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Abstract

Full Text

CHEMISTRY

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ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

THE EFFECT OF THE MEDIUM ON THE MECHANISM OF THE ISOTOPIC-EXCHANGE REACTION OF ETHYL α-BROMOMERCURIPHENYLACETATE WITH MERCURIC BROMIDE LABELED WITH Hg^{203}

As is known, the medium is one of the principal factors determining the rate and mechanism of processes. A change in the medium may lead to a change in the reaction rate or to a partial change in the mechanism, which results in a complication of the kinetics (a mixed kinetic order). Much more rarely can the mechanism of a process be completely changed by altering the properties of the medium. These cases have been studied in sufficient detail using the example of nucleophilic substitution at a saturated carbon atom. In recent years, intensive investigation of electrophilic-substitution reactions has begun; however, no systematic study has yet been carried out of the effect of the nature of the solvent on the mechanism of electrophilic-substitution reactions at a saturated carbon atom. A certain exception is the series of works by Cram ([1–9]), in which the effect of the solvent on the stereochemical (but not kinetic) result of heterolytic cleavage of the carbon—carbon bond was studied.

In the present work, a change in the kinetic order and mechanism of an electrophilic-substitution reaction at a saturated carbon atom upon changing the solvent is reported for the first time. The object chosen for study was the isotopic-exchange reaction of ethyl α-bromomercuriphenylacetate with mercuric bromide labeled with Hg^{203}:

$$R_1R_2R_3C{-}HgBr + {}^*HgBr_2 \rightleftarrows R_1R_2R_3C^*{-}HgBr + HgBr_2$$

$$(R_1 = C_6H_5;\ R_2 = H;\ R_3 = COOC_2H_5)$$

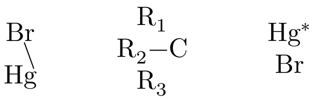
The kinetics of the reaction were measured in pyridine and in 70% aqueous dioxane*. It was shown that in pyridine the reaction has an overall second order (first order in each of the components)

$$K_2 = 6.60 \cdot 10^{-2}\ \text{L/mol} \cdot \text{sec} \quad \text{at } 60^\circ.$$

The parameters of the Arrhenius equation are: $E = 16.3$ kcal/mol, $\lg A = 9.5$. The activation entropy is $\Delta S = -15.5$ entropy units at 60°.

$$K_2 = 10^{9.5} \exp\left(-\frac{16300}{RT}\right).$$

We assume that the reaction proceeds between the molecules of the organomercury compound and mercuric bromide through a reaction complex with one –



temporary nucleophilic solvation by pyridine of the departing mercury atom, which considerably facilitates the course of the process. Probably the pyridine complex of mercuric bromide, $C_5H_5N \cdot HgBr_2$, takes part in the reaction.

In studying isotopic exchange in 70% aqueous dioxane it was found that the reaction has an overall first order: first order with respect to the organomercury compound and zero order with respect to mercuric bromide.

$$K_1 = 5.58 \cdot 10^{-4}\ \text{sec}^{-1} \quad \text{at } 60^\circ.$$

The parameters of the Arrhenius equation are: $E = 26.7$ kcal/mole, $\lg A = 14.3$. The activation entropy $\Delta S = +4.6$ entropy units at 60°.

Kinetic first order in electrophilic isotopic exchange is observed for the first time. This result may be explained by assuming that the slowest stage of the process, determining its overall rate, is the ionization stage of the organomercury compound*. In all probability, such ionization proceeds with formation of an internal ion pair**.

$$R_1R_2R_3C{-}HgBr \rightleftharpoons R_1R_2R_3C :^{\ominus}\ \ HgBr^{\oplus},$$

which, in a second, fast stage, exchanges with mercuric bromide.

$$R_1R_2R_3C :^{\ominus}\ [HgBr^{\oplus} + HgBr_2^{*}] \rightleftharpoons R_1R_2R_3C :^{\ominus}\ \ HgBr^{\oplus *} + HgBr_2.$$

* The experimental work will be published in full in *Izv. AN SSSR, OKhN.*

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Thus, the change of solvent apparently led to a change in the reaction mechanism. As far as we know, no cases have yet been published of kinetic confirmation of an S_E1 mechanism.

Comparison of the results obtained when carrying out the reaction in pyridine and in aqueous dioxane shows that the reaction is greatly facilitated in pyridine; this is expressed above all in a sharp decrease of the activation energy. It should be noted that additions of pyridine strongly accelerate the exchange reaction in dimethylformamide. It is possible that by varying the medium it will be possible to create conditions under which a gradual shift of the kinetics from first order to second order can be observed.

For the case of isotopic exchange in aqueous dioxane, whose kinetics obey first order, we studied the influence of structural factors on the reaction rate using as examples ethyl esters of various α-bromomercuriaryl acetic acids

$$\underset{X}{\langle}-CH(COOC_2H_5)HgBr + {}^*HgBr_2 \rightleftharpoons HgBr_2 + \underset{X}{\langle}-CH(COOC_2H_5){}^*HgBr$$

where $X = p$-F, p-Cl, p-Br, p-I, p-CH_3, p-tert.-C_4H_9, o-CH_3. In their effect on the reaction rate, the substituents fall into the following series*** (in order of retardation):

X	p-I, Br, Cl	$> p$-F	$> H$	$> o$-CH_3	$> p$-CH_3	$> nC_4H_9$
Half-life period (min.)	340	500	620	1500	2000~3000	

which is consistent with the concept of an S_E1 mechanism.

Indeed, alkyl substituents (whether, in a first approximation, para or ortho), by donating electrons, should increase the electron density at the reaction center and thereby hinder ionization, whereas halides, by withdrawing electrons, can partially neutralize the charge of the incipient benzyl carbanion, stabilizing it and thereby facilitating ionization.

$$Alk-C_6H_4-\overset{\ominus}{CH}-COOR \qquad \overset{\oplus}{HgBr}$$

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* The considerable lability of the C–Hg bond in compounds of the structure studied is well known ([10,11]).

** In our opinion, in this case it is precisely ionization that takes place ([13,12]), and not dissociation, since it is unlikely that this reaction could proceed through kinetically free charged particles.

*** The accuracy of the method does not allow detection of differences between the effects of chlorine, bromine, and iodine.

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$$\mathrm{Hal{-}C_6H_4{-}\overset{\ominus}{C}H{-}COOR} \qquad \mathrm{\overset{\oplus}{Hg}Br}$$

The question of the stereochemistry of this S_E1 reaction remains open for the time being.

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