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Abstract

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STUDIES IN THE FIELD OF RADIATION CHEMISTRY OF ORGANOMETALLIC COMPOUNDS

GAMMA RADIATION IN THE REACTION BETWEEN METALLIC TIN AND ALKYL HALIDES

In the field of radiation chemistry, a considerable number of works have been devoted to the study of reactions under the action of high-intensity radiation on water and aqueous solutions. To a much lesser extent, the reactions of organic compounds, as well as nonaqueous media, have so far been touched upon. Finally, as far as we know, processes in organometallic chemistry under the influence of such radiation have not been studied at all.

In a systematic study of this question in various directions, we investigated the reaction of the interaction of alkyl and aryl halides with various metals, and, as one example of interest both theoretically and practically*—the reaction of the interaction of alkyl halides with metallic tin.

This reaction, expressed by the overall equation

$$2\mathrm{RBr} + \mathrm{Sn} \rightarrow \mathrm{R_2SnBr_2}$$

and proceeding, probably, by a more complex mechanism (see below), does not take place at ordinary temperature. Its implementation requires relatively high temperatures (200°(1), 300–350°(2))**.

Owing to the severe reaction conditions, the final product is contaminated with an admixture of considerable amounts (up to 25%) of $\mathrm{R_3SnX}$, etc. With the inevitable use here of sealed vessels, strong explosions were observed(1) as a result of the accumulation of gaseous products.

Moreover, as was shown by Vanderkerk and Luijten(5), the above reaction is limited to lower alkyls (methyl, ethyl). When *n*-butyl bromide and tin are heated to 180° for several hours, the substances do not interact with one another: vapors of *n*-butyl bromide passed through molten tin give the same negative result; finally, in contrast to what occurs in obtaining methylmercury or methylgermanium halide derivatives(2), passing vapors of *n*-butyl chloride over a tin—copper alloy at 300° leads only to the formation of butene, tin chloride, and other nonorganometallic products.

Therefore, organic salts of di-*n*-butyltin, for example the maleate or laurate, which give the greatest effect in the stabilization of polyvinyl chloride plastics—

* Organotin compounds of the class R_2SnX_2 are described in the literature as stabilizers for polyvinyl chloride plastics$^{(3)}$, and also as catalysts in the preparation of polyesters$^{(4)}$.

** Only for practically little-acceptable alkyl iodides could the reaction be carried out (Cahours, 1860) in sunlight (simultaneously there was partial decomposition with liberation of iodine).

which were obtained by the authors indicated by a roundabout route, through disproportionation of tetraalkyl tin compounds by the Kochetkov method (6):

$$(C_4H_9)_5Sn + SnCl_4 \rightarrow 2(C_4H_9)_2SnCl.$$

Although the yields here were close to quantitative, preliminary preparation of tetrabutyltin was necessary.

Consequently, it was of substantial interest to find a new route for the direct preparation of dihalogenated alkyltin, which would make it possible to carry out the process at ordinary pressure and temperature and would use new sources of energy.

Therefore we set ourselves the task of studying the reaction of alkyl halides with metallic tin under conditions of irradiation with γ-rays. As follows from the data presented below, the reaction between alkyl bromides and tin occurs at ordinary temperature, reaching a yield of 55 moles per 100 eV (calculated on the alkyl halide).

In contrast to the reaction between RBr and tin under heating conditions ($\sim$ 200°), here only traces of R_3SnX are formed.

When alkyl chlorides are used (in the example of *n*-propyl chloride) the reaction does not proceed. In the case of mobile chlorine (example—benzyl chloride), it leads to the formation of small amounts of dibenzyl and tin dichloride.

Alkyl iodides react readily under irradiation; the yields reach 60 moles per 100 eV.

As for the mechanism of the reaction, one may assume (as one of the possible schemes) its chain character, with the formation of free radicals $R^{\cdot}$ followed by the intermediate formation of an organotin radical*:

1. $\mathrm{RBr} \rightsquigarrow \mathrm{R}^{\cdot} + \mathrm{Br}$
2. $\mathrm{R}^{\cdot} + \mathrm{Sn} \longrightarrow \mathrm{RSn}^{\cdot}$
3. $\mathrm{RBr} + \mathrm{RSn}^{\cdot} \longrightarrow (\mathrm{RSnBr}) + \mathrm{R}^{\cdot}$
4. $(\mathrm{RSnBr}) + \mathrm{RBr} \longrightarrow \mathrm{R_2SnBr_2}$

Comparing, on the basis of our data and literature data, the behavior of various alkyl halides in reaction with tin under different types of action (thermal, γ-irradiation, and ultraviolet light), we note the following:

1. Alkyl chlorides and tin (in the absence of a catalyst) do not give organotin compounds under any type of action (the reactions proceed in another direction).
2. Alkyl bromides and tin form organotin compounds under γ-ray irradiation and under thermal action (in the latter case with a limitation for lower radicals). Ultraviolet illumination has no effect.
3. Alkyl iodides and tin, on the contrary, give organotin compounds under all the above-mentioned types of action.

Experimental Section

Method of work and reagents. As the source of radiation, Co^{60} was used, corresponding to $21 \cdot 10^3$ g-eq of radium. Irradiation was carried out in glass ampoules 10 mm in diameter and 150 mm high, drawn out into an open capillary. The temperature during the experiments did not exceed 30°. In the case of ethyl bromide, partial volatilization of the bromide occurred during the experiment, and the experiments were stopped somewhat earlier. In all cases, one side of the ampoule was turned toward the source of rad–

* Compare, for example, the mechanism of the reaction between alkyl halides and mercury under ultraviolet irradiation (7).

irradiation and remained motionless during irradiation; we also did not carry out any stirring, which would probably have improved the yields.

The alkyl halides were purified and dried in the usual way. We used preparations boiling within 1-2°, and as a rule worked with freshly distilled halogen derivatives. Metallic tin ("pure" grade) was ground to powder in its brittle state above 200°. After cooling, the powder was washed with alcohol and dry ether and dried in air at ordinary temperature. Tin that had not entered into the reaction could be used again.

Reaction of tin with *n*-butyl bromide under γ-ray irradiation. Metallic tin powder (prepared as described above), in an amount of 33 g (0.278 g-atom), was charged into an ampoule with 4 ml (5.1 g; 0.037 mole) of *n*-butyl bromide. (Thus, a very considerable excess of tin is taken relative to the equation; above the metal there is a small layer of bromide.) A series of experiments was carried out with different irradiation times, which made it possible to establish the yield as a function of the integral irradiation dose (see Table 1).

Table 1

Integral dose, 10^6, r	n-$(C_3H_7)_2 \cdot SnBr_2$, g	Yield, mol/100 eV	n-$(C_4H_9)_2 \cdot SnBr_2$, g	Yield, mol/100 eV
13.4	–	–	1.7	52
15.5	1.9	57	–	–
21.0	2.1	57	–	–
24.0	2.4	58	2.8	58
29.0	2.7	55	3.3	58
32.0	2.9	52	–	–
36.7	3.5	55	–	–
42.0	4.2	55	–	–
49.0	–	–	4.9	56
61.0	–	–	6.7	57

After irradiation was completed, the liquid portion, consisting of a mixture of unreacted bromide and reaction product, was decanted through a filter. It is of interest to note that, in contrast to experiments at high temperature (for example, with C_2H_5Br according to Grüttner and Krause (^{1})), the liquid portion retained its initial color, did not turn brown, did not resinify, and did not fume (hydrogen bromide). It had a faint odor of R_3SnX (as is known, this impurity is very considerable in thermal preparation). The tin, which had clumped into a dense mass, was washed several times with low-boiling (~40°) petroleum ether, and the wash petroleum ether was combined with the main filtrate. After distillation of the ether and of the unreacted initial butyl bromide, liquid di-*n*-butyltin dibromide remains. It is identified by conversion, with the aid of ammonia, into the oxide and then, under the action of hydrogen chloride, into the corresponding dichloride; m.p. 40°, according to the literature data (^{5}) the m.p. of di-*n*-butyltin dichloride is 40.5°. The yield (calculated on the bromide taken) reaches 55 mole per 100 eV.

Reaction of tin with *n*-propyl bromide or ethyl bromide under γ-ray irradiation. Under analogous ratios and irradiation conditions, irradiation of a mixture of *n*-propyl bromide and powdered tin leads to the formation of di-*n*-propyltin dibromide. After the usual workup, distillation of the petroleum ether and of the unreacted bromide, and cooling, a crystalline substance was obtained with m.p., after recrystallization from *n*-hexane, 48°; in the literature the m.p. is 49° (^{8}).

As in the preceding experiment, the reaction mixture after irradiation is almost not contaminated with the impurity of tri-*n*-propyltin bromide, does not fume, and shows no signs of resinification. For the yields see Table 1.

On irradiation, as described above, of 4 cm^3 of a mixture of ethyl bromide and 33 g of tin, followed by the usual workup, we obtained diethyltin dibromide in a yield of 38 mole per 100 eV (integral dose $50 \cdot 10^6$ r). After the usual workup, 4.4 g of diethyltin dibromide with m.p. 63° was obtained; according to the literature, m.p. 64° (1).

It was of interest to investigate, in passing, the behavior of the dibromides obtained under irradiation. A small amount of pure diethyltin dibromide or di-*n*-propyltin dibromide was irradiated with γ-rays. At least at an integral dose of $30 \cdot 10^6$ r, no noticeable decomposition occurs. The melting points remain unchanged.

Irradiation with ultraviolet light of a mixture of ethyl bromide and tin. A mixture of ethyl bromide (or, correspondingly, *n*-propyl bromide) with an excess of tin powder was irradiated in a quartz ampoule for 50 hours at 50° with a quartz lamp at a distance of about 20 cm from the source. After the usual work-up, we were unable to establish the presence of any organotin compound.

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