gas stream by a train of dry sodium hydroxide but cannot be distinguished from bromine by this method because the latter also reacts, although less efficiently.

Reaction of Bromine with Ethylene Bromide.—Table I gives the results of experiments on the rate at which elemental radiobromine enters organic combination when dissolved in liquid ethylene bromide in the dark. The apparent activation energy obtained from the log k vs. $1/T$ plot of the data is 31.7 kcal./mole. Fractionation of the organic products with carriers indicated that $\geqq 75\%$ of the organically bound radiobromine was in the form of 1,1,2-$C_2H_3Br_3$. Radiobromine dissolved in ethylene bromide entered organic combination at room temperature when illuminated.

TABLE I

REACTION OF BROMINE WITH ETHYLENE BROMIDE

INITIAL BROMINE CONCN. 1×10^{-3} M./L. IN ALL CASES

Temp., °C.	Time, hr.	Br_2 reacted, %[a] (1)[c]	(2)[c]	k, $(m./l.)^{1/2}$ min.$^{-1} \times 10^4$[b] (1)	(2)
25	..	4.8[d]	4.2[d]	..	..
115	4.5	31.0	31.2	0.33	0.35
120	3.5	46.0	52.9	0.73	0.87
125	2.0	43.1	37.1	1.16	0.97
133	1.0	46.2	43.3	2.5	2.4
140	0.75	59.1	55.3	4.7	4.4

[a] Assuming that the products are $C_2H_3Br_3$ and HBr and that the % reacted is therefore equal to twice the % of the radiobromine found in organic combination. [b] Assuming that $d[Br_2]/dt = -k[Br_2]^{1/2}$. [c] Columns (1) and (2) give the results of two separate series of experiments. [d] Presumably due to photochemical reaction during preparation of the reaction mixtures. This % was deducted from the total % observed at the higher temperatures in obtaining the figures recorded.

Reaction of Hydrogen Bromide with Ethylene Bromide.—Thirty determinations indicate that from 115 to 180° radiobromine present as hydrogen bromide in liquid ethylene bromide enters organic combination with a half-life in the range from 20 hours to 15 minutes. The results were too erratic to allow calculation of a temperature coefficient. Fractionation experiments indicated that the reaction products were about 70% 1,2-$C_2H_4Br_2$ and 30% higher boiling materials.

When sealed 300-ml. Pyrex flasks containing 150 mm. of hydrogen bromide (tagged with Br^{82}) and 200 mm. of ethylene bromide (pressures measured at room temp.) were heated no reaction occurred in thirty minutes at 225° but significant organic combination of the activity took place at 270° and above. Prolonged heating at the higher temperatures gave an equilibrium distribution of the activity. After 105 min. at 308°, 150 min. at 317°, 90 min. at 320°, 120 min. at 338° the activity found in the organic products was 46.5, 45.3, 44.1 and 42.9%, respectively. A total of 73% organically bound activity would be expected in the equilibrium mixtures if they contained the original pressures of hydrogen bromide and ethylene bromide. Fractionation experiments on the organic products of the 308 and 317° reactions indicated that about 61% of the activity was in a form lower boiling than ethyl bromide (probably C_2H_3Br), 4% was 1,1-$C_2H_4Br_2$ and 35% was 1,2-$C_2H_4Br_2$. It is probable that the bromine originally in hydrogen bromide entered organic combination through the equilibrium $C_2H_4Br_2 \rightleftarrows C_2H_3Br + HBr$. Decomposition of ethylene bromide at 340–370° has been reported previously.[3]

Reaction of Ethylene Bromide with Bromine which has Undergone Radiative Neutron Capture.—When tubes of purified, degassed ethylene bromide were bombarded with neutrons from a 100 mg. Ra–Be source it was regularly observed that about 50% of the bromine which underwent radiative neutron capture could be extracted by an aqueous solution of sulfite ion and bromide ion.

When similar tubes were heated to 119° and above following irradiation the inorganic bromine which had been produced by radiative neutron capture re-entered organic combination at a measurable rate. For example, after 90 min. at 119° only 24% rather than 50% was extractable. When the organic products from the combined hot atom and thermal reactions which had occurred in such a sample were fractionated with carriers about half the activity was found as 1,2-$C_2H_4Br_2$, about a third as 1,1-$C_2H_4Br_2$, about 10% as 1,1,2-$C_2H_3Br_3$ and a few per cent. as ethyl bromide.

Reaction of Ethylene Bromide with Br^{80} (18 min.) Produced by the Isomeric Transition.—When purified degassed ethylene bromide which had been synthesized from bromine containing Br^{80} (4.4 hr.) was allowed to stand at room temperature and then extracted with aqueous sulfite–bromide solution, approximately 50% of the Br^{80} (18 min.) daughter of the Br^{80} isomeric transition was always found in inorganic form. At higher temperatures, up to 220°, the results were somewhat variable but did not show any definite trend away from 50% extractable. Since the system was maintained at the reaction temperature for nearly four half lives of the Br^{80} (18 min.) just prior to extraction, essentially all of the daughter activity measured at the time of extraction had been formed at the reaction temperature.

When molecular bromine containing Br^{80} (4.4 hr.) was allowed to stand in liquid 1,2-$C_2H_4Br_2$ at room temperature the fraction of the isomeric transitions which resulted in organic combination of the Br^{80} (18 min.) was about 20% and essentially all of this organically bound activity appeared as 1,2-$C_2H_4Br_2$. At liquid air temperatures the total organic yield was somewhat higher but approximately two-thirds of the organically bound Br^{80} (18 min.) was in the form of 1,1,2-$C_2H_3Br_3$ and only one-third as $C_2H_4Br_2$. This effect of change in phase and temperature is qualitatively similar to that reported for the radiative neutron capture reaction on the propyl bromides.[4] It shows an increase in proportion of polybromination products not observed in the isomeric transition reaction in bromotrichloromethane.[5]

Acknowledgment.—This work was supported in part by the Atomic Energy Commission and in part by the Research Committee of the Graduate School with funds made available by the Wisconsin Alumini Research Foundation. The Br^{80} was obtained from the Argonne National Laboratory and the Br^{82} from the Oak Ridge National Laboratory.

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RECEIVED NOVEMBER 30, 1950

The Uranyl Nitrate–Water System Above 60°[1]

BY W. L. MARSHALL, JR., J. S. GILL AND C. H. SECOY

Although there are some data in the literature[2–5] for the solubility of uranyl nitrate in water, the discrepancy of these data indicated the necessity for a check on the measurements. We have measured the solubility from the incongruent melting point of the hexahydrate at about 60° to the melting point of the dihydrate at 184°. Our results show a lower solubility than that given in most of the earlier data and also indicate an incongruent melting point for the trihydrate rather than the congruent point inferred in some of the previous work. The system is thermally stable up to the revised melting point of the dihydrate. Above this point decomposition of the nitrate ion occurs.

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(1) This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Commission at Oak Ridge National Laboratory. Presented before the Division of Physical and Inorganic Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Illinois, September 3–8, 1950.

(2) Von Alfred Benrath, *Z. anorg. allgem. Chem.*, **249**, 245 (1942).

(3) O. Guempel, *Bull. soc. chim., Belg.*, **38**, 443 (1929).

(4) J. A. Lane, Plutonium Project Handbook, Revised Edition, CL-697, Ch. 2, "Physical and Chemical Properties," May, 1945.

(5) A. Wasilieff, *J. Russ. Phys.-Chem. Soc.*, **42**, 570 (1910).

Experimental.—Mallinckrodt C.P. uranyl nitrate hexahydrate was used for the preparation of uranyl nitrate dihydrate and for the preparation of solutions which contained more water than the hexahydrate composition. The dihydrate was prepared by dehydration of the hexahydrate at 115–120°, the product being kept under vacuum. Analysis of the dihydrate showed 55.34% uranium (theoretical 55.36%).

Since the presence of an amount of either UO_3 or HNO_3 in the salt would be expected to have a measurable effect on the solubility, the ratio of UO_3 to HNO_3 was checked by comparing the titration curve of a prepared salt solution with those obtained with solutions to which a weighed amount of UO_3 had been added. The solutions were titrated with standard nitric acid using a glass electrode *p*H meter. A sample titration curve of a $UO_2(NO_3)_2$ solution containing an amount of added UO_3 is shown in Fig. 1. In this manner the stoichiometric end-point *p*H for a solution of a given concentration was determined. Solutions of this concentration prepared from the reagent uranyl nitrate were found to have this same *p*H value, thus indicating that the salt contained neither UO_3 nor excess acid as impurity.

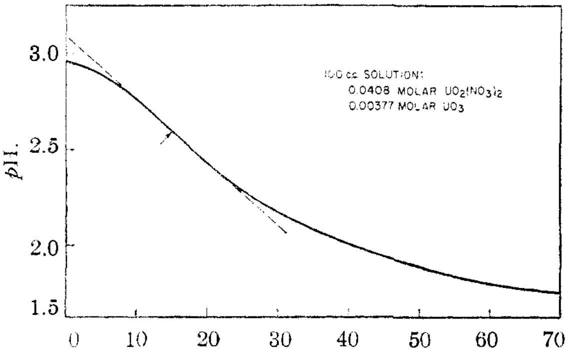


Fig. 1.—The titration of an aqueous $UO_2(NO_3)_2$-UO_3 solution.

The apparatus for the solubility measurements consisted of a 200-cc. round-bottom flask to which was sealed a side arm containing a large-bore stopcock. This side tube was scaled to the bottom of a 400-cc. beaker over the mouth of which was fitted a rubber glove. By manipulating a pipet through the rubber glove, liquid samples could be transferred from the flask to tared weighing bottles, previously placed in the beaker, without exposing the sample to the atmosphere. The neck of the flask was attached by a standard taper joint to an adapter with a tru-bore tube through which a stirrer operated. A side arm from the adapter led first to a trap containing standard ceric sulfate solution, then to a second trap containing ferrous sulfate solution and finally to a rough vacuum pump. The solubility flask was immersed in a constant temperature bath controllable to ±0.1°. The temperature of the bath was measured with a Bureau of Standards calibrated mercury thermometer or by a mercury thermometer which was calibrated in this Laboratory against a Bureau of Standards certified platinum resistance thermometer.

The procedure for making a run was as follows. Uranyl nitrate hexahydrate was placed in the flask; the flask was attached to the line in position in the thermostat set at the desired temperature. A partial vacuum was applied to the molten hexahydrate and the liquid was stirred vigorously until crystallization began. The vacuum line was then closed and air, dried by passing through sulfuric acid, calcium chloride and calcium sulfate successively, was admitted to the system. After an additional period of stirring, usually 40 to 50 minutes, samples of the clear solution were transferred to tared weighing bottles through the large bore stopcock as described above. The weighing bottles were closed with ground glass stoppers before removal from the apparatus for weighing. The uranium content was determined by ignition of the sample at 900° to U_3O_8. The attainment of equilibrium was checked by the analytical agreement of samples taken after various time intervals. The results show that 10 to 15 minutes of stirring was sufficient.

The purpose of the standard ceric sulfate and ferrous sulfate in the gas train was to detect thermal decomposition of the nitrate ion if it should occur. Any liberated nitrogen dioxide would reduce ceric ion and nitric oxide would yield the red complex, $Fe(NO)SO_4$, in the ferrous sulfate solution. The excess ceric ion was back-titrated with standard ferrous sulfate.

TABLE 1

THE SOLUBILITY OF URANYL NITRATE IN WATER, 60–184°

Temp., °C.	Liquid, % $UO_2(NO_3)_2$	Solid, % $UO_2(NO_3)_2$	Solid phase composition
70	77.25		$UO_2(NO_3)_2·3H_2O$
77		87.08 (theor., 87.95)	$UO_2(NO_3)_23H_2O$
77.2	78.49		$UO_2(NO_3)_2·3H_2O$
85	79.92		$UO_2(NO_3)_2·3H_2O$
90.5	80.98		$UO_2(NO_3)_2·3H_2O$
92	81.37	87.05	$UO_2(NO_3)_2·3H_2O$
100	82.57		$UO_2(NO_3)_2·3H_2O$
110	84.14		$UO_2(NO_3)_2·3H_2O$
113[a]	84.67		$UO_2(NO_3)_2·3H_2O$ + $UO_2(NO_3)_2·2H_2O$
120	85.25		$UO_2(NO_3)_2·2H_2O$
130	86.13		$UO_2(NO_3)_2·2H_2O$
133	86.54		$UO_2(NO_3)_2·2H_2O$
137	87.07		$UO_2(NO_3)_2·2H_2O$
141.2	87.02		$UO_2(NO_3)_2·2H_2O$
141.5		90.58 (theor., 91.63)	$UO_2(NO_3)_2·2H_2O$
147	87.75		$UO_2(NO_3)_2·2H_2O$
154.5	88.23		$UO_2(NO_3)_2·2H_2O$
159	88.74		$UO_2(NO_3)_2·2H_2O$
160	88.94		$UO_2(NO_3)_2·2H_2O$
165.5	89.22		$UO_2(NO_3)_2·2H_2O$
172	89.92		$UO_2(NO_3)_2·2H_2O$
180	90.78		$UO_2(NO_3)_2·2H_2O$
181	91.01		$UO_2(NO_3)_2·2H_2O$
184[b]	91.63		$UO_2(NO_3)_2·2H_2O$

[a] Intersection point for incongruent melting point, trihydrate. [b] True melting point, dihydrate.

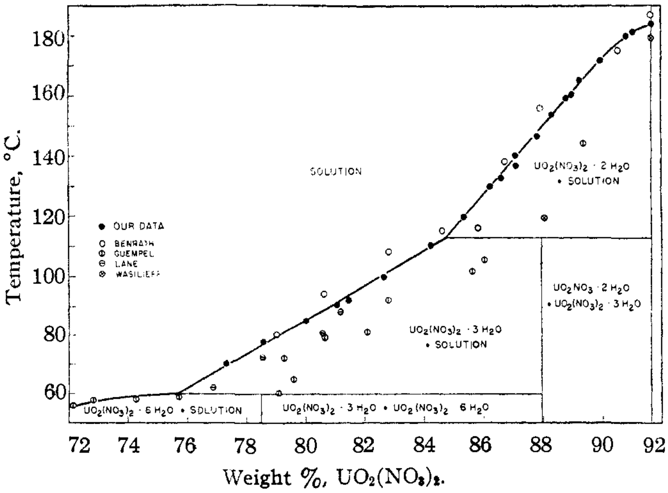


Fig. 2.—The solubility of uranyl nitrate in water.

A bent spatula was used for sampling the solid phase. After removal from the system, the crystals were quickly dried between filter paper and weighed. The uranium content was determined by ignition to U_3O_8.

The melting point of the dihydrate and the incongruent point for the trihydrate were determined by sealing samples of appropriate compositions in capillary tubes and observing the temperature at which melting first occurs. The dihydrate was prepared by dehydration of the hexahydrate at 115–120°. Compositions near that of the trihydrate were prepared by adding water with a micropipet to a sample of the dihydrate. The mixture was then finely ground and a sample taken for analysis simultaneously with the sealing of the material in the capillary tube.

Discussion.—The solubility and solid phase data given in Table I and shown graphically in Fig. 2 are the results of five separate experimental runs which overlap. Some of the values were obtained going up the temperature scale and some by proceeding from a higher to a lower temperature. No decomposition of uranyl nitrate was detected below 184° either by visual observation or by titration of the standard ceric sulfate solution contained in the gas train. Above 184° the dihydrate decomposes giving oxides of nitrogen.

The melting point data for the dihydrate and the trihydrate are given in Table II. These values check those obtained by extrapolation of the solubility curves.

TABLE II

MELTING POINT DETERMINATIONS

Weight %, $UO_2(NO_3)_2$	87.2	87.5	89.1	89.9	91.63
First observed melting, *t.*, °C.	113	113	113	112	184

Data available from the literature[2,3,4,5] are also shown in Fig. 2 and serve to indicate the amount of deviation from our values. Wasilieff[5] gives 121.5° as the trihydrate melting point compared to our value of 113° (incongruent point). Benrath[2] gives 187°, and Wasilieff[5] 179.3°, as the dihydrate melting point for which we have determined the temperature to be 184°.

OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENN.
RECEIVED OCTOBER 5, 1950

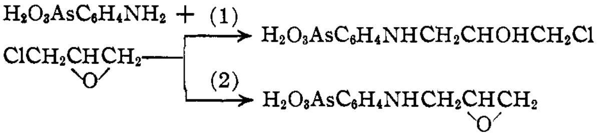
Some Substituted *p*-Arsanilic Acids[1,2]

BY ROBERT L. MCGEACHIN AND ROBERT E. COX

The reactions of 4-hydroxyphenylarsonic acid and *p*-arsanilic acid with various aliphatic chlorides and bromides have been studied by Hamilton[3,4,5,6] and his co-workers. In this investigation, we have extended the study, carrying out the reactions of *p*-arsanilic acid with 1,3-dichloropropanol-2, epichlorohydrin, β-chloro-β′-hydroxydiethyl ether (diglycolchlorohydrin) and trimethylene dibromide.

In the reaction of *p*-arsanilic acid with 1,3-dichloropropanol-2 using sodium bicarbonate as a buffer, yields were comparable to those obtained in similar reactions using unbuffered media (30%), with the bis-compound, N,N′-di-(4-arsonophenyl)-1,3-diaminopropanol-2, the only compound that could be isolated. However, when disodium phosphate was used as a buffer, both the bis-compound and N-(3-chloro-2-hydroxypropyl)-*p*-arsanilic acid were found.

With epichlorhydrin, unsatisfactory results were obtained in the buffered medium but when the reaction was run without a buffer characterizable products were obtained, although in low yields. Of the two possible mechanisms for the first stage of this reaction, (1) is the more probable



$$H_2O_3AsC_6H_4NH_2 + \underset{\diagdown O \diagup}{ClCH_2CHCH_2} \begin{cases} \xrightarrow{(1)} H_2O_3AsC_6H_4NHCH_2CHOHCH_2Cl \\ \xrightarrow{(2)} H_2O_3AsC_6H_4NHCH_2\underset{\diagdown O \diagup}{CHCH_2} \end{cases}$$

since we were able to isolate N-(3-chloro-2-hydroxypropyl)-*p*-arsanilic acid from the reaction mixture. This could then react with another molecule of *p*-arsanilic acid to give the bis-compound which was found to be the principal product.

β-N-(4-Arsonophenyl)-amino-β′-hydroxydiethyl ether, formed by the reaction of diglycolchlorhydrin on *p*-arsanilic acid, proved to be so water-soluble that the free acid could not be isolated in the pure form so that it was necessary to isolate it as the sodium salt. This was unexpected since β-(β′-hydroxy)-ethoxyethoxyphenylarsonic acid,[6] a compound closely resembling our product in structure, was easily isolated as the free acid.

In the reaction of trimethylene dibromide with *p*-arsanilic acid only the bis-compound, N,N′-di-(4-arsonophenyl)-1,3-diaminopropane, could be isolated as was the case in the reaction of ethylene dibromide with *p*-arsanilic acid.[3]

Experimental

Reaction of *p*-Arsanilic Acid with 1,3-Dichloropropanol-2.—To a solution of 2 g. of *p*-arsanilic acid (I), 3.7 g. of sodium hydroxide and 9.5 g. of sodium bicarbonate in 60 ml. of water, 7 g. of 1,3-dichloropropanol-2 (II) was added and the mixture boiled under reflux for six hours. Acidification to congo red with concd. hydrochloric acid precipitated a white solid, N,N′-di-(4-arsonophenyl)-1,3-diaminopropanol-2. This product was purified by dissolving in 10% sodium hydroxide, reprecipitating with acid, washing with water and drying over calcium chloride *in vacuo*. It does not melt below 250°; yield of 6.8 g. (30%).

Anal.[7] Calcd. for $C_{15}H_{20}O_7N_2As_2$: As, 30.6. Found: As, 30.4.

Sixty-seven grams of I was dissolved in 100 ml. of 2.3 *N* sodium hydroxide, 22 g. of disodium phosphate added and the mixture heated to boiling. Fifteen ml. (20 g.) of II was added, 1 ml. every ten minutes with each addition followed after five minutes by the addition of 1 ml. of 40% sodium hydroxide. Acidification of the cooled reaction mixture to congo red with concd. hydrochloric acid precipitated the bis-compound which was purified as described above; yield of 22 g. (29%).

Anal. Calcd. for $C_{15}H_{20}O_7N_2As_2$: As, 30.6. Found: As, 30.3.

The filtrate from above, when adjusted to a *p*H of 5 with 10% sodium hydroxide, deposited white crystals on standing in the ice-box. This product was washed with ice-cold water, dried at 120° for several hours and then *in vacuo* over calcium chloride. Qualitative tests showed it contained chlorine. It does not melt below 250°; yield of 3 g. (6%).

Anal. Calcd. for $C_9H_{13}O_4NClAs$: As, 24.2. Found: As, 24.0.

Reaction of I with Epichlorhydrin.—To 67.3 g. of I dissolved in 75 ml. of 4 *N* sodium hydroxide, 28.7 g. of epichlorhydrin was added and the mixture boiled under reflux for one hour. Acidification in the usual manner precipitated the bis-compound which was purified in the manner described above; yield of 10 g. (14%).

Anal. Calcd. for $C_{15}H_{20}O_7N_2As_2$: As, 30.6. Found: As, 30.4.

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(1) Taken in part from the M.S. thesis of Robert E. Cox.

(2) This work was aided by a grant to the University of Louisville from the Kentucky State Medical Research Commission.

(3) C. S. Hamilton, THIS JOURNAL, **45**, 2751 (1923).

(4) L. A. Sweet and C. S. Hamilton, *ibid.*, **56**, 2409 (1934).

(5) P. O. Bare and C. S. Hamilton, *ibid.*, **59**, 2444 (1937).

(6) J. Parker, Ph.D. thesis, University of Nebraska, 1940.

(7) A modification of the method of F. E. Cislak and C. S. Hamilton, THIS JOURNAL, **52**, 638 (1930), was used in the arsenic analyses.