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Abstract

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G. A. Razuvaev, G. G. Petukhov, and A. G. Artem' ev

Radical Exchange Reactions in the Presence of $AlCl_3$

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Using organometallic compounds as an example, we have investigated radical exchange with a "solvent." It was shown that exchange proceeds both in radical and in ionic reactions. In reactions with organomercury compounds, exchange proceeds through free radicals with regeneration of the reacting radical ([1]). Organosodium compounds exchange with a "solvent" through a carbanion ([2]). In the latter case, exchanges proceeded more completely and between such radicals as, for example, benzyl, which cannot exchange as a free radical.

In the present work we wanted to test the possibility of cationic exchange,

$$R^+ + R^*D \rightleftharpoons R^* + RD, \tag{1}$$

using deuterium-containing "solvents" for these purposes and $AlCl_3$ as catalyst.

The use of $AlCl_3$ as a catalyst for hydrogen exchange has been studied mainly in acid-type reactions ([3])

$$DX + RH + AlCl_3 \rightleftharpoons D^+ + RH + (AlCl_3X)^-$$

$$D^+ + RH \rightleftharpoons H^+ + RD. \tag{2}$$

Exchange reactions proceeding with the participation of carbonium ions have been studied with the aid of deuterium in reactions between aliphatic hydrocarbons and H_2SO_4 ([4,5]).

To study cationic exchange we made use of halogenated and aromatic hydrocarbons. The compounds selected as exchanging systems interact with $AlCl_3$ in two ways. Halogenated compounds, as is known, in the presence of $AlCl_3$ give carbonium ions ([6,7]). In this case exchange can proceed according to equation (1). Aromatic hydrocarbons with $AlCl_3$ form a π-complex, in which the aromatic hydrocarbon is strongly subject to protonation ([8]). Exchange may proceed according to equation (2).

As is seen from Table 1, chlorobenzene–deuterobenzene and cyclohexyl chloride–deuterocyclohexane (experiments Nos. 1–5) exchange in the presence of $AlCl_3$ to an equilibrium state:

$$RXI + R^*D \overset{AlCl_3}{\rightleftharpoons} R^*XI + RD.$$

Exchange in these systems proceeds according to equation (1) with participation of phenyl-

···and cyclohexyl carbocations, whose formation occurs according to the scheme:

$$R{-}Cl + AlCl_3 \rightleftarrows R^+ + (AlCl_4)^-,$$

$$R + R^*D \rightleftarrows (R \to R^*D) \rightleftarrows RD + R^{*+},$$

$$R^{*+} + (AlCl_4)^- \rightleftarrows R^*Cl + AlCl_3.$$

It is possible that deuterolysis of deuteriobenzene promotes the hydrogen-exchange reaction in experiments Nos. 1–4.

$$C_6D_5D + AlCl \to D^+ + (C_6D_5AlCl_3)^-.$$

However, from the example cyclohexyl chloride–deuteriocyclohexane it follows that this condition is not necessary.

Table 1

Experiment No.	Exchanging components I	Exchanging components II	Temperature, °C	Time, h	Content of D^* in initial component II, γ	D^* found in component I after the reaction, γ	Exchange, %**	Measurement error***, %
1	C_6H_5Cl	C_6D_6	18	72	2000	85	4.2	0.5
2	Same	Same	50	1/2	2740	916	33.4	0.3
3	Same	Same	100	1/3	2740	1270	43.4	0.3
4	Same	Same	100	24	4820	2240	46.5	0.2
5	$C_6H_{11}Cl$	$C_6H_{11}D$	18	21	4152	1900	45.7	2.5

Experiment No.	Exchanging components I	Exchanging components II	Temperature, °C	Time, h	Content of D^* in initial component II, γ	D^* found in component I after the reaction, γ	Exchange, %**	Measurement error***, %
6	*o*-$CH_3C_6H_4Br$	$CH_3OC_6H_4D$	18	24	10380	324	3.1	0.2
7	Same	Same	100	3	10380	442	4.2	0.2
8	*n*-$NO_2C_6H_4Cl$	$NO_2C_6D_5$	18	24	3367	259	7.6	1.8
9	Same	Same	100	3	8600	362	4.2	0.4
10	$C_6H_5CH_3$	C_6D_6	100	3	5050	3565	70.6	1.8
11	Same	Same	100	3	5050	3460	68.6	1.9
12	C_6H_{10}	C_6D_6	18	24	5050	125	2.4	0.8
13	Same	Same	100	3	5050	36	0.7	0.6
14	C_6H_{10}	$C_6H_{11}D$	18	24	4152	100	2.4	2.4
15	Same	Same	100	3	4152	350	8.4	2.4
16	$C_6H_5OCH_3$	C_6H_5D	100	3	5050	39	0.4	0.3
17	$C_6H_5CH_2OCH_3$	$C_6H_5CH_2OCH_2C_6H_5$	18	24	8600	89	1.0	0.3
18	Same	Same	100	3	8600	4.0	0.1	0.3

Table 2

Experiment No.	Exchanging components I	Exchanging components II	Temperature, °C	Time, h	Content of C^{14} in initial component II, imp/min	C^{14} found in component I from the reaction, imp/min	Exchange, %	Measurement error**, %
1	$CH_3C_6H_5$	$C_6H_6-1-C^{14}$	100	3	1536	176	11.4	0.2
2	Same	Same	100	3	1536	219	14.3	0.2
3	Same	Same	100	3	1536	190	12.4	0.2

In contrast to these systems, between toluene and deuteriobenzene (Table 1, experiments Nos. 10, 11) hydrogen exchange proceeds only according to equation

(2)

$$C_6D_6 + AlCl_3 \rightleftarrows (C_6D_5AlCl_3)^- + D^+,$$

$$C_6H_5CH_3 + AlCl_3 \rightleftarrows (C_6H_4CH_3AlCl_3)^- + H^+.$$

* The amount of deuterium per nucleus of the aromatic compound is given.
** The percentage of exchange was calculated taking into account the equilibrium state of the reaction. In experiments Nos. 16-18 it was calculated for two exchanging groups.
*** The experimental error (in %) was calculated as the ratio of the product of the measurement accuracy (15γ) to the dilution by the deuterium content in the initial component II.

The exchanging particles are a proton and a deuteron. The exchange process can also be represented as an electrophilic substitution reaction

$$C_6D_6 + H^+ \rightleftharpoons (C_6D_6H)^+ \rightleftharpoons C_6H_5H + D^+.$$

It is known that transfer of hydrogens from the CH_3 group into the ring, as well as migration of hydrogen from one position to another in the toluene molecule, does not occur ([9,10]).

Since many reactions under the action of $AlCl_3$ are accompanied by rearrangements (as, for example, the Friedel-Crafts reaction), it was necessary to check the exchange between toluene and benzene using two isotopic labels. For this purpose, deuterotoluene labeled in the ring and radiobenzene 1-6 C^{14} were taken. The experiment showed that, along with hydrogen exchange, intermolecular migration of the CH_3 group of toluene to the benzene ring takes place. At 100°, about 12.7% rearranges in 3 hours. This was established by the presence of radiocarbon in the toluene isolated in the form of benzoic acid (Table 2, experiments Nos. 1-3).

Investigation of exchange reactions between deuterobenzene and cyclohexane, cyclohexene and deuterocyclohexane (Table 1, experiments Nos. 12-15) showed that exchange in these systems is practically absent. These experiments to some extent confirm the correctness of the conclusions made above. Indeed, where one of the components does not give a π-complex with $AlCl_3$ (as, for example, cyclohexane), or where complex formation is not accompanied by protonation (as, for example, with cyclohexene), hydrogen exchange does not occur.

Using chloronitrobenzene and bromoanisole as examples, it was proposed to study the influence of substituents on the exchange process. It seemed that electrophilic substituents, increasing the charge of the carbonium ion, should promote the exchange process, while nucleophilic substituents, decreasing this charge, should, on the contrary, slow the exchange rate. However, experimental

verification showed that both *p*-chloronitrobenzene with deuteronitrobenzene and *o*-bromoanisole with deuteroanisole exchange very little under the same conditions (Table 1, experiments Nos. 6-9). Probably, in both cases $AlCl_3$ is directed to the unshared electron pair of oxygen, which forms a strong complex with $AlCl_3$. This assumption is to some extent confirmed by the fact that no exchange is detected between deuterobenzene and diphenyl ether, nor between deuterotoluene and dibenzyl ether (Table 1, experiments Nos. 16-18). Such results are in full agreement with the previously established fact concerning the strength of radicals situated at an oxygen atom ([11]).

The experiments were carried out mainly in sealed ampoules at room temperature and at 100°. The exchanging components were mixed in equimolar amounts, and the amount of $AlCl_3$ taken was 0.01 mole. After completion of the reaction, the substances were washed free of $AlCl_3$ with dilute hydrochloric acid, then with water, dried, and separated into components. In experiments Nos. 1-9 and 16 the substances were separated by ordinary distillation, and in experiments Nos. 17 and 18 by distillation in vacuo. Thereafter, from the isolated component I, traces of the deuterated component II were removed by washing. For this purpose, the corresponding nondeuterated component II in an amount of 15 ml was added to the remaining component I. A second distillation was then carried out. Cyclohexene in experiments Nos. 12-15, after removal of $AlCl_3$, was oxidized cold with $KMnO_4$ in alkaline medium to adipic acid, and in some experiments was brominated in CCl_4 at 0° to dibromocyclohexane. Toluene in experiments Nos. 10, 11 (Table 1) and 1-3 (Table 2) was isolated in the form of benzoic acid. The purity of the isolated products was checked by boiling and melting points and by mixed-melting-point tests.

The products identified in this way and the original deuterium-containing substances (component I) were burned in a stream of dry air over

with calcined copper oxide. The water obtained from combustion was analyzed for deuterium content by the flotation method. The measurement error was 15γ. Radiometric analysis of the substances in experiments Nos. 1-3 of Table 2 was carried out in the form of carbon dioxide in an internal-fill counter.

The results of the analyses are summarized in Tables 1 and 2.

Gorky State
University

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