

support the concept that the rate depends upon α and not upon some other process requiring the independent formation and growth of nuclei.

The addition of 1.0% iron(II) oxalate dihydrate as shown in Figure 2 reduced appreciably the time to reach 0.5 fraction decomposed, yet at this concentration iron(II) oxalate did not significantly alter the rate constant of the reaction. In the KD series of Table I the rate constants at 239 and 244° are 0.92×10^{-3} and $1.55 \times 10^{-3} \text{ sec}^{-1}$, respectively, and are essentially the same as the rate constants of the undoped K series of $0.83 \times 10^{-3} \text{ sec}^{-1}$ at 240° and $1.57 \times 10^{-3} \text{ sec}^{-1}$ at 244°.

The Arrhenius plot of Figure 4 includes data from two different samples and a sample containing added iron(II) oxalate. Both samples and the doped sample have the same energy of activation, and, of course, the energy of activation does not change as iron(II) oxalate is produced during the decomposition.

Reactions which increase in rate as decomposition proceeds have been called "autocatalytic."¹⁰ The addition of iron(II) oxalate or its formation *in situ* clearly increases the rate of the reaction but it does not do so by lowering the activation energy. Probably this type of reaction is not truly catalytic. A better name for the iron(II) oxalate might be an acceleratory agent. It functions in a manner that is opposite that of an inhibitor. An inhibitor in a simple sense may be considered to remove a reactive component so that the large number of events potentially possible from that active component does not take place. An acceleratory agent such as the iron(II) oxalate in the present

study makes possible the reaction of the activated complex but it does not lower the activation energy as a catalyst would be expected to do.

The activation step in the photochemical decomposition of potassium tris(oxalato)ferrate(III) has been described as the promotion of an electron from an oxalate to the antibonding E_g orbitals of the iron(III) to which it is coordinated.¹⁶ From a plot of quantum yield as a function of wavelength for solutions of potassium tris(oxalato)ferrate¹⁷ a threshold value of approximately 50 kcal mol⁻¹ can be estimated. This is sufficiently close to our value of 46 kcal mol⁻¹ that it is tempting to suggest that the thermal activation step is the same as that of the photochemical. Whatever may be the activation step, the presence of iron(II) ion is considered to be essential for the reaction of activated complex to products.

Conclusions

A new apparatus and new techniques have been used to study the kinetics and the chemistry of the decomposition of potassium tris(oxalato)ferrate(III) in the temperature range 233–262°. Both the kinetic results and the chemical observations support a simple mechanism for the decomposition that may be represented by the equation $d\alpha/dt = k\alpha(1 - \alpha)$.

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Hydrogen-1 and Indium-115 Nuclear Magnetic Resonance Hydration and Complex Formation Study of Indium Halide Solutions in Water-Acetone Mixtures

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A hydration and complex formation study of indium halide solutions in water-acetone mixtures has been carried out by proton and indium-115 nuclear magnetic resonance techniques. At -100° , the proton- and ligand-exchange rates in these solutions are slow enough to permit the direct observation of pmr signals for bulk water and water molecules in the In^{3+} primary hydration shell. From the relative intensities of these signals, cation hydration numbers were calculated. These results were correlated with indium-115 nmr measurements which revealed signals attributed to $\text{In}(\text{H}_2\text{O})_6^{3+}$ and InI_4^- in iodide solutions and InCl_4^- and InBr_4^- in the other halide systems. The data were interpreted in terms of indium hexahydrate and tetrahalide complexes, along with additional species at higher halide concentrations.

Introduction

In addition to electrochemical,^{1,2} Raman,³⁻⁵ and ion-exchange⁶⁻¹⁰ methods, recent publications have

demonstrated the utility of the direct proton magnetic resonance (pmr) technique as a complementary tool for

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investigating aqueous electrolyte solutions.¹¹⁻²⁹ When ligand and proton exchange are slowed sufficiently by lowering the temperature of the sample, separate pmr signals can be distinguished for water or other ligand molecules in the principal solvation shell of the cation and in bulk medium. This observation has resulted in the measurement of hydration numbers for several diamagnetic [Al^{3+} , Ga^{3+} , In^{3+} , Be^{2+} , Mg^{2+} ,¹¹⁻¹⁴ Sc^{3+} , Y^{3+} , Th^{4+} ,^{15,16} UO_2^{2+} , Sn^{4+} , Zn^{2+} ,¹⁷⁻²⁰ La^{3+} + 20] and paramagnetic [Co^{2+} ,²¹ Er^{3+} , Fe^{2+} , Ce^{3+} , Ni^{2+} + 20] cations, a quantitative evaluation of competitive solvation in aqueous solvent mixtures,²²⁻²⁵ a measure of proton-exchange rates,^{26,27} and an estimate of inner-shell, cation-anion complex formation.^{15-19,28,29}

In the last research area, pmr studies of tin halide¹⁸ and gallium halide^{28,29} complex formation were augmented with metal ion nmr measurements. Intercomplex exchange was slow enough ($\tau \approx 5 \times 10^{-4}$ sec) in the Ga^{3+} systems to permit the observation of separate metal ion signals for each complex. This led to an unambiguous identification of the dominant species present. A similar approach involving both pmr and indium-115 nmr techniques was used in the present study of aqueous acetone-indium halide solutions in the hope that the dominant species could be identified and the complexing behavior of In^{3+} compared to Ga^{3+} . A correlation of these nmr data with the results of prior Raman³⁰⁻³² and indium-115 nmr³³ chemical shift investigations of pure aqueous solutions of indium halides also was anticipated.

Experimental Section

The indium perchlorate and halide salts (Alfa), the ultrapure hydrogen halide solutions (Brinkmann), and spectroquality acetone were used as received. The water content of the salts was determined by pmr signal intensity measurements. Solutions were prepared by weight using deionized water.

All pmr chemical shift and signal area measurements were made with a Varian A-60 spectrometer equipped with a variable-temperature probe for studies from -150 to $+200^\circ$. The method has been described in detail elsewhere^{18,22} and it con-

sists of cooling the sample in the spectrometer probe until separate signals for bulk and coordinated water molecules are observable. At these temperatures, -90 to -110° for In^{3+} solutions, the spectra were recorded and area measurements were carried out in triplicate with the electronic integrator of the spectrometer.

The indium-115 nmr measurements were carried out at the Bell Telephone Laboratories, Murray Hill, N. J., using a Varian DP-60 spectrometer operating in the wide-line mode at 13.1 MHz and 14.1 kG. The field scan was calibrated with a fluxmeter and frequency counter. All chemical shifts were referred to the indium-115 signal of a 3.5 *m* $\text{In}(\text{ClO}_4)_3$ solution, the position of which was essentially invariant with acid and acetone concentration. The chemical shifts were determined by making several recordings of the standard $\text{In}(\text{ClO}_4)_3$ solution signal and comparing these with the spectra of other In^{3+} solutions. The $\text{In}(\text{ClO}_4)_3$ reference signal was recorded at the beginning and end of each series to check the stability of the spectrometer. For reasons to be discussed later, the indium-115 nmr measurements were possible only at $+25^\circ$.

Results

Figure 1 illustrates the significant features of the

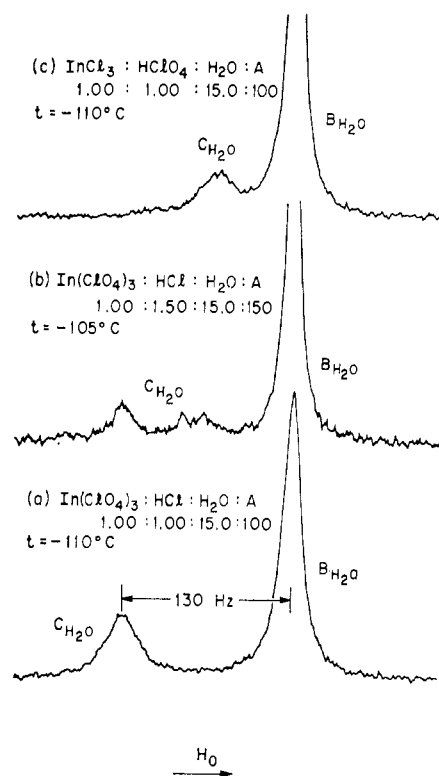


Figure 1.—The water pmr spectra of water-acetone solutions of In^{3+} containing (a) a 1:1, (b) a 1.5:1, and (c) a 3:1 mole ratio of Cl^- to cation, recorded on a Varian A-60 spectrometer. The signals arising from bulk water ($\text{B}_{\text{H}_2\text{O}}$) and water molecules in the In^{3+} solvation shell ($\text{C}_{\text{H}_2\text{O}}$) are labeled in the diagram and concentrations are given in mole ratios.

indium halide solution spectra. In addition to the bulk water signal at higher field, one or more coordinated water peaks were evident, the number depending on the halide concentration. From spectra such as these, the coordinated water pmr chemical shifts and the In^{3+} hydration numbers of Table I were determined. Since the pmr measurements were made between -90 and -110° , solution viscosity caused increased signal broadening particularly in those systems of lowest acetone content in each series. Thus, the precision of the hydration numbers is about 5% (0.1-0.2 unit) in most cases and 10% where the values are qualified with a

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TABLE I
CATION HYDRATION NUMBERS FOR INDIUM HALIDE
SOLUTIONS IN WATER-ACETONE MIXTURES

Mole ratios In ³⁺ :X ⁻ :H ₂ O:A ^a	In ³⁺ hydration no.	δ, ^b Hz		
		CH ₂ O ⁽¹⁾	CH ₃ O ⁽²⁾	CH ₂ O ⁽²⁾
Cl ⁻				
1.00:0.74:15.0:100	5.2	441
1.00:0.65:14.4:150	4.9	444
1.00:1.00:15.0:50	4.2	446
1.00:1.00:15.0:75	4.3	446
1.00:1.00:15.0:100	4.4	442
1.00:1.00:15.0:150	4.5	442
1.00:1.50:15.0:100	4.0 (overlap)	439	385 (av)	
1.00:1.50:15.0:150	3.7	443	397	381
1.00:3.00:15.0:50 ^c	2.8 (broad)	...	(Broad)	
1.00:3.00:15.0:75 ^c	3.2 (broad)	...	340 (av)	
1.00:3.00:15.0:100 ^c	3.1	...	332 (av)	
1.00:3.00:15.0:150 ^c	3.0	...	335	
1.00:4.60:15.5:100	(Broad)	...	336 (av)	
Br ⁻				
1.00:1.00:15.0:50	4.6	441
1.00:1.00:15.0:100	4.6	448
1.00:1.00:15.0:150	4.5	447
1.00:1.50:15.0:100	(Overlap)	440	398	380
1.00:3.00:8.1:50	1.3	...	394	374
1.00:3.00:14.0:100	1.2	...	400	382
1.00:3.00:15.7:100 ^c	1.2	...	388	368
1.00:3.60:16.3:100	0.6 (broad)	...	380 (av)	
1.00:4.00:16.6:100
I ⁻				
1.00:1.00:15.0:50	4.6	441
1.00:1.00:15.0:100	4.4	444
1.00:1.00:15.0:150	4.1	445
1.00:3.00:8.0:50	2.0	430	396	376
1.00:3.00:15.0:100	2.2	436	400	380
1.00:3.00:15.0:100 ^c	2.3	430	396	375
1.00:3.50:8.8:100	1.1	...	395	375
1.00:4.20:18.0:100

^a In(ClO₄)₃ was used with the particular hydrogen halide in those systems containing less than a 3:1 mole ratio of halide to In³⁺. The indium trihalides were used at 3:1 mole ratios or greater, with excess halide added in the form of the hydrogen acid. ^b δ is defined as ν(CH₂O) - ν(internal acetone). CH₂O⁽¹⁾ refers to the coordinated water peaks appearing at lowest field in the spectra (see Figures 1-3), while the higher field coordinated water peaks are designated by CH₂O⁽²⁾ and CH₃O⁽²⁾. ^c The solution was acidified with HClO₄ to a 1:1 mole ratio with In³⁺.

notation that the signals were broad. The chemical shift measurements were made with respect to internal acetone, with a precision of ~1% (~5 Hz). A calibration indicated that at these concentrations, the position of the acetone signal is constant within this precision limit. The lack of a shift or hydration number entry in Table I indicates that the particular coordinated water peak could not be detected.

The position of the bulk water signal is not listed in Table I since it varies markedly with acid and solvent concentration and temperature. Generally a decrease in temperature or the addition of acid causes a displacement of the bulk water peak to lower field, whereas an increase in acetone concentration produces an upfield shift. These observations can be interpreted qualitatively in terms of hydrogen bonding and protonation.^{34,35} It also should be noted that although the presence of large amounts of acetone is necessitated by the low temperatures which must be achieved to slow proton exchange, the inert nature of this solvent com-

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ponent has been demonstrated repeatedly.^{13,14,22,23} In all spectra no signal for coordinated acetone could be observed. Thus, the hydration numbers in Table I represent the total number of solvent molecules in the principal solvation shell of In³⁺.

Typical indium-115 nmr spectra are shown in Figures 2 and 3, and the chemical shift and line width data de-

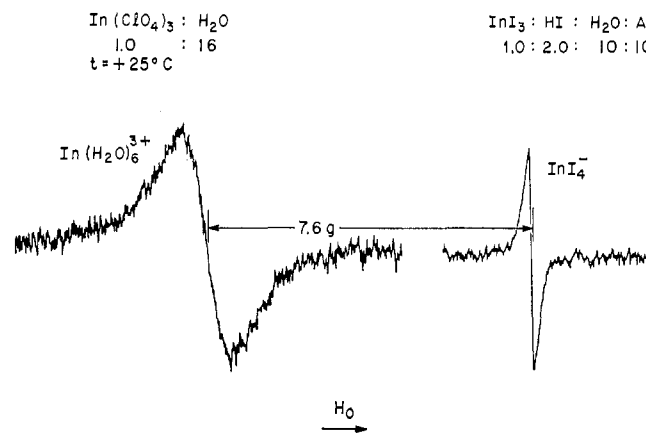


Figure 2.—The indium-115 nmr spectra for (a) an In(ClO₄)₃ solution in water and (b) a water-acetone solution of InI₃ containing added HI. The spectra were recorded on a Varian DP-60 at 13.1 MHz and 14.1 kG. The species responsible for the signals are labeled, and concentrations are given in mole ratios.

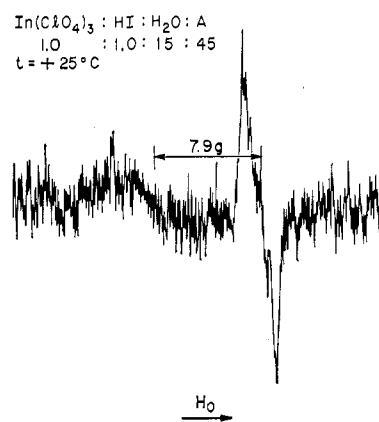


Figure 3.—The indium-115 nmr spectrum of a water-acetone solution of In(ClO₄)₃ containing a 1:1 mole ratio of I⁻ to In³⁺, recorded on a Varian DP-60. The concentration is given in mole ratios.

rived from all solutions studied are listed in Table II. The δ values were calculated from 10⁶[H(standard) - H(solution)]/H₀, where H₀ is 14.1 kG, and Δν_{1/2} is the peak to peak width of the indium-115 derivative signal. At halide to In³⁺ mole ratios of 1:1 and 2:1 in the Cl⁻ and Br⁻ systems, an indium-115 signal could not be observed. Thus, entries for only higher mole ratios are given. Studies were possible at more concentrations of iodide ion, as shown in Table II. In Figure 3, at 1:1 mole ratios of I⁻ to In³⁺, two indium-115 nmr signals were observed with the chemical shifts noted in Table II. At higher I⁻ ion concentrations, the broad signal at lower field could no longer be detected. The nmr data of Table II are precise to about 5-10%.

Discussion

A previous pmr hydration number study demonstrated that the In³⁺ ion is hexahydrated in aqueous

TABLE II
INDIUM-115 CHEMICAL SHIFT AND LINE WIDTH DATA FOR INDIUM
SALT SOLUTIONS IN WATER-ACETONE MIXTURES AT +25°

Soln mole ratios	δ^a , ppm	$\Delta\nu_{1/2}$, Hz
In(ClO₄)₃:HClO₄:H₂O:A		
1.00:0:16:0	Taken as standard	2,240
1.00:1.0:20:0	~+10	1,780
1.00:1.0:20:20	~+10	3,920
1.00:2.0:15:15	Broad	~18,000
InCl₃:HClO₄:H₂O:A		
1.00:0:4.0:4.0	Not observable	
1.00:1.0:10:10	Not observable	
1.00:0:4.0:12	+430	1,950
1.00:1.0:10:30	+465	1,680
1.00:1.0:6.0:20	+440	1,600
1.00:0:4.0:20	+480	1,120
1.00:1.0:6.0:28	+440	1,030
1.00:0:4.0:28	+430	840
InBr₃:HClO₄:H₂O:A		
1.00:1.0:10:10	+188	2,060
1.00:1.0:10:30	+210	470
1.00:1.0:10:40	+160	185
1.00:1.0:10:80	+180	185
InBr₃:HBr:H₂O:A		
1.00:1.0:5.0:5.0	+195	560
1.00:1.0:5.0:15	+185	260
1.00:2.0:10:10	+180	310
1.00:2.0:10:20	+180	190
1.00:2.0:10:100	+185	160
In(ClO₄)₃:HI:H₂O:A		
1.00:1.0:15:15	-555, -2	470 ^b
1.00:1.0:15:30	-560, -15	140
1.00:1.0:15:45	-600, -30	190
1.00:1.0:15:60	-555, -4	190
1.00:1.0:15:75	-575, -4	220
1.00:1.0:15:150	-620, -7	210
1.00:2.0:20:20	-500	280
InI₃:HClO₄:H₂O:A		
1.00:1.0:10:10	-540	470
1.00:1.0:10:30	-530	280
1.00:1.0:10:40	-550	220
1.00:1.0:10:80	-550	170
InI₃:HI:H₂O:A		
1.00:1.0:5.0:5.0	-530	1,330
1.00:2.0:10:10	-540	390

^a δ is defined as $10^6[H(\text{standard}) - H(\text{soln})]/H_0$, where H_0 is 14,092 G. A positive value indicates resonance at a lower magnetic field than the standard In(ClO₄)₃ solution. ^b The line widths in this series refer to the high-field (-500 to -620 ppm) signal. The low-field peak was approximately 5000 Hz wide in all cases.

acetone solutions of the perchlorate salt.¹³ In fact, at solvent concentrations similar to those of Tables I and II, this anion is unable to displace water molecules from the solvation shell of any cation studied thus far.^{13,16-18} This property is not surprising in view of the low relative basic strength of ClO₄⁻ ion, and it allows the determination of the maximum hydration number of the cation present. In contrast to this behavior, the complexing tendencies of the halide ions are much greater as seen from the pmr hydration data of Table I. Since competitive solvation on the part of acetone can be ruled out, the decrease of the In³⁺ hydration number can be interpreted reasonably in terms of inner-shell complex formation, that is, a replacement by halide ions of water molecules in the primary solvation sheath of the cation. For example, at a 1:1 mole ratio of halide to In³⁺, the average In³⁺ hydration number has decreased from 6.0 to about 4.4-4.6. This value decreases to 3.9 at a 1.5:1 mole ratio of Cl⁻ to In³⁺, and

in the 3:1 solutions, In³⁺ hydration numbers of 3.0, 1.3, and 2.2 were measured in the presence of Cl⁻, Br⁻, and I⁻ ion, respectively. Measurements at 1.5:1 (Br⁻ and I⁻) and 2:1 (all halides) mole ratios were precluded by the low field displacement of the bulk water peak and subsequent signal overlap. More evidence for the presence of indium(III) halide complexes in these solutions is provided by the multiple patterns observed for the signals of coordinated water shown in Figure 1.

It is tempting to account for these data by postulating the formation of successive In³⁺-X⁻ complexes, but this approach is not consistent with the experimental observations. For example, as seen in Figure 1, at halide to In³⁺ mole ratios of 1:1 or less, only one coordinated water peak is observed, rather than the pattern that would arise from the simultaneous presence of species represented by InX_{*n*}(H₂O)_{6-*n*}^{3-*n*}, where *n* is 0, 1, 2, 3, etc. Rapid proton or ligand exchange between these complexes or selective exchange between one or more of these species with bulk water could produce the one bound water peak observed. This does not seem likely since signals for other complexes are observed at slightly higher halide concentrations. The possible superposition of the bulk water signal and coordinated water peaks was checked by addition of paramagnetic Cu²⁺ to several of these systems. This procedure has the effect of selectively broadening the bulk water signal.³⁶ No other coordinated peaks were evident. Thus, the assumption that only one hydrated In³⁺ complex is present up to a 1:1 mole ratio of halide to cation is reasonable. If so, the choice of this complex must be consistent with the observed average In³⁺ hydration number, the chemical shift of the coordinated water protons in each halide solution, and the lack of appreciable dependence of the hydration number on acetone concentration, that is, dielectric constant. This last feature indicates that complex formation is essentially complete over the acetone range covered. The similar chemical shifts observed for bound water in the three 1:1 halide systems, that is, 444, 445, and 443 Hz downfield from internal acetone for the Cl⁻, Br⁻, and I⁻ ion solutions, may reflect the presence of the same species in each case, one whose chemical shift would not depend critically on the anion. In addition, the average In³⁺ hydration number of ~4.4 narrows the possible choices of complexes, particularly if only one hydrated complex is present. A combination which is consistent with all these experimental results is In(H₂O)₆³⁺ and InX₄⁻. One bound water signal would be observed if these were the dominant species, the chemical shift of the water protons of In(H₂O)₆³⁺ would not be expected to vary significantly from one halide system to another, and provided complexing were complete, an average In³⁺ hydration number of 4.5 would be predicted. It is important to note that the combination of In(H₂O)₆³⁺ and InX₆³⁻ would imply a hydration number of 5.0, a value higher than that observed.

At higher halide ion concentrations, it is apparent from Figure 1 that the formation of one or more additional complexes has occurred. The coordinated water portion of the pmr spectra of 1.5:1 halide to In³⁺ solutions consists of three signals, that is, the peak previ-

ously assigned to $\text{In}(\text{H}_2\text{O})_6^{3+}$ and a doublet at slightly higher field. The doublet designated by $\text{C}_{\text{H}_2\text{O}}^{(2)}$ and $\text{C}_{\text{H}_2\text{O}}^{(3)}$ in Table I can arise from different complexes or water molecules experiencing different electronic environments in the same complex. Within the limits introduced by line width, the two high-field bound water peaks are roughly equally intense, and their appearance and intensity vary similarly with halide concentration. These features, however, provide only qualitative evidence that one complex is responsible for both signals. At a 3:1 mole ratio of X^- to In^{3+} , the coordinated water signal at lowest field [$\text{C}_{\text{H}_2\text{O}}^{(1)}$ in Table I] is no longer apparent in the Cl^- and Br^- solution spectra (see Figure 1) but it is still present in the I^- case.

In view of the possible mixed or even polymeric complexes which may exist at these intermediate halide concentrations, a detailed identification of all the species present was not possible. However some general observations are of interest. The Cl^- and Br^- data of Table I show that the complexing process varies to some extent in each halide system. The principal features at a 3:1 halide to In^{3+} mole ratio are (a) the coordinated water signal at lowest field is no longer present (Figure 1c), (b) the bound water pattern that remains is a broadened singlet displaced ~ 50 Hz upfield from the previous doublet in the Cl^- solutions, while the doublet appearance and position is essentially unchanged in the Br^- solution spectra, and (c) the hydration numbers decrease to 3.0 and 1.3 in the presence of Cl^- and Br^- , respectively. The spectra rule out the presence of appreciable amounts of $\text{In}(\text{H}_2\text{O})_6^{3+}$ in these two systems, leaving a combination of InX_4^- and intermediate species to account for the hydration data. The lower In^{3+} hydration number in the presence of Br^- is evidence for a higher concentration of InBr_4^- . This proposed reduced tendency for the formation of InCl_4^- is supported by the higher Cl^- concentration (5:1) required to eliminate the bound water signal entirely.

The above discussion emphasizes the need for supplemental metal ion nmr measurements in studies of this type. This is particularly true when nonhydrated complexes, such as InX_4^- , possibly are present. In turn, such experiments are complicated by the quadrupole moment exhibited by metal ions such as indium-115. If the local environment of an In^{3+} ion in solution is asymmetrical, as it would be in any complex containing both water molecules and halide ions in its principal solvation shell, strong interactions of the quadrupole moment with surrounding fluctuating electric field gradients result, the nucleus relaxation time is shortened, and the nmr signal is broadened, even to the point of no longer being observable. In symmetrical complexes, such as $\text{In}(\text{H}_2\text{O})_6^{3+}$ and InX_4^- , the metal ion nucleus experiences only small electric field gradients, the relaxation time is longer, and the nmr signal is sharp and detectable at surprisingly low concentrations. If the In^{3+} complexes are undergoing rapid exchange, one observes only a single resonance peak, with a chemical shift and line width which are the weighted average of all species involved. This is the situation in pure aqueous indium salt solutions at $+25^\circ$.³³ By analogy to the proton experiments just described, when the lifetime of an In^{3+} nucleus in a particular complex is longer than the reciprocal of the nmr signal separation

of the complexes, a signal can be observed for each species, in the absence of excessive quadrupole broadening.

Typical indium-115 spectra for $\text{In}(\text{ClO}_4)_3$ and InI_3 solutions are shown in Figure 2, with the probable In^{3+} species labeled. Recall the pmr spectra of comparable systems showed that $\text{In}(\text{H}_2\text{O})_6^{3+}$ dominates in ClO_4^- solutions and no coordinated water signal was observed at a 4:1 I^- to In^{3+} mole ratio. Although the indium-115 chemical shift of the $\text{In}(\text{ClO}_4)_3$ solution signal was invariant with acid and solvent concentration, the line width was sensitive to these parameters. The constancy of the chemical shift indicates that mixed complex formation or polymerization is not occurring, while the broadening observed with increasing acetone and perchloric acid concentration may reflect solvent-separated ion pairing between $\text{In}(\text{H}_2\text{O})_6^{3+}$ and ClO_4^- . At any rate, the $\text{In}(\text{ClO}_4)_3$ spectrum of Figure 2 was taken as a chemical shift value for uncomplexed In^{3+} .

In view of the pmr hydration number results, it was not surprising that the indium halide spectra were markedly dependent on salt and solvent concentration. At 1:1 and 2:1 mole ratios of Cl^- or Br^- to In^{3+} , an indium-115 signal could not be observed. This is not a sensitivity problem since more dilute solutions were studied successfully at higher halide concentrations. Rather, this feature must reflect signal broadening produced by rapid intercomplex exchange involving all species in solution, including asymmetrical types at the higher halide concentration.

However, exchange is definitely slower in the 1:1 I^- to In^{3+} solutions, for which, as seen in Figure 3, two indium-115 signals were evident. In Table II it is important to note the concentration range covered for these solutions; that is, the acetone to water mole ratio varied from 1:1 to 10:1, and the salt concentration varied from 0.9 to 0.1 *m*. Particularly at the lowest molality, indium-115 signals probably would be detectable only if the complexes involved were highly symmetrical. Moreover, the chemical shift of the broader signal at lower field corresponds closely to that of the reference $\text{In}(\text{ClO}_4)_3$ solution (see Table II), indicating that $\text{In}(\text{H}_2\text{O})_6^{3+}$ is responsible for this peak.

The much sharper signal observed with these 1:1 solutions occurred ~ 570 ppm upfield from the reference peak. At 2:1–5:1 I^- to In^{3+} mole ratios, only the sharper indium-115 peak could be observed, with a chemical shift varying from 500 to 550 ppm upfield from the reference. This is probably the same species in each case, demonstrating a chemical shift dependence on acid and solvent concentration. Single signals also were observed in the spectra of 3:1 Cl^- to In^{3+} solutions and 3:1–5:1 Br^- to In^{3+} solutions, pointing again to the probable presence of a symmetrical metal ion complex. The signals were broader by a factor of about 5 in the Cl^- solution spectra, presumably because of more rapid exchange, and they were positioned ~ 450 ppm downfield from the reference. The indium-115 signals arising from the Br^- solutions were ~ 185 ppm downfield from the reference, and they narrowed considerably with increasing acetone content. At these high halide concentrations, the amount of $\text{In}(\text{H}_2\text{O})_6^{3+}$ that could be present would be small. Recall, also, that the pmr spectra revealed no signal for this species in the 3:1 Cl^- and Br^- cases. As previously stated,

quadrupole broadening in any asymmetrical complexes most likely would prevent the detection of signals at these salt concentrations.

Attempts were made to slow exchange in the 1:1 and 2:1 Cl⁻ and Br⁻ systems by cooling the samples to 0°, but a signal still could not be detected. Calibration experiments with InI₄⁻ solutions showed that below 0°, viscosity broadening would be too severe to observe any peak. Bromine-79 nmr measurements also were made with these solutions, but complex formation with In³⁺ and the resultant quadrupole interactions broadened the signals beyond detection.

Based on the pmr and indium-115 nmr data of this study and the results of Raman³⁰⁻³² and indium-115 nmr measurements with similar indium halide systems,³³ the sharp indium-115 signal observed in all halide solutions can be attributed to the particular InX₄⁻ complex. The Raman spectrum obtained with a pure aqueous InI₃ solution containing excess HI corresponded unambiguously to tetrahedral InI₄⁻. Rapid intercomplex exchange and, perhaps, less extensive complexing prevented this observation in aqueous InCl₃ and InBr₃ solutions, but when these solutions were extracted with ethyl ether, the Raman spectra conclusively identified the presence of only tetrahedral InCl₄⁻ and InBr₄⁻. Although the salt and halide concentrations are lower in the present study, the large acetone concentrations and subsequent lowering of the dielectric constant would induce comparable complex formation. The previous indium-115 nmr study³³ revealed (a) a sharp signal for pure aqueous InI₃ solutions, shifted ~583 ppm upfield from a similar In(ClO₄)₃ reference peak, (b) one broad signal attributed to In³⁺ complexes undergoing rapid exchange in pure aqueous InCl₃ and InBr₃ solutions, and (c) single sharp signals shifted 440 and 180 ppm downfield from the reference peak, for ether-extracted solutions of InCl₃ and InBr₃, respectively. Based on symmetry considerations, the assumption that complexing would be favored in the ether solutions, and the previously cited

Raman studies,³⁰⁻³² the authors concluded that these sharp signals were due to the tetrahedral InX₄⁻ complexes.³³ The remarkable similarity of the chemical shifts (and line widths in the solutions of high acetone content) listed in Table II and those reported by Cannon and Richards for the extracted halide solutions means the same species are being observed in each case. Since the dielectric constants of the systems are both low, ~4 in ether and ~20 in the acetone solutions, complexing to a comparable extent would be expected.

Finally, the conclusions of this study may be compared briefly to the results of studies of similar gallium halide solutions.^{28,29,37-39} The formation of tetrahedral GaX₄⁻ complexes was demonstrated in pure aqueous solutions by Raman^{37,39} and ion-exchange³⁹ methods and in water-acetone mixtures by pmr and gallium-69 nmr techniques.^{28,29} However, the nmr data were consistent with combinations of GaX₄⁻ with only Ga(H₂O)₆³⁺, and no evidence was found for significant amounts of intermediate complexes.^{28,29} Thus, the complexing tendencies are stronger in the gallium halide solutions.

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Reactions of Lower Fluorides of Sulfur with Hydrogen Sulfide

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The reactions of H₂S with FSSF, SSF₂, SF₄, and SOF₂ were studied at low temperature, and the products were analyzed by nmr spectroscopy. In each case, one or more members of the sulfanes, H₂S_x, were produced. With excess H₂S, the major product is H₂S₆; with deficit H₂S, only H₂S_{≥6} is observed. The formation of sulfane is interpreted as resulting from a simple condensation process in the case of FSSF, condensation followed by rearrangement in the case of SSF₂, and formation of SSF₂ as an intermediate step in the case of SF₄.

Introduction

The reaction of SSF₂ with H₂S was reported by Seel and Göllitz² to give predominantly sulfur. Under cer-

tain unspecified conditions, the products consisted almost entirely of yellow oils. It was suggested that these oils might be fluorosulfanes, FS_nF, by analogy with the known reactions of chlorosulfanes with H₂S.³

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