diffraction pattern showed that $h + k + l = 2n$, the requirement for a body centered lattice. This is consistent with the space group possibilities for K_2NiF_4.[8] By analogy with this structure the z parameters for oxygen and strontium were assigned the values $z_O = 0.151$ and $z_{Sr} = 0.347$. The calculated relative intensities are compared with the observed intensities in Table I. No correction was made for absorption. The agreement is good and appears to establish the structure of Sr_2IrO_4 as the K_2NiF_4 type.

TABLE I

OBSERVED AND CALCULATED INTERPLANAR SPACINGS AND INTENSITIES (FORWARD REFLECTIONS)

hkl	*d*/*n*(obs.)	*d*/*n*(calcd.)	*I*(obsd.)	*I*(calcd.)
002	6.48	6.42	m^{+}	41.8
101	3.72	3.72	m^{-}	22.7
004	3.23	3.23	$w^{=}$	1.2
103	2.88	2.89	s^{+}	100.0
110	2.74	2.75	s^{-}	55.5
112	2.53	2.53	w	4.6
105	2.143	2.148	m^{+}	13.1
006		2.150		16.6
200	1.942	1.944	m	27.6
202	1.859	1.861	w	5.7
211	1.720	1.722	w	4.7
116	1.689	1.692	m^{-}	22.2
204	1.667	1.665	$w^{=}$	0.7
107		1.667		0.1
213	1.612	1.612	s^{-}	51.5
215	1.441	1.442	m	6.9
206		1.443		19.0
118	1.392	1.392	w	3.3
220	1.374	1.374	w	3.1
222	1.345	1.344	w^{+}	0.2
109		1.346		8.5
301	1.288	1.289	$w^{=}$	0.9
217	1.264	1.265	$w^{=}$	0.4
224		1.265		0.1
303	1.242	1.241	w^{++}	8.4
208		1.242		5.2
310	1.229	1.229	w^{++}	10.9
312	1.207	1.208	w^{-}	3.9
226	1.158	1.158	w^{++}	8.7
305		1.158		1.7
1,0,11	1.124	1.124	w	3.5

Discussion

The formation of Sr_2IrO_4 as a pure phase by the reaction of mixtures containing excess strontium indicates that all of the excess strontium oxide is volatilized at 1200° since no change in lattice constant was observed. With less than stoichiometric quantity of strontium, the excess iridium is liberated and the pattern of Sr_2IrO_4 again shows no change in spacing. The compound Sr_2IrO_4 is therefore assumed to be stoichiometric.

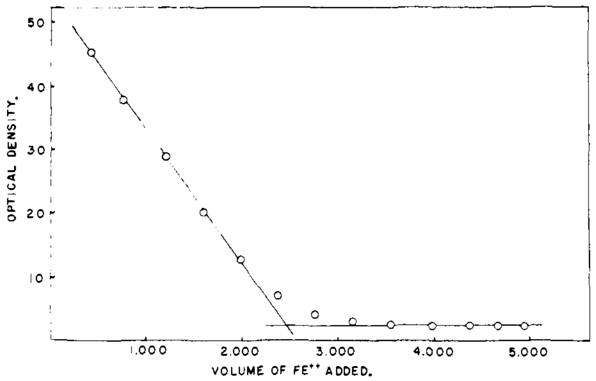

Fig. 1.—Typical photometric titration curve for $(IrCl_6)^{-4}$.

Other transition metals which have been shown to give A_2BO_4 phases are titanium, manganese and molybdenum.[8] Each of these elements also gives a perovskite-type oxide with strontium but all attempts to prepare a phase of this type in the strontium–iridium–oxygen system have failed. Lower temperatures and reactions in which only stoichiometric amounts of oxygen were allowed to react have been tried without success. This cannot be explained on the basis of relative ionic radii since the Goldschmidt radius of Ir^{+4} is 0.66, which lies close to the range covered by the other elements ($Ti^{+4} = 0.64$, $Mn^{+4} = 0.52$, $Mo^{+4} = 0.62$). The tolerance factor for the perovskite structure $t = [(R_A + R_O)/\sqrt{2}\ (R_B + R_O)]$ for iridium is 0.95, well within the common range.

Acknowledgment.—The authors wish to thank Dr. David Hume for his suggestion of the photometric method for iridium and Mr. Donald Klein for his advice concerning the experimental procedure.

STORRS, CONN.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

The Solubility of Several Metal Sulfates at High Temperature and Pressure in Water and in Aqueous Uranyl Sulfate Solution[1]

BY ERNEST V. JONES, M. H. LIETZKE AND WILLIAM L. MARSHALL

RECEIVED AUGUST 15, 1956

The solubility of several metal sulfates at high temperature and pressure has been determined in H_2O and in aqueous UO_2SO_4. In most of the systems investigated a large increase in solubility of the metal sulfate is observed at a given temperature as a function of increasing UO_2SO_4 concentration. This type of behavior points to a considerable degree of complexing in the saturated solutions. Several heats of solution have been determined and a possible relationship between these values and the amount of complexing is suggested.

Introduction

Two general methods are available for the determination of the solubility of salts at elevated temperature. In the analytical method saturated solutions are prepared and separated from the solid phase at the equilibrium temperature, and analyzed. In the synthetic method known ratios of salt and water are heated and the temperature

---

[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

is observed at which the disappearance or appearance of a solid phase occurs. In the present investigation the synthetic method was used to determine the solubilities of the sulfates of lanthanum, yttrium, cadmium, cesium and silver at high temperatures in water and in aqueous UO_2SO_4. In addition, the solubility of zinc sulfate in water alone at high temperatures was investigated while the solubility of $BaSO_4$ in aqueous UO_2SO_4 at 250° was studied by the analytical method. Since uranyl sulfate is known to complex the sulfate ion,[2] it seemed of interest to determine how much the solubilities of these salts increase in UO_2SO_4 solutions. The solutions used were 0.1272, 1.145 and 1.348 *m* in UO_2SO_4.

Experimental Methods

With the exception of the determinations below 100° and the filter technique for $BaSO_4$, all solubility measurements were made by the silica tube method described by Etard[3] and A. Benrath.[4,5] The silica tube method depends upon the visual observation of the appearance or disappearance of crystals in synthetic "mixtures" of known concentration. In the case of Cs_2SO_4 and Ag_2SO_4, both of which showed a positive temperature coefficient of solubility, the water and crystals were weighed directly into the silica tubes for each determination. In all other cases the solutions were prepared by dilution of a more concentrated stock solution.

In place of the 2 to 3 mm. i.d. heavy wall tubes used in most of the previous work, both 4 and 6 mm. i.d., conventional wall silica tubes were employed in the present experiments. These tubes did not permit as high temperatures to be reached, but made easier the visual observation of the appearance or disappearance of crystals. The tubes were heated in aluminum block furnaces which were mounted on motor driven rockers so that thorough mixing of the solution and crystals could be accomplished. The temperature, which was controlled to about ±1°, was measured by an iron–constantan thermocouple placed directly above the silica tube in the furnace and recorded on a calibrated Brown recording potentiometer.

A temperature correction curve was obtained by the use of two thermocouples. One thermocouple was placed within a silica tube in the position to be occupied by a tube containing the synthetic mixture. The other thermocouple was placed in its true position to be occupied during a run. The $\Delta(t°, \text{C.})$, which was used as a correction factor, was insignificant at 100° but increased to approximately −3° at 300°.

The lowest solubility measured was limited in each case by the ability to detect the first appearance of crystals in the tube. In some cases the crystals were visible in much more dilute solutions than in the case of other salts. For example, the measurement of the solubility of $La_2(SO_4)_3$ in UO_2SO_4 solution could be extended to 0.04% $La_2(SO_4)_3$ while the cadmium and zinc sulfate limits were much higher (2 to 3%). In all cases the measurements were extended to as dilute solutions as possible using the experimental methods available. The temperatures at which crystals dissolved or appeared in the tubes could be reproduced to about ±1°.

The solubility of $BaSO_4$ at 250° was determined by the use of a two-cell filtration-type apparatus similar to that of Booth and Bidwell.[6] The solutions and excess radioactive $Ba^{140}SO_4$ were equilibrated at 250° in one of the two compartments, which were separated by a sintered platinum filter obtained from the American Platinum Works. After equilibrium had been established the apparatus was inverted and the empty end cooled somewhat below 250°. The saturated solution was forced through the filter by means of the vapor pressure differential. The entire apparatus was then cooled to room temperature, the solution sample removed and the barium concentration in the solution determined by radioactive analysis. Equilibrium was checked by making a series of runs as a function of time. It was found that equilibrium was attained within 24 hours.

Experimental Results

Lanthanum Sulfate.—The high temperature solubility of $La_2(SO_4)_3$ in H_2O, in 0.1271 *m*, and in 1.348 *m* UO_2SO_4 solution is given in Table I. An experimental point is given at which temperature two liquid phases appeared. The formation of two liquid phases at elevated temperatures is characteristic of the system UO_2SO_4–H_2O.[7]

In all three cases the solubility of $La_2(SO_4)_3$ showed a negative temperature coefficient. Since the $La_2(SO_4)_3$ solutions all showed a strong tendency to supersaturate it was necessary to heat them 50 to 70° above the solubility equilibrium temperature before crystals appeared. The temperatures given represent the points at which the last crystals redissolved upon slow cooling. The $La_2(SO_4)_3$ crystals did not adhere to the sides of the tubes.

Several solutions of $La_2(SO_4)_3$ in water and in 0.1272 *m* UO_2SO_4 were heated to 300° to check on the possible existence of double solubility points at a particular concentration. No such points were observed. However, a metastable solubility point was observed at 149° for 3.97 wt. % $La_2(SO_4)$ in 1.348 *m* UO_2SO_4 solution.

Table I

The Solubility of Lanthanum Sulfate in Water and in Uranyl Sulfate Solutions

t (°C.)	$La_2(SO_4)_3$, wt. %	*t* (°C.)	$La_2(SO_4)_3$, wt. %
	In water		In 1.348 *m* UO_2SO_4
108	0.61	78	4.39
113	.46	91 and 149	3.97
115	.37	148	3.80
117	.31	150	3.75
	In 0.1272 *m*	150.5	3.70
	UO_2SO_4	151	3.60
97	2.04	152	3.46
105	1.74	154	3.25
120	0.87	160	2.69
145	.29	168	2.30
169	.15	178	1.85
199	.083	202	1.22
215	.042	222	0.88
		Two liquid layers at 291°	0.57

To check on the stability of $La_2(SO_4)_3$ solutions at high temperature a 0.31% $La_2(SO_4)_3$ solution in water was held at 260° for 48 hours and an 0.87% $La_2(SO_4)_3$ solution in 0.1272 *m* UO_2SO_4 was held at 250° for 72 hours. No change was observed in either system in the amount or form of the $La_2(SO_4)_3$ crystals. When the tubes were cooled the crystals redissolved at the expected temperatures. The solutions of $La_2(SO_4)_3$ in water and in dilute UO_2SO_4 solutions seemed to be stable at 250°. The increased solubility of $La_2(SO_4)_3$ in UO_2SO_4 solution is probably due to strong sulfate complexing by UO_2SO_4.

Cadmium Sulfate.—The solubility of $CdSO_4$ in H_2O, in 0.1272 and in 1.348 *m* UO_2SO_4 solution is shown in Table II. $CdSO_4$, like $La_2(SO_4)_3$,

---

(2) R. H. Betts and R. K. Mickels, *J. Chem. Soc.*, Suppl., **2**, 286 (1949).

(3) Etard, *Ann. chim.*, [7] **503**, 2 (1894).

(4) A. Benrath, *Z. anorg. allgem. Chem.*, **231**, 285 (1937).

(5) A. Benrath, *ibid.*, **247**, 147 (1941).

(6) H. S. Booth and R. W. Bidwell, This Journal, **72**, 2567 (1950).

(7) C. H. Secoy, *ibid.*, **72**, 3343 (1950).

shows a negative temperature coefficient of solubility; and the presence of UO_2SO_4 in the solution increases the solubility of $CdSO_4$ at a given temperature. The $CdSO_4$ solutions also show a tendency to supersaturate; hence the temperatures given represent the points at which the last crystals redissolved as the systems cooled. The crystals obtained at the higher temperatures and lower concentrations either of $CdSO_4$ or of UO_2SO_4 adhered to the walls of the tube, while the crystals from the more concentrated solutions were non-adherent.

$CdSO_4$, like $La_2(SO_4)_3$, shows no double solubility points up to 300° in water and in 0.1272 *m* UO_2SO_4 solution. Two double solubility points were observed in $CdSO_4$ solutions in 1.348 *m* UO_2SO_4. A 31.33 wt. % $CdSO_4$ solution shows a metastable point at 209.0° and a 30.12% $CdSO_4$ solution shows a similar point at 215.8°. This system also shows a transition point at 216° for 29.37% $CdSO_4$ solution as can be shown by plotting the data in Table II.

TABLE II

THE SOLUBILITY OF CADMIUM SULFATE IN WATER AND IN URANYL SULFATE SOLUTIONS

t (°C.)	$CdSO_4$, wt. %	*t* (°C.)	$CdSO_4$, wt. %
	In water		In 1.348 *m* UO_2SO_4
124	29.6		
160	14.8	21	31.62
182	7.4	47.8 (209)[a]	31.33
190	3.0	84.2	30.50
	In 0.1272 *m* UO_2SO_4	102.9 (215.8)[a]	30.12
		215.8	29.37
175	28.5	216.8	29.69
200	14.2	220.8	28.68
219	7.1	228.7	26.54
251	2.8	230.6	25.83
		244.3	22.51

[a] Metastable solubility points.

The $CdSO_4$–UO_2SO_4–H_2O system did not appear to be as stable as the corresponding $La_2(SO_4)_3$–UO_2SO_4–H_2O system. When the 2.8% $CdSO_4$ solution, in 0.1272 *m* UO_2SO_4, was held for 24 hours at 230° or for one hour at 240° (below the point at which crystals normally appeared in the solution) a brownish-orange precipitate appeared in the tube. The precipitate redissolved when the solution was cooled. Analysis revealed that the precipitate did not contain any uranium. When the brownish crystals were dissolved in dilute sulfuric acid a colorless solution resulted. When NaOH was added to the solution a white precipitate, probably $Cd(OH)_2$, was obtained. Hence it appears that the precipitate may have been CdO.

Zinc Sulfate.—The solubility of $ZnSO_4$ in water also decreased as the temperature increased. The data obtained are shown in Table III. The $ZnSO_4$ solutions, unlike the $La_2(SO_4)_3$ and $CdSO_4$ solutions, did not exhibit the strong tendency to supersaturate. No double solubility points at a given concentration were found below 300°. The crystals of $ZnSO_4$ that appeared adhered to the walls of the tube. Occasionally the $ZnSO_4$ solutions showed very peculiar behavior. For example, when the 2.1% solution was heated for the first time, non-adherent crystals appeared in the solution at 225°. The crystals redissolved on cooling. When the solution was heated again no crystals appeared at 225° but the "normal" adherent crystals were observed at 257°. The non-adherent crystals could not be produced in the tube again upon several subsequent heatings. This phenomenon was also observed in the 5.1% and in the 11.3% solutions. No explanation is given for this behavior although the points may indicate an extension of the lower half of the zinc sulfate solubility curve. The 2.1% $ZnSO_4$ solution contained 0.39 mg. silica/ml. after 3 heatings to 260° while a similar solution that had been heated only once contained 0.03 mg. silica/ml.

When the 11.3% $ZnSO_4$ solution was held at 250° (2° above the point at which crystals appeared in the tube) for 24 hours a very large amount of crystalline material was deposited in the tube. The X-ray analysis of these crystals showed them to be a mixture of $ZnSO_4 \cdot H_2O$ and $ZnSO_4$ which seems to preclude a hydrolytic reaction as the cause of the increased number of crystals. When the 17.0% $ZnSO_4$ solution was held overnight at 210° (28° below the point at which crystals normally appear) crystals appeared in the solution. These crystals redissolved readily when the solution was cooled. Their composition was not determined.

TABLE III

THE SOLUBILITY OF ZINC SULFATE IN WATER

t (°C.)	$ZnSO_4$, wt. %	*t* (°C.)	$ZnSO_4$, wt. %
	In water	248	11.3
178	34.0	253	8.5
203	25.5	255	5.1
219	22.7	257	2.1
238	17.0		

Cesium Sulfate.—The solubility of Cs_2SO_4 in water, in 0.1272 and 1.348 *m* UO_2SO_4, is shown in Table IV.

Throughout the range investigated the solubility of Cs_2SO_4 showed a positive temperature coefficient. No crystals reappeared in any of the solutions when they were heated to *ca.* 310°. The cesium sulfate solutions showed no tendency to supersaturate. In all cases at the elevated temperatures the crystals dissolved and reappeared at the same temperature. The point at 23° was obtained merely by stirring excess Cs_2SO_4 crystals with water in a beaker. No attempt was made to thermostat the solution; and an ordinary mercury thermometer was used to measure the temperature. The agreement with the values obtained by Berkeley[8] was satisfactory.

This system is the only system of the particular ones studied in which the presence of dissolved UO_2SO_4 *decreased* rather than increased the solubility of the saturating species. The solid phase in equilibrium with 1.348 *m* UO_2SO_4 is more than likely a double salt of UO_2SO_4 and Cs_2SO_4.

Yttrium Sulfate.—The solubility of $Y_2(SO_4)_3$ in water, in 0.1272 *m*, in 1.145 *m*, and in 1.348 *m* UO_2SO_4, is shown in Table V. Also included in the table are experimental data showing the temperatures at which the two liquid phase region appears.[7]

---

[8] Earl of Berkeley, *Phil. Trans. Roy. Soc. (London)*, **203A**, 210 (1904).

Higher temperatures are shown in the two liquid phase region at which precipitation had not yet occurred.

In all cases the solubility of $Y_2(SO_4)_3$ shows a negative temperature coefficient. Since the $Y_2(SO_4)_3$ solutions all showed a strong tendency to supersaturate it was necessary to heat them 50 to 70° above the equilibrium solubility temperature before crystals appeared. The temperatures given represent the points at which the last crystals redissolved upon slow cooling. The $Y_2(SO_4)_3$ crystals did not adhere to the sides of the tubes. Just as in the case of $La_2(SO_4)_3$ no double solubility points were observed at any given concentration below 300°. The $Y_2(SO_4)_3$–UO_2SO_4–H_2O system seemed to be stable at temperatures as high as 320°.

Table IV

The Solubility of Cesium Sulfate in Water and in Uranyl Sulfate Solutions

t (°C.)	Cs_2SO_4, wt. %	t (°C.)	Cs_2SO_4, wt. %
	In water		In 1.348 m UO_2SO_4
23	63.5	167.7	0.30
175	71.8	178.5	.33
211	73.5	187.3	.37
270	75.0	214.8	.44
292	75.5	245.3	.49
	In 0.1272 m UO_2SO_4	285.6	.54
53.8	64.19	288.6	.78[a]
61.6	66.00		
77.3	67.12		
84.2	67.55		
104.8	68.58		
140.2	70.07		
177.5	71.66		
228.6	73.48		

[a] Two liquid layers at 293°, much undissolved.

Table V

The Solubility of Yttrium Sulfate in Water and in Uranyl Sulfate Solutions

t (°C.)	$Y_2(SO_4)_3$, wt. %	t (°C.)	$Y_2(SO_4)_3$, wt. %
	In water		In 1.145 m UO_2SO_4
108	4.76	208	4.32
150	2.38	215	3.41
155	1.59	217	3.44
160	1.19	230	2.78
161	0.95	245	2.12
163	.64	[a]	1.43
176	.48	[a]	1.08
186	.23		In 1.348 m UO_2SO_4
195	.12	212	4.31
	In 0.1272 m UO_2SO_4	221	3.62
153	4.47	224	3.43
162	2.23	231	2.99
189	0.81	237	2.74
229	0.22	[b]	2.34
		[b]	2.14

[a] Two liquid layers at about 277°. No crystals up to 320°. Held at 320° for 2 hr. [b] Two liquid layers at about 270°. No crystals after several hours above 280 to 310° for 2.14 wt. % $Y_2(SO_4)_3$ solution.

Silver Sulfate.—The solubility of silver sulfate[9] in 0.1272 m and in 1.348 m UO_2SO_4 solution is shown in Table VI. In this case as with Cs_2SO_4 there is a positive temperature coefficient of solubility. However, the solubility is increased in UO_2SO_4 solution above the solubility in pure water,[9] whereas in the case of Cs_2SO_4 there is a decrease. The phase equilibria of this system were sufficiently reversible to permit precise data to be obtained.

Barium Sulfate.—The solubility of $BaSO_4$ at 250° as a function of uranyl sulfate concentration is shown in Table VII. It is interesting to note that a plot of log $BaSO_4$ molality against the square root of the UO_2SO_4 molality is linear. Also, if the log of the $BaSO_4$ molality is plotted against 25° pH data obtained by Orban[10] for the particular concentrations of UO_2SO_4 in water alone a linear plot is obtained with a slope of unity. As yet this observation has not been explained.

These data point out, at least at 250°, the rather large increase in solubility of $BaSO_4$ in UO_2SO_4–H_2O solution. The amount of increase is far in excess of that expected on the basis of Debye–Hückel effects.

Heat of Solution.—If the solubility data for any particular solid phase in a given solution are plotted as the log solubility, expressed as mole fraction or molality against $1/TK$°., then, from thermodynamic considerations, the tangent to the curve at any given temperature will yield a heat of solution. For the ideal system, in which heat capacities of the individual constituents remain constant and the interionic interaction changes are negligible over the same temperature range, the tangent will also remain con-

Table VI

The Solubility of Silver Sulfate in Uranyl Sulfate Solutions

t (°C.)	Ag_2SO_4, wt. %	t (°C.)	Ag_2SO_4, wt. %
	In 0.1272 m UO_2SO_4		In 1.348 m UO_2SO_4
36.0	1.04	42.5	1.54
54.0	1.46	52.0	2.36
83.3	2.18	84.6	3.63
107.8	2.72	106.5	5.38
127.4	3.01	131.4	7.43
140.0	A red product formed[a]	161.6	9.89
		174.3	11.01
		197.1	12.82
		214.9	14.14
		237.5	15.75
		259.1	17.25

[a] Initial composition = 3.01% Ag_2SO_4.

Table VII

The Solubility at 250° of Barium Sulfate in Water and in Uranyl Sulfate Solutions

UO_2SO_4, m	UO_2SO_4,[a] M	Molal solubility $BaSO_4 \times 10^5$	$BaSO_4$[a] $\times 10^5$, M
0.000	0.000	0.53	0.53
.126	.125	1.47	1.46
.319	.313	3.38	3.32
.647	.625	9.26	8.95
.809	.775	10.8	10.3
1.06	1.00	18.4	17.4
1.22	1.15	23.8	22.4
1.34	1.25	40.0	37.3

[a] Molarities are for volumes at 25°.

---

(9) M. Barre, *Ann. chim. phys.*, [8] **24**, 211 (1911).

(10) E. Orban, "The pH Measurement of Uranyl Sulfate Solutions from 25 to 60° C.," AEC Declassified Report 3583 (1952).

stant, thus producing a linear function of log solubility against $1/T$ °K. When the data for the various systems described in this paper are plotted in this way it is found that the majority of the slopes do remain constant and yield the approximate heats of solution given in Table VIII. In the case of the plots showing two slopes the values are for the portions of the curves corresponding to the higher temperature range except in the case of the solubility of Ag_2SO_4 in 1.35 m UO_2SO_4 where the converse is true. Solid phase transitions are clearly shown by discontinuities in the solubility curves.

TABLE VIII

THE ΔH_{soln} FOR SEVERAL METAL SULFATES IN UO_2SO_4 SOLUTION

	ΔH_{soln} (kcal./mole)		
Salt	In H_2O	In 0.1272 m UO_2SO_4	In 1.348 m UO_2SO_4
$Y_2(SO_4)_3$	−130	−80	−48
$La_2(SO_4)_3$	−120	−60	−43
$CdSO_4$	.....	−33	−13
Ag_2SO_4	3.8	6.6	11
Cs_2SO_4	1.6	1.6	4.9

The large decrease in the heat of solution of the solid phase as a function of increasing uranyl sulfate in the solution appears indicative of a large degree of interaction and/or complexing of the solute with either UO_2SO_4 or the ionic species in solution. Aqueous salt systems which do not complex the solute exhibit negligible change in the heat of solution as the aqueous salt concentration is increased. Perhaps some theoretical quantitative relationships can be derived to correlate the change in the heat of solution per unit change of concentration of the electrolyte species in solution with complexing constants of the reacting species.

OAK RIDGE, TENN.

[CONTRIBUTION FROM TECHNICAL DEVELOPMENT LABORATORIES, COMMUNICABLE DISEASE CENTER, PUBLIC HEALTH SERVICE]

Chlorine Exchange between Aluminum Chloride and γ-1,2,3,4,5,6-Hexachlorocyclohexane

BY GEORGE W. PEARCE AND SONJA KRAUSE

RECEIVED JULY 23, 1956

Chlorine exchanges readily between aluminum chloride and γ-1,2,3,4,5,6-hexachlorocyclohexane (γ-HCC) at temperatures above 100° with some decomposition and isomerization, primarily to α-HCC and δ-HCC. Mechanisms for both exchange and isomerization are proposed.

Chlorinated hydrocarbon insecticides labeled with chlorine-36 would be very helpful in studies of the fate and toxicology of this class of compounds in resistant strains of arthropods as well as in higher animals. The use of exchange reactions appeared to offer a simpler way of preparing Cl-36 labeled compounds than their complete synthesis. In addition, study of exchange reactions can provide knowledge of the structural nature of compounds in relation to their properties in general. Using lindane, the γ-isomer of 1,2,3,4,5,6-hexachlorocyclohexane (γ-HCC), as a chlorinated hydrocarbon insecticide of importance chlorine exchange reactions between it and $AlCl_3$ labeled with Cl-36 have been attempted.

1,2,3,4,5,6-Hexachlorocyclohexane has previously been labeled by direct chlorination of benzene with chlorine-36.[1]

Experimental

Both the apparatus and the method of preparing labeled aluminum chloride were based on the work of Willard and colleagues[2,3] in which the reactions

$$HCl^* + AgNO_3 \longrightarrow AgCl^* + HNO_3$$

$$AgCl^* + Al \longrightarrow Ag + AlCl_3^*$$

are employed. The latter reaction is carried out under rigorously anhydrous conditions in an evacuated system. Two solutions of chlorine-36[4] one containing 41.6 mg. Cl/microcurie and the other 3.62 mg. Cl/microcurie, were available for this work. The silver nitrate was Mallinckrodt Reagent grade and the aluminum was Baker and Adamson, 16 to 60 mesh.

The AgCl was prepared in a tube protected from light and fused to a flask containing the γ-HCC[5] which was used without further purification. After the AgCl had been melted under vacuum to remove the last traces of water, Al was added, still under vacuum. When the mixture was heated to 460–500°, $AlCl_3$ was evolved as a gas and could be driven over into the flask containing the γ-HCC if this was cooled in liquid nitrogen. Heat had to be applied for one to two hours for complete conversion of the AgCl to $AlCl_3$. The flask containing $AlCl_3$ plus γ-HCC was then sealed off completely from the rest of the apparatus and could be treated as desired with the contents still under vacuum. A number of runs were made in which the heat treatment of the $AlCl_3$ and lindane and/or the shape of the reaction container were varied. Products from the reaction mixture were recovered by dissolving in ether and water and extracting each layer with small portions of the other solvent. Aliquots of the water phase and products obtained from the ether phase were assayed for Cl-36 activity after conversion to AgCl. A shielded end-window Geiger tube was used to count samples. The approximate disintegration rate was estimated by standardizing this count against a Q-gas flow counter which was assumed 50% efficient. Percentage exchange was calculated as percentage of total possible exchange at equilibrium.

Experimental Results

Run 1: 500 mg. lindane in 100-ml. reaction flask, 42.6 mg. Cl containing 1 microcurie. Lindane and $AlCl_3^{36}$ heated about 7 minutes at 115–130°; no discoloration m.p. 111.5–112.5° (recrystallized product); exchange, 16%.

Run 2: 500 mg. lindane in Y-shaped tube, 41.84 mg. Cl containing 11.5 microcuries. Lindane and $AlCl_3^{36}$ driven back and forth several times by heating alternate arms of

---

(1) J. T. Craig, P. F. Tryon and W. G. Brown, *Anal. Chem.*, **25**, 1661 (1953).

(2) C. H. Wallace and J. E. Willard, THIS JOURNAL, **72**, 5275 (1950).

(3) M. Blau and J. E. Willard, *ibid.*, **73**, 442 (1951).

(4) Cl-36-P Processed, Oak Ridge National Laboratory, AEC, Isotope Catalogue, July, 1952.

(5) Pure samples of α-, β-, γ-, δ- and ε-isomers were obtained from the Ethyl Corporation.