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Corresponding Member of the Academy of Sciences of the USSR O. A. REUTOV and V. I. SOKOLOV

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Abstract

Full Text

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RADIOCHROMATOGRAPHY OF ORGANOMERCURY COMPOUNDS

In the last 5-6 years the number of works devoted to organomercury compounds has increased considerably; these compounds have proved to be very convenient objects for studying the mechanism of electrophilic and homolytic substitution at a carbon atom.

In the course of a systematic study of the reactions (I–VI) of isotopic exchange of organomercury compounds,

$$R_2Hg + {}^*Hg \rightleftharpoons R_2{}^*Hg + Hg \tag{1}$$

$$R_2Hg + R'_2{}^*Hg \rightleftharpoons R_2{}^*Hg + R'_2Hg \tag{2}$$

$$R_2Hg + R^*HgX \rightleftharpoons R_2{}^*Hg + RHgX \tag{3}$$

$$RHgX + {}^*Hg \rightleftharpoons R^*HgX + Hg \tag{4}$$

$$RHgX + {}^*HgX_2 \rightleftharpoons R^*HgX + HgX_2 \tag{5}$$

$$RHgX + R'^*HgX \rightleftharpoons R^*HgX + R'HgX \tag{6}$$

(I)

(II)

(III)

(IV)

(V)

(VI)

we repeatedly encountered experimental difficulties caused by the difficulty of separating the reacting substances, which often have very similar solubilities. It was necessary to develop, for kinetic measurements, a suitable method for separating organomercury compounds from one another and from inorganic mercury salts. Such a method, based on radiochromatography, is described in the present work. As model systems we chose mixtures of esters of various α-bromomercurarylalkylacetic acids, $XC_6H_4CH(HgBr)COOR$, with one another and with mercuric bromide.

It was found that organomercury salts are readily separated from mercuric bromide by chromatography on paper* impregnated with a 10% solution of ethylene glycol in acetone (the paper is treated several hours before use). Various solvents may be used as the mobile phase. The best separation is achieved by using an octane–benzene mixture in a ratio of 3 : 2 (by volume). In this case mercuric bromide remains at the place where the solution was applied, while the organomercury compound moves directly behind the solvent front. For good separation it is sufficient for the front to move approximately 4–5 cm, which takes less than 5 min. If the substances were applied to the chromatogram in the form of pyridine solutions, the spot of mercuric bromide lags only slightly behind the spot of the organomercury compound; in this case the required length of the chromatogram is 8–9 cm.

* We note that chromatography of organometallic compounds is represented in the literature by only isolated examples. In particular, for organomercury compounds there is only one report (5), devoted to the chromatography of substances of the type RHgCl, where $R = CH_3, C_2H_5$, [[unclear: text]] . No quantitative chromatographic measurements are described.

Development of the zones was carried out with a dilute solution of dithizone in chloroform or carbon tetrachloride; dithizone gives a violet-pink coloration with organomercury salts and a pink-yellow coloration with mercuric bromide ([6]).

We carried out the separation of mixtures of the organomercury salts $XC_6H_4CH(HgBr)COOR$ and $YC_6H_4CH(HgBr)COOR$ in two examples: X = H, Y = n-Br and X = n-Br, Y = o-CH_3. The separation was performed on a reversed phase, for which a 10% solution of olive oil in petroleum ether was used. The mobile phase was aqueous (60–80%) ethyl or methyl alcohol. The dependence of R_f on the alcohol concentration was as follows:

X	65% C_2H_5OH	70% C_2H_5OH	80% CH_3OH
H	0.19	0.20	–
n-Br	0.07	0.09	0.18
o-CH_3	–	–	0.30

Radiochromatography was used by us to study the kinetics of isotopic exchange of ethyl esters of α-bromomercuriarylacetic acids with mercuric bromide labeled with Hg^{203}, in pyridine and 70% aqueous dioxane ([7])

$$XC_6H_4CH(HgBr)COOR + {}^*HgBr_2 \rightleftharpoons XC_6H_4CH({}^*HgBr)COOR + HgBr_2.$$

The work was carried out according to the procedure described below.

Weighed portions of the organomercury salt and mercuric bromide were dissolved separately in pyridine or aqueous dioxane, kept at the temperature of the experiment, and combined. The total volume of the reaction mixture was 4 ml, and the amounts of substances did not exceed 30–70 mg. A sample was taken with a glass capillary (each capillary is used to take only one sample) and applied to paper*. In kinetic measurements the solution should be applied not as a spot, but as a band on narrow strips of paper (width 1 cm). This achieves unification of the geometry of the spots, which considerably reduces the error in radiochemical measurements on end-window counters. The degree of exchange is calculated from the ratio of the activities of the zones corresponding to the organomercury compound and mercuric bromide on each paper,

$$F = \frac{A_{\text{Hg–OC}}}{A_{\text{Hg–OC}} + A_{\text{HgBr}_2}} \cdot \frac{C_{\text{Hg–OC}} + C_{\text{HgBr}_2}}{C_{\text{Hg–OC}}},$$

so that there is no need to maintain a constant sample volume. (The index Hg –OC denotes the organomercury compound, A is activity, C is concentration.)

Special experiments established that, under our conditions, secondary exchange on the paper does not occur.

The results obtained by the chromatographic method coincide with the results obtained in the usual way, i.e., by preparative isolation of one of the substances followed by measurement of its activity, as is evident from the following data.

Time (min.)	35	60	100	205	405
Degree of exchange (%): preparative	5.0	8.2	13.0	24.0	53.5
Degree of exchange (%): chromatography	5.0	8.7	12.9	22.5	55.5

It should be noted that at high degrees of exchange (above 70%) the agreement of the results in parallel chromatographic samples in many cases decreases considerably, and the scatter increases.

Comparison of these two methods leads to the conclusion that radiochromatography has considerable advantages: simplicity and low labor consumption, saving of time (one can work approximately 4 times faster) and of substances (the required amounts are 10 times smaller than usual; this is especially important

* Leningrad paper, type "B."

in the case of hard-to-obtain compounds); naturally, in this case one is dealing with smaller activities. An important advantage is also the complete independence of the method from the nature of the solvent, which often complicates quantitative preparative separation.

The present method may find application in studying the kinetics of isotope-exchange reactions of types II, III, V, VI, and also, probably, the kinetics of reactions of organomercury salts with acids and halides under conditions in which radioactive RHgX is used:

$$^{*}\mathrm{RHgX} + \mathrm{HX} \rightarrow \mathrm{RH} + {}^{*}\mathrm{HgX_2}$$

$$\mathrm{RHgX} + \mathrm{X_2} \rightarrow \mathrm{RX} + {}^{*}\mathrm{HgX_2}$$

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CITED LITERATURE

1. O. A. Reutov, G. M. Ostapchuk, DAN, **117**, 826 (1957).

2. O. A. Reutov, T. A. Smolina, Kh. Khun-ven, Izv. AN SSSR, OKhN, **1959**, 559.

3. O. A. Reutov, T. P. Karpov et al., Izv. AN SSSR, OKhN, **1960**, No. 7, 1311.

4. O. A. Reutov, G. M. Ostapchuk, ZhOKh, **29**, 1614 (1959).

5. J. Chromatogr., **2**, No. 1, D1 (1959); J. Agric. Chem. Soc., Japan, **31**, 872 (1957).

6. F. D. Snell, C. T. Snell, *Colorimetric Methods of Analysis*, **2**, N. Y., 1949.

7. O. A. Reutov, V. I. Sokolov, I. L. Beletskaya, DAN, **136**, No. 3 (1960).

Note: Figure translations are in progress. See original paper for figures.