EQUILIBRIUM IN THE EXCHANGE INTERACTION OF TRIALKYLOXONIUM SALTS WITH ESTERS

UDC 541.121+541.48+547.29'26

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In recent years it has been shown that heterochain macromolecules are rather active under the conditions of their formation and may enter into various chemical reactions, the most important of which, from the standpoint of the properties of the polymer formed, is the reaction of chain transfer with cleavage of bonds [1, 2]. This reaction, as a rule, proceeds with heterolytic, and sometimes with homolytic cleavage of the heterobonds of the macromolecules as well. An investigation of the mechanism of reactions of exchange interaction of polymer chains is extremely complex, and frequently cannot be accomplished in practice as a result of the difficulty of analyzing polymer systems. At the same time, the indicated reactions can easily be simulated by model studies on low-molecular compounds, the analysis of which at present has basically been rather well developed.

The purpose of the present work was to investigate the equilibrium in the exchange interaction of triethyloxonium hexachloroantimonate with butyl acetate, simulating the reaction of interchain exchange of esters and ethers. The exchange of oxonium salts with esters had not been described heretofore and was investigated by us for the first time.

EXPERIMENTAL

In view of the high reactivity of trialkyloxonium salts with respect to various nucleophilic reagents, all the substances used were thoroughly purified, primarily from moisture. Nitrobenzene was boiled three times over fresh portions of P_2O_5 and redistilled over P_2O_5 at 210°C collecting the middle fraction. Bu – tyl acetate was repeatedly washed with conc. K_2CO_3 , with distilled water, subsequently dried over anhy– drous K_2CO_3 , and with boiling over P_2O_5 , then redistilled at 126°C. Triethyloxonium hexachloroantimonate was synthesized from freshly redistilled epichlorohydrin, dried over calcium hydride, and antimony penta– chloride in a solution of diethyl ether, preliminarily dried over a potassium – sodium alloy, according to the procedure of Meerwein, somewhat modified [3].



Fig. 1. Kinetic curves of the formation of ethyl acetate (a) and ethyl butyl ether (b) at 30° C in nitrobenzene solution in the interaction of butyl acetate 0.186 M with triethyloxonium hexachloroantimonate, M: 1) 0.008; 2) 0.016; 3) 0.033; 4) 0.055; 5) 0.110.

Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 801-807, April, 1969. Original article submitted April 22, 1968.



Fig. 2. Influence of temperature on the kinetics and equilibrium in the exchange of triethyloxonium hexachloroantimonate, 0.055 M, with butyl acetate, 0.186 M, in a solution of nitrobenzene at: 1) 30°; 2) 50°; 3) 70°. a) Accumulation of ethyl acetate; b) accumulation of ethyl butyl ether.



Fig. 3. Kinetic curves of the formation of ethyl acetate at 30° C in nitrobenzene solution in the interaction of triethyloxonium hexachloroantimonate, 0.055 M, with butyl acetate, M: 1) 0.186; 2) 0.372; 3) 0.745; 4) 1.487.

The reaction was conducted in nitrobenzene solution in the temperature interval 10-70°C. The reaction mixture was analyzed chromatographically on a chromatograph with an ionization-flame detector of the DIP-1 type with a column with dimensions 200 $\times 0.6$ cm, filled with polyethylene glycol adipate-600, 20%, and phosphoric acid, 1%, applied on celite-545. Column temperature 90°C, helium velocity 40 ml /min. To increase the accuracy of the results of the analysis, the latter was conducted with an internal standard of chlorobenzene.

DISCUSSION OF RESULTS

From the results of an analysis of the reaction mixture it follows that in addition to the expected

ethyl acetate, as a result of the reaction at 30° C diethyl and ethyl butyl ethers are also formed, while at higher temperatures dibutyl ether is formed in addition. The accumulation of the reaction products proceeds to some limiting value, which in the region of the investigated reagent concentrations depends to a significant degree on the initial concentration of the oxonium salt (Fig. 1) and the temperature of the reaction (Fig. 2), and to a lesser degree on the initial butyl acetate concentration (Fig. 3). Special experiments have shown that the indicated limiting concentrations of the reaction products are equilibrium concentrations, while the equilibrium established in the system is a true equilibrium and can be reached from both directions by varying the reaction temperature. Thus, the reaction equilibrium mixture at 30° C was heated at 50° C. After two days, the equilibrium characteristic of 50° C was established in the reaction mixture. Exposure of this mixture for two days at 30° C restores the reaction system to the initial equilibrium state.

On the basis of general considerations, as a result of exchange we might have expected the formation

of 16 products (including the unreacted starting materials): EtOAc, EtOEt, Et_3O , Et_2OAc , Ac_3O , BuOAc, EtOBu, Et_2CBu , $EtOAc_2$, Ac_2O , BuOBu, $EtOBu_2$, EtBuOAc, Bu_3O , $BuOAc_2$, Bu_2OAc . The anions here and henceforth will be omitted for the sake of brevity in the description of the salt forms. Moreover, it has been shown [4] that the reaction proceeds through the formation of an intermediate complex $[Et_3O \cdot BuOAc]^+$. A complete analysis of all the products of this complex system is practically impossible as a result of the absence of methods of analysis of oxonium salts with different natures of the radical at the present time. However, qualitative and even semiquantitative conclusions on the various oxonium salts formed as a result of the reaction can be drawn on the basis of an analysis of the free reaction products, which are not bound in complexes (oxonium salts may be considered as complex compounds).

TABLE 1. Results of an Investigation of the Equilibrium of the Exchange of Triethyloxonium Hexachloroantimonate with Butyl Acetate at 30°C

[A ₀]·10², ^M eq	[B ₀]·10 ¹ , Meq	[C _{eq}] •10 ² , M	[AB] _{eq} .10 ² . Meq	a	к ³⁰ eq	[A1]·10 ² , Meq	[B₀]·10³, Meq	[C _{eq}] •10 ² , M	[AB]eq .10², Meq	α	K ³⁰ eq
11,0 5,5 3,3 1,6	1,86 1,86 1,86 1,86 1,86	5,6 3,2 2,2 1,2	2,2 0,8 0,4 0,1	8 7 7 7	0,90 0,47 0,44 0,28	0,8 5,5 5,5 5,5	1,86 3,72 7,45 14,87	0,7 3,6 3,9 4,1	0,0 1,0 1,1 1,2	7 7 8	0,28 0,44 0,44 0,57
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Согласно данным табл. 1 $K_{p^{30}} = 0.48 \pm 0.13$; $K_{p_1} = 3.5 \pm 1.1 \ a/M$; $K_{p_2} = 0.14 \pm 0.01 \ M/a$.

Of the possible reaction products enumerated above, it is evident that each compound can be formed from the corresponding salt forms. The absence of dibutyl ether and acetic anhydride in the equilibrium mixture at 30°C indicates that only eight products are formed as a result of exchange:

EtOAc,
$$Et_3 \vec{O}$$
, $EtOEt$, $Et_2 OAc$,
BuOAc, $Et_2 \vec{O}Bu$, $EtOBu$, $EtBu \vec{O}Ac$. (1)

At 50°C the appearance of dibutyl ether is evidence that at this and higher temperatures, reactions with the participation of the intermediate product – the diethylbutyloxonium salt – begin to take place. Thus, the reaction under consideration is an interesting case in which the realizable equilibrium is incomplete, metastable. This indicates that under the investigated conditions, certain existing pathways of development of the reaction are kinetically hindered, although the formation of all possible reaction products apparently is not thermodynamically prohibited.

The experimental results obtained permit us to assume the following sequence of reversible reactions of the exchange influence under consideration at 30°C and at lower temperatures:

 $Et_{3}\dot{O} + BuOAc$ $keq_{1} \qquad \downarrow keq_{2} \qquad (2)$ $Et_{2}O + EtBu\dot{O}Ac = EtOAc + Et_{2}\dot{O}Bu = EtOBu + Et_{2}\dot{O}Ac . \qquad (2)$ keq_{6}

Each of the reactions indicated above proceeds through preliminary formation of an intermediate complex with the composition $[Et_3O\cdot BuOAc]^+$. Therefore the equilibrium constants on scheme (2) represent essentially products of the equilibrium constants of formation of the complex from the starting materials and its decomposition into the reaction products.

On the basis of the established composition of the equilibrium reaction mixture, we can write the following balance equations:

$$\begin{split} & \text{BuOAc}_{\text{J}_{0}} = [\text{BuOAc}_{\text{leq}} + [\text{EtOAc}_{\text{leq}} + [\text{Ac}\overset{\circ}{\text{D}}\text{Et}_{2}]_{\text{eq}} + [\text{Ac}\overset{\circ}{\text{D}}\text{EtBu}_{\text{leq}} + [\text{Et}_{3}\text{O} \\ & + [\text{BuOAc}]_{\text{eq}} + [\text{EtOBu}_{\text{leq}} + [\text{Et}_{2}\overset{\circ}{\text{D}}\text{Bu}]_{\text{eq}} \\ & + [\text{Ac}\overset{\circ}{\text{D}}\text{EtBu}_{\text{eq}} + [\text{Et}_{3}\text{O} \cdot \text{BuOAc}]_{\text{eq}} + \\ & \text{Et}_{3}\overset{\circ}{\text{O}}_{\text{lo}} = [\text{Et}_{3}\overset{\circ}{\text{O}}]_{\text{eq}} + [\text{Et}_{2}\text{O}]_{\text{eq}} + [\text{Et}_{3}\text{O} \cdot \text{BuOAc}]_{\text{eq}} + \\ & \text{Et}_{3}\overset{\circ}{\text{O}}_{\text{lo}} = [\text{Et}_{3}\overset{\circ}{\text{O}}]_{\text{eq}} + [\text{Et}_{2}\text{O}]_{\text{eq}} + [\text{Et}_{2}\text{O}\text{Bu}]_{\text{eq}} + [\text{Et}_{3}\text{O} \cdot \text{BuOAc}]_{\text{eq}} + \\ & \text{Et}_{3}\overset{\circ}{\text{O}}_{\text{lo}} = 3 [\text{Et}_{3}\overset{\circ}{\text{O}}]_{\text{eq}} + [\text{Et}_{2}\text{O}]_{\text{eq}} + [\text{Et}_{2}\text{O}\text{Bu}]_{\text{eq}} + 2 [\text{Et}_{2}\overset{\circ}{\text{O}\text{Bu}}]_{\text{eq}} + 2 [\text{Et}_{2}\overset{\circ}{\text{O}\text{Bu}}]_{\text{eq}} + \\ & \quad + [\text{Ac}\overset{\circ}{\text{D}}\text{E}\text{IBu}]_{\text{eq}} + 2 [\text{Ac}\overset{\circ}{\text{O}}\text{E}_{2}] + [\text{Et}\text{OAc}]_{\text{eq}} + 3 [\text{Et}_{3}\text{O} \cdot \text{BuOAc}]_{\text{eq}}^{+}. \end{split}$$

Combining the indicated equations with one another, it can be shown that

$$[\text{Et}_{2}\text{O}]_{eq} + [\text{EtOBu}]_{eq} = [\text{AcOEt}_{2}]_{eq} + [\text{AcOEtBu}]_{eq}.$$

From the experimental data it follows that

$$[Et_2O]_{eq} + [EtOBu]_{eq} \ll [EtOAc]_{eq}$$

TABLE 2. Equilibrium Constants at 30°C for the Reactions Indicated in Scheme (2)

Equilibrium constant at 30°	Value	Equilibrium constant at 30°	Value	Equilibrium constant at 30°	Value
K _{eq1}	$\leq 1,2 \cdot 10^{-3}$	K _{eq3}	$1,2 \cdot 10^{-3}$	K _{eq5}	2,5.10-3
K _{eq2} †	0,48	K _{eq4}	$\leq 2,5 \cdot 10^{-3}$	K _{eq6}	

*Unfortunately, on account of technical difficulties the exact accumulation of diethyl ether could not be measured; it is evident only that $[Et_2O]_{eq} \leq [EtOBu]_{eq}$ $\dagger K_{eq2} = K_{eq}^{30}$ for reaction (4), considered above.

Consequently,

$$[AcOEt_2]_{eq} + [AcOEtBu]_{eq} \ll [EtOAc]_{eq}$$

The same can also be assumed for the general sum:

$$[Et_2O]_{eq} + [EtOBu]_{eq} + [AcOEt_2]_{eq} + [AcOEtBu]_{eq} \leq [EtOAc]_{eq}.$$

This analysis gives a basis for asserting that the bulk of the equilibrium mixture is comprised of esters and trialkyloxonium salts, and the reaction of exchange proceeds predominately according to the equation:

$$Et_3O + BuOAc \rightleftharpoons [Et_3O \cdot BuOAc]^+ \rightleftharpoons EtOAc + Et_2OBu , \qquad (3)$$

which for convenience can be rewritten in the following form:

$$A + B \xrightarrow{K_{eq^1}} AB \xrightarrow{K_{eq^2}} C + D$$
(4)

where $A = E t_3 \dot{O}$; B = BuOAc; $AB = [Et_3O \cdot BuOAc]^+$; C = EtOAc; $D = Et_2 \dot{O}Bu$. For scheme (4) at equilibrium, the following ratios are correct:

$$K_{eq} = K_{eq1} K_{eq2} = \frac{C_{eq}^{2}}{(A_{0} - C_{eq} - [AB]_{eq} (B_{0} - C_{eq} - [AB]_{eq})}$$
(5)
$$K_{eq2} = \frac{[AB]_{eq}}{(A_{0} - C_{eq} - [AB]_{eq}) (B_{0} - C_{eq} - [AB]_{eq})}$$

from which it follows that

$$\frac{K_{eq}}{K_{eq_1}} = K_{eq^2} = \frac{C_{eq^2}}{[AB]_{eq}}$$

 \mathbf{or}

$$[AB]_{eq} = \frac{1}{K_{eq^2}} C_{eq}^2 \equiv \alpha C_{eq^2}$$
(6)

Substituting function (6) into Eq. (5), this equation can be rewritten for two independent experiments with different initial concentrations of the reagents:

$$K_{eq} = \frac{C_{eq1}^{2}}{(A_{0_{1}} - C_{eq1} - \alpha C_{eq1}^{2}) (B_{0_{1}} - C_{eq1} - \alpha C_{eq2}^{2})}$$

$$K_{eq} = \frac{C_{eq2}^{2}}{(A_{0_{2}} - C_{eq2}^{2} - \alpha C_{eq2}^{2}) (B_{0_{2}} - C_{eq2} - \alpha C_{eq1}^{2})}$$
(7)

From this system of two equations with two unknowns (α and K_{eq}), considering functions (5) and (6), we can determine all the equilibrium constants of reaction (4) (Table 1).



According to the data of Table 1, $K_{eq}^{30} = 0.48 \pm 0.13$; $K_{eq_1} = 3.5 \pm 1.1$ liters/mole; $K_{eq2} = 0.14 \pm 0.01$ M.

It is easy to show that for scheme (2) the following ratios are correct for an equilibrium reaction mixture:

$$\left(\frac{[\text{Et}_2\text{O}]_{eq}}{[\text{EtOAc}]_{eq}}\right)^2 = \frac{K_{eq_1}}{K_{eq_2}} = K_{eq_4} \quad \left(\frac{[\text{EtOBu}]_{eq}}{[\text{EtOAc}]_{eq}}\right)^2 = \frac{K_{eq_3}}{K_{eq_2}} = K_{eq_5}$$

and

Fig. 4. Dependence of the equilibrium concentration of ethyl acetate on the equilibrium concentration of ethyl butyl ether.

 $\left(\frac{[\text{EtzO}]_{eq}}{[\text{EtOBu}]_{eq}}\right)^2 = \frac{K_{eq_1}}{K_{eq_3}} = K_{eq_6}$ ⁽⁸⁾

These ratios can be rewritten in the following form:

$$\frac{[\text{Et}_2\text{O}]_{eq}}{[\text{EtOAc}]_{eq}} = \text{const}; \quad \frac{[\text{EtOBu}]_{eq}}{[\text{EtOAc}]_{eq}} = \text{const}; \quad \frac{[\text{Et}_2\text{O}]_{eq}}{[\text{EtOBu}]_{eq}} = \text{const}$$
(9)

Figure 4 presents the dependence of the equilibrium concentration of ethyl acetate on the equilibrium concentration of ethyl butyl ether for one of the series of experiments. As can be seen from Fig. 4, functions (9) are fulfilled with satisfactory accuracy.

Thus, it seems possible to evaluate the equilibrium constants of all the reactions presented in scheme (2) according to Eq. (8). These values are cited in Table 2.

As has already been indicated, at temperatures higher than $30^{\circ}C$, one must reckon with the presence of secondary exchange reactions with the participation of the diethylbutyloxonium salt [scheme (10)]:

$$EtBuOAc + EtOBu \neq Et_2OBu + BuOAc \Rightarrow Bu_2O + Et_2OAc$$

$$H$$

$$EtOBu_2 + EtOAc \Rightarrow Et_2O + Bu_2OAc$$
(10)

An analysis of the balance of the reaction products at temperatures higher than 30° C (50 and 70° C) shows that reaction (3) no longer predominates; other conversions, indicated in schemes (2) and (10) also have greater relative importance. Therefore, it is practically impossible to calculate the equilibrium constants at these temperatures.

At 10°C a calculation of the equilibrium constant for reaction (3) gave a value of $K_{eq}^{10} = 0.18 \pm 0.18$ M. An estimation of the heat of reaction (3) according to the calculated equilibrium constants at 10 and 30°C leads to a value of $\Delta H = 8.5$ kcal/mole. This means that there is a rather strong dependence of the heats of formation of the RC- \dot{O} bonds in oxonium salts and the RC-O bond in esters on the nature of the hydrocarbon radical. In the case under consideration

$$\Delta H = (H_{\rm Et-0} - H_{\rm Bu-0}) - (H_{\rm Et-0} - H_{\rm Bu-0^+}),$$

where H_{Et-O} and H_{Bu-O} are the heats of formation of the Et-O and Bu-O bonds in the corresponding esters of acetic acid; $H_{Et-\dot{O}}$ and $H_{Bu-\dot{O}}$ are the heats of formation of the $C-\dot{O}$ bond in oxonium salts for ethyl and butyl radicals, respectively.

The results cited are evidence that relatively small changes in the heats of formation of the C-O bond for alkyl radicals (in the case under consideration for the ethyl and butyl radicals) in the molecules of ethers and esters produce substantial changes in the state of equilibrium in exchange reactions.

CONCLUSIONS

1. The equilibrium of the exchange of triethyloxonium hexachloroantimonate with butyl acetate in nitrobenzene solution was investigated in the temperature interval 10-70°C. 2. The exchange reaction is complex, but the basic direction of the exchange reaction consists of transalkylation of the reagents. As a result of kinetic hindrances at low temperatures, 30° C, the exchange reaction does not take place in all possible directions.

3. The values of the equilibrium constants were estimated and the thermal effect was determined for the transalkylation reaction.

4. Small differences in the heats of formation of the C-O bond in the molecules of esters and oxonium salts with various lengths of the alkyl radical produce substantial changes in the state of equilibrium in exchange reactions.

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