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Abstract

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EQUILIBRIUM DISTRIBUTION OF DEUTERIUM IN HYDROGEN EXCHANGE WITH LIQUID HYDROGEN CHLORIDE

(Presented by Academician V. A. Kargin on 9 VI 1958)

The present work is the first investigation of deutero-exchange in liquid hydrogen chloride and is devoted to the study of isotope equilibria in certain systems that include hydrogen chloride.

In previous works we revealed ([1], [2]) and analyzed ([3]) a general regularity determining the character of the equilibrium distribution of deuterium in hydrogen isotope-exchange reactions, making it possible to predict the magnitude of the deuterium distribution coefficient (α) in any system of hydrogen-containing substances. The numerous experimental data available in the literature are in good agreement with this regularity ([3]). The only exception was the value of α for the benzene–hydrogen chloride system ([4]), the reliability of which, however, was doubtful. There were grounds to suppose that equilibrium had not been attained in the cited work (only direct exchange was studied) and that the value obtained, $\alpha_{20^\circ} = 1.6$, was therefore too low. In another, later work ([5]), by experimental determination of the magnitude of the deuterium distribution coefficient between an aromatic C–H bond in the phenol molecule and hydrogen chloride, a more satisfactory value, $\alpha_{50^\circ} = 2.18$, was obtained. It should be noted that this value was calculated from experimental data under the erroneous assumption that the value of α for O–H and H–Cl bonds is 1.1. The corresponding recalculation, however, does not lead to a significant change in this quantity and gives $\alpha_{50^\circ} = 2.0$. In that work, too, equilibrium was attained only from one side.

Thus, it was of interest to obtain a reliable value of α for the isotope equilibrium between hydrogen chloride and an aromatic C–H bond, and also to compare this value with the values of α in the case of an O–H bond and an aliphatic C–H bond, for which there are no experimental data at all in the literature. Knowledge of the corresponding values is also necessary for the investigation we are presently carrying out of deutero-exchange with liquid hydrogen chloride.

The isotope equilibrium between hydrogen chloride and benzene, cyclopentane, and also water was studied. The experiments were carried out in liquid-phase systems under pressure, for which sealed ampoules and valves made of Monel metal or platinum were used (^{6}), Figs. 3 and 4. After equilibrium had been reached, the hydrogen chloride was evaporated, passing its first portion through a vessel heated to 350° (^{4}), and the water obtained as a result of neutralization was analyzed for deuterium content. Evaporation was carried out slowly, without removing the test tube from the thermostat. In addition, at the end of the exchange experiment the deuterium content in the organic substances and in the water was determined. In experiments with benzene and cyclopentane the hydrocarbons were burned in a stream of oxygen and the isotopic composition of the resulting water was determined. In the experiments with water, the -

···acid, which remained after evaporation of the hydrogen chloride, was neutralized by passing its vapors through soda heated to 350°. In doing so, a correction was introduced for the difference in the concentrations of deuterium in water and in hydrogen chloride, the relative contents of which in the analyzed sample of hydrochloric acid were determined by titration. Isotopic analysis of the water was in all cases carried out by the drop method (^{7}).

Equilibrium in the isotopic exchange was reached from both sides, by carrying out experiments on direct and reverse exchange (with the exception of the experiments with cyclopentane). The experiments on isotopic exchange in hydrocarbons were carried out under catalysis by aluminum chloride. The data obtained are given in Table 1.

Table 1

Temperature, °C	Exchange time, h	Initial deuterium conc., at. % in HCl	Initial deuterium conc., at. % in substance	Final deuterium conc., at. % in HCl	Final deuterium conc., at. % in substance	Distribution coefficient α
System HCl–water	**System HCl–water**	**System HCl–water**	**System HCl–water**	**System HCl–water**	**System HCl–water**	**System HCl–water**
0	6.0	1.10	–	0.80	2.10	2.66
0	6.0	1.10	–	0.80	1.96	2.48
0	3.8	–	1.96	0.42	1.14	2.73
0	4.5	–	1.96	0.43	1.17	2.73
25	3.2	0.95	–	0.78	1.84	2.38
25	21.0	1.10	–	0.86	2.04	2.40
25	22.3	1.10	–	0.97	2.18	2.28
25	2.5	–	1.96	0.49	1.23	2.52
25	2.6	–	1.96	0.48	1.23	2.58
40	2.3	0.95	–	0.70	1.57	2.26
40	2.1	0.95	–	0.64	1.43	2.25
40	4.8	1.10	–	0.83	1.81	2.20

Temperature, °C	Exchange time, h	Initial deuterium conc., at. % in HCl	Initial deuterium conc., at. % in substance	Final deuterium conc., at. % in HCl	Final deuterium conc., at. % in substance	Distribution coefficient α
40	4.4	–	1.96	0.50	1.24	2.49
40	5.1	–	1.96	0.56	1.36	2.48
System HCl—benzene	**System HCl—benzene**	**System HCl—benzene**	**System HCl—benzene**	**System HCl—benzene**	**System HCl—benzene**	**System HCl—benzene**
25	3.6	0.95	–	0.52	1.26	2.44
25	24.0	0.95	–	0.48	1.10	2.31
25	24.5	1.10	–	0.96	2.27	2.40
25	20.5	–	1.10	0.29	0.74	2.57
25	21.0	–	1.26	0.27	0.70	2.61
System HCl—cyclopentane	**System HCl—cyclopentane**	**System HCl—cyclopentane**	**System HCl—cyclopentane**	**System HCl—cyclopentane**	**System HCl—cyclopentane**	**System HCl—cyclopentane**
~ 20	530	0.95	–	0.47	1.11	2.38
~ 20	549	0.95	–	0.49	1.10	2.26
~ 20	771	1.10	–	0.60	1.44	2.42

Despite the fact that the experiments were carried out in liquid-phase systems, the values of α indicated in Table 1 refer to the systems: dissolved (liquid) substance—gaseous hydrogen chloride, since at the end of the experiment the deuterium concentration was determined not in liquid but in gaseous hydrogen chloride, which was in isotopic equilibrium with the liquid phase. For this purpose, for analysis, a small fraction of hydrogen chloride was taken at the very beginning of its evaporation from the ampoule. The accuracy of the data obtained was $\pm 5\%$ of the value of α.

In addition to the direct experimental determination of the values of α for the system water (liquid)—hydrogen chloride (gas), these values were also calculated from spectral data, taking into account corrections for anharmonicity of vibrations in the molecules H_2O, HDO (^{8}), HCl, and DCl (^{9}), and corrections for the ratio of the vapor elasticities of H_2O and HDO (^{8}). The values obtained as a result of the calculation: $\alpha_{0^\circ} = 2.79$; $\alpha_{25^\circ} = 2.45$; $\alpha_{40^\circ} = 2.32$, coincide with those given···

in Table 1 within the experimental errors. The corresponding exact calculations for systems including benzene and cyclopentane were not carried out because of the absence in the literature of corrections for the anharmonicity of vibrations, as well as ratios of force constants for pairs for the various isotopic forms of these compounds.

The data obtained indicate that the values of α (for one and the same temperature) in the isotopic exchange of hydrogen chloride with compounds containing an O—H bond, as well as an aromatic or aliphatic C—H bond, are practically identical. This fact, as well as the magnitude itself of the excess of the values of α over unity, is in complete agreement with the general regularity of the equilibrium distribution of deuterium (1–3).

Especially noteworthy is the hydrogen exchange discovered in this work, which proceeds in a medium of liquid hydrogen chloride in the presence of $AlCl_3$ (as also in solutions of $AlBr_3$ in HBr and BF_3 in HF (10)) with a saturated hydrocarbon containing no tertiary carbon atom, for which cyclopentane was taken.

The comparative ease of hydrogen exchange between hydrocarbons and liquid hydrogen chloride testifies to the possibility of using it (along with other liquid hydrogen halides (11,12)) as a medium for studying the capacity of organic compounds for electrophilic substitution reactions by the deuterium-exchange method. The corresponding investigations are currently being carried out.

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