Chemistry

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Abstract

Full Text

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On the Mechanism of Electrophilic and Homolytic Substitution at an Olefinic Carbon Atom

Among the three possible types of substitution reactions at an olefinic carbon atom:

$$
\begin{aligned}
&>C{=}C:X + Z^- \longrightarrow >C{=}C{-}Z + X^- && S_N\\
&>C{=}C:X + Z^+ \longrightarrow >C{=}C{-}Z + X^+ && S_E\\
&>C{=}C:X + Z\cdot \longrightarrow >C{=}C{-}Z + X\cdot && S_R
\end{aligned}
$$

from the stereochemical standpoint the electrophilic and homolytic substitutions have been studied most extensively. Starting from cis- and trans-β-chlorovinyl organomercury compounds with strictly established configurations, A. N. Nesmeyanov and A. E. Borisov studied the stereochemistry of numerous transitions of the chlorovinyl group from one metal to another (1), as a result of which the Nesmeyanov–Borisov rule was formulated, concerning the preservation of the geometric configuration in reactions of electrophilic and radical substitution at a carbon atom attached by a carbon–carbon double bond.

Direct confirmation of this rule was obtained subsequently (2) in the example of readily occurring isotope-exchange reactions. Strict preservation of the geometric configuration is observed in exchange reactions of cis- and trans-β-chlorovinylmercury chlorides both with radioactive sublimate (S_E^2) and with metallic mercury labeled with the radioactive isotope Hg^{203} (S_R).

However, until recently it had been impossible to form any definite conception of the nature of the elementary act, since the kinetics of the reactions under consideration remained unclear.

With the aim of studying in detail the mechanism of electrophilic and homolytic substitution at an olefinic carbon atom, we undertook a combined investigation of the kinetics and stereochemistry of replacement of a mercury atom by a halogen in stereoisomeric β-chlorovinyl and ω-bromostyryl organomercury compounds.

On the basis of the totality of the stereochemical and kinetic data obtained by us, one may attempt to judge the mechanism of the reactions studied.

We established that in polar solvents (methyl alcohol, dioxane, dimethylformamide) the reaction of β-chlorovinylmercury chloride with iodine in the presence of iodide ion proceeds as a bimolecular electrophilic substitution (has overall second kinetic order: first order with respect to the organomercury compound and first order with respect to iodine) and takes place in accordance with the Nesmeyanov–Borisov rule, with strict preservation of the geometric configuration (^{3}). In all the cases studied, the reactivity of the cis isomer is greater than that of the trans isomer. The values of the reaction rate constants, activation energies, and activation entropies are given in Table 1.

As is evident from the experimental data obtained, the solvents, in order of decreasing influence on the reaction rate, are arranged in the following series: methyl alcohol > 80% dioxane > dimethylformamide. An analogous series for the effect of solvents on the reaction rate with halide was obtained in our laboratory for organomercury compounds in which mercury is bonded to saturated and aromatic carbon atoms.

Table 1

Solvent	k_2, l/mol · sec at 15°C	E, kcal/mol	$\Delta S^{\neq}$, e.u.	Solvent	k_2, l/mol · sec at 15°C	E, kcal/mol	$\Delta S^{\neq}$, e.u.
trans-β-chlorovinylmercuric chloride				**cis-β-chlorovinylmercuric chloride**			
Methyl alcohol	40.40	11.7	−11.0	Methyl alcohol	45.50	11.4	−11.6
85% aqueous dioxane	0.516	13.6	−12.8	Dimethylformamide	0.391	9.5	−27.6
Dimethylformamide	0.356	10.1	−25.8				

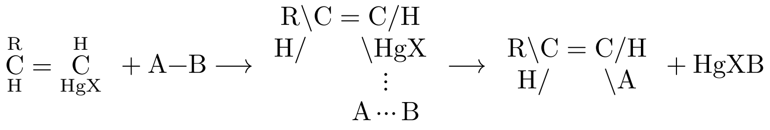
The study of the stereochemistry of reactions of the S_{E2}-type for isomeric ω-styrylmercuric bromides with bromine (in methyl alcohol in the presence of NH_4Br) also showed complete retention of the geometric configuration (^{4}).

Retention of the geometric configuration in reactions of the S_{E2}-type at an olefinic carbon atom was further confirmed in the protolysis of cis- and trans-β-chlorovinylmercuric chlorides with DCl in absolute dioxane (^{5}).

The reaction has overall second order (first order in each of the components, $k^{\text{cis}}_{2(\text{HCl})} = 7.9 \cdot 10^{-4}$ l/mol • sec, $k^{\text{trans}}_{2(\text{HCl})} = 8.8 \cdot 10^{-4}$ l/mol • sec), the isotope effect in this reaction is $k_{\text{H}}/k_{\text{D}} = 1.12$ (at 60°), $E_{\text{trans}} = 14.5 \pm 0.4$ kcal/mol, $\Delta S^{\neq} = -31.6$ e.u.

It was shown by the NMR method that from each isomer of the organomercury compound there is obtained the single corresponding isomer of deuterated vinyl chloride.

These results make it possible to propose the following mechanism for reactions of electrophilic bimolecular substitution (S_{E2}-type) at an olefinic carbon atom, with formation of a cyclic transition state,



$$\underset{\text{H}}{\overset{\text{R}}{\text{C}}} = \underset{\text{HgX}}{\overset{\text{H}}{\text{C}}} + \text{A—B} \longrightarrow \begin{matrix} \text{R}\backslash\text{C} = \text{C/H} \\ \text{H/} \qquad \backslash\text{HgX} \\ \vdots \\ \text{A} \cdots \text{B} \end{matrix} \longrightarrow \begin{matrix} \text{R}\backslash\text{C} = \text{C/H} \\ \text{H/} \qquad \backslash\text{A} \end{matrix} + \text{HgXB}$$

$$1.\ \text{X} = \text{R} = \text{Cl},\ \text{A} = \text{B} = \text{J};\quad 2.\ \text{R} = \text{C}_6\text{H}_5,\ \text{X} = \text{A} = \text{B} = \text{Br};\quad 3.\ \text{X} = \text{R} = \text{Cl},\ \begin{matrix}\text{A} = \text{H} \\ \text{or D}\end{matrix},\ \text{B} = \text{Cl}$$

Using a solvent with high ionizing power—dimethyl sulfoxide (DMSO)—we succeeded for the first time in carrying out monomolecular electrophilic substitution of the S_{E1} type at an olefinic carbon atom.

The reaction of trans-β-chlorovinylmercuric chloride with iodine in DMSO is first order with respect to the organomercury compound and zero order with respect to iodine (S_{E1}-mechanism): $k_1^{\text{trans}} = 3.6 \cdot 10^{-3}$ sec^{-1} at 20°; $E = 11.6$ kcal/mol; $\Delta S^{\neq} = 32.4$ e.u.

$$\text{Cl—CH=CH—HgCl} + \text{J}_2 \xrightarrow{\text{DMSO}} \text{Cl—CH=CH—J} + \text{HgClJ}$$

Of interest is the stereochemical result of this reaction. It turned out that, in contrast to S_E^1-reactions at a saturated carbon atom, monomolecular electrophilic substitution of the S_E^1 type at an olefinic carbon atom proceeds with complete retention of the geometric configuration.

Apparently, in the first, slow stage, which determines the kinetics of the process as a whole, ionization of the organomercury compound occurs with formation of an ion pair

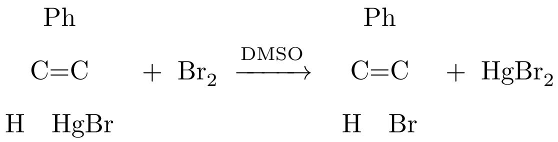
$$\text{Cl—CH=CH—HgCl} \overset{\text{slow}}{\rightleftharpoons} \text{Cl—CH=CH:HgCl},$$

which then, in the second stage, rapidly reacts with halide

$$\text{Cl—CH=CH:HgCl} \xrightarrow{\text{rapid}} \text{Cl—CH=CH—J} + \text{HgClJ},$$

Retention of the geometric configuration in reactions of the type under consideration indicates that, in this case, in the absence of free rotation, the free electron pair at the olefinic carbon atom is capable of fixing the geometric configuration.

In analogous fashion, the reaction of isomers of ω-styrylmercury bromide with bromine in DMSO proceeds with complete retention of the geometric configuration (^{4}).

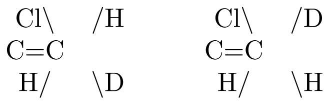


$$\underset{\text{H}\quad\text{HgBr}}{\overset{\text{Ph}}{\text{C=C}}} + \text{Br}_2 \xrightarrow{\text{DMSO}} \underset{\text{H}\quad\text{Br}}{\overset{\text{Ph}}{\text{C=C}}} + \text{HgBr}_2$$

Retention of the geometric configuration in S_E^1-type reactions at an olefinic carbon atom was confirmed in the study of the stereochemistry of another electrophilic substitution reaction.

The protolysis reaction of the cis–trans isomers of β-chlorovinylmercury chloride under the action of HCl and DCl in DMSO also proceeds by the S_E^1 mechanism (^{5}). The reaction is first order with respect to the organomercury compound and zero order with respect to the acid: $k_{1(\text{trans})}^{\text{HCl}} = 1.3 \cdot 10^{-3}$ s^{-1} (at 30°), $E = 11.9$ kcal/mol, $\Delta S^{\neq} = -38.5$ e.u. The absence of an isotope effect in this reaction confirms the proposed mechanism.

From comparison of the reaction rates of trans-β-chlorovinylmercury chloride with iodine and HCl in DMSO, it is seen that in the case of monomolecular electrophilic substitution the rates of reaction with J_2 and HCl are of approximately the same order, which, apparently, is connected with the common character of the first stage of these reactions. A study of the NMR spectra of deuterated vinyl chlorides showed



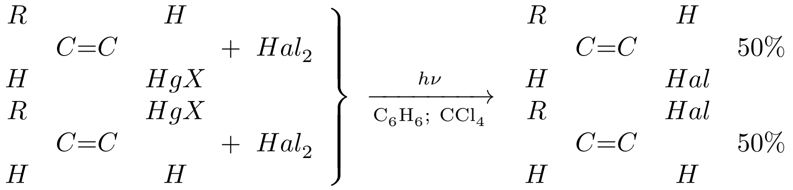
$$\begin{array}{ccc} \text{Cl}\backslash & & /\text{H} \\ & \text{C=C} & \\ \text{H}/ & & \backslash\text{D} \end{array} \qquad \begin{array}{ccc} \text{Cl}\backslash & & /\text{D} \\ & \text{C=C} & \\ \text{H}/ & & \backslash\text{H} \end{array}$$

that the protolysis reaction of the S_E^1 type also proceeds with retention of the geometric configuration.

We next studied the mechanism of homolytic substitution at an olefinic carbon atom. Obviously, reactions of homolytic substitution may in principle be either free-radical reactions or reactions in the course of which radicals, as kinetically independent particles, are not formed. There is no certainty that among the homolytic reactions studied previously there is even a single free-radical one.

In this connection we set ourselves the goal of studying the kinetics and stereochemistry of a deliberately free-radical reaction. The photochemical reaction of isomers of β-chlorovinylmercury chloride with iodine, as well as of cis-trans-styrylmercury bromides with bromine in nonpolar solvents—benzene and carbon tetrachloride—was chosen as the object.

Under these conditions the reaction has an overall first order (first with respect to iodine and zero with respect to the organomercury compound). The determination of the orders is, of course, formal, since the reaction apparently constitutes a radical chain process in which the slow step is the photochemical decomposition of the halogen into radicals. In all cases, from both the trans- and the cis-isomer of the organomercury compound there is formed one and the same mixture of isomers (50% trans- and 50% cis-form) of the corresponding olefins. Parallel experiments established that secondary isomerization of cis- and trans-chloroethylenes and cis- and trans-bromostyrenes is not superimposed on this result.*



$$\left.\begin{array}{ccccc} R & & H & & \\ & C{=}C & & + & Hal_2 \\ H & & HgX & & \\ R & & HgX & & \\ & C{=}C & & + & Hal_2 \\ H & & H & & \end{array}\right\} \xrightarrow[C_6H_6;\ CCl_4]{h\nu} \begin{array}{cccc} R & & H & \\ & C{=}C & & 50\% \\ H & & Hal & \\ R & & Hal & \\ & C{=}C & & 50\% \\ H & & H & \end{array}$$

1. $R = X = Cl,\ Hal = J$;   2. $R = C_6H_5,\ X = Hal = Br$

Thus, in free-radical substitution of a mercury atom by a halide, the geometric configuration of the chlorovinyl group is not retained.

On the basis of the material presented, the regularities of the mechanism of electrophilic and homolytic substitution at an olefinic carbon atom may be formulated as follows:

1. Reactions of bimolecular electrophilic substitution at an olefinic carbon atom proceed with retention of the geometric configuration (S_{E2} rule).
2. Reactions of monomolecular electrophilic substitution at an olefinic carbon atom proceed with retention of the geometric configuration (S_{E1} rule).
3. Homolytic substitution reactions at an olefinic carbon atom, in the course of which radicals are not formed as kinetically independent particles, proceed with retention of the geometric configuration; in reactions of free-radical substitution the configuration is not retained (S_R rule).

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* Cis-chloroethylene and trans-chloroethylene, upon prolonged standing in the light, are converted into one and the same equilibrium mixture of isomers, containing 17.5% trans-chloroethylene and 82.5% cis-chloroethylene. In our experiments, however, an approximately equimolecular mixture of chloroethylenes was formed. The equilibrium mixture of ω-bromostyrene isomers contains 30% cis- and 70% trans-form.

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

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