the pentaamminechromium(III) complexes, Table III shows the second-order rate constants for the base hydrolysis of the chloro compounds. For comparison the rate constants for the corresponding chloropentaamminecobalt(III) complexes<sup>18</sup> are also listed.

An S<sub>N</sub>1CB mechanism for the alkaline hydrolysis would be expected to have  $k_{\text{OD}} > k_{\text{OH}}$  by analogy with the chlorohydrin hydrolysis.<sup>19</sup> Calculation of  $k_{\text{OD}}/k_{\text{OH}}$  for the (conjugate base) hydrolysis of 2-chloroethanol was effected by reasonable estimates of

(17) M. L. Tobe, *J. Chem. Soc.*, 3667 (1959).

(18) A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

(19) C. G. Swain, A. D. Ketley, and R. F. W. Bader, *J. Am. Chem. Soc.*, **81**, 2353 (1959).

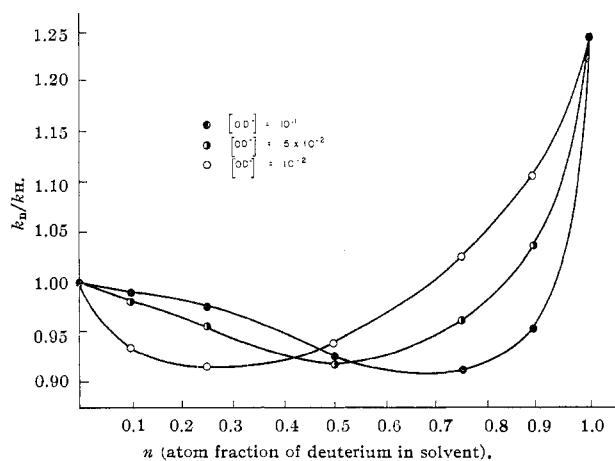
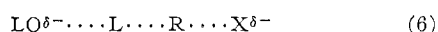


Fig. 3.—The variation of the rate of the base hydrolysis of  $\text{Cr}(\text{NL}_3)_6\text{Cl}$  as a function of the atom fraction of deuterium in the solvent  $\text{L}_2\text{O}$  at various  $[\text{OL}^-]$ .

hydrogen-bonding vibrational frequencies.<sup>20</sup> These same calculations cannot be carried out here owing to insufficient information concerning the NH vibrations in the complex ion. Nevertheless, the opposite effects in the cobalt(III) and chromium(III) systems are very interesting. It will be recalled that alkaline hydrolysis is much less important relative to acid hydrolysis for the chromium compounds than for the cobalt compounds. On a conjugate base mechanism, this would imply that the hypothetical base is weaker in the case of  $\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}^+$  and that the basicity change in the solvent structure breaking during halide solvation is of much greater importance in determining the rate ratio. Thus, the base hydrolysis reaction of the cobalt complex more nearly approximates the acid hydrolysis reaction than does the base hydrolysis of the chromium complex. For the stronger hypothetical base  $\text{Cr}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}^+$  the higher base strength of the  $\text{OD}^-$  ion will necessitate  $k_{\text{OD}} > k_{\text{OH}}$ . The circumstances are more complex than indicated here, for contributions from the secondary halide solvation isotope effect and the primary effect upon the ammine lyon-donating power in addition to the secondary effect upon the lyoxide ion basicity mentioned above must be considered. The situation is analogous to eq. 5,<sup>21</sup> which considers the transition state represented in eq. 6. Figure 3 shows the varia-

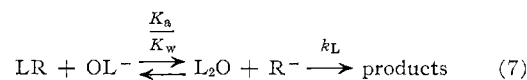
$$\frac{k_{\text{D}}}{k_{\text{H}}} = \xi \left( 1 + \left( \frac{k_{\text{D}}}{k_{\text{HSD}}} - 1 \right) \phi \right) \quad (5)$$



tion of  $k_{\text{n}}/k_{\text{H}}$  with  $n$  for the hydroxide ion catalyzed hydrolysis of the chloropentaamminechromium(III) ion. No attempt has been made to calculate the  $k_{\text{n}}/k_{\text{H}}$  values. It must be noted that the marked concavity is a necessary result of reducing the basicity of an attacking molecule to a value comparable to that of the solvent, *e.g.*, an  $\text{OL}^-$  has been changed to an  $\text{OL}$ . This isotope effect cannot on this basis be distinguished from that resulting when a transition state of the type

$\text{LO} \cdots \text{R} \cdots \text{X}^{\delta-}$  forms, where there is direct ( $\text{S}_{\text{N}}2$ ) attack of the lyoxide ion upon the metal of the complex ion.

If the reaction does follow an  $\text{S}_{\text{N}}1\text{CB}$  mechanism,<sup>4</sup> then it takes the course indicated in eq. 7 and the



isotope effect upon the acid dissociation constant of the ammine,  $(K_{\text{a}})_{\text{h}}/(K_{\text{a}})_{\text{d}}$ , may be estimated<sup>16</sup> from eq. 8 for the over-all reaction. For the chloropenta-

$$\frac{k_{\text{OH}}}{k_{\text{OD}}} = \frac{k_{\text{H}}(K_{\text{a}})_{\text{h}}(K_{\text{w}})_{\text{D}}}{k_{\text{D}}(K_{\text{a}})_{\text{d}}(K_{\text{w}})_{\text{H}}} \quad (8)$$

amminechromium(III) ion, taking  $k_{\text{OH}}/k_{\text{OD}} = 0.73$ , the observed base-hydrolysis isotope effect, and  $k_{\text{D}}/k_{\text{H}} = 0.43$ , the observed acid hydrolysis isotope effect (a reasonable approximation for the second step of reaction 7), then

$$\frac{(K_{\text{a}})_{\text{h}}}{(K_{\text{a}})_{\text{d}}} = \frac{(K_{\text{w}})_{\text{H}}}{(K_{\text{w}})_{\text{D}}} \times 0.31 \quad (9)$$

In view of the increase of  $(K_{\text{a}})_{\text{h}}/(K_{\text{a}})_{\text{d}}$  as  $K_{\text{a}}$  decreases observed empirically for oxyacids<sup>22</sup> and given some support by estimates of the vibrational frequencies of the acidic protons,<sup>5</sup> this value of  $(K_{\text{a}})_{\text{h}}/(K_{\text{a}})_{\text{d}}$  would suggest a relatively high value for  $K_{\text{d}}$  for the chloropentaamminechromium(III) ion. The same procedure applied to the chloropentaamminecobalt(III) ion<sup>16</sup> indicates  $(K_{\text{a}})_{\text{h}}/(K_{\text{a}})_{\text{d}}$  is approximately equal to  $(K_{\text{w}})_{\text{H}}/(K_{\text{w}})_{\text{D}}$ , and this would suggest a relatively low value for  $K_{\text{a}}$ . Any large difference in the acidities of these two complexes appears to be ruled out by a comparison of the N-H stretching frequencies determined from the crystalline salts, *viz.*,  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ , 3130  $\text{cm}^{-1}$ ,<sup>23</sup> and  $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$ , 3120  $\text{cm}^{-1}$ .<sup>24</sup> Although the corresponding frequencies in water are not known, it seems reasonable that these two complexes should exhibit similar frequency shifts in going from the same crystalline environment to the same aqueous environment. If this be true, then the treatment given by Bunton and Shiner<sup>6</sup> will lead to very similar values for  $(K_{\text{a}})_{\text{h}}/(K_{\text{a}})_{\text{d}}$  for the two complexes. Consequently, if the dependence of  $(K_{\text{a}})_{\text{h}}/(K_{\text{a}})_{\text{d}}$  upon acid strength observed for aquo acids is also valid for aminic acids, the complexes in question must have similar values for  $K_{\text{a}}$ .

Pearson, Stellwagen, and Basolo<sup>16</sup> have argued that a value for  $(K_{\text{a}})_{\text{h}}/(K_{\text{a}})_{\text{d}}$  in the vicinity of 6.5 is not unreasonable for an acid such as  $\text{Co}(\text{NH}_3)_6^{+3}$ . If such a value can be applied to the chromium system then it is seen that  $k_{\text{D}}/k_{\text{H}}$  has the value 1.37. This value is far from the pure solvent isotope effect (0.43) observed for the acid hydrolysis of the chloropentaamminechromium complex. It further contrasts with the cobalt case, where the assumption of 6.5 as a reasonable value for  $(K_{\text{a}})_{\text{h}}/(K_{\text{a}})_{\text{d}}$  leads to a residual isotope effect quite analogous to that observed for acid hydrolysis.

(22) C. K. Rule and V. K. La Mer, *ibid.*, **60**, 1974 (1938).

(23) M. Kobayashi and J. Fujita, *J. Chem. Phys.*, **23**, 1354 (1954).

(24) E. P. Bertin, I. Nakagawa, S. Mizushima, T. J. Lane, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 525 (1958).

(20) C. A. Bunton and V. J. Shiner, *J. Am. Chem. Soc.*, **83**, 3207 (1961).

(21) C. G. Swain and E. R. Thornton, *ibid.*, **83**, 3890 (1961).

These observations and comparisons suggest that the base hydrolyses of the chloropentaamminechromium(III) and chloropentaamminecobalt(III) complexes do not proceed through a common mechanism.

It seems likely that the chromium complex hydrolyzes *via* a mechanism which involves direct interaction and charge transfer between the metal ion and the hydroxide ion.

CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY  
CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MISSOURI

## Exchange on Triply Connected Arsenic of the Substituents: Methoxyl, Dimethylamino, and the Halogens<sup>1</sup>

BY KURT MOEDRITZER AND JOHN R. VAN WAZER

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Proton nuclear magnetic resonance (n.m.r.) was used to study interchange of substituents in seven systems: 1,  $\text{As}(\text{OCH}_3)_3$  vs.  $\text{As}[\text{N}(\text{CH}_3)_2]_3$ ; 2-4,  $\text{As}(\text{OCH}_3)_3$  vs.  $\text{AsX}_3$ ; and 5-7,  $\text{As}[\text{N}(\text{CH}_3)_2]_3$  vs.  $\text{AsX}_3$ , where X stands for F, Cl, or Br. In addition,  $\text{F}^{19}$  n.m.r. was employed on the fluorine-containing compounds to check the reliability of the n.m.r. analytical procedure. In accord with previous work in our laboratory on exchange of these substituents on triply connected phosphorus and on silicon, it was found that the exchange equilibria of the methoxyl with the dimethylamino group do not deviate much from the values expected from ideal random sorting. On the other hand, there is a large deviation for the exchange of the dimethylamino group with halogens and a significant but lesser deviation for the exchange of methoxyl groups with halogens. These deviations are due to exothermic reactions between the end-member compounds to make the mixed species. For the arsenic systems, the values of  $\Delta H$  corresponding to these nonrandom equilibria were measured calorimetrically and are compared herein with the  $\Delta H$  values calculated from the deviations from randomness of the equilibrium constants. The rate of substituent interchange on the triply connected arsenic was found to be quite rapid in all cases. For all systems except  $\text{As}(\text{OCH}_3)_3$ - $\text{As}[\text{N}(\text{CH}_3)_2]_3$ , the average rate of interchange was estimated as a function of concentration and temperature from the n.m.r. line shapes.

Previous studies<sup>2</sup> in this laboratory have indicated that exchange reactions of halogen atoms with either the dimethylamino or methoxyl group proceed to equilibrium points which deviate considerably from those corresponding to ideally random sorting of the substituents. It was postulated that the deviation from randomness, as measured by a free-energy difference, might in general be independent of the central atom to which these substituents are bonded, and this paper presents a test of this postulate for triply connected arsenic as the central atom.

In 1896, Michaelis and Luxembourg<sup>3</sup> described dialkylaminodichloroarsine. Articles<sup>4</sup> concerning this type of compound as well as bis(dialkylamino)chloroarsine have been published occasionally since that time. Although esters of arsenous acid were first investigated<sup>5</sup> nearly a century ago, the halo esters were apparently not studied<sup>6</sup> until fifty years later.

### Experimental

**Reagents.**—Arsenic trifluoride was purchased from Chemical Procurement Laboratories (College Point 56, N. Y.), arsenic tri-

bromide was from Bios Laboratories (New York 23, N. Y.), and arsenic trichloride was a Baker and Adamson reagent grade chemical. The arsenic halides were carefully redistilled in a dry nitrogen atmosphere before use. Tris(dimethylamino)arsine was made according to the procedure developed by one of us<sup>7</sup> and trimethyl arsenite was made as described below.

A 2-mole sample of arsenic trichloride was added slowly at a temperature of 5° to a well-stirred ice-cooled mixture consisting of 1.5 l. of *n*-hexane, 1.5 l. of diethyl ether, 6.5 moles of methanol, and 6.1 moles of triethylamine. After standing overnight, the solution was filtered and the solvent distilled off to give 236 g. (1.4 moles) of  $\text{As}(\text{OCH}_3)_3$ , b.p. 129–130° (760 mm.) (70% yield). A single sharp peak in the proton n.m.r. spectrum of the product indicated at least 99.5% purity with respect to hydrogen-containing materials. A qualitative test showed the absence of halogen in the product.

**Equilibration.**—Due to the hydrolytic sensitivity of the arsenic compounds, all materials were carefully handled in a nitrogen atmosphere in a drybox, having a dew point below -78°. Glassware was baked at 150° and cooled to room temperature *in vacuo*. Equilibration was carried out by either sealing the correct proportions of starting materials in glass tubes and heating to 120° for 5 days or by mixing the selected proportions of the starting ingredients and holding at 25° for 5 days. The same quantitative results were found in either case.

**Analytical Procedures.**—A Varian A-60 analytical n.m.r. spectrometer running at a frequency of 60 Mc. was employed for the  $\text{H}^1$  n.m.r. determinations at room temperature. In general, a sweep rate of 0.1 c.p.s. was used at a sweep width of 50 cycles for full scan. The  $\text{F}^{19}$  n.m.r. determinations, as well as the  $\text{H}^1$  spectra obtained at various temperatures, were run on a Varian HR-60 spectrometer at frequencies of 56.444 and 60.000 Mc., respectively. Spinning was not used in the  $\text{F}^{19}$  n.m.r. determinations since the samples were contained in 15-mm. o.d. Teflon tubes; but all samples determined by  $\text{H}^1$  n.m.r. were spun in 5-mm. thin-walled precision-bore glass tubes.

(1) Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 2, 1963.

(2) (a) E. Fluck and J. R. Van Wazer, *Z. anorg. allgem. Chem.*, **307**, 113 (1961); J. R. Van Wazer and L. Maier, *J. Am. Chem. Soc.*, in press; (b) K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, in press; *Inorg. Chem.*, in press; also see (c) H. A. Skinner and N. B. Smith, *J. Chem. Soc.*, 2324, 3930 (1954).

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