Chemistry

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1960

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Abstract

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ON THE MECHANISM OF BIMOLECULAR ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

The mechanism of electrophilic substitution at a saturated carbon atom still remains insufficiently elucidated. One of the reasons for this lies in the difficulty of simultaneously studying the stereochemical and kinetic aspects of electrophilic-substitution reactions.

In 1953, one of us, together with A. N. Nesmeyanov and S. S. Poddubnaya (^{1}), studied the stereochemistry, and in 1957 we, together with R. E. Mardaleishvili, studied the kinetics (^{2}) of the symmetrization reaction of esters of α-bromomercuriphenylacetic acid under the action of ammonia in chloroform in the cold. Thus, for the first time, the stereochemistry and kinetics of a reaction of electrophilic substitution at a saturated carbon atom were studied simultaneously:

$$R_1R_2R_3C{-}\cdots HgBr + R_1R_2R_3C{-}Hg\cdots Br \xrightarrow{NH_3} R_1R_2R_3C{-}Hg{-}CR_1R_2R_3 + HgBr_2 \cdot 2NH_3$$

$$(R_1 = C_6H_5; \quad R_2 = H; \quad R_3 = COOC_2H_5 \text{ or } COO_{10}H_{19})$$

After our work on the simultaneous study of the stereochemistry and kinetics of electrophilic-substitution reactions using as an example the symmetrization of esters of α-bromomercuriphenylacetic acids (^{1,2}), only one work appeared—that of Ingold (^{3}) (1959)—on the simultaneous study of the stereochemistry and kinetics of the racemization reaction of di-*tert*-butylmercury under the action of $HgBr_2$.

On the basis of the kinetic (reversibility of the reaction, second order with respect to $R_1R_2R_3CHgBr$ and second order with respect to ammonia) and stereochemical (retention of configuration) data, the mechanism of the reaction under consideration may be represented by the following scheme:

$$(a) \quad 2R_1R_2R_3C{-}HgBr \rightleftharpoons (\mathrm{A}) \rightleftharpoons R_1R_2R_3C{-}Hg{-}CR_1R_2R_3 + HgBr_2$$

$$(b) \quad HgBr_2 + 2NH_3 \rightleftharpoons HgBr_2 \cdot 2NH_3$$

The first stage (a) is a reaction of bimolecular electrophilic substitution (S_E2) at a saturated carbon atom*.

$$a) \quad R_1R_2R_3CHgBr + NH_3 \rightleftharpoons R_1R_2R_3CHgBr \cdot NH_3,$$

$$b) \quad 2R_1R_2R_3CHgBr \cdot NH_3 \rightleftharpoons (R_1R_2R_3C)_2Hg + HgBr_2 \cdot (NH_3)_2$$

* An alternative mechanism (satisfying the stereochemical and kinetic requirements) is less probable, since the symmetrization reaction proceeds under the influence of the most diverse reagents that irreversibly bind $HgBr_2$. Thus, together with L. R. Filippienko (^{4}), we found that esters of α-bromomercuriphenylacetic acid (like other organometallic compounds with readily mobile mercury) are readily symmetrized under the action of diphenylmercury:

$$2R_1R_2R_3C{-}HgBr + (C_6H_5)_2Hg \rightarrow (R_1R_2R_3C)_2Hg + 2C_6H_5HgBr.$$

The intermediate formation of the complex $R_1R_2R_3CHgBr \cdot (C_6H_5)_2Hg$ in this reaction is unlikely, in particular because it contradicts the stoichiometry of the reaction.

Together with U Yan-tsze[1] we studied the kinetics of another electrophilic reaction at a saturated carbon atom—the isotopic exchange reaction of esters of α-bromomercuriphenylacetic acid with bromine mercury labeled with Hg^{203},

$$\mathrm{R_1R_2R_3CHgBr + Hg^*Br_2 \rightleftharpoons R_1R_2R_3CHg^*Br + HgBr_2},$$

$$(\mathrm{R_1 = C_6H_5;\ R_2 = H;\ R_3 = COOC_2H_5 \text{ or } COOC_{10}H_{19}})$$

This reaction is of overall second order and, possibly, proceeds by an analogous two-stage mechanism, the first stage of which (a) is identical with the first stage of the symmetrization reaction:

$$(a) \quad \mathrm{2R_1R_2R_3CHgBr \rightleftharpoons R_1R_2R_3C - Hg - CR_1R_2R_3 + HgBr_2},$$

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[1] Reference number as printed on the page.

(b) $(R_1R_2R_3C)_2Hg + Hg^*Br_2 \rightleftharpoons R_1R_2R_3CHg^*Br + R_1R_2R_3CHgBr$.

In all probability, through a transition state (A), reactions of the types considered may also proceed in the case of other organomercury salts having a relatively weak C—Hg bond.

We studied the influence of structural factors on the rate of bimolecular electrophilic substitution at a saturated carbon atom, choosing as the model reaction the symmetrization of compounds of the type n-$YC_6H_4CH(HgBr)COOR$ under the action of ammonia in chloroform. The first slow stage of this reaction evidently also proceeds through a transition state of type (A).

$$2\,Y{-}C_6H_4{-}CH(HgBr)COOR \rightleftharpoons (A) \rightleftharpoons$$
$$ROOC{-}CH(YC_6H_4){-}Hg{-}CH(COOR)(C_6H_4Y) + HgBr_2$$

1. $Y = H;\ R = CH_3,\ C_2H_5,\ \text{iso-}C_3H_7,\ \text{tert-}C_4H_9,\ \text{n-}C_9H_{19},\ \text{l-}C_{10}H_{19}$
2. $Y = Cl,\ Br,\ H,\ CH_3;\ R = C_2H_5$.

The considerable influence of the nature of substituents R on the rate of symmetrization may be judged from the following values of the reaction rate constants, calculated by the method proposed earlier[2].

R	CH_3	C_2H_5	iso-C_3H_7	tert-C_4H_9	n-C_9H_{19}	$C_{10}H_{19}$ (l-menthyl)
K_2, ml/mol·sec	181.5	110	25.9	negligibly small	10.2	6.9

The rate of reaction of the methyl ester is more than 25 times greater than the rate of reaction of the l-menthyl ester.

Naturally, the influence of the nature of R on the reaction rate is due to the sum of polar and steric factors.

The nature of substituent Y also influences the rate of symmetrization, as is evident from the values of the corresponding reaction rate constants for compounds of the type n-$YC_6H_4CH(HgBr)COOC_2H_5$.

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[2] Reference number as printed on the page.

Reaction scheme: transition state (A) with substituents Y and X, structures (I) and (II)

Figure 1: Reaction scheme: transition state (A) with substituents Y and X, structures (I) and (II)

Y	Cl	Br	H	CH_3
K_2, ml/mol · sec	470	400	110	0

Replacement of the hydrogen atom in the n-position of the benzene ring by chlorine accelerates the reaction by more than 5-fold, while replacement by a methyl group leads to the reaction practically not occurring. Naturally, in the case of bimolecular nucleophilic substitution in analogous systems

an inverse dependence is observed when comparing the influence of substituents on the reaction rate*.

Since the influence of the substituents Y on the rate of the reaction under consideration is apparently due purely to polar factors, the data presented lead to the conclusion that withdrawal of electrons from the reaction center (the saturated carbon atom) facilitates the bimolecular reaction of electrophilic substitution (S_E2). This fact indicates that, even in bimolecular substitution, cleavage of the old bond, rather than formation of the new one, may play the more important role. This circumstance brings the bimolecular S_E2 mechanism closer to the unimolecular, dissociative S_E1 mechanism, since in the latter cleavage of the old bond is the stage determining the rate of the entire process.

The results obtained by us show that reactions of electrophilic substitution at a saturated carbon atom proceed considerably more complexly than had previously been assumed on the basis of the simple limiting cases S_E1 and S_E2.

Since in the transition state (A) not only the old C—Hg bond but also the old Hg—Br bond is being cleaved, one might expect that the symmetrization reaction will proceed faster in the case where unlike molecules of organomercury salts, containing different substituents in the p-position of the benzene ring, react with each other. If, for example, Y is an electron-accepting substituent and X an electron-donating substituent, then the transition state (A)

will be reached more easily than in the case of reaction of identical molecules. In the first of the reacting molecules, cleavage of the old C—Hg bond is facilitated; in the second, cleavage of the Hg—Br bond.

Cosymmetrization of this type was carried out for the following pairs of compounds: $X = H,\ Y = Cl;\ X = H;\ Y = Br;\ Y = H,\ X = CH_3$. For each case the initial reaction rate was calculated. The following result was obtained: for the first two cases the total rate of the process proved to be greater than the sum of the initial rates for the individual components, taken at the same concentrations, by an amount exceeding the individual rates of the most rapidly reacting components. In the case $X = CH_3$, the result proved especially interesting. Although symmetrization of the p-methyl-substituted ester alone practically does not occur, in a mixture with the unsubstituted ester it does take place, though not to completion, to a certain extent. The total rate of the process proves greater than for the unsubstituted ester at the same concentration.

One of the interesting and important questions is the effect on the rate of the process of additives of various compounds not participating in the reaction. Such an effect of additives of polar molecules on the rate of nucleophilic reactions was studied by Ingold ($^{10-14}$) and by Swain (^{15,16}), who drew from their results diametrically opposite conclusions about the nature of this phenomenon.

We studied the influence of additives in S_E2 reactions. It was found that additives of polar agents to the reaction mixture considerably accelerate the symmetrization of esters of α-bromomercuriphenylacetic acid. Table 1 gives the values of the second-order reaction constants, calculated from the half-lives of the substance at an initial ester concentration

* For example, in the reactions of substituted benzyl chlorides with amines (^{6}), azides (^{7}), or in Finkelstein substitution (^{8,9}).

α-bromomercuriphenylacetic acid $6.8 \cdot 10^{-5}$ mole/ml, ammonia $\sim 1 \cdot 10^{-3}$ mole/ml, and various concentrations of additives.

It was further shown that the solvent itself (in our case, chloroform), being a polar molecule, has an accelerating effect on the reaction. For this purpose the reaction was carried out in an inert solvent—benzene—with additions of various amounts of chloroform.

A similar result was obtained in studying the rate of isotopic exchange of $C_6H_5CH(HgBr)COOC_2H_5$ with $Hg^{203}Br_2$. Thus, if in benzene the percentage of exchange is negligibly small, then on going over to a solvent possessing appreciable polarity, for example 70% aqueous dioxane, the rate increases almost 9-fold.

Table 1

Added substance	$C \cdot 10^3$, mole/ml*	$\tau_{1/2}$, sec	K_2, ml/mole · sec
Nitromethane	0	136	108
Nitromethane	0.469	75	197
Nitromethane	0.937	57	258
Nitrobenzene	0	170	86.7
Nitrobenzene	0.902	128	114.8
Methyl alcohol	0	136	108

Added substance	$C \cdot 10^3$, mole/ml*	$\tau_{1/2}$, sec	K_2, ml/mole • sec
Methyl alcohol	0.309	110	133
Methyl alcohol	0.618	93	158.5

* On average this is 1/25 of the amount of solvent.

The rate of the isotopic-exchange reaction of esters of α-bromomercuriphenylacetic acid with $Hg^{203}Br_2$ is accelerated by additions of both acids and bases. For example, we found an extremely strong effect of additions of pyridine on the rate of isotopic exchange of the *l*-menthyl ester of α-bromomercuriphenylacetic acid in acetone (reactant concentration 0.03 mole/ml) at 50°. Whereas in the absence of additives exchange in 6 hours proceeds only to 1%, the addition of 5 parts by weight of pyridine (relative to the amount of acetone) leads to 35% exchange after 3 hours, and 10 parts by weight—to 92% after 4.5 hours.

It remains an open question whether polar additives enter into the transition state (i.e., whether there is a definite kinetic order with respect to the additives), or whether their role is reduced to changing the polarity of the reaction medium, which in turn affects the reaction rate. This question is subject to further study.

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Received
19 XII 1959

CITED LITERATURE

1. A. N. Nesmeyanov, O. A. Reutov, S. S. Poddubnaya, DAN, **88**, 479 (1953); Izv. AN SSSR, OKhN, 1953, 850.
2. O. A. Reutov, I. P. Beletskaya, R. E. Mardaleishvili, DAN, **116**, 617 (1957); ZhOKh, **33**, No. 1, 153 (1959); ZhOKh, **33**, No. 9, 1962 (1959); O. A. Reutov, Angew. Chem., No. 21, 688 (1957).
3. H. B. Charman, E. D. Hughes, C. K. Ingold, J. Chem. Soc., 1959, 2530.
4. O. A. Reutov, I. P. Beletskaya, L. R. Filippenko, Nauchn. dokl. vyssh. shkoly, khim. i khim. tekhnol., No. 4, 754 (1958).
5. O. A. Reutov, I. P. Beletskaya, U Yang-chei, Collection "Kinetics and Catalysis," Publ. Acad. Sci. USSR, 1960.

6. T. Mukaiyama, H. Tanaka, Bull. Chem. Soc. Japan, **29**, No. 8, 914 (1956).
7. T. Mukaiyama, H. Tanaka, Bull. Chem. Soc. Japan, **29**, No. 8, 908 (1956).
8. M. Simonetta, G. Favini, Rend. Ist. lombardo sci. e lettere ce sci. mat. e natur., **87**, No. 2, 279 (1954).
9. J. Charlton, E. Hughes, C. Ingold, J. Chem. Soc., 1956, 855.
10. E. Hughes, C. Ingold et al., J. Chem. Soc., 1957, 1220.
11. E. Hughes, C. Ingold et al., J. Chem. Soc., 1957, 1230.
12. E. Hughes, C. Ingold et al., J. Chem. Soc., 1957, 1265.
13. E. Hughes, C. Ingold et al., J. Chem. Soc., 1957, 1238.
14. I. Pocker, J. Chem. Soc., 1957, 1279.
15. C. Swain, J. Am. Chem. Soc., **72**, 2794 (1950).
16. C. Swain, M. Kreevoy, J. Am. Chem. Soc., **77**, 1122 (1955).

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