given by Åkerlöf[7] were used. Values of r based on Åkerlöf's constants and the experimental data seem to be a linear function of the mole fraction of the non-electrolyte in the solution. This function may be expressed by $r = a + bN$. The constants a and b vary from alcohol to alcohol, whereas a at least would be expected to be the same for all of the non-electrolytes involved.

The experimental results and the values of r calculated on the basis of Åkerlöf's dielectric constants are given in the Table. S denotes the solubility in millimoles per liter, and P denotes the weight per cent. of the alcohol.

Summary

The solubility of silver bromate in mixtures of methanol, ethanol, n-propanol and isopropanol with water was determined at 25°. The data were found to be incompatible with the Born electrostatic formula.

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[7] Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 33]

Some Reactions of Anhydrous Thorium Tetrabromide with Organic Liquids

BY RALPH C. YOUNG

As the first step in the study of reactions of metals on non-aqueous solutions of thorium tetrabromide, experiments were carried out to find the results of the action of thorium tetrabromide alone on certain organic liquids.[1] With ethyl alcohol, ethyl acetate, methyl cyanide and pyridine at temperatures as high as the boiling points of the respective solutions, molecular compounds were formed having the formulas, $ThBr_4\cdot 4C_2H_5OH$, $ThBr_4\cdot 2CH_3COOC_2H_5$, $ThBr_4\cdot 4CH_3CN$, $ThBr_4\cdot 3C_5H_5N$. At room temperature $ThBr_4\cdot 4C_6H_5NH_2$ was formed but at the boiling point of the solution of thorium tetrabromide in aniline other reactions occurred. Matthews has reported the formation of $ThBr_4\cdot C_5H_5N$ and $ThBr_4\cdot 4C_6H_5NH_2$ both in ether solution.[3]

The molecular compounds $ThBr_4\cdot 3C_6H_5COOC_2H_5$, $2ThBr_4\cdot 7C_6H_5COCH_3$ and $ThBr_4\cdot 4C_6H_5CHO$ were obtained in the reaction of thorium tetrabromide with ethyl benzoate, acetophenone and benzaldehyde at room temperature, while at their respective boiling points, thorium tetrabromide reacted rapidly as follows with these liquids; ethyl bromide and thorium benzoate were formed from the reaction of the halide with the ester, and the hydrated thoryl bromide organic complexes, $ThOBr_2\cdot 0.5C_6H_5COCH_3\cdot H_2O$ and $ThOBr_2\cdot 2C_6H_5CHO\cdot H_2O$ were precipitated when solutions of the tetrabromide in these other solvents were boiled; an equivalent amount of hydrogen bromide was eliminated and water was also formed by condensation reactions of the solvents. The tendency of thorium to retain two of its bromine atoms is also shown in reaction with propiophenone, in which case, $ThOBr_2\cdot 0.5C_6H_5COC_2H_5\cdot 2H_2O$ precipitated from the boiling solution. Continued heating of these reaction mixtures, accompanied by a slow distillation of the solvents, caused a further removal of the bromine only at a very slow rate.

Rosenheim, Santer and Davidson[4] report that benzaldehyde and thorium tetrachloride when heated together react, hydrogen bromide being evolved, and they suggest a formula, $ThCl_2(C_6H_5CO)_2$, for the resulting product, which formula they say "must be taken with reserve" as there was no analysis made for the organic residue and that for thorium failed to check well the above formula. With thorium tetrabromide it has been found that if oxygen was not carefully excluded in its reaction with benzaldehyde or if the benzaldehyde was not free from benzoic acid, the bromine was partially displaced by the benzoic acid radical, hydrogen bromide being evolved, and there was formed a product, insoluble in benzaldehyde, of composition, $ThBr_2(C_6H_5COO)_2\cdot 3C_6H_5CHO$.

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(1) Comparison of the stabilities toward heat of the lower anhydrous bromides of titanium and zirconium[2] indicates that at only relatively low temperatures would a lower valence bromide of thorium be stable. Anhydrous titanous bromide has been produced by the action of mercury or silver on titanium tetrabromide in benzene solution.[2]

(2) Young with Schumb, THIS JOURNAL, **52**, 4233 (1930); Young, *ibid.*, **53**, 2148 (1931).

(3) Matthews, *ibid.*, **20**, 839 (1898).

(4) Rosenheim, Santer and Davidson, *Z. anorg. Chem.*, **35**, 424 (1903).

Experimental

In the production of thorium tetrabromide, nitrogen was bubbled through bromine and then passed into a quartz tube containing a mixture of dry thorium dioxide and dry sugar charcoal at a temperature of approximately 900°. The product which collected at the cool end of the tube in the form of a white powder and crystalline masses was resublimed. The resublimed white crystalline thorium tetrabromide, which analysis showed to be pure, was collected in a 10-mm. Pyrex tube connected at one end to a vacuum pump operating at 1 mm.; the other end joined to a 22-mm. Pyrex tube which served to hold the crude material was heated to approximately 550° in an electric furnace. Glass wool at the junction of the two tubes prevented accidental mixing.

The organic solvents used were all of Eastman grade, carefully dried and fractionated. Reactions were carried out in an atmosphere of dry nitrogen with 2 g. of thorium tetrabromide and 20 g. of the solvent. Compounds in Table I numbered 1, 2, 3, 5, 6, 8 and 11 were obtained from solutions which had been boiled for approximately twenty-five minutes. A small amount of solvent was distilled, to remove water and hydrogen bromide, from the reaction mixtures of 3, 5 and 8. In other cases reactions were carried out at room temperature. Table II gives the analytical results.

TABLE I

PREPARATION AND PROPERTIES OF COMPOUNDS

	Compound	Method of separation from reaction mixture	Dried in vac. after washing with	Color and solubility
1	$ThBr_4 \cdot 4CH_3CN$	Filtration	Pet. ether	White, sl. sol. in acetonitrile, sol. in water
2	$ThBr_4 \cdot 4C_2H_5OH$	Solvent distilled	Pet. ether	White feathery crystals, sol. in alc., water
3	$ThOBr_2 \cdot 0.5C_6H_5COCH_3 \cdot H_2O$	Filtration	Benzene	Yellow, insol. in acetophenone, sol. in water
4	$2ThBr_4 \cdot 7C_6H_5COCH_3$	Pptd. by pet. ether, filtered	Pet. ether	White, sol. in acetophenone, water
5	$ThOBr_2 \cdot 0.5C_6H_5COC_2H_5 \cdot 2H_2O$	Filtration	Benzene	Pale yellow, insol. in propiophenone, sol. in water
6	$ThBr_4 \cdot 2CH_3COOC_2H_5$	Solvent distilled	Pet. ether	White needle-like crystals, sol. in ethyl acetate, water
7	$ThBr_4 \cdot 3C_6H_5COOC_2H_5$	Pptd. by pet. ether, filtered	Pet. ether	White, sol. in ethyl benzoate, water
8	$ThOBr_2 \cdot 2C_6H_5CHO \cdot H_2O$	Filtration	Benzene	Pale brown, sol. in benzaldehyde, water
9	$ThBr_4 \cdot 4C_6H_5CHO$	Pptd. by pet. ether, filtered	Pet. ether	White, sol. in benzaldehyde, water
10	$ThBr_4 \cdot 4C_6H_5NH_2$	Ppt. by sol. of benzene ($^1/_3$) and pet. ether ($^2/_3$), filtered	Bz–pet. ether	White, sl. sol. in aniline, sol. in water
11	$ThBr_4 \cdot 3C_5H_5N$	Filtration	Benzene	White, very sl. sol. in pyridine, sol. in water

TABLE II

ANALYTICAL RESULTS

Compound	Thorium, %		Bromine, %		Nitrogen, %						Atomic ratios	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Th:Br	H:C
1	32.43	32.42	44.65	44.85	7.82	7.47					1:4.03	
		32.70		44.57		8.14					1:3.96	
									C_2H_5OH, %			
2	31.54	31.86	43.46	43.52					25.00	25.05	1:3.97	
		31.85		43.75						24.82	1:3.99	
					Hydrogen, %		Carbon, %		$C_6H_5COCH_3$, %			
3	47.76	47.28	32.92	32.94	1.23	1.55	9.88	10.96	12.34	11.24	1:2.01	1.66:1
		47.25		32.86		1.60		11.17		12.09	1:2.03	1.73:1
									$C_6H_5COCH_3$, %			
4	23.68	23.87	32.89	32.52					43.20	41.15	1:3.97	
		24.07		32.99						39.14	1:4.00	
									$C_6H_5COC_2H_5$, %			
5	45.43	45.81	31.28	32.02	1.76	1.93	10.56	9.54	13.11	12.44	1:2.03	2.35:1
		46.34		32.20		1.68		9.82		13.01	1:2.01	2.11:1

TABLE II (*Concluded*)

Compound	Thorium, %		Bromine, %		Nitrogen, %						Atomic ratios	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Th:Br	H:C
									$CH_3COOC_2H_5$, %			
6	31.89	31.92	43.92	43.79					24.18	24.36	1:3.98	
		32.12		43.12						24.34	1:3.99	
									$C_6H_5COOC_2H_5$, %			
7	23.17	23.00	31.91	32.48					44.92	44.19	1:4.10	
		23.74		32.48						44.54	1:3.97	
									C_6H_5CHO, %			
8	36.49	36.64	25.06	25.48	2.19	2.26	26.33	26.82	33.23	27.51[a]	1:2.02	1:0.99
		36.13		25.86		2.35		26.15		27.21	1:2.07	1:0.94
9	23.79	25.22[b]	32.76	34.05					43.45	39.25	1:3.84	
		25.60		33.83						39.75	1:3.93	
									$C_6H_5NH_2$, %			
10	25.12	25.05	34.61	35.55					40.27	40.15	1:4.12	
		25.61		35.58						39.70	1:4.03	
									C_5H_5N, %			
11	29.42	28.47	40.52	41.15					30.04	28.59	1:4.19	
		28.32		41.07						28.86	1:4.21	

[a] The low percentage of benzaldehyde found is likely due to its conversion into benzoic acid.

[b] The analyses of (9) indicate that the bromine was being displaced slowly at room temperature.

Summary

With certain organic liquids, anhydrous thorium tetrabromide reacts only to form molecular compounds up to temperatures as high as the boiling points of the respective solutions. The following compounds were formed with this class of liquids: $ThBr_4 \cdot 4C_2H_5OH$, $ThBr_4 \cdot 2CH_3COOC_2H_5$, $ThBr_4 \cdot 4CH_3CN$ and $ThBr_4 \cdot 3C_5H_5N$.

Anhydrous thorium tetrabromide reacts with other organic liquids to form molecular compounds at room temperature, but at the boiling point of the solutions other reactions ensue and in several cases hydrated thoryl bromide organic complexes were formed. The formulas of such substances are: $ThBr_4 \cdot 4C_6H_5CHO$, $2ThBr_4 \cdot 7C_6H_5COCH_3$, $ThBr_4 \cdot 4C_6H_5NH_2$, $ThOBr_2 \cdot 2C_6H_5CHO \cdot H_2O$, $ThOBr_2 \cdot 0.5C_6H_5COCH_3 \cdot H_2O$ and $ThOBr_2 \cdot 0.5C_6H_5COC_2H_5 \cdot 2H_2O$.

Ethyl benzoate and thorium tetrabromide form the molecular compound $ThBr_4 \cdot 3C_6H_5COOC_2H_5$ at room temperature but at the boiling point of the solution a reaction takes place: $ThBr_4 + 4C_6H_5COOC_2H_5 = (C_6H_5COO)_4Th + 4C_2H_5Br$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Transition Point of Carbon Tetrachloride as a Fixed Point in Thermometry. The Melting Point. Heats of Transition and of Fusion

BY HERRICK L. JOHNSTON AND EARL A. LONG

The existence of an allotropic change in solid carbon tetrachloride, under atmospheric pressure, was first observed by Goldschmidt[1] who reported a change from "doubly refracting" to "optically isotropic" crystals at about 45° below zero centigrade. Latimer[2] set the temperature of transition at approximately $-48.5°$. More recently, McCullough and Phipps,[3] who describe the transition as a change from monoclinic crystals (low temperature) to cubic crystals (high temperature) reported the transition point at $-48.54 \pm 0.02°$. They claimed that this point was constant and reproducible and recommended its use as a fixed point in thermometry. However, Skau and Meier,[4] who criticize the temperature scale of McCullough and Phipps, were unable to confirm the results of these earlier authors. Skau and Meier obtained a mean value of $-47.55 \pm 0.12°$ for the transition and reported variations between successive determinations of as much as 0.2°. Both McCullough and Phipps and Skau and

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[1] V. M. Goldschmidt, *Z. Krist.*, **51**, 26 (1913).

[2] Latimer, THIS JOURNAL, **44**, 90 (1922).

[3] McCullough and Phipps, *ibid.*, **50**, 2213 (1928).

[4] Skau and Meier, *ibid.*, **51**, 3517 (1929).