

Photochemical Coupling between Tin Tetrabromide and Simple Aliphatic Bromine Compounds

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Photochemical coupling in the presence of oxygen between bromine-substituted methanes, ethanes, and ethylenes and tin tetrabromide has been investigated in carbon tetrachloride solutions. Solid reaction products have been isolated and analysed.

Two different types of coupling have been found, *i.e.* Sn—O—C and Sn—C. The latter type is found only in the case of 1,1-dibromoethylene. Besides, formation of C—C bonds has been shown in the cases of carbon tetrabromide and bromoform.

Exchange between bromine and hydrogen and vice versa is observed in different cases. Carbonyl groups appear in all compounds except in the products from carbon tetrabromide and bromoform. With decreasing content of bromine in the organic reactant the rate of reaction and yields are decreasing.

The photochemical reaction between tin tetrabromide and tetrabromoethylene in the presence of free oxygen has been reported previously.¹ The reaction product was found to consist of simple, linear molecules with Sn—O—C couplings. A free-radical type of mechanism is involved.

In order to study the scope of the reaction we have performed the reactions between tin tetrabromide, oxygen, and bromine derivatives of methane, ethane, and ethylene in carbon tetrachloride solution and examined the reaction products. Only solid deposits have been isolated and examined. Due to their extremely great sensitivity towards moisture it has not been practically possible to obtain samples for analysis which have not undergone hydrolysis or absorbed water, to some extent.

The compounds are amorphous and our investigations are mainly based on elementary analyses and spectroscopic examinations supported by different other tests. Group analyses of the compounds are difficult to perform on account of their reactivity and special character.

EXPERIMENTAL

All reactions were performed in a cylindrical flask of 500 ml volume which was placed in a thermostated bath and illuminated with a 125 W mercury-vapour lamp.

All operations were carried out with great care to exclude moisture. The tin tetrabromide was distilled in vacuum over phosphorus pentoxide just before use. The organic compounds were recrystallized and dried, or distilled in vacuum, before use. Carbon tetrachloride of analytical quality, usually 300 ml, was used as a solvent after treatment with phosphorus pentoxide and active carbon and subsequent distillation. A small amount of bromine was added. Oxygen from a steel flask was dried over sulphuric acid and phosphorus pentoxide and bubbled through the solution at a pressure of 1 atm.

The solid products were washed several times in the reaction flask with carbon tetrachloride, which was finally removed by freeze drying in vacuum, yielding the products in a voluminous and fine-powdered state.

Infrared spectroscopic investigations were carried out on a Perkin-Elmer spectrophotometer, model 21, with sodium chloride and cesium bromide optics. The spectra were obtained from potassium bromide disks.

For NMR studies a Varian A 60 A spectrometer has been used.

Table 1. Experiments with tin tetrabromide and organic reactants.

Organic reactant	Reaction temperature °C	Time of reaction h	Conc. mole/l of SnBr ₄	Conc. mole/l of organic reactant	Thermic stability of products. Visible decomp. °C
CBr₄					
Sample 1	20	3.0	0.058	0.067	> 150 ^a
» 2	20	1.5	0.126	0.016	> 200
» 3	20	1.7	0.025	0.017	> 200
» 4	0	1.8	0.025	0.027	> 200
CHBr₃					
Sample 1	20	3.0	0.013	0.046	~ 100
» 2	20	6.7	0.013	0.038	> 200
» 3	20	1.5	0.026	0.076	> 200
» 4	0	16.3	0.051	0.038	> 200
CH₂Br₂					
Sample 1	0	31.5	0.026	0.048	> 200
» 2	20	17.5	0.104	0.020	> 200
CBr₂=CBr₂					
Sample 1	20	4.5	0.038	0.048	~ 180 ^a
» 2	20	3.0	0.044	0.051	~ 180 ^a
CHBr=CBr₂					
Sample 1	20	5.5	0.013	0.034	> 100 ^a
» 2	0	36.0	0.026	0.034	~ 100 ^a
» 3	20	7.3	0.026	0.017	~ 90
CH₂=CBr₂					
Sample 1	0	23.0	0.076	0.009	~ 100
» 2	0	29.0	0.145	0.018	> 200
» 3	0	27.5	0.150	0.022	~ 90
» 4	20	4.5	0.051	0.039	> 200
CH₂Br-CH₂Br					
Sample 1	0	14.5	0.115	0.018	~ 100
» 2	0	22.5	0.153	0.039	> 200
» 3	0	12.5	0.025	0.039	~ 100 ^a
» 4	0	24.5	0.101	0.020	~ 100

^a Not freeze-dried.

Table 2. Analytical data for reaction products.

Organic reactant	C	Sn	Br	H	O	Br ^a	H	O	Br+		Br ^b	H _a ^c	H _a ^c	H _a ^c	O	H _a ^c	O	Br ^c -O
									H+O	Br								
CBr ₄	Sample 2	1.-	0.35	0.67	3.06	1.75	0.50	2.27	1.30	4.06	2.76	1.79	3.50	2.27	1.75	0.65	0.37	2.20
	Sample 3	1.-	1.97	3.99	5.08	7.00	1.34	1.71	2.36	5.41	3.05	3.70	2.66	1.71	0.72	0.64	0.89	0.30
	Sample 4	1.-	1.47	2.78	5.31	5.40	1.13	2.15	2.19	5.46	3.28	3.31	2.87	2.15	0.98	0.75	0.76	0.68
CHBr ₃	Sample 1	1.-	1.40	3.57	4.07	1.34	1.49	1.70	0.56	3.75	3.18	2.05	2.10	1.28	2.30	0.61	0.27	1.54
	Sample 2	1.-	1.03	3.07	4.13	3.74	1.51	2.03	1.84	5.39	3.55	3.35	2.00	1.54	0.84	0.77	0.92	0.16
	Sample 3	1.-	1.58	3.66	7.64	8.89	1.42	2.96	3.45	7.83	4.38	4.87	2.19	2.57	0.74	1.17	1.58	1.26
CH ₂ Br ₂	Sample 1	1.-	0.92	2.12	3.48	5.20	1.10	1.81	2.71	5.63	2.92	3.81	1.85	0.77	0.28	0.42	1.46	0.86
	Sample 2	1.-	1.23	2.59	5.50	5.36	1.16	2.47	2.40	6.03	3.63	3.57	1.94	1.57	0.65	0.81	1.24	0.46
CBr ₂ =CBr ₂	Sample 1	1.-	0.64	1.44	3.32	3.49	0.88	2.02	2.12	5.03	2.90	3.01	1.90	2.02	0.95	1.06	1.12	0.22
	Sample 2	1.-	0.78	1.63	3.24	4.12	0.92	1.82	2.31	5.05	2.74	3.23	1.96	1.82	0.78	0.93	1.18	0.35
CHBr=CBr ₂	Sample 1	1.-	0.98	2.41	3.88	3.49	1.22	1.96	1.76	4.94	3.18	2.98	1.52	1.71	0.97	1.12	1.16	0.24
	Sample 3	1.-	0.53	2.16	3.55	0.84	1.41	2.32	0.55	4.28	3.73	1.96	0.95	1.99	3.62	2.09	0.58	0.40
CH ₂ =CBr ₂	Sample 2	1.-	1.00	2.20	3.52	0.77	1.10	1.76	0.39	3.25	2.86	1.49	1.40	1.26	3.27	0.90	0.28	1.01
	Sample 3	1.-	0.83	1.90	3.08	1.04	1.04	1.68	0.57	3.29	2.72	1.61	1.32	1.14	2.00	0.86	0.43	0.75
CH ₂ Br-CH ₂ Br	Sample 2	1.-	0.76	1.35	4.59	1.14	0.77	2.61	0.65	4.03	3.38	1.41	1.53	1.47	2.27	0.96	0.42	0.88
	Sample 3	1.-	0.63	2.73	2.33	9.57	1.67	1.43	5.87	8.98	3.10	7.54	0.48	0.20	0.03	0.42	12.23	5.39
	Sample 4	1.-	0.95	3.10	8.40	7.50	1.59	4.31	3.85	9.74	5.90	5.44	0.87	3.28	0.85	3.77	4.43	2.98

^a red.: Reduced to the sum 1.00 for carbon and tin atoms^b Br^c: Eliminated bromine^c H_a: Absorbed hydrogen

RESULTS

The different experiments which gave solid reaction products are specified in Table 1. Similar runs at different concentrations within the same ranges with tin tetrabromide and 1,2-dibromo-ethylene, ethyl bromide, and 1,1-dibromo-ethane, respectively, gave no solid products or only small, sticky deposits. 1,2-Dibromo-ethane gave no solid products at 20°C.

Runs at higher temperatures usually gave smaller yields of solid products, and a more rapid decomposition of the organic reactants. However, reactions with carbon tetrabromide, bromoform, and tetrabromoethylene, respectively, which generally proceed fairly rapidly with formation of considerable amounts of solid products, were also found to give good yields at 50°C.

All isolated products were white or creamy-white. X-Ray powder diagrams showed that all products were amorphous. On heating they did not melt, but decomposed over a range of temperature. No puffing, characteristic of peroxides, was observed on heating.

The reaction compounds were soluble in Lewis bases like formamide, dimethyl sulfoxide, and acetone; the reaction product from carbon tetrabromide, however, being markedly less soluble than the others. Solid adducts were isolated in some cases.

Due to the reactivity with solvents as well as moisture, no method suitable for molecular weight determinations has been found. Iso-piestic determinations in a closed system have given some support to the conclusions.

DISCUSSION

The infrared spectra of the different compounds, tabulated in Table 3, show common features.

The strong and broad absorption in the region around 3000 cm^{-1} , which is present in all spectra, is assumed to be due to water and associated hydroxyl groups in a hydrogen-bonded complex. The presence of water is confirmed by the method of Karl Fischer and in other ways (see below). The absorption band about 1600 cm^{-1} is probably, at least partly, caused by the deformation vibration of water, which is usually observed at 1630 cm^{-1} in hydrates.

The broad band about 1080 cm^{-1} has been correlated with the C—O stretching vibration (C—O—Sn)² and vibrations involving the stretching of the C—OH bond in alcohols. This band is lacking in the spectra of the 1,1-dibromo-ethylene compound.

The absorption at 950 cm^{-1} is supposed to arise from the Sn—O—H deformation.³

The absorption in the region about 525 cm^{-1} , which shows an indication of two maxima, is assumed to arise from C—Br and Sn—O stretching vibrations.

Bands are also present in the region 1410—1330 cm^{-1} , which at least partly arise from C—O—H deformations in alcohols or carboxylic acids.

Principally the compounds under consideration, with the exception of the product from 1,1-dibromo-ethylene, are supposed to be built up by oxygen

Table 3. Infrared spectroscopic data for reaction products. s: strong, m: medium, w: weak, br: broad, sh: shoulder.

Organic reactant	Absorption bands in wave numbers
CBr_4	Ca. 3450 and 2990, (s, br). 1610–1590 ^a (s). 1405 (m). Ca. 1065 (s, br). Ca. 940 (m). Ca. 525 (s, br) sh ca. 480.
CHBr_3	Ca. 3450 and 2990, (s, br). 1610 (s). 1400 (w). Ca. 1070 (s, br). Ca. 940 (m). Ca. 525 (s, br) sh ca. 480.
CH_2Br_2	Ca. 3450 and 2990, (s, br). 1590 (s) sh ca. 1700 and ca. 1550. 1405 (m). 1340 (m). 1205 (w). Ca. 1060 (s, br). 940 (m). ^b
$\text{CBr}_2=\text{CBr}_2$	Ca. 3400 and 2930, (s, br). Ca. 2450 (m). 1700 (m). 1670 (m). 1615 (s). 1370–1330 (m). ^a 1215 (w). Ca. 1090 (s, br). Ca. 940 (m). Ca. 525 (s, br) sh ca. 480.
$\text{CHBr}=\text{CBr}_2$	Ca. 3450 and 2990, (s, br). 1710 (s). 1610 (s) sh ca. 1550. 1375 (m). Ca. 1080 (s, br). Ca. 960 (w). ^b
$\text{CH}_2=\text{CBr}_2$	Ca. 3400, ca. 3100 and ca. 2650, (s, br). Ca. 1720 (s, br). 1475 (w). 1400 (m). 1230 (s) sh ca. 1300. 1160 (s). Ca. 820 (br). Ca. 715 (m). 675 (m). ^b
$\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$	Ca. 3450 and 2990, (s, br). 1710 (s). Ca. 1670 (m). 1610–1585 (s). ^a 1395 (m). Ca. 1080 (s, br). Ca. 960 (m). Ca. 525 (s, br). sh. ca. 480.

^a The position of the band varies for different samples.

^b Spectrum in the cesium bromide region not taken.

bridges between carbon and tin atoms. Peroxides are excluded because of the thermic stability of the compounds. The presence of other types of coupling cannot be confirmed from the infrared spectra. However, by a further treatment of the results from the elementary analyses, based on certain assumptions given below, it is possible to get additional information concerning the molecular structure.

Firstly it is assumed that tin is tetravalent in all cases and that all compounds are saturated, due to the reaction conditions with free bromine and illumination.

Hydrogen, oxygen, and bromine are supposed to be taken up or eliminated in the following ways or possibly by other reactions of equivalent effects:

Hydrogen addition. 1. Association of water. 2. Hydrolysis (with elimination of hydrogen bromide).* 3. Exchange of bromine with hydrogen.

Hydrogen elimination. 1. Exchange of hydrogen with bromine.**

* If hydrogen bromide is not eliminated, the situation in this respect is equivalent to association of water.

** Hydrogen elimination by coupling is equivalent to elimination of bromine combined with hydrogen-bromine exchange.

Oxygen addition. 1. Association of water. 2. Hydrolysis. 3. Reaction of free oxygen with formation of oxygen bridges. 4. "Exchange" of bromine with oxygen, *i.e.* formation of carbonyl groups.*

Bromine addition. 1. Addition to multiple bonds. 2. Exchange of hydrogen with bromine.

Bromine elimination. 1. Elimination by coupling. 2. Hydrolysis. 3. Exchange of bromine with hydrogen. 4. "Exchange" of bromine with oxygen.

For comparison of different compounds and samples it is convenient to relate corresponding numbers of atoms of oxygen, hydrogen, and bromine to the sum 1 for carbon and tin atoms (see Table 2). The same applies to the numbers of couplings and free valences. The reduced numbers of couplings, c , with or without oxygen, between carbon atoms, tin atoms, and carbon and tin atoms depend on the total numbers of carbon and tin atoms in the molecules.

Open structures, linear or branched: $0.5 \leq c \leq 1$

Cyclic structures, more or less chelated: $1 \leq c \leq 2$ (see structure of silicon dioxide)

For numbers of free valences, v , *i.e.* valences which are not engaged in couplings, we get correspondingly:

Open structures, linear or branched: $2 \leq v \leq 3$

Cyclic structures, more or less chelated: $0 \leq v \leq 2$

Based on these relations and the assumptions mentioned, the values quoted in Table 2 can be used to point out or indicate certain features of the molecules. The following examples may be illustrative:

$O < 0.5$ shows coupling without oxygen bridges, at least to some extent, and may possibly indicate association of water and hydrolysis only to a minor extent.

$\text{Br}_e < 2$ shows open structure and/or "exchange" of hydrogen with bromine.

$O/\text{Br}_e > 1$ shows association of water.

$\text{H} + \text{O} + \text{Br} < 2$ shows a cyclic structure and/or exchange of bromine with oxygen.

Compounds from carbon tetrabromide. The values given in Table 2 show that the different samples vary somewhat in composition. Their infrared spectra are, however, quite similar and show that the structural features are closely related. The composition of the samples varies with the degree of coupling, which has been followed by rough determinations of molecular weights by an iso-piestic method, usable only for relative measurements. The differences in the degree of coupling can not easily be explained on the basis of concentrations, temperature, and time of reaction. As a free radical mechanism probably is involved, the presence of impurities and moisture may play a part, perhaps also the after-treatment of the samples.

The absence of absorption bands in the region $1800\text{--}1650\text{ cm}^{-1}$ implies that carbonyl groups are not present or only to a small extent. NMR spectra show only one peak for hydroxyl, although the infrared spectra suggest the presence of water, C—OH, and Sn—OH. A rapid exchange of protons is suggested.

* Carbonyl groups may be formed by hydrolysis followed by elimination of water.

The values in Table 2 for sample 2 indicate a fairly high degree of coupling and probably ring formation (see values for Br_c and $\text{Br}_c\text{-O}$). To some extent direct coupling without oxygen bridges has taken place, probably between carbon atoms (see values for O and O/Br_c).⁴ Samples 3 and 4 with carbon to tin proportions about 1:2 and 2:3, respectively, probably consist of smaller molecules. Thus for sample 3 the molecular structure Sn-O-C-O-Sn with 4 hydroxyl groups and 0.75 molecules of associated water per molecule, gives the following weight per cents of elements: C 1.76; Sn 34.78; Br 46.83; H 0.81; O 15.82. Observed values are: C 1.76; Sn 34.34; Br 46.75; H 0.76; O 16.40.

Compounds from bromoform. The products from bromoform seem to be closely related to those from carbon tetrabromide as the infrared spectra are quite similar. Differences in composition for different samples due to variations in the degree of coupling are found.

NMR spectra show one peak for hydroxyl. A signal at 115 cps downfield from tetramethylsilane (TMS) is due to hydrogen bonded to carbon. The Sn-H stretching vibration which absorbs near 1870 cm^{-1} is not observed.

The value $\text{H}_a/\text{O} = 2.30$ for sample 1 (Table 2) shows that an exchange of bromine with hydrogen has taken place at carbon atoms. There is also evidence of coupling to some extent without oxygen bridges, probably between carbon atoms.

Samples 2 and 3 probably consist of smaller molecules with oxygen bridges.

Compounds from dibromo-methane. The values from Table 2 and the infrared spectra show absorption of water and coupling with oxygen bridges. Hydrogen-bromine exchange is indicated. Infrared absorption near 1700 cm^{-1} arise from carbonyl grouping in these samples. Absorption bands about 1550 and 1400 cm^{-1} may indicate ionized carboxyl groups. NMR spectra show one peak for hydroxyl. No signal due to carbon-bonded hydrogen is observed, confirming the hydrogen-bromine exchange.

The rate of the reaction is markedly slower than for the carbon tetrabromide and bromoform reactions and the yield is smaller.

Compounds from tetrabromo-ethylene. These compounds are described earlier.¹ They consist of the unit C-C-O-Sn , which yields oxalate groupings on hydrolysis.

Compounds from tribromo-ethylene. Infrared absorption at 1710 cm^{-1} shows presence of carbonyl groups. Bands about 1550 and 1375 cm^{-1} may be due to ionized carboxyl groups. NMR spectra show one peak for hydroxyl and further the presence of hydrogen bonded to carbon. (113 cps downfield from TMS.) The values in Table 2 suggest structures Sn-O-C-C-O-Sn and Sn-O-C-C , respectively, for samples 1 and 3. Water absorption and hydrolysis have taken place to some extent.

The reaction is slow compared to the reaction of tetrabromo-ethylene and the yield is much smaller.

Compounds from 1,1-dibromo-ethylene. The values in Table 2 show that couplings without oxygen bridges exist. Bromine-hydrogen exchange is further evident. For open structures the corresponding total numbers of

carbon and tin atoms in the molecules, a , and the numbers of couplings related to the sum 1 for carbon and tin atoms, c , are:

$$\begin{array}{ccccccc} a: & 2 & 3 & 4 & \dots & \infty & \\ c: & 0.50 & 0.67 & 0.75 & \dots & 1.00 & \end{array}$$

For sample 1 with the carbon to tin proportion 1:1 the corresponding values for other couplings than those between carbon atoms must be equal to or greater than 0.5. The value 0.39 for the oxygen content thus shows that couplings Sn—C or Sn—Sn are present. A coupling Sn—Sn is rather unlikely to appear only in these compounds. The value 0.57 for sample 2 is indicative of the same type of coupling, *i.e.* Sn—C.

This view is in agreement with the infrared spectra which are principally different from those discussed so far. The strong band near 1080 cm^{-1} previously correlated with the C—O stretching vibration (C—O—Sn), is lacking. In this case two new, strong bands at 1230 and 1160 cm^{-1} appear, of which the former may be due to carboxylic acid. The broad carbonyl band is observed near 1700 cm^{-1} . The band near 1600 cm^{-1} which has been correlated with the deformation vibration of water is also lacking. The presence of oxygen in carbonyl and hydroxyl groups further supports the presence of couplings of the type Sn—C.

The rate of reaction is relatively slow and the yields are low for these compounds. The thermic stability is markedly lower than generally for the group of compounds discussed above (see Table 1).

Compounds from 1,2-dibromo-ethane. The values in Table 2 show that sample 2 differs considerably in oxygen contents from samples 3 and 4. Absorption of water and hydrolysis have taken place in all samples. Exchange of bromine with hydrogen is found in sample 2, while an exchange of hydrogen with bromine is indicated for samples 3 and 4. These results are partly confirmed by NMR spectra, as there is no signal found from carbon-bonded hydrogen in the case of sample 3.

The infrared spectra show strong absorption about 1080 cm^{-1} due to the C—O stretching vibration in the C—O—Sn grouping. Absorption bands at 1710 and 1670 cm^{-1} show the presence of carbonyl groups.

The reaction, which does not proceed at room temperature, gives fairly small yield at 0°C . The thermic stability of the product is comparatively low.

Acknowledgements. We are grateful to *Norges almenvitenskapelige forskningsråd* for financial support. We also thank Professor Haakon Haraldsen for his help and for placing laboratory facilities at our disposal.

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Received November 19, 1966.