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Abstract

Full Text

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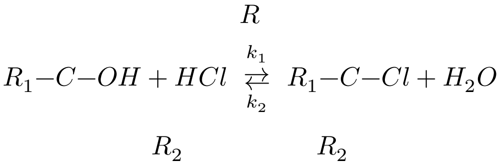
On the Reactions of Hydrogen Exchange of Alkyl Chlorides with Hydrochloric Acid and of tert-Butyl Alcohol upon Replacement of Hydroxyl by Chlorine

Reactions of tertiary aliphatic alcohols with a saturated aqueous solution of hydrogen chloride proceed at a high rate and practically irreversibly, with formation of the corresponding alkyl chlorides.



$$R_1{-}\underset{R_2}{C}{-}OH + HCl \overset{R}{\underset{k_2}{\overset{k_1}{\rightleftarrows}}} R_1{-}\underset{R_2}{C}{-}Cl + H_2O$$

(saturated aqueous solution) $k_1 \gg k_2$

There are no reliable data in the literature on the mechanism of this reaction; however, the mechanism of the reverse reaction—the hydrolysis of tertiary alkyl chlorides—has been established (^{1}) and is a monomolecular nucleophilic substitution reaction (S_N1).

It could be assumed that the reaction of formation of tertiary chlorides from the corresponding alcohols also proceeds by a carbonium-ion mechanism.

In the present work we investigated whether this reaction is accompanied by hydrogen exchange. It is evident that the presence of deuterium in the chlorides obtained could serve as an indication of the occurrence, at an intermediate stage of this reaction, of sufficiently long-lived carbonium ions (^{2}).

For this purpose, the reaction of tert-butyl alcohol with a saturated aqueous solution of hydrochloric acid enriched with deuterium was investigated. The studies showed that the tert-butyl chloride formed at a high rate contained only an insignificant amount of deuterium. At the same time, upon further contact of the chloride with deutero-hydrochloric acid, the deuterium content in tert-butyl chloride increased, and, for example, after 38 hours of contact the extent of exchange exceeded 30%* (Table 1). Similar results were also observed for other tertiary chlorides—tert-amyl chloride and 1-methylcyclohexyl chloride-1.

It was established that the number of hydrogen atoms exchanged for deuterium corresponds only to the α-hydrogen atoms. Under the same conditions, a primary alkyl chloride—butyl chloride—does not enter into the hydrogen-exchange reaction (Table 2).

Numerous studies (⁴) of the mechanism of various solvolytic reactions of tertiary alkyl halides have shown that all these reactions proceed by the S_N1 mechanism, the rate-determining stage being

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* Our data on the absence of hydrogen exchange in the process of the reaction of tertiary alcohols with hydrochloric acid agree with the data of Shalev (³) and co-workers, who established that in the process of obtaining tert-butyl chloride-d_9 from tert-butyl alcohol-d_9 and hydrochloric acid, no exchange of deuterium for hydrogen is observed. However, on the basis of the present study it should be taken into account that, during prolonged contact of the components, a considerable change in the isotopic composition of the chlorides may occur.

Table 1

Experiment No.	Alcohol	Experimental conditions: molar ratio alcohol/DCl	Experimental conditions: reaction time	EBC* of chloride, γ/ml: calculated for exchange of all H	EBC* of chloride, γ/ml: found	Exchange, % of calculated
1	$(CH_3)_3C—OH$	1 : 1	10 min.	7800	30	0.4
2	Same	1 : 1.34	20 min.	42960	1000	2.3
3	””	1 : 1.42	10 min.	40750	445	1.1
4	””	1 : 1.42	38 hr.	40750	12470	31.0

* Here and below, EBC is the excess density of the combustion water.

Table 2

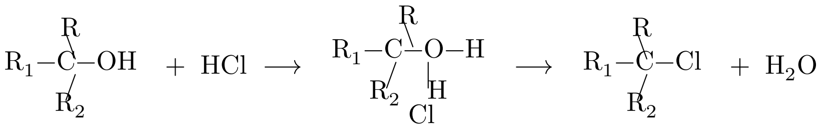
Experiment No.	Chloride	Experimental conditions: molar ratio chloride/DCl	Experimental conditions: reaction time, hr.	EBC of chloride, γ/ml: calculated for all H	EBC of chloride, γ/ml: calculated for α-H	EBC of chloride, γ/ml: found	Exchange, % of calculated for α-H
1	$(CH_3)_3CCl$	1 : 3.6	105	58200	58200	55700	96.0
2	$(CH_3)_2C(Cl)CH_2CH_3$	1 : 2.4	113	47030	38570	30530	79.2
3	Same	1 : 3.3	250	37820	30250	29890	98.8
4	1-chloro-1-methylcyclohexane	1 : 3.4	106	50800	32970	23240	70.5
5	Same	1 : 2.9	250	38810	20480	18590	90.7
6	n-C_4H_9Cl	1 : 4.5	110	31900	31900	414	1.3

their rate is the rate of ionization of tertiary halides. It is evident that the reaction under consideration of tertiary alkyl chlorides with deuterohydrochloric acid should likewise be a special case of solvontic monomolecular reactions. On this basis one should suppose that the hydrogen-exchange reaction of tertiary alkyl chlorides is also connected with their ability to ionize in a hydrochloric-acid solution having a high dielectric constant. The nature of the ionization of the chlorides, depending on a number of external and internal factors, may vary from the state of ion pairs to solvated carbonium ions. A consequence of ionization of the chlorides is their hydrogen exchange.

The fact that only the α-hydrogen atoms of chlorides take part in the hydrogen-exchange reaction can be explained by the impossibility, under the conditions investigated, of migration of the carbonium center along the chain of carbon atoms, owing to the electrostatic attraction of the carbonium center by anions (in ion pairs) or to the influence exerted by the solvation shell of the carbonium carbon (in free carbonium ions).

The absence of deuterium in tertiary butyl chloride, formed as the result of the rapidly proceeding process of nucleophilic substitution of hydroxyl by chlorine during the interaction of tertiary butyl alcohol with deuterohydrochloric acid, permits one to consider that either carbonium ions are not formed at all in the course of this reaction, or their lifetime is so short that they do not have time to exchange to any noticeable extent with acidic deuterium donors.

The first assumption is apparently the more probable. In its favor, in particular, are the cases described in the literature (5) of preservation of optical activity upon replacement of hydroxyl by chlorine at an asymmetric carbon. This view corresponds to a synchronous reaction mechanism:



Experimental Part*

Reaction of tertiary butyl alcohol and enriched aqueous HCl. I. 7.55 g (102 mmol) of freshly distilled over calcium hydride tertiary butyl alcohol was shaken for 10 min with 11.55 g (125 mmol HCl) of 30% hydrochloric acid of isotopic density 10000 γ/ml. The chloride layer was washed with ice water, bicarbonate solution, again with water, dried over $CaCl_2$, and distilled. The isolated chloride had the following constants: b.p. 52°, n_D^{20} 1.3847, d_4^{20} 0.8425, IDVS 30 γ/ml. The IDVS calculated for exchange of 9H was 7800 γ/ml. The study showed that, during replacement of the hydroxyl of the alcohol by chlorine under the action of HCl, hydrogen exchange is not observed.

II. 7.61 g (103 mmol) of tertiary butyl alcohol and 12.71 g (138 mmol HCl) of a saturated aqueous solution of hydrochloric acid of isotopic density 79000 γ/ml were stirred for 20 min. The isolated tertiary butyl chloride had b.p. 50–51°, n_D^{20} 1.3848, d_4^{20} 0.8400, IDVS 1000 γ/ml. The IDVS calculated for exchange of 9H was 42960 γ/ml.

III. 7.80 g (105 mmol) of tertiary butyl alcohol was stirred with 12.6 g (138 mmol HCl) of hydrochloric acid of isotopic density 80500 γ/ml. A sample of chloride taken after 10 min had the following constants: b.p. 50–50.5°, n_D^{20} 1.3850, d_4^{20} 0.8436, IDVS 445 γ/ml. The chloride isolated after 38 h of shaking had b.p. 49–50°, n_D^{20} 1.3841, d_4^{20} 0.8519, IDVS 12470 γ/ml. The IDVS calculated for isotopic equilibrium was 40750 γ/ml.

Hydrogen exchange of tertiary butyl chloride with hydrochloric acid. 3.95 g (43 mmol) of tertiary butyl chloride (b.p. 52°, n_D^{20} 1.3852, d_4^{20} 0.8435) and 14.17 g (1 mmol HCl) of a saturated aqueous solution of hydrochloric acid of isotopic density 80500 γ/ml were shaken in a sealed tube for 105 h. The isolated chloride had b.p. 51–52°, n_D^{20} 1.3830, d_4^{20} 0.8899, IDVS 55700 γ/ml. The IDVS calculated for exchange of 9H was 58200 γ/ml.

Hydrogen exchange of tertiary amyl chloride with hydrochloric acid. I. 4.1 g (38.5 mmol) of tertiary amyl chloride (b.p. 82°, n_D^{20} 1.4043, d_4^{20} 0.8627) and 8.38 g (91.8 mmol HCl) of hydrochloric acid of isotopic density 80500 γ/ml were stirred for 113 h. The isolated chloride had b.p. 83°, $n_D^{20.3}$ 1.4016, d_4^{20} 0.8954, IDVS 30530 γ/ml. The IDVS calculated for exchange of 8H was 38570 γ/ml.

II. 2.48 g (23.3 mmol) of chloride and 6.94 g (76 mmol HCl) of hydrochloric acid (80500 γ/ml) were stirred for 250 h. The IDVS of the chloride after the experiment was 29890 γ/ml; the IDVS calculated for exchange of 8α-H was 30250 γ/ml.

Hydrogen exchange of 1-methylcyclohexyl chloride with hydrochloric acid. I. 3.28 g (25 mmol) of 1-methylcyclohexyl chloride (b.p. 58°/30 mm, n_D^{20} 1.4572, d_4^{20} 0.9666) and 7.70 g (84 mmol HCl) of hydrochloric acid (80500 γ/ml) were stirred for 106 h. The isolated

* A. N. Astakhova and L. E. Andreeva took part in the work.

The chloride had b.p. 69-70°/42-43 mm, n_D^{20} 1.4567, d_4^{20} 0.9967, SRA 23240 γ/ml. SRA calculated for exchange of 7α-H: 32970 γ/ml.

II. 3.33 g (25 mmoles) of methylcyclohexyl chloride and 6.37 g (73 mmoles HCl) of hydrochloric acid (42000 γ/ml) were stirred for 250 hours. The isolated chloride had b.p. 49.5°/24-25 mm, n_D^{20} 1.4569, d_4^{20} 0.9920, SRA 18590 γ/ml. SRA calculated for exchange of 7α-H: 20480 γ/ml.

Hydrogen exchange of normal butyl chloride with hydrochloric acid. 2.25 g (24 mmoles) of *n*-butyl chloride (b.p. 78°, n_D^{20} 1.4015, d_4^{20} 0.8850) and 9.91 g (109 mmoles HCl) of hydrochloric acid (41870 γ/ml) were stirred for 110 hours. The isolated chloride had b.p. 77-78°, n_D^{20} 1.4014, d_4^{20} 0.8869, SRA 414 γ/ml. SRA calculated for exchange of 9 H: 31900 γ/ml.

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