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Abstract

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DEUTERIUM EXCHANGE BETWEEN AROMATIC HYDROCARBONS AND LIQUID DEUTERIUM CHLORIDE

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The use of liquid deuterated hydrogen halides (HF, HBr, and HI) as media for studying the rate of deuterium exchange in hydrocarbons and their derivatives made it possible to estimate the relative ability of individual hydrogen atoms in the molecules of these compounds to undergo electrophilic substitution reactions and to reveal the influence of the physical properties of the solvent (polarity, dielectric constant, etc.) on the rate of deuterium exchange ([1–9]). The absence of data on the rate of exchange with liquid hydrogen chloride, however, did not make it possible to obtain a complete picture characterizing the protogenic properties of hydrogen halides in hydrogen-exchange reactions.

In the present work the main results of a study of the reactions of isotopic hydrogen exchange with liquid deuterium chloride are briefly presented. Hydrogen chloride enriched with deuterium (1.5–2%), which hereafter we shall conventionally call deuterium chloride—DCl, was obtained from a mixture of concentrated sulfuric and hydrochloric acids, to which a calculated amount of D_2O had previously been added.

The experimental procedure was in its main features analogous to the procedures used in works ([10,11]). However, the high vapor pressure of DCl at room temperature ($\sim$ 40 atm) ruled out the possibility of using glass ampoules, as was done in experiments with hydrogen bromide ([10]). The vessel for storing deuterium chloride and the ampoules for carrying out exchange experiments were made of Monel metal and equipped with valves, the design of which is described in ([11]). Teflon was used as the gasket material. The method of working with liquid DCl was partially described by us in ([12]).

The required amount of DCl was transferred by siphoning* from the vessel into a cooled glass test tube, from which it was distilled in vacuum into a Monel-metal test tube into which a weighed portion of the hydrocarbon under study had been introduced beforehand. The solution was kept for the required time in a thermostat, after which the deuterium chloride was evaporated, the hydrocarbon was purified, burned in a stream of oxygen, and, after purification of the water obtained, the deuterium concentration was determined by the drop method (13). Before combustion, the purity of the organic substance under study was checked by monitoring its boiling or melting temperature. The rate of isotopic exchange was characterized by the number (n) of atoms exchanged over a given time interval or by the rate constant (k). The quantities n and k were calculated from the formulas given in work (14). The value of the coefficient (α) of deuterium distribution between the hydrocarbon and hydrogen chloride, taking into account the phase state, was taken to be 2.2 (15). As the values of n and k, values averaged over all exchangeable hydrogen atoms in the hydrocarbon molecules were taken.

The results of the experiments are presented below.

Benzene. Exchange in benzene proceeds very slowly. In 1 year at room temperature (~ 20°), approximately two H atoms are exchanged.

* To avoid fractionation.

$k_{C_6H_6}^{\sim 20^\circ} = 4 \cdot 10^{-8}$ sec^{-1} (average value from 4 experiments with durations from 146 to 11,400 hr.).

Hydrocarbons with condensed rings. An increase in the number of aromatic rings leads to a sharp increase in the rate of exchange. Thus, isotopic equilibrium at 25° is reached in the case of naphthalene in less than 71 hr ($n = 7.6$), for phenanthrene in less than 23 hr ($n = 10$), and for pyrene in less than 6 hr ($n = 9.6$). The values of k decrease as the duration of the exchange experiment increases, which indicates a pronounced nonequivalence of different hydrogen atoms in the molecules of these compounds with respect to their ability to undergo electrophilic substitution. In the case of naphthalene, k changes from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-5}$ sec^{-1}; in the case of phenanthrene, from $0.9 \cdot 10^{-4}$ to $0.6 \cdot 10^{-4}$ sec^{-1}; and for pyrene, from $6 \cdot 10^{-4}$ to $1 \cdot 10^{-4}$ sec^{-1}. The rate of exchange in the compounds studied increases in the sequence: benzene $\ll$ naphthalene $<$ phenanthrene $<$ pyrene.

Biphenyl. The hydrogen atoms of biphenyl enter into exchange more readily than the hydrogen atoms of benzene, but less readily than those of naphthalene. At 25° the exchange rate is characterized by the following values of n: 2 hr $n = 0.5$; 10 hr $n = 0.7$; 21 hr $n = 1.7$; 49 hr $n = 2.9$. At room temperature (~ 20°): 79 hr $n = 3.0$; 279 hr $n = 5.2$; 1200 hr $n = 6.0$; 4800 hr $n = 6.0$. The data presented, according to which 4 hydrogen atoms (in the meta positions) enter into isotopic exchange with great difficulty, indicate a very weak ability of these atoms to participate in electrophilic substitution reactions, which is consistent with the chemical properties of biphenyl.

Alkylbenzenes. The rate of hydrogen exchange for various monoalkylbenzenes is the same within experimental error. For toluene, ethylbenzene, and isopropylbenzene, respectively, the following values of n were obtained: 6 hr $n = 0.4$; 0.4; 0.5 (25°); 10 hr $n = 0.7$; 0.7; 0.7 (25°); 24 hr $n = 1.7$; 1.5; 1.4 (25°); 1200 hr $n = 4.4$; 4.0; 4.1 (~ 20°). This result indicates that the structure of the alkyl group has practically no effect on the ability of the H atoms of the ring to undergo electrophilic substitution.

We give the data for toluene in greater detail. 1 hr $n = 0.1$; 2 hr $n = 0.2$; 4 hr $n = 0.4$; 6 hr $n = 0.4$; 10 hr $n = 0.7$; 20 hr 40 min $n = 1.3$; 24 hr $n = 1.7$; 70 hr $n = 2.6$ (25°C); 96 hr $n = 3.0$; 963 hr $n = 4.4$; 2400 hr $n = 4.4$; 4800 hr $n = 5.2$ ($\sim 20^{\circ}$).

By the method described in work (^{5}), the individual exchange-rate constants were determined for the H atoms of monoalkylbenzenes in the ortho and para positions and in the meta position; they proved to be, respectively, $k_{o,p} \simeq 1 \cdot 10^{-5}$ sec^{-1}, $k_m \simeq 3 \cdot 10^{-7}$ sec^{-1}. It is easy to see that the H atoms in the meta positions of the aromatic ring of monoalkylbenzenes, in contrast to the corresponding H atoms in biphenyl, are characterized by an increased ability (compared with benzene) to undergo electrophilic substitution. This is connected with the fact that, in the case of alkylbenzenes, the inductive effect and the σ, π-conjugation effect of the alkyl group (in contrast to the phenyl group) have the same sign.

Hydrogen exchange in the aromatic ring of polymethylbenzenes (mesitylene, durene, pentamethylbenzene) proceeds very rapidly—in the course of 1 hr at 25°, isotopic equilibrium is reached for the corresponding H atoms; moreover, the value of n in experiments lasting 240 hr remains unchanged.

In the case of hexamethylbenzene, exchange is not observed even over 240 hr. This indicates that, just as in the case of other hydrogen halides (DF, DBr), the hydrogen atoms of methyl groups do not enter into isotopic exchange with DCl.

Phenylated alkanes. For diphenylmethane (I) and triphenylmethane (II), the following values of n were obtained: 10 hr at 25°, $n = 0.2$ (I); $n = 0$ (II); 24 hr at 25°, $n = 0.5$ (I); $n = 0.3$ (II); 73 hr at $\sim 20^{\circ}$, $n = 1.2$ (I); $n = 0.4$ (II); 240 hr at $\sim 20^{\circ}$, $n = 3.4$ (I); $n = 0.8$ (II); 1200 hr at $\sim 20^{\circ}$, $n = 5.4$ (I); $n = 3.8$ (II). In the case of diphenylmethane, for

1340 h at $\sim 20^{\circ}$, $n = 6.2$, and for triphenylmethane at $\sim 20^{\circ}$: 2420 h, $n = 5.6$; 4800 h, $n = 6.4$. In both of these hydrocarbons, in contrast to toluene, only the H atoms in the ortho and para positions enter into exchange, whereas exchange in the meta positions does not occur under the experimental conditions. The averaged values of $k^{\sim 20^{\circ}}$ for diphenylmethane (I) and triphenylmethane (II) are, respectively, $k_{\mathrm{I}} \simeq 0.8 \cdot 10^{-6}$ sec^{-1}; $k_{\mathrm{II}} \simeq 1.1 \cdot 10^{-7}$ sec^{-1}. The ratio between the rate constants of benzene, triphenylmethane (II), diphenylmethane (I), and toluene is

$$k^{\sim 20^{\circ}}_{\mathrm{H_6C_6}} : k^{\sim 20^{\circ}}_{\mathrm{II}} : k^{\sim 20^{\circ}}_{\mathrm{I}} : k^{25^{\circ}}_{\mathrm{C_6H_5CH_3}} = 4 : 11 : 80 : 1000.$$

This ratio indicates that, as the number of phenyl groups attached to one aliphatic C—H bond increases, the ability of the ring H atoms toward electrophilic substitution decreases, although it remains higher than that of benzene.

The rate of exchange in the case of fluorene is considerably higher than that of diphenylmethane. Within 1 h at 25°, 4.4 hydrogen atoms of fluorene are exchanged; in 24 h at 25°, $n = 5.0$; in 48 h at $\sim 20°$, $n = 5.6$; in 240 h at $\sim 20°$, $n = 6.6$. The value of k for the first four H atoms of fluorene is $k^{25°} = 2.2 \cdot 10^{-4}$ sec^{-1}, and for the remaining ones, $k^{\sim 20°} \simeq 1.2 \cdot 10^{-5}$ sec^{-1}. The hydrogen atoms of the methylene group do not enter into exchange.

Naphthalene derivatives. Hydrogenation of one ring in the naphthalene molecule sharply increases the ability of the H atoms of the other ring to undergo electrophilic-substitution reactions. Within 6 h at 25° in the tetralin molecule, four H atoms enter into exchange with a rate constant $k = 2 \cdot 10^{-4}$ sec^{-1}. This number of exchanged atoms remains unchanged over 240 h.

Methylation of naphthalene in the α position leads to acceleration of exchange of the ring H atoms. In 1 h at 25°, $n = 4.5$. In the case of β-methylnaphthalene, the exchange rate is higher than the exchange rate in naphthalene: in 6 h at 25°, all seven H atoms are exchanged ($k_{25°} = 5 \cdot 10^{-4}$ sec^{-1}). Introduction of electronegative substituents slows the exchange. In 1 h at 25°, in α-chloro-, α-bromo-, and α-nitronaphthalene, respectively 0.4, 0.2, and 0.06 hydrogen atoms enter into exchange.

Table 1

Comparison of the rate of deuterium exchange in different liquid hydrogen halides at 25°

Compounds	HF (2)	HCl (our data)	HBr (5,6)	HJ (9)
Benzene	$1 \cdot 10^{-3}$	$4 \cdot 10^{-8}$ ($\sim 20°$)	$5 \cdot 10^{-8}$ ($\sim 20°$)	–
Toluene (o-atoms)	$\gg 10^{-2}$	$\sim 1 \cdot 10^{-5}$	$5.3 \cdot 10^{-5}$	$1.4 \cdot 10^{-6}$
Toluene (p-atoms)		$\sim 1 \cdot 10^{-5}$	$1.9 \cdot 10^{-4}$	$3.7 \cdot 10^{-6}$
Toluene (m-atoms)		$\sim 3 \cdot 10^{-7}$ ($\sim 20°$)	$2.7 \cdot 10^{-7}$	
Naphthalene		$11 \div 1 \cdot 10^{-5}$	$30 \div 0.5 \cdot 10^{-4}$	
Phenanthrene		$0.9 \div 0.6 \cdot 10^{-4}$	$0.8 \cdot 10^{-3}$	
Diphenyl (o-atoms)			$2.6 \cdot 10^{-5}$	$1.1 \cdot 10^{-6}$
Diphenyl (p-atoms)		$11 \div 2 \cdot 10^{-6}$	$1.4 \cdot 10^{-4}$	$4.0 \cdot 10^{-6}$
Diphenyl (m-atoms)		$11 \div 2 \cdot 10^{-6}$	$< 1 \cdot 10^{-8}$	
Diphenylmethane		$1.0 \div 0.5 \cdot 10^{-6}$	$3 \div 1.5 \cdot 10^{-5}$	
Triphenylmethane		$4 \div 0.7 \cdot 10^{-7}$	$3 \cdot 10^{-6}$	

Catalytic acceleration of exchange under the action of $AlCl_3$. In work (15) it was shown that addition of $AlCl_3$ sharply accelerates hydrogen exchange between benzene and DCl: at room temperature equilibrium is reached in less than 4 h. However, exchange in the aliphatic C—H bonds of alkylbenzenes in the presence of $AlCl_3$ is not substantially accelerated. Thus, in toluene over 46 h in the presence of $AlCl_3$, no more than 5 hydrogen atoms enter into exchange. In the case of saturated hydrocarbons that do not contain a tertiary C atom, addition of $AlCl_3$ leads to a noticeable

exchange. In cyclopentane, after 24 hours at 25°, $n = 4.5$, and after 96 hours at room temperature $n = 6.1$. In cyclohexane, after 24 hours at 25°C, $n = 0.8$, and after 214 hours at room temperature $n = 2.9$ (in these experiments isomerization of cyclohexane to methylcyclopentane is not excluded).

Comparison of the rate of exchange in different hydrogen halides. The results obtained make it possible to compare the rate constants of deuterium exchange in various hydrogen halides (see Table 1). From the data presented it is evident that the "activity" of the hydrogen halides as electrophilic reagents [16] increases in the sequence

$$\mathrm{HJ} \ll \mathrm{HCl} < \mathrm{HBr} \ll \mathrm{HF}.$$

Unfortunately, at present there are no data on the acidity constants of liquid hydrogen halides. If the dissociation constant in water is used as a measure of acidity, as is often done, it is easy to see that the capacity for hydrogen exchange is not directly related to the acidity of the hydrogen halide, which increases in the sequence [17]

$$\mathrm{HF} \ll \mathrm{HCl} < \mathrm{HBr} < \mathrm{HJ}.$$

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