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## Abstract

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## STUDY OF THE EXCHANGE OF ETHYL RADICALS IN THE SYSTEM $Al(C_2H_5)_3$–$\overset{*}{C}_2H_5Br$

*(Presented by Academician M. I. Kabachnik, 11 VII 1960)*

In previous works, the possibility and conditions of radical exchange were studied in certain organic derivatives of mercury ([1]), lead ([2]), and magnesium ([3]). Taking into account the growing interest in organoaluminum compounds, which are widely used in organic synthesis, we carried out a study of the exchange of ethyl radicals between triethylaluminum and ethyl bromide. It should be noted that the study of exchange of identical alkyl or aryl radicals is possible only by the method of radioactive indicators. Therefore, one of the components of the system under study, namely ethyl bromide, was labeled with carbon $C^{14}$. The synthesis of labeled ethyl bromide was carried out according to the procedure described earlier ([2]).

Because of the high sensitivity of triethylaluminum to moisture and oxygen, all work on filling the reaction ampoules with the starting components was carried out in an atmosphere of purified nitrogen. The filled reaction ampoules were frozen with liquid nitrogen, evacuated, sealed, and thermostated under the required conditions. If radical exchange occurs in the system under study, then the ethane collected upon decomposition of the triethylaluminum after the exchange reaction should contain carbon $C^{14}$. Radiometric analysis of ethane for its carbon $C^{14}$ content was carried out with an internal-counting counter after preliminary combustion of the ethane to carbon dioxide ([4]).

Summarizing the experimental material obtained in the study of the exchange of ethyl radicals in the triethylaluminum–ethyl bromide system, the following features should be noted: a) a necessary condition for radical exchange in the system studied is the presence of metal halides, without whose addition exchange is not observed even under rather severe conditions (150° C, 20 hr); b) in the presence of $TiCl_4$ and $NiCl_2$, either an explosion of the reaction ampoule or polymerization of the starting substances occurs, as a result of which a thick resinous mass is formed that is not decomposed by alcohol and water; c) in the presence of $BiCl_3$, $FeCl_3$, $CuCl_2$, CuCl, $CoCl_2$, AgBr, and $SnCl_2$, the exchange reaction proceeds smoothly, as a rule without explosion; d) no gases are formed as by-products of the reaction; e) the exchange reaction is monomolecular. The rate constant of the exchange reaction is calculated from the equation:

$$K = -\frac{1}{t} \ln \left(1 - \frac{A_t}{A_\infty}\right),$$

where $t$ is the time in seconds, $A_t$ is the activity of triethylaluminum at time $t$, and $A_\infty$ is the activity of triethylaluminum at equilibrium, i.e., at 100% exchange; f) in diethyl ether as solvent, the rate of exchange drops sharply.

The experimental data are summarized in Table 1.

Table 1

| Additive | Solvent | Temp., °C | $K \cdot 10^{-5}$, $sec^{-1}$ | $E$, kcal/mol | Additive | Solvent | Temp., °C | $K \cdot 10^{-5}$, $sec^{-1}$ | $E$, kcal/mol |
|---|---|---|---|---|---|---|---|---|---|
| $BiCl_3$ | – | 90 | 6,13 | 10,5 | CuCl | – | 85 | 4,33 | 6,5 |
| $BiCl_3$ | – | 100 | 8,82 | 10,5 | CuCl | – | 100 | 6,23 | 6,5 |
| $BiCl_3$ | – | 115 | 15,54 | 10,5 | CuCl | – | 115 | 8,82 | 6,5 |
| $BiCl_3$ | ether | 100 | 0,052 | 9,0 | $CoCl_2$ | – | 85 | 1,92 | 9,0 |
| $BiCl_3$ | ether | 115 | 0,072 | 9,0 | $CoCl_2$ | – | 100 | 3,36 | 9,0 |
| $BiCl_3$ | ether | 120 | 0,096 | 9,0 | $CoCl_2$ | – | 115 | 5,09 | 9,0 |
| $FeCl_3$ | – | 85 | 3,37 | 8,0 | AgBr | – | 100 | 0,50 | 11,0 |
| $FeCl_3$ | – | 100 | 6,13 | 8,0 | AgBr | – | 115 | 0,96 | 11,0 |
| $FeCl_3$ | – | 115 | 8,18 | 8,0 | AgBr | – | 135 | 1,82 | 11,0 |
| $FeCl_3$ | ether | 100 | 0,041 | 13,0 | $SnCl_2$ | – | 100 | 0,38 | 6,0 |
| $FeCl_3$ | ether | 110 | 0,052 | 13,0 | $SnCl_2$ | – | 115 | 0,53 | 6,0 |
| $FeCl_3$ | ether | 125 | 0,086 | 13,0 | $SnCl_2$ | – | 135 | 0,77 | 6,0 |
| $CuCl_2$ | – | 85 | 4,13 | 7,0 | | | | | |
| $CuCl_2$ | – | 100 | 6,80 | 7,0 | | | | | |
| $CuCl_2$ | – | 115 | 9,34 | 7,0 | | | | | |

On the basis of the features set forth above, we believe that the exchange reaction proceeds through the formation of a six-membered cyclic complex with alternating bonds being broken and formed ([5,6]). As additives we used metal halides having $d$-electrons in their orbitals. For elements with $d$-electrons, proximity of the $s$-, $p$-, and $d$-levels is characteristic; owing to this, mutual transitions between them are possible as the number of lone electrons increases. Pairing of electrons leads to increased valence, as a result of which additional bonds, in comparison with the principal valence, may arise, leading to interaction between molecules that would seem to be "saturated" with one another.

In our opinion, the exchange reaction includes three stages:

1. The haloalkyl and the metal halide form a polarized molecular compound, in which, as a result of polarization, the covalent carbon–halogen bonds are loosened

$$^{*}RX + MX_3 \rightarrow {}^{*}RX \cdots MX_3 \qquad \text{(A)}$$

2. Triethylaluminum and the polarized molecular compound form a six-membered cyclic complex

$$R_3Al + {}^{*}RX \cdots M_3X \longrightarrow R_2Al\begin{matrix}{}^{*}R \cdots X \\ \cdots \quad \cdots \\ {}^{*}R - X\end{matrix}MX_2 \qquad \text{(B)}$$

3. The six-membered cyclic complex decomposes both with rupture of the bonds that have arisen (dotted lines, crossed out once) and with rupture of the old loosened bonds (solid lines, crossed out twice)

$$R_2Al\begin{matrix}R \cdots X \\ {}^{*}R - X\end{matrix}MX_2 \longrightarrow \begin{cases} R_2AlR + {}^{*}RX + MX_3, & \text{no exchange,} \\ R_2Al{}^{*}R + RX + MX_3, & \text{exchange occurs.} \end{cases} \qquad \text{(V)}$$

The stage of decomposition of the cyclic complex, which may be regarded as a pseudomolecule, is a monomolecular reaction. The reaction scheme does not assume the formation of gases as by-products of the exchange reaction.

The presence of an empty orbital at the aluminum atom in triethylaluminum facilitates the formation of the cyclic complex. It was natural to suppose,

that if the empty orbital of the aluminum atom is occupied, this will hinder the formation of a cyclic complex and, consequently, will also hinder radical exchange. It is known that triethylaluminum forms with diethyl ether an etherate, which is a very stable compound. Therefore, we studied the exchange in the system under investigation in a diethyl ether medium, when the empty orbital of the aluminum atom is occupied through the formation of a donor–acceptor bond between aluminum and the ether oxygen. In this case the exchange drops sharply (Table 1).

Thus, the features of the reaction noted above are in good agreement with the proposed exchange mechanism.

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