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Abstract

Full Text

Chemistry

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Isotopic Exchange of Hydrogen Between Hydrocarbons, Catalyzed by Alkoxides in Electron-Donor Solvents

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In discussing the acid–base properties of hydrocarbons, the idea was put forward that isotopic exchange of hydrogen between hydrocarbons is possible if one of them is present in the form of a carbanion ([1]). Later such reactions were indeed carried out. G. A. Razuvaev and co-workers ([2]) observed deuterium exchange between benzene and phenylnatrium, and also between toluene and benzylnatrium. Hart ([3]) carried out deuterium-exchange reactions between alkylbenzenes by heating their mixture at 150° with the addition of metallic potassium, which partially converts the more acidic hydrocarbon into a carbanion. Earlier we showed ([4–6]) that, in the presence of an electron-donor solvent that well solvates the alkoxide cation and does not form a hydrogen bond with its anion, the latter proves to be a strong base capable, in particular, of converting fluorene into a carbanion. Such solvents include, for example, 1,2-dimethoxyethane (DME), diglyme—diethylene glycol dimethyl ether (DG), tetrahydrofuran (THF), and 1,2-diethoxyethane (DEE). Depending on the solvating ability of the solvent, the degree of metalation of the hydrocarbon changes.

Taking the above into account, we expected that, in the indicated solvents, reactions of isotopic hydrogen exchange between the CH bonds of sufficiently acidic hydrocarbons, catalyzed by alkoxides, should take place, and we assumed that measurement of the rate of the exchange reaction carried out in different solvents could serve as a method for estimating their solvating ability with respect to cations. Obtaining such data is of great interest for the whole field of carbanion reactions, including the interpretation of the influence of solvents on anionic polymerization reactions.

In our work, deuterium-exchange reactions were studied with two pairs of hydrocarbons: indene—fluorene and indene—triphenylmethane. In addition to the solvents named above, 1,4-dioxane (DO) was used. The catalysts were CH_3OK and $(CH_3)_3COLi$. Experiments with CH_3OK were carried out in heterogeneous systems. $(CH_3)_3COLi$ is soluble in many organic solvents ([7]), including those used by us. A two-limbed ampoule, in which the experiment was carried out, was attached at its ground joint to a manifold, evacuated, filled with argon, and, in a stream of argon, a weighed portion of CH_3OK was introduced into it in the form of a solution in CH_3OH. The latter was distilled off in vacuum, and the ampoule was evacuated for 1-2 hours, heating the alkoxide at 100°. $(CH_3)_3COLi$ was introduced in a sealed ampoule, which was broken in a stream of argon. Weighed portions of the hydrocarbons were introduced into the other limb of the ampoule, and the solvent, which had been standing over potassium in another ampoule attached to the manifold, was vacuum-transferred into it. The two-limbed ampoule was sealed off, all components were mixed, and the ampoule was immersed in a thermostat. After the experiment, the contents of the ampoule were poured into water, the hydrocarbons were extracted with ether, the extract was washed with water, the ether was evaporated, and the solid hydrocarbon was re-

crystallized from alcohol, dried, checked for melting point, burned, and the deuterium (D) content in the purified water from combustion was determined by the drop method.

For the experiment, 3-6 ml of a solution containing 0.2 mole of each of the hydrocarbons and 0.1 mole of alkoxide in 1000 ml of solvent was prepared. In all solvents in the presence of CH_3OK, solutions of indene and fluorene were colored dark violet; solutions of indene and triphenylmethane were dark red. In the presence of $(CH_3)_3COLi$, the first pair of hydrocarbons gave a light-green solution in DME, and a colorless solution in DO.

Table 1

Deuterium exchange between indene and D-fluorene ($C_0 = 2.42$). Catalyst—CH_3OK, 25°

Solvent	Duration, h	C	C_∞	$C - C_\infty$
DME	0.5	0.84	0.86	−0.02
DME	3	0.76	0.82	−0.06
DME	6	0.64	0.76	−0.12
DME	18	0.89	0.86	0.03
DO*	0.5	0.76	0.72	0.04

* $C_0 = 2.06$.

By special experiments we verified that, in a mixture with indene, fluorene is not appreciably metalated in the presence of CH_3OK. Heavy water (98 at. % D) was added to a reaction mixture in DME that had been kept for 3 hours at 25°. The water obtained by combustion of the isolated fluorene contained 0.5; 0.0; 0.5 at. % D. Consequently, beyond the limits of accuracy of our experiments lies the error that could have been caused by decomposition of the metalated deutero-fluorene by ordinary water. It will not be significant in experiments with $(C_6H_5)_3CD$ either, since its acidity is considerably lower than that of fluorene (^{8}).

We proceed to describe the results obtained.

Deuterium exchange between indene and fluorene deuterated in the CH_2 group, catalyzed by CH_3OK, proceeds rapidly and under mild conditions; moreover, three hydrogen atoms of indene ([9]) and two deuterium atoms of fluorene participate in the exchange reaction. Equilibrium of the exchange reaction is established at 25° already after 0.5 hour (Table 1). C_0 is the deuterium concentration (at. % D) in the water from combustion of the substance before the experiment; C—after the experiment; C_∞—the calculated equilibrium concentration. C and C_∞ in all experiments were determined for fluorene (or triphenylmethane).

Under more severe conditions, deuterium exchange occurs between indene and triphenylmethane deuterated in the CH group. The equilibrium of the exchange reaction in DO, in contrast to DME, is not attained after 5 hours at 100°. The degree of attainment of equilibrium is characterized by the quantity $(C_0 - C) \cdot 100/(C_0 - C_\infty) = \alpha\%$ (Table 2).

Table 2

Deuterium exchange between indene and D-triphenylmethane ($C_0 = 2.16$). Catalyst—CH_3OK

Solvent	Temp., °C	Duration, h	C	C_∞	$C - C_\infty$	α
DME	50	22	0.52	0.51	0.01	100
DME	100	1	0.26*	0.25	0.01	100
DME	100	5	0.57	0.48	0.09	94
DO	100	0.5	2.00	0.49	1.51	12
DO	100	5	0.98	0.46	0.52	70

* $C_0 = 1.10$.

The lower rate of deuterium exchange in DO than in DME can also be established in experiments with the pair of hydrocarbons indene—fluorene, if instead of CH_3OK one takes the weaker catalyst, $(CH_3)_3COLi$. At 25°, equilibrium of the exchange reaction in the first solvent is not attained after 24 hours, whereas in the second the reaction reaches equilibrium already after 0.5 hour. In this series of experiments, both deutero-fluorene with ordinary indene and ordinary fluorene with deutero-indene, which contains 2 D atoms, were mixed (Table 3).

The deuterium-exchange reaction between deutero-indene and triphenylmethane under catalysis by $(CH_3)_3COLi$ in DME was not detected after 3-hour heating at 100°, and between fluorene and toluene deuterated in the CH_3 group it was not observed under catalysis by CH_3OK in DG at the same temperature even after 45 hours.

Table 4 gives the results of a series of experiments on deuterium exchange between deuterioindene and fluorene in several solvents. Since deuterium passed from indene into fluorene and the latter was analyzed, $\alpha_1 = 100C/C_\infty$.

The order of the solvents, similar to that indicated in Table 4, was established in our laboratory in the study of the reactions of metalation of fluorene by alcoholates (6), in the formation of anion radicals of toluene (10) and diphenyl (6), and in the anionic polymerization of α-methylstyrene initiated by dianions of its tetramer (11). Similar results on the influence of the same solvents on the reaction of metalation of fluorene by metallic potassium and on deuterium exchange between fluorene and KOD were obtained by Scherf and Brown (12).

Table 3

Deuterium exchange between indene and fluorene. Catalyst $(CH_3)_3COLi$, 25°

Solvent	Duration, h	C	C_∞	$C - C_\infty$
Indene—deuterofluorene ($C_0 = 3.40$)	**Indene—deuterofluorene** ($C_0 = 3.40$)	**Indene—deuterofluorene** ($C_0 = 3.40$)	**Indene—deuterofluorene** ($C_0 = 3.40$)	**Indene—deuterofluorene** ($C_0 = 3.40$)
DME	0,5	1,36	1,32	0,04
DME	3	1,47	1,42	0,05
DME	3	1,46	1,43	0,03
DO	0,5	3,23	1,22	2,01
DO	2	2,81	1,28	1,53
DO	3	2,72	1,48	1,24
Deuterioindene ($C_0 = 4.58$)—**fluorene**	**Deuterioindene** ($C_0 = 4.58$)—**fluorene**	**Deuterioindene** ($C_0 = 4.58$)—**fluorene**	**Deuterioindene** ($C_0 = 4.58$)—**fluorene**	**Deuterioindene** ($C_0 = 4.58$)—**fluorene**
DME	3	1,47	1,65	−0,18
DO	3	0,13	1,40	−1,27

In summary, it may be said that the work carried out by us has confirmed the assumption that it is possible to effect the reaction of isotopic hydrogen exchange between hydrocarbons under catalysis by alcoholates, and to compare the solvating ability of solvents by the rate of hydrogen exchange. The use of this method is a task for further investigation, to be carried out under conditions of a more exact experiment. The mechanism of the hydrogen-exchange reaction considered in this work may not be entirely the same in different cases and probably depends, in particular, on the degree of acidity of the hydrocarbons participating in the reaction and on the electron-donor properties of the catalyst and solvent. If both hydrocarbons are partially converted into carbanions in the reaction with the alcoholate, then the reaction may proceed through a stage of isotopic exchange between the deuterated and the ordinary alcohol that are formed. One should also bear in mind the equilibrium of the reaction between the carbanion of one hydrocarbon and the molecule of another hydrocarbon, as is clearly expressed in papers (^{2,3}). However, the formation of stable carbanions is apparently not an obligatory condition for the exchange reaction to occur. This is suggested by the fact that deuterium exchange between indene and fluorene, catalyzed by $(CH_3)_3COLi$, occurs in colorless solutions when DO is the solvent. It is not excluded that in the transition state, under the influence of the negatively charged oxygen atom of the alcoholate, the bond of carbon with the deuterium (or protium) atom in the molecule of the more acidic hydrocarbon is strongly polarized.

Table 4

Deuterium exchange between deuterioindene ($C_0 = 3.8$) and fluorene for 3 h. Catalyst–$(CH_3)_3COLi$*, 25°

Solvent	C	C_∞	α_1
DME	0,87	1,35	64
DP	0,81	1,26	64
DEE	0,20	1,20	17
DEE	0,24	1,25	19
DO	0,12	1,23	9
DO	0,08	1,26	6

* The activity of the catalyst was lower than that of the preparation used earlier.

In a single act, its cleavage occurs and the addition to the negatively charged carbon atom of a proton (deuteron) from another hydrocarbon, to whose negatively charged carbon atom a deuteron (proton) is added. It would be of interest to measure the kinetic isotope effect and the activation energy in reactions proceeding in different solvents, in order to clarify the general picture of the mechanism outlined above.

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