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Abstract

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ON THE MECHANISM OF PROTOLYSIS OF CIS- AND TRANS-β-CHLOROVINYLMERCURY CHLORIDES UNDER THE ACTION OF HCl AND DCl

In the present work we set forth the results of a study of the protolysis of isomeric β-chlorovinylmercury chlorides in abs. dioxane and dimethyl sulfoxide (DMSO)

$$\mathrm{Cl{-}CH{=}CH{-}HgCl + HCl(DCl) \rightarrow Cl{-}CH{=}CH{-}H(D) + HgCl_2}.$$

It has been shown that in dioxane this reaction is bimolecular (of the S_E2 type), whereas in DMSO it is a monomolecular electrophilic substitution (of the S_E1 type). Thus, we have obtained a second example of a reaction of the S_E1 type at an olefinic carbon atom ([1]). The use of deuterated hydrogen chloride made it possible to obtain isomeric chlorinated vinyls. Study of the NMR spectra showed that both reactions, in agreement with previously obtained data ([1, 2]), proceed with complete retention of configuration.

The kinetics of the reaction in dioxane were studied titrimetrically by the change in the concentration of hydrogen chloride at equimolecular reactant concentrations of 0.1 mol/l at temperatures of 50, 60, 70, and 80°. Titration was carried out with 0.085 N potassium hydroxide using methyl red. The data obtained obey a second-order law (Fig. 1). Table 1 gives the values of the half-periods and the second-order rate constants for the corresponding temperatures for both isomers.

Table 1

t°,C	Trans-isomer + HCl, $\tau_{1/2}$, min	Trans-isomer + HCl, $k_2 \cdot 10^4$, l/mol · sec	Cis-isomer + HCl, $\tau_{1/2}$, min	Cis-isomer + HCl, $k_2 \cdot 10^4$, l/mol · sec	Trans-isomer + DCl, $\tau_{1/2}$, min	Trans-isomer + DCl, $k_2 \cdot 10^4$, l/mol · sec
40	876	1.9				
50	474	3.5			504	3.3

t°,C	Trans-isomer + HCl, $\tau_{1/2}$, min	Trans-isomer + HCl, $k_2 \cdot 10^4$, l/mol · sec	Cis-isomer + HCl, $\tau_{1/2}$, min	Cis-isomer + HCl, $k_2 \cdot 10^4$, l/mol · sec	Trans-isomer + DCl, $\tau_{1/2}$, min	Trans-isomer + DCl, $k_2 \cdot 10^4$, l/mol · sec
60	210	7.9	189	8.8	234	7.1
70	108	15.4	96	17.4		
80	58	28.7				

Table 2

t°,C	Trans-isomer + HCl, $\tau_{1/2}$, sec	Trans-isomer + HCl, $k_1 \cdot 10^3$, sec^{-1}	Trans-isomer + DCl, $\tau_{1/2}$, sec	Trans-isomer + DCl, $k_1 \cdot 10^3$, sec^{-1}	Cis-isomer + HCl, $\tau_{1/2}$, sec	Cis-isomer + HCl, $k_1 \cdot 10^3$, sec^{-1}
30	540	1.28	–	–	–	–
35	369	1.88	372	1.86	408	1.70
40	282	2.46	–	–	–	–
50	168	4.13*	169	4.10	192	3.61

* The average value is given for measurements carried out at $C_{0\mathrm{RHgX}} : C_{0\mathrm{HCl}} = 1:1$ and $1:2$.

As can be seen from the data obtained, the cis-isomer, as in the previously studied reaction with iodine, reacts faster than the trans-isomer; $k_{2\mathrm{cis}}/k_{2\mathrm{trans}} = 1.12$. From the data in Table 1, a plot of the dependence $\lg k_2 = f(1/T)$ (Fig. 2b) was constructed for the trans-isomer, from which the parameters of the Arrhenius equation were found: $E = 14.5 \pm 0.4$ kcal/mol, $\lg A = 6.4$; activation entropy $\Delta S^{\neq} = -31.6$ e.u.

Under these same conditions, the reaction of trans-β-chlorovinylmercury chloride with deuterated hydrogen chloride was carried out at 50 and 60° (Table 1). The isotope effect of the reaction is 1.06 at 50° and 1.10 at 60°.

The kinetics of the reaction of isomeric β-chlorovinylmercury chlorides with hydrogen chloride in DMSO was studied titrimetrically (mercurimetrically) by following the change in chloride-ion concentration.

The study was carried out at equimolecular concentrations of the reagents, 0.1 mole/liter, and also in an excess of HCl at temperatures of 30, 35, 40, and 50°. The reaction is first order. A plot of the dependence $\lg(C_0/C) = f(\tau)$ for various temperatures is given in Fig. 3. Table 2 summarizes the values of

the half-periods, the first-order reaction rate constants, and the corresponding absolute temperatures.

Fig. 1. Dependence of $C_0/C - 1$ on τ at various temperatures:
I–40°, II–50°, III–60°, IV–70°. a–trans isomer + HCl, b–cis isomer + HCl, v–trans isomer + DCl

Fig. 2. Dependence of $\lg k_1$ (a) and $\lg k_2$ (b) on $1/T$

A tenfold excess of HCl does not change the reaction rate.

From the data of Table 2 a plot of $\lg k_1 = f(1/T)$ was constructed (Fig. 2a), from which the parameters of the Arrhenius equation were found: $E = 12.1 \pm 0.4$ kcal/mole, $\lg A = 4.9$; activation entropy $\Delta S^{\neq} = -38.5$ entropy units.

It is interesting to note that under the conditions of a monomolecular reaction the trans isomer reacts faster than the cis isomer. $k_{1\text{trans}}/k_{1\text{cis}} = 1.12$. The reason for the change in the reactivity of the isomers upon a change in the reaction mechanism is not yet clear.

Fig. 3. Dependence of $\lg C_0/C$ on τ at various temperatures:
I–30°, II–35°, III–40°, IV–50°.
a–$C_{0\text{RHgX}} : C_{0\text{HCl}} = 1 : 1$; trans isomer + HCl;
b–$C_{0\text{RHgX}} : C_{0\text{HCl}} = 0.5 : 1$;
v–trans isomer + DCl;
g–cis isomer + HCl

The mechanism of the protolysis reaction of β-chlorovinylmercury chloride in DMSO can be represented by a scheme analogous to that which was proposed in the previously studied reaction of this compound with iodine in DMSO (1). The reaction proceeds in two stages, with the formation, in the first slow stage, of an ion pair (S_E1)

$$\text{Cl–CH=CH–HgCl} \overset{\text{slow}}{\rightleftharpoons} \text{Cl–CH=}\overline{\text{CH}}\text{–}\overset{\oplus}{\text{H}}\text{gCl}$$

$$\text{Cl–CH=}\overset{\ominus}{\text{C}}\text{H} : \; - \overset{\oplus}{\text{H}}\text{gCl} + \text{HCl} \xrightarrow{\text{fast}} \text{Cl–CH=CH–J} + \text{HgClJ}.$$

Thus, we have an example of another reaction apparently proceeding by a mechanism of the S_E1 type at the olefinic carbon atom.

Replacement of HCl by DCl in DMSO does not lead to any noticeable changes in the reaction rate (see Table 2); the deviations in the values of the con-

fall within the experimental error. This result, as well as the independence of the reaction rate from the concentration of HCl, is in complete agreement with the proposed monomolecular reaction mechanism.

Acid cleavage of the C–Hg bond is the simplest and best-studied reaction of organomercury compounds. However, the stereochemistry of this reaction has

Fig. 4. NMR spectra of the isomers of vinyl chloride: a $-\overset{\mathrm{Cl}\backslash}{\mathrm{H}/}C=C\overset{/\mathrm{D}}{\backslash\mathrm{H}}$, b $-\overset{\mathrm{Cl}\backslash}{\mathrm{H}/}C=C\overset{/\mathrm{H}}{\backslash\mathrm{D}}$, c $-$Cl—$C\equiv CH_2$.

Figure 1: Fig. 4. NMR spectra of the isomers of vinyl chloride: a $-\overset{\mathrm{Cl}\backslash}{\mathrm{H}/}C=C\overset{/\mathrm{D}}{\backslash\mathrm{H}}$, b $-\overset{\mathrm{Cl}\backslash}{\mathrm{H}/}C=C\overset{/\mathrm{H}}{\backslash\mathrm{D}}$, c $-$Cl—$C\equiv CH_2$.

not yet been studied even for a saturated carbon atom. The study of the stereochemistry of protolysis of optically active sec-butylmercury bromide and of the geometrical isomers of 4-methylcyclohexylmercury bromides, carried out by Jensen ([3]) with the aid of labeled acids, unfortunately was not successful. Under the action of acids, racemization and isomerization of the starting substances occurred. However, the author suggests that the reaction itself proceeds with retention of configuration.

Fig. 4. NMR spectra of the isomers of vinyl chloride:

$$a\ —\ \overset{\mathrm{Cl}}{\mathrm{H}}{>}\mathrm{C}=\mathrm{C}{<}\overset{\mathrm{D}}{\mathrm{H}},\qquad b\ —\ \overset{\mathrm{Cl}}{\mathrm{H}}{>}\mathrm{C}=\mathrm{C}{<}\overset{\mathrm{H}}{\mathrm{D}},\qquad c\ —\ \mathrm{Cl—C}\equiv\mathrm{CH_2}$$

The stereochemistry of the acid-cleavage reaction was studied by us using, as an example, the reaction of isomeric cis- and trans-β-chlorovinylmercury chlorides with deuterium-labeled hydrogen chloride. In a blank experiment, the vinyl chloride isolated quantitatively (b.p. -15°) was identified as the dibromide Cl—CHBr—CH_2Br, yield 94%. B.p. 162—163°, n_D^{20} 1.5544. Lit.: b.p. 160° ([4]).

The reaction was carried out in absolute dioxane and DMSO, in which, as follows from the kinetic data, it proceeds, respectively, by the S_E2 and S_E1 mechanisms.

Identification of the isomeric vinyl chlorides, in which the presence of isomers is associated with replacement of hydrogen by deuterium in Cl—CH=CH—D, was carried out by studying high-resolution proton-resonance spectra on a JNMR-3 instrument with an operating frequency of 40 MHz.

The spectra obtained for vinyl chloride and the deuterated isomers are given in Fig. 4.

It is known that the constant (J) of spin-spin interaction of atoms at a carbon-carbon double bond in the trans position considerably exceeds their spin-spin interaction constant from the cis position ([5]). In this connection, in the case of trans-vinyl chloride-2(D)

$$\overset{\mathrm{Cl}}{\mathrm{H}}{>}\mathrm{C}=\mathrm{C}{<}\overset{\mathrm{H}}{\mathrm{D}}$$

we are dealing with a typical two-spin system, which in the NMR spectrum

gives a quadruplet with chemical shift $\delta = 9 \cdot 10^{-7}$ and $J_{\text{trans}} = 15$ Hz. However, owing to quadrupole relaxation, the line widths in the quadruplet are different.

The result obtained for the trans compound proves that both reactions, S_E2 and S_E1 (in dioxane and DMSO), proceed with complete retention of the geometrical configuration.

The cis system represents a more complicated case,

$$\overset{\text{Cl}}{\text{H}}\!> \text{C} = \text{C} <\!\overset{\text{D}}{\text{H}},$$

since nuclei with different spin values are in the trans position. The spectrum of cis-vinyl chloride-2(D) differs sharply from the spectrum of the trans isomer. Unfortunately, it is not amenable to simplified consideration. The question of which of the quadrupole nuclei (Cl^{35} or H^2) located in the trans position relative to the protons is responsible for the complication of the spectrum requires separate consideration. It should be noted that these interactions must also be taken into account in a more rigorous consideration of the spectrum of trans-vinyl chloride-2(D), since,

as already noted, the distribution of intensities in its spectrum does not correspond to a simple two-spin system.

From a comparison of the spectra of trans- and cis-chloroethylenes-2 (D), one may conclude that they differ sharply, in full agreement with theory. It follows from this that we have for the first time isolated truly pure isomers of deuterated vinyl chloride, i.e., the reaction of bimolecular and monomolecular substitution at the olefinic carbon atom proceeds with complete retention of the geometric configuration.

Experimental Part

Study of the stereochemistry of the reaction of cis- and trans-β-chlorovinylmercuric chlorides with DCl in abs. dioxane and DMSO.

To a solution of 10 g (0.034 mole) of trans-β-chlorovinylmercuric chloride in 10 ml of abs. dioxane was added dropwise 1.2 ml of a 10 N solution of deuterated hydrogen chloride in dioxane (deuterium content 99.6%). The deuterated vinyl chloride formed (b.p. -15°) was dried over anhydrone and condensed in a receiver cooled with a mixture of dry ice and methanol (-50°). Four ml of vinyl chloride with b.p. -15.5° was obtained, yield 96%. The vinyl chloride was then distilled into an ampoule and its NMR spectrum was recorded.

The reaction for obtaining deuterated vinyl chloride from cis-β-chlorovinylmercuric chloride in dioxane was carried out analogously, as were the reactions of both isomers with DCl in DMSO. The yields in both solvents are close to quantitative.

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