2805 w, 2776 w, 2760 sh, 1950 w, 1728 m, 1686 s, 1681 s, 1502 m, 1487 sh, 1455 m, 1437 m, 1404 s, 1384 s, 1314 w, 1257 m, 1152 w, 1088 s, 1063 m, 865 w, and 657 s.

Infrared spectrum of Er(thd)$_3$·DMF: 2963 s, 2954 sh, 2929 sh, 2903 m, 2866 w, 2809 w, 1666 s, 1604 m, 1589 s, 1574 s, 1548 m, 1538 s, 1504 s, 1491 sh, 1478 m, 1459 sh, 1450 m, 1418 sh, 1414 s, 1403 s, 1385 s, 1357 s, 1284 w, 1244 w, 1225 m, 1195 m, 1177 w, 1140 m, 1102 w, 1085 sh, 1061 w, 1022 w, 960 w, 929 w, 869 m, 818 w, 719 w, 677 m, and 611 m. The bands at 791 m, 762 m, 755 m, and 735 m which were obscured in the spectrum of the sample dissolved in CCl$_4$ were observed in a mineral oil mull.

Infrared spectrum of Er(thd)$_3$: 2965 s, 2958 sh, 2932 sh, 2905 m, 2868 m, 1596 s, 1577 sh, 1571 s, 1567 sh, 1561 sh, 1555 sh, 1550 s, 1546 sh, 1537 sh, 1530 sh, 1522 sh, 1517 sh, 1509 s, 1502 s, 1493 sh, 1479 m, 1460 m, 1449 s, 1419 sh, 1406 s, 1401 s, 1388 s, 1357 s, 1300 sh, 1288 w, 1247 m, 1225 s, 1196 w, 1177 m, 1141 s, 1023 w, 961 w, 933 w, 929 w, 870 s, 720 m, and 611 m. The following bands, which were obscured in the CCl$_4$ solution, were observed in the spectrum of the sample run as a mineral oil mull: 819 w, 769 s, 765 s, 736 m, and 731 m.

New bands appearing in the Er(thd)$_3$·DMF spectrum which are not found in the spectrum of Er(thd)$_3$ are located at 1666, 1102, 1061, and 677 cm^{-1}, and are apparently due to the presence of DMF in the adduct. The absorption band at 657 cm^{-1} in the DMF spectrum, attributed to an N—C═O bending frequency, was shifted to 677 cm^{-1} in Er(thd)$_3$·DMF. The shift of this band to higher frequencies has been observed in the spectra of complexes of DMF with metal halides.[14] The band in DMF located at 1088 cm^{-1} has been variously assigned and observed to shift mostly to higher frequencies in DMF adducts of metal halides.[15] That this band may have shifted to 1102 cm^{-1} in the Er(thd)$_3$·DMF adduct is subject to question. The third absorption located at 1061 cm^{-1} in the adduct appears to originate from the unassigned 1063-cm^{-1} band in DMF.[16] Perhaps the most significant evidence for interaction between DMF and the erbium chelate is the shift of the carbonyl stretching frequency in DMF from 1686 to 1666 cm^{-1} in the Er(thd)$_3$·DMF adduct. The shift of this absorption to lower frequencies in DMF adducts of metal halides[15,16] appears to be a reliable criterion upon which to choose coordination by DMF through oxygen rather than nitrogen. This conclusion is also supported by our nmr evidence. The exact nature of the complex cannot be specified with the information available; the DMF could either be bonded to the metal or to some electron-acceptor site in the ligand shell. An X-ray analysis or perhaps fluorescence measurements of the type reported in ref 4 should shed further light on this problem.

The experimental evidence presented in this study demonstrates conclusively that the complexes prepared using the method of Hammond, *et al.*, are adducts with the formula Ln(thd)$_3$·DMF while those obtained by following the procedure suggested by Eisentraut and Sievers are unsolvated chelates with the formula Ln(thd)$_3$.

Acknowledgment.—This research was supported in part by the ARL In-House Independent Laboratory Research Funds, Office of Aerospace Research, U. S. Air Force.

---

(14) M. A. J. Jungbauer and C. Curran, *Nature*, **202**, 290 (1964).

(15) E. W. Randall, C. M. S. Yoder, and J. J. Zuckerman, *Inorg. Chem.*, **5**, 2240 (1966), and references therein.

(16) J. Archambault and R. Rivest, *Can. J. Chem.*, **36**, 1461 (1958).

CONTRIBUTION FROM THE LABORATORY OF
ANALYTICAL CHEMISTRY, FACULTY OF SCIENCE,
NAGOYA UNIVERSITY, CHIKUSA-KU, NAGOYA, JAPAN

Ionic Equilibria in Mixed Solvents. II. Hydrolysis of Beryllium Ion in a 0.1 Mole Fraction Dioxane–Water Mixture and in Aqueous Solution Containing 3 *M* LiClO$_4$ as an Ionic Medium

BY HITOSHI OHTAKI AND HIDEKI KATO

Received June 6, 1967

The preceding paper of this series[1] described the hydrolytic reaction of beryllium ion in a 0.2 mole fraction dioxane–water mixture containing 3 M LiClO$_4$ as an ionic medium and concluded that Be$_3$(OH)$_3$$^{3+}$ was the predominant species in the solution in which beryllium ion hydrolyzed.

In the present study the hydrolytic reaction of beryllium ion was examined in different solvent systems such as a 0.1 mole fraction (35.21% w/w) dioxane–water mixture and an aqueous solution containing 3 M LiClO$_4$ as an ionic medium, and results obtained were compared with the previous findings. Symbols used in the present paper are the same as those used in part I.[1]

Method of Measurements

The method of measurements was essentially the same as that employed in part I of this series. In aqueous solutions with $B \leq 0.0050\ M$, a technique of coulometric generation of hydroxide ions in the forward titrations and of hydrogen ions in the back titrations was employed and no solutions were added from the burets to the test solution.

The emf of the cell used may be written, at 25°, as

$$E = E^\circ - 59.15 \log h + E_j(h, B)$$

assuming the constant activity coefficient of hydrogen ion. E° is a constant involving the activity coefficient. h and B represent concentrations (moles per liter) of hydrogen and beryllium ions, respectively. The liquid junction potential, $E_j(h, B)$, is experimen-

---

(1) H. Ohtaki, *Inorg. Chem.*, **6**, 808 (1967).

tally estimated by the same methods described in part I.[1] The result is formulated as

$$E_j(h, B) = -11h + 7.4B \text{ (in mv)}$$

for a 0.1 mole fraction dioxane–water mixture, and for aqueous solution we have

$$E_j(h, B) = -16h + 4.1B \text{ (in mv)}$$

Experimental Section

All reagents and apparatus used were the same as those used in the preceding work.[1] For coulometric titration, a coulometric analyzer (Leeds and Northrup Co., Phila., Pa.) was employed as a current source. A constant current of 6.43 ma (4.000 μF/min) was used. Variation of the current was within 0.05%.

The cell assembly for coulometric titrations was

$$(-)\mathrm{Pt}\left|\,\mathrm{soln}\,\right|\begin{array}{l}3.00\ M\ \mathrm{LiClO_4}\\ \mathrm{soln}\end{array}\vdots\begin{array}{l}2.90\ M\ \mathrm{LiClO_4}\ \text{and}\\ 0.10\ M\ \mathrm{LiCl}\ \text{in aq soln}\end{array}\Big|\mathrm{Ag}(+)$$

for generation of hydroxide ions and

$$(-)\mathrm{Pt}\Big|\begin{array}{l}2.90\ M\ \mathrm{LiClO_4}\ \text{and}\\ 0.10\ M\ \mathrm{AgClO_4}\ \text{in aq soln}\end{array}\vdots\begin{array}{l}3.00\ M\\ \mathrm{LiClO_4}\ \text{soln}\end{array}\Big|\,\mathrm{soln}\,\Big|\mathrm{Pt}(+)$$

for generation of hydrogen ions.

All titrations were performed at 25.00 ± 0.01° in a paraffin oil thermostat, which was placed in a room thermostated at 25 ± 1°.

Evaluation of the Composition of Products and the Equilibrium Constants of Hydrolysis Reactions

Values of Z and log h at each series of B are represented graphically in Figures 1 and 2. The results in the present work are corrected for protolytic impurities which existed in solutions.[2] Thirty micromoles per liter of protolytic impurities of the apparent dissociation constant of pK = 4.6 was found for the solution of 3 M $\mathrm{LiClO_4}$ in a 0.1 mole fraction dioxane–water mixture, while the aqueous 3 M $\mathrm{LiClO_4}$ solution contained 45 μM protolytic impurities of pK = 5.4.

Table I

The Equilibrium Constants of the Hydrolytic Reactions of Beryllium Ion in the Systems of 0.2 and 0.1 Mole Fraction Dioxane–Water Mixtures and Aqueous Solution

System	Log $^*\beta_{1,1}$	Log $^*\beta_{1,2}$	Log $^*\beta_{2,1}$	Log $^*\beta_{2,2}$	Log $^*\beta_{3,3}$
0.2 mole fraction dioxane–water[1]	≤ -6.0	-3.66 ± 0.10	-10.84 ± 0.1	-7.15 ± 0.1	-8.75 ± 0.04
0.1 mole fraction dioxane–water	. . .	-3.29 ± 0.10	-11.5 ± 0.1	. . .	-8.65 ± 0.05
Aqueous solution	≤ -5.4	-3.27 ± 0.10	-11.5 ± 0.1	. . .	-8.74 ± 0.05

The composition of hydrolysis products was estimated by a method similar to that described in the preceding paper.[1] A plot of $\bar{q}$ *vs.* $2\bar{q} - \bar{p}^3$ suggested the presence of $\mathrm{BeOH^+}$, $\mathrm{Be_2OH^{3+}}$, and $\mathrm{Be_3(OH)_3{}^{3+}}$ complexes at $Z < 0.8$. In the region of lower B and higher Z, the formation of $\mathrm{Be(OH)_2}$ and $\mathrm{Be_2(OH)_2{}^{2+}}$ is anticipated.

Equilibrium constants $^*\beta_{1,1}$, $^*\beta_{1,2}$, $^*\beta_{2,1}$ $^*\beta_{2,2}$, and $^*\beta_{3,3}$ were refined by means of the least-squares method with a help of a computer, HITAC 5020E.

In the system of a 0.1 mole fraction dioxane–water mixture, neglect of $^*\beta_{1,1}$ and $^*\beta_{2,2}$ gave rise to only a slightly larger error-square sum than that of the five constants, so the existence of $\mathrm{BeOH^+}$ and $\mathrm{Be_2(OH)_2{}^{2+}}$ is not conclusive. In the aqueous solution system, on the other hand, neglect of $^*\beta_{1,1}$ and $^*\beta_{2,2}$ gave an appreciably larger error-square sum. Neglect of only $^*\beta_{2,2}$ gave almost the same error-square sum as that for the five constants. Thus the existence of $\mathrm{Be_2(OH)_2{}^{2+}}$ is doubtful in aqueous solution. The above considerations lead to the conclusion that the data in the system of a 0.1 mole fraction dioxane–water mixture could be explained with the set of $^*\beta_{1,2}$, $^*\beta_{2,1}$, and $^*\beta_{3,3}$. In the aqueous solution system, the data are better explained with the set of $^*\beta_{1,1}$, $^*\beta_{1,2}$, $^*\beta_{2,1}$, and $^*\beta_{3,3}$ than the set of $^*\beta_{1,2}$, $^*\beta_{2,1}$ and $^*\beta_{3,3}$. The final values of the constants are tabulated in Table I together with values reported previously.[1]

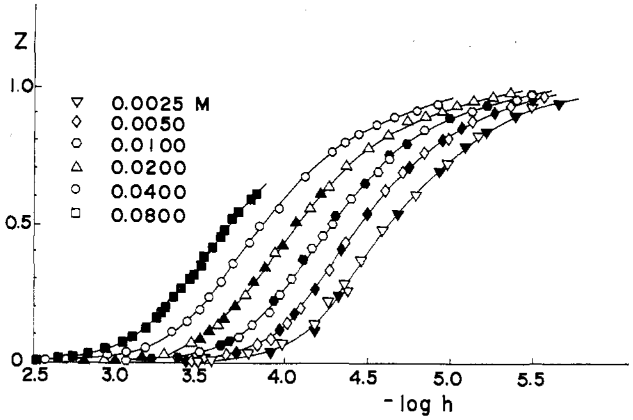

Figure 1.—Z as a function of $-\log h$ in a 0.1 mole fraction dioxane–water mixture system. Points with open symbols were obtained by forward titrations, and points with black symbols, by back titrations. Drawn curves were calculated with the final values of the equilibrium constants given in Table I.

Discussion

A brief survey has been described in part I for previous results on the beryllium hydrolysis. It has been confirmed by many investigators that $\mathrm{Be_3(OH)_3{}^{3+}}$ is the main product in aqueous solutions.[4–8] Now it is concluded that the species is the main one not only in the aqueous solution but also in dioxane–water mixtures.

The formation of $\mathrm{Be_2OH^{3+}}$ was also ascertained in all systems of aqueous and dioxane–water mixed solutions studied. The $\mathrm{Be(OH)_2}$ complex was evident in three systems in the present series of works. The species was also found by Kakihana and Sillén,[4] although the equilibrium constant determined in the aqueous 3 M

---

(2) H. Ohtaki, H. Kato, and K. Kunda, *Bull. Chem. Soc. Japan*, **40**, 1279 (1967).

(3) H. S. Dunsmore, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, **17**, 2644 (1963).

(4) H. Kakihana and L. G. Sillén, *ibid.*, **10**, 985 (1956).

(5) P. Schindler and A. B. Garrett, *Helv. Chim. Acta*, **43**, 2176 (1960).

(6) B. Carell and Å. Olin, *ibid.*, **15**, 1875 (1961).

(7) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **18**, 1015 (1964).

(8) E. Matijevic, *J. Colloid Sci.*, **20**, 322 (1965).

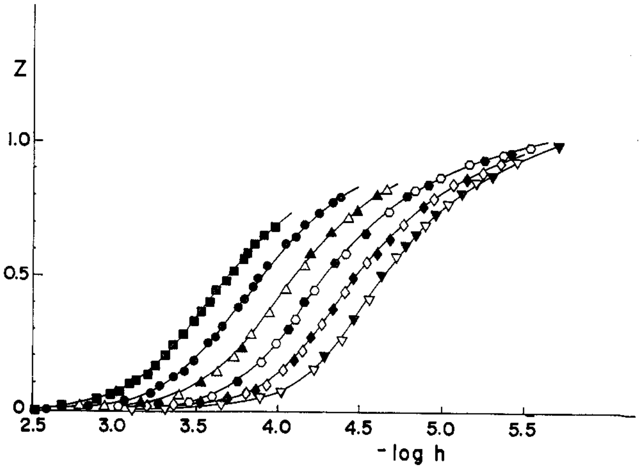

Figure 2.—*Z* as a function of −log *h* in the aqueous solution system. Symbols were the same as those in Figure 1. Curves were calculated with the values in Table I.

$LiClO_4$ medium in the present series of work was about 0.6 lower in the log $^*\beta$ unit than that reported by them in 3 *M* $NaClO_4$ medium. The change of the constant may be caused by the change of the medium salt.

The $Be_2(OH)_2^{2+}$ complex was found only in the system of the highest dioxane concentration studied. The presence of the species was thus not sure.

A slight decrease in the equilibrium constant of the formation of Be_2OH^{3+} was observed with an increasing concentration of dioxane in the solvent and an increase in the constant for $Be(OH)_2$ was found when the concentration of dioxane increased from 0.1 to 0.2 mole fraction. However, for such minor components the values of the equilibrium constants might be sensitive by a small uncertainty of the equilibrium constant of the main species and small experimental errors. Therefore, it seems reasonable to give a conclusion only for the main species: the equilibrium constant for the formation of $Be_3(OH)_3^{3+}$ is changed only to a very small extent with the solvent composition of dioxane–water mixtures.

Acknowledgment.—The authors wish to thank Professor Motoharu Tanaka for his great interest and valuable criticism.

CONTRIBUTION FROM THE CHEMICAL ENGINEERING
AND CHEMISTRY DIVISIONS OF ARGONNE NATIONAL LABORATORY,
ARGONNE, ILLINOIS 60439

Raman Spectrum of Xenon Hexafluoride

BY EARL L. GASNER AND HOWARD H. CLAASSEN

Received June 8, 1967

The structure of XeF_6 molecules has been the subject of a number of studies over a period of about 3 years. Because of experimental difficulties due to the reactivity of the material and because some of the properties of this molecule seem to be unique, the problem of structure continues to be a challenge.

Only incomplete infrared and Raman spectra have been reported. Smith[1] studied the infrared spectrum of the vapor from 400 to 1400 cm^{-1} and also reported an observation by George Begun of Raman bands for the solid at 655, 635, and 582 cm^{-1}. Hyman and Quarterman[2,3] observed Raman bands at 660, 620, and 600 cm^{-1} for XeF_6 dissolved in HF.

We have measured the Raman spectra of XeF_6 for the solid at ∼40°, for the liquid at 54 and 92°, and for the vapor at 94° and ∼2 atm pressure. A Spectra-Physics Model 125 laser was used as a source of ∼50 mw of exciting light at 6328 A. The exciting light was mechanically chopped at 400 cps. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ∼−50°, and an ac lock-in amplifier. The samples were contained in a cell that was a nickel block suitably drilled and fitted with sapphire or CaF_2 windows and thin Teflon gaskets. A hole 2 mm in diameter is drilled all the way through the 1 × 2 × 2 in. nickel block. It is closed at the top by a sapphire window through which the laser beam could enter and at the bottom by a mirror. A 20-mm long section of the 2-mm hole is milled open in the central section and covered by a calcium fluoride window 30 mm in diameter to permit the scattered radiation to escape at right angles to the laser beam. The cell was designed for liquid samples, but was used also to study solid XeF_6 and to obtain preliminary results for the vapor.

The results of the study are shown in Figures 1–4. The traces of Figures 1 and 3 were obtained with the incident light polarized perpendicular to the line from sample to spectrophotometer slit. On Figures 2 and 4 traces are shown for both perpendicular and parallel polarizations of incident light. Polarization characteristics are indicated qualitatively in these figures rather than quantitatively because of the reflections from the cylindrical sample container. The frequencies given in the figures are, in most instances, average values obtained from several scans.

Figure 1 shows that definite changes in relative intensities and band shapes occur with changing temperature in the liquid. Comparison of Figures 2 and 3 shows a striking similarity between the spectra of the solid and of the lower temperature liquid. These observations indicate that the groups of four molecules whose xenon atoms are at corners of a tetrahedron in the solid[4] tend to persist in the liquid as polymers, probably tetramers. The band at 506 cm^{-1} increases by a factor of 3 to 5 in warming from 54 to 92° and is probably the only monomer band that is not overlapped by polymer bands. In the vapor, which is

---

[1] D. F. Smith, "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 300.

[2] H. H. Hyman and L. A. Quarterman, ref 1, p 278.

[3] H. H. Hyman, *Science*, **145**, 3634 (1964).

[4] P. A. Agron, C. K. Johnson, and H. A. Levy, *Inorg. Nucl. Chem. Letters*, **1**, 145 (1965).