iodide, since this implies that HI is a product of the radiolysis. The effect seems to be greater than can be attributed to experimental error.

According to the discussions above the rate of iodine production in ethyl iodide and presumably in the other alkyl iodides must depend on: (1) the net rate of I_2 production in the spurs; (2) the rate of production of thermal radicals in the spurs; (3) the ratio of HI to I_2 production. The question may be raised as to which of these factors is responsible for the fact that G_{I_2} with no added scavengers increases with increasing number of β-hydrogens in the molecule.[2,23] From Table II it may be seen that the effect is not attributable to the rate of thermal radical production (columns 2 and 6), that the net rate of I_2 production in the spurs does increase with increase in the β-hydrogen content, except in going from C_2H_5I to *sec*-C_4H_9I, (column 5) and that the ratio of thermal radical reaction with HI to reaction with I_2 also increases (column 7). The G value for reaction of thermal radicals with HI shows the smoothest increase as a function of the number of β-hydrogens in the molecule (column 8). Column 7 gives the total rate at which iodine is produced in the spurs by reactions 5 and 6, including the iodine which back reacts via the exchange reaction 9. As the carbon chain length of the alkyl iodide increases the number of bonds in the molecule other than the C–I bond increases. As a result of this the rate for C–I bond rupture might be expected to decrease; this was found experimentally. It can also be seen that the secondary iodides (isopropyl and *sec*-butyl) show slightly higher rates of C–I bond rupture than the corresponding primary compounds, which might be expected on the basis of bond strengths.

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MADISON, WISCONSIN

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[CONTRIBUTION NO. 503 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

The Formation of Thallium Chloride Complexes and their Extraction into Ether[1]

BY DONALD L. HORROCKS AND A. F. VOIGT

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The extraction of thallium(III) chloride into isopropyl ether has been studied using tracer techniques with Tl^{204}. Appreciable extraction occurs under conditions of high acidity, and the extraction is markedly dependent upon the ionic strength of the solution. In order to study the effect of varying acidity and chloride concentration over a wide range, the study was run at rather high ionic strength. The temperature coefficient and heat of extraction were determined in the range of 20–30°. The empirical formula of the extracted species was found to be $HTlCl_4$ and a higher complex, H_2TlCl_5, was found not to be extractable. At low chloride concentrations and low acidity the extraction cannot be explained completely by this mechanism and it is postulated either that $TlCl_3$ extracts or that $HTlCl_4$ ionizes in ether under these conditions.

The extraction of thallium(III) from hydrohalic acids into ether has been reported by several investigators.[2–6] It has been developed into an analytical method for separating thallium from most elements, except iron(III), gallium(III), gold(III), and some others. Aside from noting the optimum conditions for complete extraction of the thallium, no investigations of the nature of the extraction process have been made. This research was undertaken to obtain information about the thallium compound present in the ether phase, the dependence of the extraction upon the concentrations of acid and chloride, the temperature coefficient of the extraction and the extraction equilibrium constant. These should be of interest in comparison with the analogous Fe(III) which has been shown to extract into ether as $HFeCl_4$.[7]

Preliminary investigations of the extraction of thallium(III) from $HClO_4$–LiCl–$LiClO_4$ solutions into isopropyl ether showed appreciable extraction only at relatively high acid and chloride concentrations and also showed that the extraction depends very markedly upon the ionic strength. It was thus necessary to perform the investigations in solutions of constant, high ionic strength. On the other hand the sensitivity of the tracer method made it possible to do the experiments at low concentration, about 10^{-3} M, of thallium.

The results of these conditions was that the determination of the activity coefficients of the various ionic species was difficult, but not as difficult as it would have been at higher thallium concentrations. In estimating activity coefficients it was necessary to make some assumptions which may not be completely valid.

The distribution of thallium between phases was measured by tracer techniques over a range of

[1] Based in part on a thesis presented by Donald L. Horrocks to Iowa State College in partial fulfillment of the requirements for the Ph.D. degree, November, 1955.

[2] Rothe, *Stahl und Eisen*, **12**, 1052 (1892); **13**, 333 (1893).

[3] (a) A. A. Noyes, W. C. Bray and E. B. Spear, THIS JOURNAL, **30**, 489, 515, 559 (1908); (b) E. H. Swift, *ibid.*, **46**, 2375 (1924).

[4] I. Wada and R. Ishii, *Bull. Inst. Phys. Chem. Res. Tokyo*, **13**, 264 (1934); [*C. A.*, **28**, 3334 (1934)].

[5] H. M. Irving, *Quart. Rev.*, **5**, 200 (1951).

[6] H. M. Irving and F. J. C. Rossotti, *Analyst*, **77**, 801 (1952).

[7] N. H. Nachtrieb and J. C. Conway, THIS JOURNAL, **70**, 3547 (1948).

TABLE I

EMPIRICAL FORMULA OF SPECIES IN ETHER PHASE

Initial conditions	[Tl] × 10^4, moles/l.	[Cl^-] × 10^4, moles/l.	[H^+] × 10^4, moles/l.	Cl^-/Tl	H^+/Tl
3.0 *M* total concn., 0.10 *M* LiCl, 0.4 *M* $HClO_4$	6.66	2.75	5.7	4.13	0.86
3.0 *M* total concn., 0.4 *M* LiCl, 1.6 *M* $HClO_4$	8.63	3.8	8.6	4.39	1.00
2.0 *M* total concn., 1.0 *M* LiCl, 1.0 *M* $HClO_4$	5.75	2.70	5.9	4.69	1.02

chloride ion, acid and total salt concentrations. In the interpretation of the data, it was found advantageous to use formation constants determined by Benoit[8] for the various thallium(III) chloride complexes up to $TlCl_4^-$. Experimentally, this species, in the form of the acid, was essentially the only thallium compound found in the ether phase. Hence the distribution could be represented by a constant

$$K = \frac{(HTlCl_4)_e}{(H^+)_w(TlCl_4^-)_w} = \frac{[Tl_e]\,\gamma^e HTlCl_4}{(H^+)(Tl^{+3})(Cl^-)^4K_4} \quad (1)$$

in which ( ) represents activity, [ ] concentration, $K_4 = (TlCl_4^-)/(Tl^{+3})(Cl^-)^4$ and γ^e $HTlCl_4$ is the activity coefficient of $HTlCl_4$ in ether. This extraction coefficient, *K*, can be expressed in terms of the measured distribution ratio, $K_T = [Tl]_e/[Tl]_w$ by considering all of the aqueous chloride complexes of thallium, their formation constants of the form

$$K_n = \frac{(TlCl_n^{3-n})}{(Tl^{+3})(Cl^-)^n} \quad (2)$$

and the appropriate activity coefficients. The equation obtained is

$$K = K_T\frac{\gamma^e HTlCl_4}{(H^+)(Cl^-)^4K_4}\left[\sum_{n=0}^{5} K_n\gamma^n{}_{Cl^-}[Cl^-]^n/\gamma TlCl_n{}^{3-n}\right] \quad (3)$$

in which K_0 is set equal to 1. Hydrolyzed forms of thallium(III) were assumed to be unimportant at the acid concentrations used. Several series of extractions were made, each one at constant acidity and ionic strength, but with varying chloride concentration. Since the concentration of the ethereal thallium species was always small its activity coefficient was assumed constant. Thus a new extraction constant could be defined, as

$$K' = \frac{K(H^+)}{\gamma^e HTlCl_4} = \frac{K_T}{(Cl^-)^4K_4}\left[\sum_{n=0}^{5} K_n\gamma^n{}_{Cl^-}[Cl^-]^n/\gamma TlCl_n{}^{3-n}\right] \quad (4)$$

Materials.—Thallium(I) nitrate, obtained by dissolving thallium metal in HNO_3, was oxidized to thallium(III) by aqua regia. The thallium(III) chloride was extracted into ether from a 6 to 7 *N* HCl solution and precipitated as $Tl(OH)_3$ by shaking with a dilute NaOH solution. The $Tl(OH)_3$ was purified by repeated solution in 6 to 7 *N* HCl, extraction into ether and reprecipitation as $Tl(OH)_3$. The $Tl^{204}NO_3$ obtained from the Oak Ridge National Laboratory, Oak Ridge, Tennessee, was purified in this same manner.

A desired amount of the purified active and inactive Tl_2O_3 was dissolved in excess $HClO_4$ and the resulting solution standardized, the thallium determined as Tl_2CrO_4 as reported by Kleinberg[9] and the excess $HClO_4$ by titration with standard base, allowing for the titration of the thallium. The solution was 0.0106 *M* $Tl(ClO_4)_3$ in 4.05 *M* $HClO_4$.

The chloride and hydrogen ion concentrations were varied and the ionic strength was maintained constant by the use of standard solutions of LiCl, $HClO_4$ and $LiClO_4$.

Technique.—Aqueous solutions of the desired thallium(III), Cl^- and H^+ concentrations and ionic strength were extracted with equal volumes of isopropyl ether by mixing in a constant temperature bath with an automatic shaker. The temperature was 30° except for the study of temperature dependence. The solutions were shaken for 40 minutes and then allowed to separate for 30 minutes before the samples were removed with pipets. The ether samples were evaporated into 2 to 3 ml. of water. Analyses were made for acid, chloride and thallium. The acid and chloride analyses were done volumetrically, the thallium analyses radiochemically, with the addition of known amounts of carrier $Tl(NO_3)_3$ in HNO_3 to facilitate precipitation and filtration. The thallium, precipitated as Tl_2CrO_4, was filtered onto small paper discs, washed with alcohol and dried at 110°. The samples were covered with 3.3 mg./cm.^{2} cellophane discs and mounted on cardboard backing for counting.

Discussion

The temperature dependence of the extraction was determined in two series of extractions at temperatures of 20, 25 and 30°. In each series the chloride concentration was varied at constant acidity and ionic strength. The distribution ratio, K_T, decreased markedly as the temperature was increased, for example from a solution 0.2 *M* in LiCl, 0.6 *M* in $HClO_4$ and 1.53 *M* in $LiClO_4$, K_T was 4.0 at 20°, 2.5 at 25° and 1.5 at 30°. Values of ΔH of extraction were calculated by the Van't Hoff equation to be 9.5 ± 0.7 and 9.9 ± 0.3 kcal./mole at 0.4 and 0.6 *M* $HClO_4$, respectively, at an ionic strength of 2.33. Each of these values is the average of six or more calculations at different chloride concentrations.

The empirical formula of the compound in the ether phase was determined by analyzing this phase for chloride, ionizable hydrogen and thallium. Results in Table I have been corrected for the extraction of chloride and acid under identical conditions except for the absence of thallium. The high values observed for the Cl^-/Tl ratios are due principally to the small amounts present. From these data, it was assumed that the empirical formula of the ethereal species was $HTlCl_4$.

The observed distribution ratio, K_T, decreased as the chloride concentration was increased. Data at an ionic strength of 3.0 are shown in Fig. 1. Similar results were obtained at an ionic strength of 2.0. A reasonable explanation of this effect is the formation of a non-extractable species, such as $TlCl_5^{=}$. Since it was not possible to obtain sufficient data at low chloride concentrations to evaluate the constants for the mono to tetra-chloro complexes independently, the values of Benoit[8] were used. His determinations of these constants, defined as in equation 2 are for K_1, 1.38 × 10^8; K_2, 4 × 10^{13}; K_3, 6 × 10^{15}; and K_4, 10^{18}. Equation 4 was used with these constants in successive approximations to determine a value of K_5 which would give the best evaluation of K'. This treatment gave 2.96 × 10^{17} for K_5. In the region of very high ionic strength, about 5, the formation of

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[8] R. Benoit, *Bull. soc. chim. France*, 518 (1949).

[9] J. Kleinberg, "Collected Radiochemical Procedures," A.E.C. Document LA-1721, Los Alamos Scientific Laboratory, 1954.

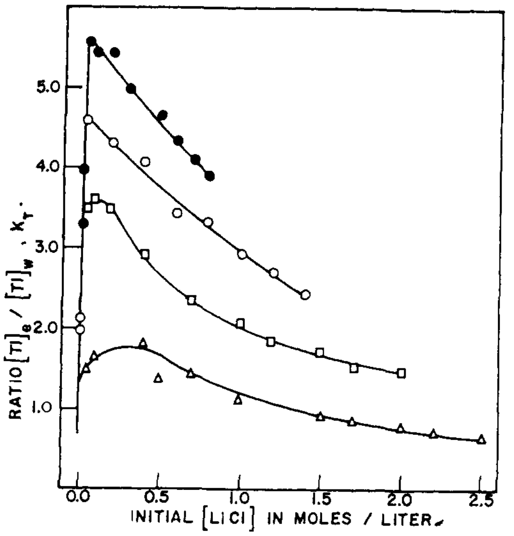

Fig. 1.—Extraction at total salt and acid concentration of 3.0 *M*: ●, 2.2 *M* $HClO_4$; O, 1.6 *M* $HClO_4$; □, 1.0 *M* $HClO_4$; △, 0.4 *M* $HClO_4$.

three phases was observed which has been described in the cases of $FeCl_3$ and $GaCl_3$ extraction.[10-12] The three phases are a "light ether," a "heavy ether" and an aqueous phase with 90–96% of the thallium in the heavy ether phase. Repetition of these experiments in the absence of thallium gave rise to the same phenomenon so that under these conditions it is caused by the high salt and acid concentration and not by the heavy metal complexes. In the case of solutions 4 *M* in $HClO_4$ and 1 *M* in LiCl plus $LiClO_4$, large amounts of the acid were found in the heavy ether layer. The explanation by Nachtrieb and Fryxell for the similar phenomenon in $FeCl_3$ extraction was that the acid H_2FeCl_5 was forming ethereal polymers by multiple hydrogen bonds. In the present case $HClO_4$ may be replacing the H_2FeCl_5 in such a polymer with ether molecules.

The difficulties of interpretation which were brought about by the three phase behavior at very high ionic strength made it necessary to conduct the more detailed study of the extraction at lower ionic strength. The total salt plus acid concentrations were kept at 2.0 and 3.0 *M* while the chloride and acid concentrations were varied. Equation 4 was used to calculate *K'* using the Debye–Hückel equation[13] for the estimation of the activity co-

$$-\log \gamma_i = \frac{AZ_i^2\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}}$$

efficients of the thallium species. As the various forms of thallium(III) are large ions, the product $B \times a_i$ was taken as 3 for all species. The activity coefficient of the chloride ion was assumed to be equal to the mean activity coefficient of HCl under the same conditions; values of 0.993 at 2.0 *M* HCl and 1.288 at 3.0 *M* HCl at 30° were used. The calculated values of *K'* are shown in Figs. 2 and 3.

The constant values of *K'* at all but the lowest chloride concentrations indicate that the description of the extraction in terms of extractable $HTlCl_4$ and non-extractable H_2TlCl_5 is valid. The sharp increase in the values of *K'* at low chloride

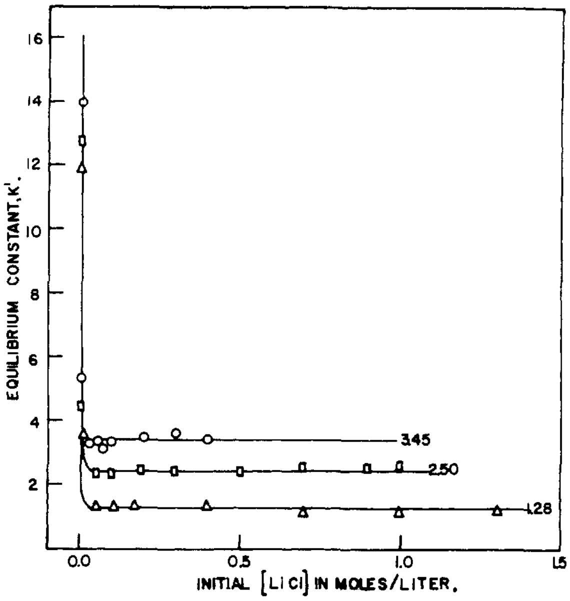

Fig. 2.—Dependence of *K'* upon [LiCl] at constant acid concentration for ionic strength equal to 2.0: O, 1.6 *M* $HClO_4$; □, 1.0 *M* $HClO_4$; △, 0.4 *M* $HClO_4$.

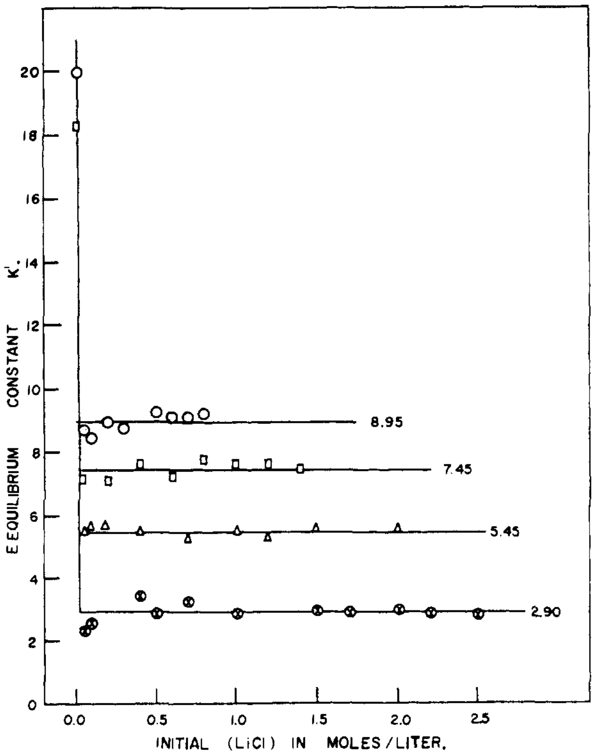

Fig. 3.—Dependence of *K'* upon [LiCl] at constant acid concentration for ionic strength equal to 3.0: O, 2.2 *M* $HClO_4$; □, 1.6 *M* $HClO_4$; △, 1.0 *M* $HClO_4$; ⊗, 0.4 *M* $HClO_4$.

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[10] R. W. Dodson, G. J. Forney and E. H. Swift, THIS JOURNAL, **58**, 2573 (1936).

[11] R. J. Myers and D. E. Metzler, *ibid.*, **72**, 3772 (1950).

[12] N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **71**, 4035 (1949); **74**, 897 (1952).

[13] I. M. Klotz, "Chemical Thermodynamics," Prentice-Hall, New York, N. Y., 1950, p. 329.

concentrations is attributed to one or both of two factors, the co-extraction of $TlCl_3$ or the ionization of $HTlCl_4$ in highly dilute ether solutions.

The directly measured extraction coefficient, K_T, showed a first-order dependence on the concentration of hydrogen ion. The quantity K', involving formation constants and activity coefficients, also showed such a relationship when plotted against the $HClO_4$ concentration as in Fig. 4. The linear acid dependence agrees with the idea that $HTlCl_4$ is the extracted species and in addition indicates that the activity coefficient of the hydrogen ion is constant at a given ionic strength.

The acid dependence is expressed in equations 1 and 4 and if these truly represent the data one would expect the curves of Fig. 4 to pass through the origin. The fact that they do not, indicates that at lower acid concentrations some other process is taking place which could be either the ionization of $HTlCl_4$ in ether or the co-extraction of $TlCl_3$.

Conclusions

The following results and conclusions can be drawn from this study.

The extraction was found to have a negative temperature coefficient in the range of 20 to 30°. An average value of ΔH of 9.7 ± 0.5 kcal. per mole was found under the conditions of the experiments.

In order to explain the reduced extraction at high acidities a non-extractable species with formula H_2TlCl_5 was postulated. The data were used to calculate its formation constant as 3.0×10^{17}.

The empirical formula of the extracted species was found to be close to $HTlCl_4$.

At a given ionic strength and acid concentration the extraction equilibrium constant was found to be essentially constant, independent of the chloride concentration except when this was quite low. The lack of constancy was possibly due to ionization of $HTlCl_4$ in the ether phase or to coextraction of the $TlCl_3$ species.

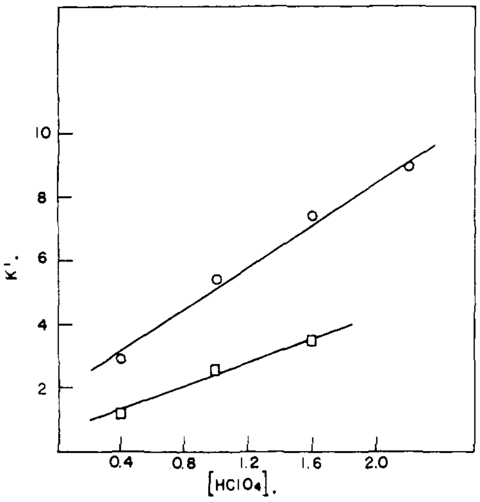

Fig. 4.—Dependence of K' upon $HClO_4$ concentration: ○, 3.0 *M* total salt and acid concentration; □ 2.0 *M* total salt and acid concentration.

The extraction was found to have a linear dependence on the hydrogen ion concentration in agreement with the supposition that $HTlCl_4$ was the species extracted. The fact that the extraction did not extrapolate to zero at low acidity agrees with the idea that $TlCl_3$ is extracting or that $HTlCl_4$ is ionizing in the ether phase. Values of the extraction coefficient at 30° are about 2.3 at an ionic strength of 2 and 4.3 at an ionic strength of 3 and relatively high acidities.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Solid Arsenic Hydrides

BY W. L. JOLLY, L. B. ANDERSON AND R. T. BELTRAMI

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Various methods for preparing solid arsenic hydrides have been evaluated as to yield and product composition. Atom ratios of hydrogen/arsenic as high as 0.52 have been observed for solid hydrides. A method has been developed for preparing an unstable, volatile arsenic hydride (probably biarsine, As_2H_4) from arsine by use of a silent electrical discharge.

I. Introduction

The literature contains many conflicting statements regarding the solid arsenic hydrides. Not only the compositions of these hydrides, but also their methods of preparation, have been the subject of dispute.[1] We have evaluated various preparative methods in terms of both yield and hydrogen content of the product. Several new preparative methods have been developed, including a method for the preparation of an unstable, volatile hydride (probably biarsine).

Some studies of the adsorption of arsine on arsenic have been made, in an attempt to elucidate the nature of the solid arsenic hydrides.

II. Results and Discussion

A. Reduction of Arsenic Solutions. 1. Reduction by $SnCl_2$.—Weeks and Druce[2] reported that a brown, amorphous arsenic hydride may be prepared by the action of an ether solution of stannous chloride on a solution of arsenic trichloride in aqueous hydrochloric acid

$$2AsCl_3 + 4SnCl_2 + 2H^+ + 2Cl^- = As_2H_2 + 4SnCl_4$$

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[1] See, for example, "Gmelins Handbuch der Anorganischen Chemie," System-Nummer 17, Verlag Chemie, G. m. b. H., Weinheim/Bergstrasse, 1952, pp. 195–200.

[2] E. J. Weeks and J. G. F. Druce, *Chem. News*, **129**, 31 (1924).