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Abstract

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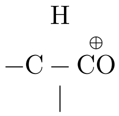
ON THE PROTON MOBILITY OF HYDROGEN ATOMS IN ACETYL CHLORIDE

At present there are experimental data confirming that, in aliphatic carbonium ions, the hydrogen atoms at the α-carbons possess proton mobility (^{1}). It was of interest to determine whether the hydrogen atoms of acylium ions of the type



$$-\overset{\mathrm{H}}{\underset{|}{\mathrm{C}}}-\overset{\oplus}{\mathrm{CO}} \tag{I}$$

also possess proton mobility.

Acylium ions are relatively stable particles. As early as 1922, Meerwein and Maier-Hüser established that acid halides form solid compounds with salts of coordinatively unsaturated metals (aprotic acids) (^{2}). In 1947, Zeel and Bauer (^{3}) studied these reactions by conductometric titration in liquid sulfur dioxide. It was found that addition of antimony pentachloride to acetyl chloride causes, up to attainment of an equimolecular ratio of these substances, a rapid increase in electrical conductivity. From the moment equimolecularity is reached, the increase in conductivity practically ceases. These data led the authors to conclude that, in the interaction of acetyl chloride with antimony pentachloride, an ionized substance is formed, the formation of which corresponds to the equation:

$$\mathrm{CH_3COCl + SbCl_5 = [CH_3 - \overset{\oplus}{CO}] + [SbCl_6]^{\ominus}}.$$

In 1959 the structure of this and analogous addition products received further convincing confirmation in the work of Sandhu and co-workers (^{4}).

Thus, salts containing the acylium cation can readily be obtained. To solve the problem we posed, we studied the reactions of isotopic exchange of the hydrogen atoms of acetyl chloride under the action of deuterium chloride on it in the presence of aprotic acids.

On the basis of what has been said, it was to be expected that, if the hydrogen atoms of acylium ions (I) are indeed capable of entering into isotopic-exchange reactions, then addition to the corresponding acid halide of an aprotic acid should promote this reaction.

Table 1 gives the results obtained by us in studying the kinetics of the isotopic-exchange reaction of the hydrogen atoms of acetyl chloride in the presence and in the absence of aprotic acids. The reactions were carried out at 25°. Acetyl chloride was dissolved in nitrobenzene containing DCl and the corresponding aprotic acid. The molar ratios of the components were $1 : 5 : 0.2 : 0.05$, respectively. The rate constants were calculated from the equation for first-order reactions.

Table 1 shows that the effect anticipated by us does occur. This permits the assertion that the hydrogen atoms in acylium ions possess proton mobility.

It is interesting to note that the rate of hydrogen exchange of acetyl chloride in nitrobenzene solution with DCl, in the presence of strong aprotic acids, is considerably lower than the rate of hydrogen exchange of alkyl chlorides under the same conditions (^{5}). Thus, for example, the rate of hydrogen exchange of isopropyl chloride with DCl in the presence of 5 mole % $FeCl_3$ in nitrobenzene solution at 25° is so high that it practically cannot be measured, whereas the rate constant for hydrogen exchange of acetyl chloride under the same conditions is only $28 \cdot 10^{-6}$ $\sec^{-1}$. This fact is probably explained by the structural features of acylium ions, in which the positive charge is distributed between the carbonyl carbon and the oxygen bound to it.

Table 1

Aprotonic acid	$K \cdot 10^6$, $\sec^{-1}$
Absent	1
$HgCl_2$	5
BF_3	9
$AlCl_3$	12
$FeCl_3$	28

The data of Table 1 also show that aprotonic acids of different strength accelerate the isotope exchange reaction of the hydrogens of acetyl chloride to different degrees. We observed an analogous phenomenon in studying the hydrogen exchange of alkyl halides (^{6}). It is significant that, in terms of the magnitude of the effect they produce, the aprotonic acids in both cases fall into the same series.

It is also interesting to note that even in the absence of aprotonic acids acetyl chloride is capable, although very slowly, of undergoing hydrogen exchange. Probably in this case as well, hydrogen exchange is associated with ionization of the acetyl chloride molecule.

Experimental Part*

Acetyl chloride (b.p. 50—51°) was purified by distillation on a column with an efficiency of 30 theoretical plates. Traces of hydrogen chloride were removed by adding dimethylaniline to the distillation flask.

Nitrobenzene and aprotonic acids (ferric chloride, antimony pentachloride, aluminum chloride, stannic chloride, boron trifluoride, and sulema) were purified in the same way as in the experiments with alkyl chlorides ([5]).

Experiments on the hydrogen exchange of acetyl chloride. Portions of aprotonic acids were dissolved in nitrobenzene (saturated with deuterium chloride) in an atmosphere of dry nitrogen in a special chamber ([5]). The solution was placed in a thermostat, acetyl chloride was added, and at specified intervals a portion of the solution was pumped (under pressure of dry nitrogen) into a distillation flask. From the samples taken, acetyl chloride was isolated by distillation under vacuum, at the same temperature at which the experiment was carried out. Traces of hydrogen chloride (deuterium chloride) were removed from the acetyl chloride by treatment with dimethylaniline, after which the acetyl chloride was distilled under vacuum and purified by repeated "freeze-transfer" under vacuum into vessels cooled with solid carbon dioxide. To avoid contact of acetyl chloride with atmospheric moisture, a quartz ampoule of volume 0.1-0.2 ml was placed in the final vessel and filled with acetyl chloride. The contents of the ampoule were burned in a stream of dry oxygen, and the deuterium content was determined in the combustion water**.

We give a detailed description of the kinetic experiments for two examples.

a. **Hydrogen exchange of acetyl chloride with DCl in nitrobenzene.** 8.27 g (105.3 mmole) of acetyl chloride was dissolved in 60.97 g of nitrobenzene containing 1.4% deuterium chloride (495.7 mmole nitrobenzene and 22 mmole DCl of excess weight 80,000 γ/ml). The solution was placed in a thermostat at 25°, and at specified intervals samples of 15-20 ml were taken, from which acetyl chloride was isolated by the method described above. The results are given in Table 2.

* The experiments were carried out with the participation of L. E. Andreeva.

** The isotope analysis was carried out by N. V. Kislyakova and N. F. Mironova.

b. Hydrogen exchange of acetyl chloride with DCl in nitrobenzene, in the presence of $FeCl_3$. 1.07 g (6.6 mmole) of anhydrous ferric chloride was dissolved in 80.17 g of nitrobenzene containing 1.12 g of DCl (642.7 mmole of nitrobenzene and 30 mmole of DCl, e.p.c.

Table 2

Duration, min	E.p.c.* of acetyl chloride, γ/ml (calculated)	E.p.c.* of acetyl chloride, γ/ml (found)	$K_{\text{v.o.}} \cdot 10^6$, sec^{-1}
1040	5010	595	0.92
1330	5010	738	1.13
4070	5010	1418	1.08
5590	5010	2204	1.56

* E.p.c. = excess density of combustion water.

Table 3

Duration, min	E.p.c. of acetyl chloride, γ/ml (calculated)	E.p.c. of acetyl chloride, γ/ml (found)	$K_{\text{v.o.}} \cdot 10^6$, sec^{-1}
125	4900	948	29
185	4900	1250	27
240	4900	1600	27
1385	4900	4960	–

80,000 γ/ml). To the solution obtained, 10.93 g (139.2 mmole) of acetyl chloride was added. The mixture was placed in a thermostat at 25°, and samples were taken in the same way as in the preceding experiment (see Table 3).

c. Hydrogen exchange of acetyl chloride with DCl in nitrobenzene, in the presence of MeHal$_x$. The results of experiments on the hydrogen exchange of acetyl chloride with DCl in a nitrobenzene solution, in the presence of various aprotonic acids, are presented in Table 4. The molar ratios of the components were, respectively, 1 : 5 : 0.3 : 0.1.

Table 4

MeHal$_x$	$K_{\text{v.o.}} \cdot 10^6$ sec^{-1}
Absent	1
$SnCl_4$	17
BF_3	25
$AlCl_3$	25
$SbCl_5$	26
$FeCl_3$	44

d. Hydrogen exchange of acetyl chloride with DCl. Freshly distilled acetyl chloride was saturated at room temperature with deuterium chloride. After 3 days the solution was treated with dimethylaniline, and the acetyl chloride was purified in the usual way. The e.p.c. found for the acetyl chloride was 1720 γ/ml.

Using the isotope-exchange method it was found that the hydrogen atoms in acetyl chloride possess proton mobility and enter into a hydrogen-exchange reaction with deuterium chloride. It was established that, in the presence of the aprotonic acids $FeCl_3$, $SbCl_5$, $AlCl_3$, $SnCl_4$, BF_3, and $HgCl_2$, the rate of the hydrogen-exchange reaction increases considerably; moreover, $FeCl_3$ exhibits the greatest accelerating effect, and $HgCl_2$ the smallest.

The experimental data obtained by us agree with the view that the hydrogen exchange of acetyl chloride is due to the formation of acylium ions.

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