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Abstract

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ON THE ISOTOPIC EXCHANGE OF HYDROGEN IN PRIMARY AND SECONDARY ALKYL CHLORIDES

In our previous communications it was shown ([1]) that tertiary alkyl halides are capable of exchanging hydrogen atoms for deuterium in acidic media possessing high ionizing power: in anhydrous formic acid, in concentrated hydrochloric and hydriodic acids.

In media with low ionizing power ([2]), as, for example, in anhydrous acetic acid, hydrogen exchange of tertiary alkyl halides does not proceed without a catalyst; however, it can be induced by catalytic amounts of aprotic acids: $FeCl_3$, $SbCl_5$, $ZnCl_2$, etc. These data led us to the idea that the hydrogen exchange of tertiary alkyl halides is a consequence of heterolysis of the C—Hal bond, with formation of exchange-capable carbonium ions. On this basis one could expect that isotopic hydrogen exchange in primary and secondary alkyl halides could also be induced, if conditions were found under which the carbon—halogen bond would be ionized.

Proceeding from the idea that heterolysis of the carbon—halogen bond is a characteristic stage of Friedel-Crafts reactions ([3]), we decided to study the reaction of hydrogen exchange of primary and secondary alkyl chlorides under the action of aprotic acids in a medium typical for Friedel-Crafts reactions—in nitrobenzene. The deuterium donor in these reactions was deuterium chloride, whose solubility in nitrobenzene at room temperature is $\sim 2\%$.

Table 1

Hydrogen exchange of alkyl chlorides with DCl in a solution of nitrobenzene in the presence of aprotic acids at 25°. (Molar ratios RCl : nitrobenzene : DCl = 1 : 5÷8 : 0.2÷0.3)

Experiment No.	RCl	$MeHal_x$	$MeHal_x$, mol. %	Duration, min.	IPVS*, calculated for α-H	IPVS*, found
1	*n*-C_4H_9Cl	Without catalyst	—	10060	1900	70
1	Same	$FeCl_3$	3	20	1500	1450
1	Same	$AlCl_3$	5	20	2150	580
1	Same	$SbCl_5$	2	12	1600	1300
2	sec.-C_4H_9Cl	$FeCl_3$	3	13	2240	1860**
2	Same	$AlCl_3$	10	32	1480	1380
2	Same	$SbCl_5$	6	31	1390	1240
2	Same	BCl_3	9	37	1310	660
3	tert.-C_4H_9Cl	Without catalyst	—	5570	2700	61
3	Same	$FeCl_3$	3	13	2600	2650**
3	Same	$AlCl_3$	3	10	2400	2370**
4	iso-C_3H_7Cl	Without catalyst	—	53280	2460	70
4	Same	$FeCl_3$	10	70	2570	2480
4	Same	$AlCl_3$	9	63	2570	1450

* Here and below, IPVS = excess density of the combustion water.
** The experiments were carried out at 10°.

Special experiments showed that, under the conditions studied, nitrobenzene does not enter into a hydrogen-exchange reaction with hydrogen chloride; and in the presence of aprotonic acids the rate of hydrogen exchange of nitrobenzene is very low (see Section 3 of the experimental part). These observations opened up the possibility of studying the hydrogen exchange of alkyl chlorides with hydrogen chloride in a nitrobenzene solution. It was established that, in the absence of aprotonic acids, hydrogen exchange of primary and secondary alkyl chlorides does not occur. However, in the presence of the aprotonic acids $AlCl_3$, $FeCl_3$, $SbCl_5$, and BF_3, rapid exchange of hydrogen atoms occurred both in secondary and in primary alkyl chlorides (Table 1).

To establish the relative activity of various aprotonic acids in nitrobenzene solution, we investigated the rate of hydrogen exchange of isopropyl chloride in the presence of equal molar amounts of aprotonic acids. The results of the kinetic experiments are presented in Table 2. It turned out that the greatest activity in the reactions of hydrogen

Table 2

Hydrogen exchange of isopropyl chloride with DCl in nitrobenzene solution in the presence of aprotonic acids at 15° (Molar ratios iso-C_3H_7Cl : nitrobenzene : DCl = 1 : 8 : 0.2 ÷ 0.03)

Experiment no.	$MeHal_x$	Rate constant of hydrogen exchange $K_{h.e.} \cdot 10^6$ sec^{-1}	Experiment no.	$MeHal_x$	Rate constant of hydrogen exchange $K_{h.e.} \cdot 10^6$ sec^{-1}
1	Without catalyst	No exchange	5	BF_3	2
2	$SbCl_5$	880	6	$SnCl_4$	2 (at 25°)
3	$FeCl_3$	440	7	$HgCl_2$	No exchange
4	$AlCl_3$	150			

exchange of isopropyl chloride is exhibited by antimony pentachloride, and the smallest among the listed aprotonic acids by tin chloride. Mercuric chloride proved incapable of initiating hydrogen exchange.

The relative activity of the aprotonic acids studied may, accordingly, be expressed by the following numerical values:

$SbCl_5$	$FeCl_3$	$AlCl_3$	BF_3	$SnCl_4$
440	220	75	1	1

It is interesting to note that our data on the activity of aprotonic acids are in good agreement with the recently published data of Kottar and Evans ([4]), who studied the effect of Friedel-Crafts catalysts on the ionization of triarylmethyl chlorides in acetic acid. According to these authors, the ionizing strength of metal halides decreases in the following order:

$$SbCl_5 \gg FeCl_3 > SnCl_4 \gg BiCl_3 > HgCl_2 > SbCl_3.$$

The high mobility of hydrogen atoms of primary and secondary alkyl halides, which we found in the presence of $SbCl_5$, $FeCl_3$, and $AlCl_3$ in nitrobenzene medium, is in good agreement with the assumption that strong aprotonic acids in a medium with high ionizing ability can bring about heterolysis of the carbon

–chlorine bond in aliphatic chlorides, and that hydrogen exchange in these cases is due to the formation of carbonium ions according to the scheme:

$$\begin{matrix} R \\ \text{C}-\text{Cl} + \text{MeCl}_x \end{matrix} \rightleftharpoons_{\text{solv.}} \left[\begin{matrix} R \\ \text{C} \\ H \end{matrix} \right]^{\oplus}_{\text{solv.}} [\text{MeCl}_{x+1}]^{\ominus}_{\text{solv.}}.$$

Experimental Part*

1. Starting materials. Alkyl chlorides. Secondary butyl chloride (b.p. 67.5-67.8°; n_D^{20} 1.3949; d_4^{20} 0.8726) was obtained from secondary butyl alcohol and thionyl chloride (5) and purified by distillation on a column with an efficiency of 30 theoretical plates. Tertiary butyl chloride with b.p. 51°, n_D^{20} 1.3852; d_4^{20} 0.8439, was obtained from tertiary butyl alcohol by treatment with HCl and distilled on a 16-theoretical-plate column. *n*-Butyl chloride (b.p. 77-78°, n_D^{20} 1.4018; d_4^{20} 0.8858) and isopropyl chloride (b.p. 34.5-35°, n_D^{20} 1.3771; d_4^{20} 0.8592) were obtained from commercial products by distillation on a column with an efficiency of 30 theoretical plates.

Nitrobenzene. Commercial nitrobenzene was dried over phosphorus anhydride and distilled in vacuum, b.p. 85-86° at 10 mm, n_D^{20} 1.5524; d_4^{20} 1.2032. Dry nitrobenzene was saturated with deuterium chloride, the concentration of which at room temperature was $\sim 2\%$.

Aprotonic acids. In our investigations we used commercial chemically pure metal chlorides $FeCl_3$, $SbCl_5$, $SnCl_4$, $AlCl_3$, $HgCl_2$. Aluminum chloride, tin chloride, and antimony pentachloride were additionally purified by distillation in vacuum, in an atmosphere of nitrogen. Ferric chloride and mercuric chloride were not subjected to additional purification. Boron fluoride, obtained by the method of Meerwein and Pannwitz, was absorbed by dry nitrobenzene and in this form was metered into the reaction mixture.

Table 3

No. of sample	Duration, min.	Specific activity of chloride, γ/ml, calculated for α-H	Specific activity of chloride, γ/ml, found	$K \cdot 10^4$, sec.$^{-1}$
1	10	2020	842	8.97
2	15	2020	1100	8.84
3	20	2020	1158	7.08
4	1263	2020	2180	

2. Experiments on the hydrogen exchange of alkyl chlorides.** Weights of aprotonic acids were dissolved in nitrobenzene in an atmosphere of dry nitrogen in a special chamber. Addition of alkyl chlorides to the reaction mixture and withdrawal of samples were also carried out in an atmosphere of nitrogen. Alkyl chlorides were isolated from the withdrawn samples by distillation in vacuum. In the case of rapid reactions, hydrogen exchange was stopped by pouring the withdrawn samples into ice water. The isolated chlorides were washed with ice water, a solution of potash, dried with calcium chloride, and distilled. Since all kinetic experiments were carried out under similar conditions, we shall confine ourselves to describing only one experiment.

Hydrogen exchange of isopropyl chloride with DCl in nitrobenzene solution in the presence of $SbCl_5$. 1.03 g (3.4 mmole) of $SbCl_5$ was dissolved in 44.52 g (362 mmole) of dry nitrobenzene. To the resulting solution were added 9.0 g (114.7 mmole) of isopropyl chloride dissolved in 67.88 g (54.6 mmole) of nitrobenzene containing 0.75 g (20 mmole) of deuterium chloride (86200 γ/ml). The solution was placed in a thermostat at 15°. At definite intervals, samples of 25–30 ml were withdrawn from the reaction medium; from these, isopropyl chloride was isolated by distillation in vacuum and purified in the usual manner. The results are given in Table 3.

3. Experiments on the hydrogen exchange of nitrobenzene. Dry nitrobenzene was saturated with deuterium chloride, the concentration of which was determined by titration with alkali using phenolphthalein. The deuterium content was determined from the excess density of the combustion water of such a solution. Samples of nitrobenzene were washed with alkali, dried with P_2O_5, distilled, and the deuterium content in the nitrobenzene was determined by the usual meth–

* A. N. Astakhova took part in the experiments.
** The isotopic analysis was performed by N. V. Kislyakova and N. F. Mironova.

among themselves. The hydrogen exchange of nitrobenzene with DCl in the presence of aprotonic acids was determined in an analogous manner (Table 4).

Thus, it has been established that primary and secondary alkyl chlorides enter, at a high rate, into a hydrogen-exchange reaction with DCl in a solution of nitrobenzene in the presence of strong aprotonic acids

Table 4

Hydrogen exchange of nitrobenzene with DCl at 25–28°

No.	$MeHal_x$	$MeHal_x$ (molar ratio)	DCl (molar ratio)	Nitrobenzene (molar ratio)	Duration, min.	EASD, γ/ml, calculated for meta-H	EASD, γ/ml, found
1	O	0	1.5	53	20000	580	0
2	$FeCl_2$	1	1.5	53	20000	580	160
2	$FeCl_2$	1	1.5	53	60500	580	470
3	$AlCl_3$	1	1.6	43	20000	580	160
3	$AlCl_3$	1	1.6	43	60500	580	410

$SbCl_5$, $FeCl_3$, $AlCl_3$. In the presence of BF_3 and $SnCl_4$ the hydrogen exchange proceeds at a considerably lower rate. Under the same conditions, mercuric chloride does not initiate the hydrogen exchange of primary and secondary alkyl chlorides at all. The data obtained confirm that the hydrogen exchange of alkyl chlorides is due to heterolysis of the carbon–chlorine bond and the formation of carbonium ions.

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