[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Chemical Effects of the Nuclear Isomeric Transition in Bromine; Evidence for Atomic Bromine and Some of its Properties

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Introduction

This study was an investigation of the chemical processes induced by the isomeric transition in which the Br^{80} nucleus changes from its upper state of 4.5 hr. half-life to the lower one of 18 min. half-life.[2,3,4] Certain evidence was obtained during the work for the occurrence of atomic bromine detectable by its radioactivity and stable for an hour or more because its concentration was very small.

The procedure was to allow compounds made with 4.5 hr. bromine to stand under various conditions for about two hours or more and then to perform chemical separations on them. The lifetime of any molecular form into which the daughter 18 min. bromine goes is limited at least by the 18 min. half-life of its nucleus and so the two hours is necessarily sufficient for the attainment of steady-state conditions to an accuracy of 1%. The steady-state amounts of the various forms of the 18 min. bromine extractable from the parent compound by the chemical separations used were determined by comparing the relative radioactivities of extract and parent compound.

One of the first results was the apparent impossibility of obtaining more than 90% separation of the 18 min. bromine although 85% was easily obtained. This has been interpreted as a limitation imposed by the nuclear processes themselves or by some part of the atomic processes which is not easily influenced by neighboring atoms. The data relating to this and a discussion of several possible explanations have already been presented.[5]

Discussion of the Radiations Involved

The isomeric transition radiations of the 4.5 hr. bromine are known to consist of conversion electrons of 23.6, 35.5 and 47.2 kev.[6,7] energy, gamma rays of approximately 37 kev.,[5,8] the regular bromine X-rays of 12 kev. or less energy,[9,10] and "Auger" electrons of 10 kev. or less from conversion of X-rays. None of these radiations affects appreciably the counter used in this work. The amount of 4.5 hr. bromine present in any sample was measured always by counting the penetrating beta-rays of 2 mev. upper limit emitted by the 18 min. bromine in equilibrium with the 4.5 hr.

Possibly about 15% of the 4.5 hr. bromine atoms emit beta rays, but this question is not settled. It has been raised as a possible explanation of the apparent 85% upper limit of extraction found in this work. If so, then some of the beta rays counted in this work should be attributed to 4.5 hr. bromine rather than 18 min. and the "percentages of extraction" listed should be raised by a factor of 100/85.

The chemical effects studied here are of course initiated by the isomeric transition radiations. Although more than one gamma ray transition must be involved in the isomeric transition,[6] the exact level scheme and relative proportions of the different rays emitted by a given atom are not yet known with certainty. According to the scheme of Grinberg and Roussinow[8] every atom emits first either a 47 kev. electron from the L shell or a 35 kev. electron from the K shell and then from 37[5] to 67[8] % of the atoms emit a 37 kev. gamma ray while in the other cases a second conversion electron is ejected from either the K or L shell. In addition to these, the X-rays and Auger electrons follow. As has been noted by many workers these radiations are all of too low momentum for the recoil of the bromine atom from their emission to disrupt the molecule.

However, the large ionization resulting from the Auger effect does furnish sufficient cause for decomposition. Measurements of X-ray fluorescence yields[11] show that a vacancy in the K shell of a bromine atom (as would be caused here by emission of a K conversion electron) has a 44% chance of being filled by Auger process. That is, an electron from

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[2] L. I. Roussinow and A. A. Yusephovich, *Compt. Rend., U. R. S. S.*, **20**, 645 (1938).

[3] E. Segrè, R. S. Halford and G. T. Seaborg, *Phys. Rev.*, **55**, 321 (1939).

[4] D. DeVault and W. F. Libby, *Phys. Rev.*, **55**, 322 (1939).

[5] D. DeVault and W. F. Libby, *ibid.*, **58**, 688 (1940).

[6] G. E. Valley and R. L. McCreary, *ibid.*, **56**, 863 (1939).

[7] L. I. Roussinow and A. A. Yusephovich, *Compt. rend., U. R. S. S.*, **24**, 129 (1939).

[8] A. P. Grinberg and L. I. Roussinow, *Phys. Rev.*, **58**, 181 (1940).

[9] P. A. Abelson, *ibid.*, **55**, 424 (1939).

[10] L. I. Roussinow and A. A. Yusephovich, *ibid.*, **55**, 979 (1939).

[11] A. H. Compton and S. K. Allison, "X-Rays in Theory and Experiment," D. Van Nostrand Co., Inc., New York, N. Y., 1935.

the L shell falls into the K vacancy and in doing so transfers its energy without radiation to a second L electron which is ejected from the atom leaving two L vacancies. Wentzel[12] has made theoretical calculations of the Auger effect on the basis of a simplified model, but does not predict its dependence on shell.[12a] The data available, however, all show increasing Auger effect with higher shells. Using these and other relevant data,[13] one obtains that at least 15% of the isomeric transitions cause loss of all the valence electrons, over 60% cause loss of four or more, less than 10% lose only 2 and less than 2% lose only one.

The loss of one valence electron probably does not often decompose the molecule. The loss of more, however, will be distributed among different atoms of the molecule and will produce coulombic repulsions between the atoms sufficient to decompose it. Possibly the small percentage of cases which result in single positive charges and some of the doubly charged may constitute the main portion of the 15% or so that has never yet been extracted.[5]

Apparatus and Methods

Counter.—A cylindrical aluminum walled counter tube 0.008 inch thick, $^7/_8$ inch diam. and 4 inches long was used for measuring the activities. The central wire was pure tungsten 0.1 mm. in diameter, and the tube was filled with alcohol vapor to a pressure of 4 cm. of mercury and argon to a total pressure of 10 cm. This mixture became stable to high counting rates after being allowed to discharge continuously for an hour or so. Its characteristics then remained constant for as much as a month of intensive use. A standard gamma ray sample giving about 16,000 counts per minute was used to check the sensitivity frequently. Even at this high rate the number of counts recorded per minute varied less than 0.03% per volt change in potential applied to the counter tube over a range of 400 volts. An 8° rise in temperature was found to raise the threshold by 80 volts but did not change the sensitivity in the plateau region.

The counter-tube was coupled directly to a two-stage amplifier with a resistance and condenser, no quenching tube being used. The impulses from the amplifier were fed to a vacuum scale of sixteen circuit.[14] The recorder consisted of an improved scale-of-ten thyratron ring circuit and a modified Veeder-Root electric impulse counter.

The counting loss correction for the apparatus as determined from the decay curves of activities of known half-lives was about 4.5% at 16,000 counts per minute and 25% at 50,000 counts per minute. By using samples with activities of between 2000 and 12,000 counts per minute the "possible statistical error" (3σ)[15] and the counting loss correction could be kept below 3% each with only five-minute counts. In the range from 8000 to 12,000 counts per min. "the possible statistical error" is less than 1.5% for a five-minute count and so is the possible error in calculating the counting loss correction.

It should be noted that there was always Br^{82} (34 hour half-life) present. It emits beta rays of about 0.5 mev. upper limit and gamma rays of 0.547, 0.787, and 1.35 mev.[16] The gamma rays produced 90% of the 34 hr. counts on the counter tube used. The amount of 34 hr. bromine present was easily estimated therefore by absorbing out all beta rays with a lead absorber. The 18 min. bromine also emits a much smaller percentage of approximately 1 mev. gamma rays which can be corrected for but was usually negligible.

The half lives used in correcting the various activities for decay are: 33.9 ± 0.3 hr. and 4.54 ± 0.10 hr. from Snell[17] and 17.9 ± 0.4 min. obtained in the course of this work.

Preparation for Counting.—Most of the activities were measured in the form of silver bromide. The precipitates were spread out evenly over a piece of filter paper 9 cm. in diameter. They were confined to an area 8 cm. in diameter by means of a glass cylinder of that size open at both ends. The surface of the Büchner funnel was ground flat so that the filter paper fitted tightly between it and the glass cylinder at all points of the circumference, to prevent escape of precipitate. A sheet of cellophane was folded around the precipitate, which was then wrapped around a bronze gauze cylinder, precipitate side inside, and held on with a rubber band. The bronze cylinders were made to fit over the counter tube with just enough clearance for inserting a cylindrical lead absorber. They made it easy to take samples from the counter tube and put them back on in reproducible positions as often as desired. A wire support held the screen cylinders concentric with the counter tube when the lead absorber was not in. A series of tests showed this method to have a reproducibility of about 3%.

The activities of liquids were determined by placing them between the two co-axial cylindrical walls of a glass cell that could be slipped over the counter tube. The inner wall was very thin (about 0.1 mm.) to pass the beta rays and of such a diameter that the cell just fitted over the counter tube when the cylindrical lead absorber was on.

Preparation of Compounds.—The radio-compounds were usually prepared by ordinary synthetic methods starting

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(12) G. Wentzel, *Z. Physik*, **43**, 524 (1927).

(12a) Dr. E. P. Cooper has considered the problem of the Auger effect and its application to the isomeric ejection process in a paper to appear soon in the *Physical Review*.

(13) First gamma ray: 100% converted, 67% K and 33% L. Second gamma ray: 40% minimum converted, assumed same ratio K to L. Of K X-rays which are emitted, 84% are L to K; 14% M to K; 2% N to K; while of the L X-rays roughly 90% are M to L and 10% are N to L. Fluorescence yields (*i. e.*, non-Auger effect): K shell, 56%; L shell, 20% max. (comparison with data for Kr would indicate 10%): M shell, 10% max. if the whole atom has lost only one or two electrons, 50% max. otherwise. The limits were widened for this case because it is uncertain how large ionization will affect the fluorescence yield. Data on X-rays from Compton and Allison, *loc. cit.*

(14) D. DeVault, *Rev. Sci. Inst.*, **12**, 83 (1941).

(15) $\sigma = \sqrt{R/n}$ = "the standard deviation," where R is the average number of counts per minute and n is the number of minutes taken for the count. There is only 0.3% chance that fluctuations in the rate due to randomness of the rays can throw a count off by more than 3 σ.

(16) M. Deutsch and A. Roberts, *Phys. Rev.*, **60**, 362 (1941).

(17) A. H. Snell, *ibid.*, **52**, 1007 (1937).

with either radio Br_2 or radio Br^-. These were obtained by irradiating a liter or more of bromobenzene with neutrons from the Berkeley cyclotron, then adding two or three drops of liquid bromine (occasionally this carrier was omitted) and extracting with sodium sulfite solution. The sulfur dioxide was boiled out after acidification with sulfuric acid. Radio-Br_2 could be obtained from this by adding liquid bromine, shaking to get complete interchange (this interchange is known to be rapid) and separating the layers. The ethyl bromide preparation required solid potassium bromide, so the aqueous extract with sulfur dioxide boiled out was neutralized with potassium carbonate, the required amount of inactive potassium bromide was dissolved in, mixed thoroughly and evaporated to dryness. The potassium sulfate impurity did not interfere.

The radio BrO_3^- was prepared several times by adding bromine to potassium hydroxide solution, but a more convenient method is to dissolve inactive sodium bromate in the acidified, sulfur dioxide-free aqueous extract from the bromobenzene and keep the solution hot for half an hour. The small amount of radio Br^- originally present is converted to bromine and this interchanges quite completely with the BrO_3^-.[18] The small amount of bromine can be boiled out or it can be precipitated with $Ag(NH_3)_2^+$ after neutralizing the solution with ammonia.

The specific activity was most conveniently measured by adding excess of the same radio Br^- used in preparing the compound (or of Br^- prepared from the compound itself or from some other material or residue from its preparation that would have the same specific activity) to a measured amount of Ag^+. The precipitate was washed and its activity was measured in the usual way. The "total" activities were usually calculated from this specific activity and the pressure, volume and temperature in the case of gases, or the volumes and densities in the case of liquids.

Methods of Extracting 18 Min. Bromine.—When 4.5 hr. bromate was being studied its solution was made alkaline with ammonia to avoid the interchange that would occur between bromate and any trace of bromine that might be there if the solution were not alkaline. The extractions were made by adding carrier Br^- and excess silver nitrate or, if the bromate solution were made with $Ag(NH_3)_2^+$ already in it, then only Br^- was added to make the extraction. To make sure that the Br^- was completely precipitated no more ammonia than just enough to keep silver oxide from precipitating was present. It also served to keep silver bromate from precipitating.

Liquid organic bromine compounds were extracted by shaking them vigorously for two minutes with the aqueous agent or by shaking with metallic mercury. The results from the two methods agreed if $SO_3^=$ solutions were used.

The gases were allowed to stand for two hours in a 5-liter flask sealed to a manifold and vacuum pumps. The flask was equipped with a mercury manometer. The extracting liquids were brought into contact with the gases by injecting them through a spray built into the flask. It consisted of 25 jets in a small bulb on the bottom end of a tube which extended into the flask to a point just below the neck. The top end of this tube extended through a ring seal and a two-way stopcock to a funnel for holding the liquid to be sprayed in. The stopcock could also be turned so as to drain the funnel into an external container. Certain parts of the walls of the flask (about 10 to 20%) were never touched by the spray but repeated extractions were always used. When bromine vapor was added for carrier purposes immediately before an extraction about two drops in liquid form was put into the funnel along with considerable water to give bulk so that the stopcock could be turned off after introducing the bromine before any air entered. When this was followed by sodium sulfite solution, the immediate disappearance of the color of the bromine vapor in the flask showed that the sodium sulfite spray extracted it thoroughly and quickly. The liquids were removed from the 5-liter flask by draining through a stopcock in the bottom into a removable evacuated receiver. Each "extraction" with sodium sulfite consisted of two approximately 30 ml. portions of the solution sprayed in and drained out and then one portion of pure water.

The sodium sulfite solution used on both liquids and gases was 0.08 *M* in sodium sulfite and 0.60 *M* in sodium bicarbonate.

Data

Table I gives all of the experiments done on gases except for some crude preliminary ones and the charged plate experiment. The rest are in Table II which is divided into sections according to conditions.

In Table I the columns headed a, b, c and d tell what percentage of the total activity was found in each of several successive extracts. These values have been corrected for small amounts of new 18 min. Br formed during the few minutes between the successive extracts. The column headed "total" gives the sum of all such successive extracts made within a short time of each other. Probable errors are about 5% for each of these totals.

Experiments on a given compound at a fixed partial pressure (*e. g.*, nos. 5, 6 and 7) are for successive extracts performed at intervals of two hours or more on the same filling. The pressures are all given in mm. and are accurate to about 0.3 mm.

Each of the extracts for expts. 1 to 5 consisted of about 100 ml. of pure water sprayed into the gas in several short spurts. Those of expt. 6 were made with pure concentrated sulfuric acid in the same way. The extracts of expts. 7 and 8 were made by spraying into the gas almost continuously about a liter of pure water each. In the rest of the experiments a few drops of bromine were vaporized into the reaction mixture which was immediately extracted by spraying in dilute aqueous sodium sulfite solution.

The results are consistent enough to establish that in the gases about 55% of the 18 min. bromine

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(18) W. F. Libby, This Journal, **62**, 1930 (1940).

TABLE I

DATA ON GASES (ALL AT APPROXIMATELY 25°)

Expt.	Radio compound	Other gases present	Extn. method	Per cent. of 18 min. extd. a	b	c	d	Total
1	20 mm. EtBr		Water	33	14	3	5	55
2	21 mm. EtBr		Water	62				62
3	21 mm. EtBr	20 mm. H_2O vap.	Water	54	5	4		62
4	21 mm. EtBr	20 mm. H_2O vap.	Water	38	9	4		51
5	22 mm. EtBr	+503 mm. A	Water	32	5	3		40
6	22 mm. EtBr	H_2O vap.	H_2SO_4	33	8	11		52
7	22 mm. EtBr	Sl. amt. air	Much water	63				63
8	20.5 mm. EtBr		Much water	44	14			58
						Average		55 ± 6
9	9.2 mm. EtBr		Br_2-$SO_3^=$	80	5			86
10	9.2 mm. EtBr	H_2O vap. + A to 104 mm.	Br_2-$SO_3^=$	81	2			83
11	9.2 mm. EtBr	H_2O vap. + A to 404 mm.	Br_2-$SO_3^=$	76	8			84
12	12.3 mm. EtBr	H_2O vap. + A to 394 mm.	Br_2-$SO_3^=$	66	11			77
13	94.0 mm. EtBr		Br_2-$SO_3^=$	70	21			90
14	10.0 mm. $(CH_2Br)_2$		Br_2-$SO_3^=$	53	16			69
15	0.4 mm. EtBr		Br_2-$SO_3^=$	65	9			73
						Average		80 ± 6

in the steady state is in such a condition that it dissolves in water or concentrated sulfuric acid in preference to remaining in the gas or on the walls of the vessel. About 25% dissolves only so far as these experiments go, by treatment with bromine and then sodium sulfite. It is also seen that pressure or inert gases exert very little effect, if any. As discussed later, this striking inability of water or concentrated sulfuric acid to extract a large portion of the 18 min. activity in the absence of carrier bromine is considered to be evidence for bromine atoms. They would be present at such low concentrations that they probably could not form molecular bromine by themselves at a significant rate and consequently would behave in the extractions according to the relative fugacity of Br atoms in the two phases.

Table II contains the data obtained on condensed phases. Part A bears on two points. First expts. 18 and 19 show, in agreement with Willard's results on a mixture of bromine and carbon tetrachloride, that solidifying at −184° produces only a small effect. It is interesting, however, that freezing and cooling do appear to increase the activity retained in the organic layer. Ice was present in the frozen mixture. The extraction was made by warming the mixture until melted and then shaking, all within 3 minutes.

Experiments 19 and 20 indicate the occurrence of atomic bromine in the liquid. In them 1 ml. of pure ethyl bromide stood at 0° for nearly two hours and was then extracted by shaking with pure water; 43% of the activity went into the water layer. Then one or two drops of bromine were added and the liquid was immediately shaken with sodium sulfite solution. This second extract contained activity equal to 24% of what the total activity would have been but for the previous extract. Of this only 9% is attributable to new 18 min. bromine formed between extracts and therefore the other 15% represents 18 min. bromine not readily soluble in water (at least compared to its solubility in ethyl bromide) but soluble after treatment with bromine and then sodium sulfite.

Additional evidence appears in Expts. 22, 23, 24, 25 and 26[19] as compared with Expts. 27, 28, 29 and 30. In the former the extracts had been made with $SO_3^=$ solution either with or without bromine added as carrier (no significant effect of bromine was observed). This should have extracted any Br atoms present. In the second group the uniformly lower extractions are obtained by extracting with plain water, checking the gaseous results.

It is interesting to observe in expt. 31 how rapidly the extraction has risen with percentage of ethanol in the carbon tetrachloride solution. This is true in general for the alkyl bromides. For example, the 90% extraction by Segrè, Halford and Seaborg[3] from $CBr(CH_3)_3$ in MeOH–H_2O solution

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(19) Expt. 26 involves $(CH_3)_3CBr$ which can hydrolyze with water. The very small amount of hydrolysis that must have occurred during the extraction should be sufficient to give enough Br^- ion to interchange with the inorganic forms of 18 min. bromine. Thus higher extraction would be expected here than in cases where the water stays pure, and might be expected to give results as high as those with $SO_3^=$ as is observed.

TABLE II

A. ATOMIC BROMINE IN LIQUID PHASES, GENERAL EXTRACTION CHARACTERISTICS OF ALKYL BROMIDES (ALL AT APPROXIMATELY 20° UNLESS NOTED)

Expt.	Radio compound	Conditions	Extraction method	% Extracted
18	C_2H_5Br	Solid at −184°	Water	21±5
19	C_2H_5Br	Liquid at 0°	Water	43±4
20	C_2H_5Br	Liquid at 0°	$Br_2 + SO_3^=$	58±4
21	C_2H_5Br	2 vol. % in hexane	$SO_3^=$	59±4
22	$CHBr_3$	0.616 g. in 500 cc. CCl_4	$Br_2 + SO_3^=$	36±5
23[a]	MeCHBrCHBrEt	1 vol. % in CCl_4	$Br_2 + SO_3^=$	38±2
24[a]	MeCHBrCHBrEt	1 + 0.05 *M* Br_2	$SO_3^=$	36±3
25	C_2H_5Br	2 vol. % in CCl_4	$SO_3^=$	38±3
26[a]	$(CH_3)_3CBr$	4 vol. % in CCl_4	Water	42±4
27	C_2H_5Br	0.21 vol. % in bromobenzene	Water	18±5
28	C_2H_5Br	.20 vol. % in CCl_4	Water	21±5
29	C_2H_5Br	.25 vol. % in (1% of 95% EtOH, 99% CCl_4)	Water	13±5
30	C_2H_5Br	.25% vol. in (10% of 95% EtOH, 90% of CCl_4)	Water	23±5
31	C_2H_5Br	.20 vol. % in 95% EtOH	$CCl_4 + H_2O$	89±5
32	Bromobenzene	1 vol. % in 95% EtOH	Inactive $\varphi Br + H_2O$	89±5[b]
Ref. 4	BrO_3^-	2.5 *M* NH_4OH	$Br^- + xsAg^+$	75[c]
33	BrO_3^-	$NH_4OH + Ag(NH_3)_2^+$	Br^-	76
34	1 *M* BrO_3^-	2 *M* NH_4OH	$Br^- + xsAg(NH_3)_2^+$	66[b]
35	0.1 *M* BrO_3-	0.2 *M* NH_4OH + 0.06 *M* Br^-	$xsAg(NH_3)_2^+$	80[b]

[a] Measured by Charles H. Klute and Edward L. Wagner, undergraduate research report, May, 1939. [b] Measured by growth of the activity of the parent substance in liquid cell after extraction. [c] Measured by growth of activity of $AgBrO_3$ ppt. made from filtrate after extraction.

B. ISOMER CAPTURE BY CCl_4 AND CS_2; EFFECT OF C_2H_5OH ON CCl_4 CAPTURE; COMPETITION BETWEEN CS_2 AND CCl_4 IN MUTUAL SOLUTIONS

Expt.	Radio compound	Conditions	Extraction method	% Isomer left in organic layer
Willard[20]	Br_2	0.1 *N* in CCl_4	I^- or NO_2^-	34
41[a]	Br_2	.1 *N* in CCl_4	Hg	32.4±1
42[a]	Br_2	.1 *N* in (1 mole % EtOH, 99 mole % CCl_4)	$SO_3^=$	25±1.5
43[a]	Br_2	.1 *N* in (9 mole % EtOH, 91 mole % CCl_4)	$SO_3^=$	12±2
44	Br_2	.24 *N* in (25 mole % EtOH, 75 mole % CCl_4)	$SO_3^=$	8.3
45	Br_2	.14 *N* in (62 mole % EtOH, 38 mole % CCl_4)	$SO_3^=$	1.8
46	Br_2	.28 *N* in (89 mole % EtOH, 11 mole % CCl_4)	$SO_3^=$	0.9
47[a]	Br_2	.1 *N* in CS_2	Hg	9±2
48[a]	Br_2	.1 *N* in (95 mole % CS_2, 5 mole % CCl_4)	Hg	12.5±0.5
49[a]	Br_2	.1 *N* in (75 mole % CS_2, 25 mole % CCl_4)	Hg	20.5±5
50[a]	Br_2	.1 *N* in (50 mole % CS_2, 50 mole % CCl_4)	$SO_3^=$ or Hg	26±.5
51[a]	Br_2	.1 *N* in (25 mole % CS_2, 75 mole % CCl_4)	$SO_3^=$ or Hg	32±3
52[a]	Br_2	.1 *N* in (5 mole % CS_2, 95 mole % CCl_4)	$SO_3^=$ or Hg	34±3

[a] Measured by Nicholas Elefther, graduate research report, February, 1941.

fits in exactly with these results. It is true for bromobenzene in ethanol also as shown in expt. 32.

The only completely aqueous solution tried was that of BrO_3^-. Earlier work had shown that this also gave high extraction. This may be an effect of solvent similar to that of alcohol or it may be due to the nature of BrO_3^- ion itself. The additional work seems to show that the results from BrO_3^-, though high, are significantly lower than the 85% extractions obtained from other compounds. Experiment 35 shows, however, that the extraction may be raised toward this limit by adjusting conditions. Probably the most significant of the changes made was the addition of inactive Br^- ion to the environment.

The first section of Table IIB shows that the presence of about enough ethanol molecules to place one or two near the mother radioactive bromine molecule in the first or second layer nearest neighbors eliminates the capture reaction with carbon tetrachloride reported by Willard.[20] This indicates a preference for reaction with the alcohol molecule to form either Br^-, HBr, Br_2 or

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(20) J. E. Willard, THIS JOURNAL, **62**, 256, 3161 (1940).

Br atoms. (The Br atoms would be extracted because they would interchange rapidly with the bromine present.) The second part of the table shows that carbon bisulfide has a similar capture reaction with the fragments, the data on the dilution effect indicating no great preferential action on the part of carbon tetrachloride. In this connection also expts. 22, 23, 24 and 25 in comparison with expts. 21 and 20 show a similar reaction probably occurs from alkyl bromides as well.

In addition, certain experiments were also tried in which solutions of radio ethyl bromide or radio-2,3-dibromopentane contained unsaturated hydrocarbons. These were extracted by adding excess bromine and shaking with sodium sulfite solution. The amounts of 18 min. bromine extracted were low (2 to 15%) as would be expected. In one case the extraction was made by shaking with pure water, no bromine having been added. This took out 33%, indicating that much of the 18 min. bromine goes into a form extractable by water but not able to add to the double bonds until after it has had a chance to interchange with bromine. Hydrogen bromide would behave this way.

The possibility that the radiations cause decompositions of other molecules enough to interfere with the results is easily eliminated in this type of experiment by noting that the extracts usually had negligible amounts of 4.5 hr. or 34 hr. bromine in them. This fact also eliminates the possibility that interchanges have interfered, because any such indiscriminate reactions would not be partial to the 18 min. bromine, but would put the longer lived activities into the extracts also.

Charged Plate Experiment.—An experiment was performed to determine if much of the 18 min. bromine ejected from gaseous ethyl bromide retains its charge for very long. The radio-ethyl bromide was put at a pressure of 32.8 mm. between a series of alternate positive and negative aluminum plates 1.3 mm. apart. A potential of 103 volts was applied for four hours. The result was what would be expected if the charge had no effect: both sets collected about equal amounts of 18 min. activity. The total amounted to over three times as much as was formed in the gas immediately between the plates, showing considerable collection of activity from the surrounding gas.

At this field and pressure positive ions should be removed within 10^{-4} second. It may be concluded tentatively, therefore, that the 18 min. Br becomes neutralized in less time than this.

General Discussion

Neutralization.—The large positive charge left on the bromine by the isomeric transition is probably not neutralized by capture of free electrons because studies of ions in gases show that to be an improbable process in general. If it occurred here it should bring about a dependence of results upon concentration of electrons and therefore on the amount of radioactivity. The present data do not seem to show evidence of such an effect.

However, as long as the 18 min. bromine has more than one positive charge a transfer of an electron from any nearby neutral molecule to it will be exothermic. Such electron jumps should be rapid when the molecules are close together. Indeed, the smaller extent of decomposition observed in liquid may be attributed partly to the presence of many neutral molecules nearby which may sometimes remove the charges rapidly enough to keep the molecule from decomposing or at least to stabilize it on the event of primary recombination. In the gas, decomposition will be more certain.

The transfer of electrons from neutral molecules to singly charged ions is to be expected also. Whether the process is endo- or exothermic depends of course on relative ionization potentials. However, the entropy effect resulting from the fact that the 18 min. Br under consideration is such a small fraction (10^{-13}) of the total number of molecules present favors the dissipation of the last charge to the surrounding molecules even against an unfavorable ionization potential difference of 0.8 volt ($kT \ln 10^{13}$). *This principle is obviously of general importance in this type of experiment.* To account for the charged plate experiment the neutralization processes would have to be completed in the gas at about 0.04 atmosphere in about 10^{-4} second. This seems reasonable. Willard has already discussed neutralization of the bromine charge from another viewpoint.[20]

The Substitution Reactions.—Willard[20] observed that some 34% (depending on concentration) of the 18 min. bromine from 4.5 hr. radio-Br_2 in carbon tetrachloride goes into the organic layer on extraction. It probably forms something like CCl_3Br. Experiment 47 shows a similar though smaller effect with carbon disulfide. When carbon disulfide and carbon tetrachloride are mixed (Expts. 48 to 52) the effect is intermediate. Also substitution into carbon tetrachloride from alkyl bromide molecules is a likely explanation for the 20% lower extractions obtained in carbon tetrachloride solution of radio-organic compounds (Expts. 22, 23, 24, 25) as compared with those in other solvents (Expts. 20, 21).

These substitutions do not occur, however, in the gas phase. This has been tried by Willard[20] with $Br_2(g)$ in carbon tetrachloride vapor and by Suess[21] with radio $HBr(g)$ in inactive C_2H_5Br vapor. They are also inhibited in the liquid by the presence of alcohol to a greater extent than mere steric hindrance (Expts. 42–46).

Willard suggested that the mechanism involves a decomposition of carbon tetrachloride by one of several methods and recombination of the fragments with the 18 min. Br. A method for decomposing the carbon tetrachloride would seem to be furnished by the high positive charge on the bromine atom. For example if it has 4 positive charges it could easily take two electrons from a carbon tetrachloride molecule on collision with it. This may decompose it into CCl_3^+ and Cl^+. The CCl_3^+ and Br^{++} could have some chance of combining if enough other molecules intervene in time to remove the charges. The cage[22] effect of the liquid will serve to hold the reactants near each other an appreciable length of time. The absence of both the cage effect and other molecules to remove the charges would prevent such substitutions in gases. This mechanism avoids capture of free electrons and at the same time decomposes a carbon tetrachloride molecule next to the bromine atom where it is needed for reaction with it. The inhibiting effect of alcohol on the substitution is understandable if the highly charged bromine atom has a preference for any alcohol molecule that might be present and ties up with it, or the oxygen from it, until it has lost so much of its charge that it can no longer decompose any carbon tetrachloride and has diffused away from any already decomposed. Possibly other forms of excitation than ionization could promote a very similar mechanism.

Alcohol Effect.—The alcohol solutions (Expts. 31, 32, 45 and 46) show results similar to those given by gaseous conditions. That is, substitutions or recombinations to form water insoluble compounds or deactivation without decomposition are all eliminated. According to Expts. 41 to 46 where mixed alcohol and carbon tetrachloride solutions are used the amount of substitution that does occur is much less than proportional to the carbon tetrachloride mole fraction. The 18 min. bromine, therefore, shows a preference for the alcohol. It seems logical that a bromine atom with large positive charge would be attracted to a highly electronegative atom like oxygen and form a temporary compound with it, perhaps after decomposing the alcohol molecule. This could serve to keep the bromine from combining with any other fragments until some time after it has been neutralized and drifted away from them. Another possibility is that the bromine has a strong tendency to react with the hydrogen atom of the hydroxyl group to form hydrogen bromide.

Data of le Roux, Lu and Sugden[23] indicate that aniline in only 5% concentration has a similar effect.

Inorganic End-products.—It should be noted that the concentration of 18 min. bromine even in pure liquid ethyl bromide with the strongest samples used could not have exceeded about 10^8 atoms per cc. This, then, is the upper limit of concentration of any products of the transition-induced reaction unless some of these products are identical with substances already present in the reaction mixture. Reactions between product molecules are highly improbable since even in a gas at this concentration a given molecule undergoes only about two collisions per min. They will be expected, therefore, to react only with molecules already present in large quantity.

The possible forms for the 18 min. bromine that might be extractable from radio-organic compounds by the inorganic reagents used are Br_2, HBr, Br (free atoms), molecular fragments containing carbon atoms, such as CH_2Br, and ions. The charged plate experiment fairly well rules out that any large proportion of the 18 min. bromine exists very long in ionic form. Of the uncharged species, hydrogen bromide and bromine could be formed by combination of the 18 min. bromine with the hydrogen or the bromine atoms of the other organic compounds already present. Both would be expected to go completely into the water layer on extraction because the hydrolysis $Br_2 + H_2O \rightarrow H^+ + Br^- + HBrO$ is highly favored by the extremely low concentration of bromine that would be present in the cases where pure water was used as the extracting agent. In

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[21] H. Suess, *Z. physik. Chem.*, **45B**, 312 (1940).

[22] Frank and Rabinowitch, *Trans. Faraday Soc.*, **30**, 125 (1934).

[23] L. J. le Roux, C. S. Lu and S. Sugden, *Nature*, **143**, 517 (1939); C. S. Lu and S. Sugden, *J. Chem. Soc.*, 1273 (1939).

fact, any concentration less than 10^{-9} M for acid solutions or less than 10^{-4} M for solutions of bromine only, with no added acid, is sufficient for over 99% hydrolysis. The fraction of the activity that was readily extracted by water from either gas or condensed phase may therefore be either hydrogen bromide or bromine or both.

It has been pointed out, however, that in both the gaseous and liquid experiments a certain fraction of the activity, extractable by more drastic means, does not go into the water layer readily. We propose that this fraction is in the form of *bromine atoms* and that they are more soluble in the organic layers. The following alternatives to this proposition do not seem so likely: possibly it could be bromine, the difficulty with extraction by water being due to slowness of the hydrolysis or to excess bromine impurity causing a decrease in the hydrolysis. For the first point, the reaction would not be expected to be any slower at extremely low concentrations of bromine than it is at high concentrations unless the only possible mechanism involved collisions between two bromine molecules. For the second point, it is very unlikely that bromine impurity was present at concentrations of 10^{-6} M, though the possibility must be borne in mind. Another possibility is that it is in the form of something like CH_2Br. However, one would expect the C–Br bond to break before the others and it is difficult to see how an unstable molecule such as this would be formed in subsequent reactions of the bromine any more readily than Br atoms themselves.

If the assumption of bromine atoms is correct, we are prepared to list the following as some of the properties of thermal bromine atoms. *They are not readily soluble in water or concentrated sulfuric acid. They do not react readily with organic compounds such as ethyl bromide, but do interchange quickly with bromine.* It is obvious that we may have here a method of *producing labeled bromine atoms* in reagent form. It has not been determined whether the Br atoms are found on the walls or in the gas in the case of the gas experiments.

Bromate Ion.—In the case of bromate ion the initial decomposition probably throws off one or more oxygen atoms. The unstable product must usually end up as Br^- through decomposition of its own accord, through oxidation of ammonia or through interchange with Br^- already present. It is then extracted by precipitation with the $Ag(NH_3)_2^+$. The high extractions obtained generally from BrO_3^- show these to be probable processes.

However, the relatively low result of Expt. 34 shows that under some conditions the 18 min. bromine has a chance of getting back into the form of BrO_3^-, the only form likely to escape precipitation by the $Ag(NH_3)_2^+$. Probably, therefore, the intermediate has long enough life to interchange with BrO_3^- or to combine with oxygen atoms from the water to reform BrO_3^-. The loss of electrons during the isomeric transition insures a sufficiently high oxidation state. Interchange of the intermediate with Br^- would explain the fact that the highest extraction was obtained in Expt. 35, where Br^- was present in macroscopic quantity.

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Summary

The isomeric transition from 4.5 hr. to 18 min. half life in Br^{80} usually induces a shower of electrons from the bromine atom. If the molecule containing the bromine atom is in a gaseous state it is decomposed by the resulting large positive charge on it. The ejected 18 min. bromine atom is quickly neutralized by electron transfer on collision with neutral molecules and ends up as hydrogen bromide, bromine, or *free Br atoms.* The latter form in appreciable numbers with long life because of low concentration, appear not to be very soluble in water or concd. sulfuric acid, and do not react readily with organic compounds such as ethyl bromide.

In liquid phases substitution reactions occur. Probably the cage effect keeps the highly charged Br in contact with neighboring molecules for a longer time so that they are broken up by the charge and the fragments have a chance to com-

bine with the Br. Thus a smaller fraction of the 18 min. activity becomes water-soluble. Primary recombination or deactivation might, of course, occur also. Substitution into carbon bisulfide occurs slightly less often than into carbon tetrachloride.

Alcohol or aniline acts to release the 18 min. bromine in inorganic form either by being attracted by Br atoms undergoing transition and reacting with them enough to prevent recombinations or substitutions or by reaction with the newly formed organic bromides while they are still activated.

This tentative picture is based on the following experimental findings. (1) A portion (roughly 25%) of the 18 min. activity ejected from organic compounds in the gas and in the liquid will interchange with Br_2 or react with reducing agents, but is not extracted by water. (2) Another portion is readily extracted by pure water. (3) The amount of 18 min. bromine which goes into or remains in organic form is reduced to a minimum by gaseous conditions or by adding alcohol or aniline to liquids. (4) Substitution into carbon bisulfide is observed and into carbon tetrachloride is confirmed. The substitution into carbon tetrachloride occurs either from bromine or alkyl bromides. (5) The products from the gas phase at 21 mm. pressure do not show preference for either negative or positive charged plates. (6) A small dependence of the amount of extraction from BrO_3^- on the presence of Br^- may indicate that an intermediate form is involved there.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Colorimetric Detection and Determination of Palladium with Compounds Containing the *p*-Nitrosophenylamino Group[1]

BY LYLE G. OVERHOLSER AND JOHN H. YOE

A study of the reaction of *p*-nitrosodiphenylamine (I) with palladous chloride and its application to the colorimetric detection and determination of palladium has been presented in a previous paper.[2] Further studies on a large number of aromatic amines revealed that compounds containing the *p*-nitrosophenylamino group, *p*-$NOC_6H_4N<$, namely, *p*-nitrosoaniline (II), *p*-nitrosodimethylaniline (III), and *p*-nitrosodiethylaniline (IV) form similar highly colored complexes with palladous salts. These complexes are all of the same general type as exemplified by palladous dichlorodiammine, $Pd(NH_3)_2Cl_2$. This compound has been reported to exhibit *cis-trans* isomerism; hence it is possible that those prepared in this Laboratory may exist in *cis-trans* isomeric forms, though no experimental evidence to substantiate this view is at hand.

Numerous amines give complexes with palladous chloride but generally the product obtained is yellow. Thus aniline[3] and *p*-nitroaniline[4] both give yellow complexes with palladous chloride. In contrast, the complex of (I) with palladous chloride is dark purplish-brown, that of (II) dark brown, and of (III) and (IV) bright red. Diethylaniline, dimethylaniline, *p*-aminophenol, *p*-chloroaniline, and *p*-phenylenediamine do not give highly colored complexes with palladous salts. All this evidence indicates that the nitroso group must be present in order to form highly colored complexes and that the *p*-$NOC_6H_4N<$ structure is responsible for the characteristic reaction with palladous salts.

The presence of the nitroso group also results in a more selective reaction for palladium. Thus, diphenylamine and its amino or hydroxy derivatives give highly colored reactions with numerous oxidizing agents, whereas the nitroso derivative reacts only with strong oxidizing agents. Similarly, *p*-aminodiethylaniline gives reactions with weaker oxidizing agents than does *p*-nitrosodiethylaniline

Ogburn[5] reported reactions of palladous chlo-

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[3] A. Gutbier and A. Krell, *Ber.*, **39**, 1292 (1906).

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