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Abstract

Full Text

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On the "Anomalous" Influence of Substituents in S_E2 Reactions

We have previously studied the influence of substituents on the symmetrization reaction of the ethyl ester of α-bromomercuriphenylacetic acid under the action of ammonia

$$XC_6H_4CH(HgBr)CO_2C_2H_5 \xrightarrow{NH_3} (XC_6H_4CHCO_2C_2H_5)_3Hg + HgBr_2(NH_3)_2.$$

The following series of substituent effects on the reaction rate was obtained:

$$n\text{-}NO_2 > m\text{-}Br > n\text{-}I > n\text{-}Br > n\text{-}Cl > n\text{-}F > H > m\text{-}CH_3 > n\text{-}C_2H_5 >$$

$$> n\text{-iso-}C_3H_7 > n\text{-}CH_3 < n\text{-tert.-}C_4H_9.$$

As can be seen, this series proved to be the opposite of what would have been expected on the basis of ideas about the mechanism of S_E2. The Hammett equation is applicable to the series obtained. The value $\rho = 2.8$ indicates a high sensitivity of the reaction to the influence of substituents.

Fig. 1. Dependence of the optical density d on concentration.

To explain the influence of substituents, it was suggested that in the given reaction, although it is a reaction of the S_E2 type, cleavage of the old C—Hg bond precedes formation of the new one* ([1]).

Some confirmation of this point of view is provided by the character of the substituent effect obtained for these same objects in the study of the isotope-exchange reaction with bromomercury labeled with Hg^{203}:

reaction scheme: transition state with two arylmercury bromide fragments, substituents X, R, R′, and Br/Hg interactions

Figure 2: reaction scheme: transition state with two arylmercury bromide fragments, substituents X, R, R′, and Br/Hg interactions

$$XC_6H_4CH(HgBr)CO_2C_2H_5 + {}^*HgBr_2 \rightleftharpoons XC_6H_4CH({}^*HgBr)CO_2C_2H_5 + HgBr_2.$$

In 70% aqueous dioxane ([3]) and in dimethyl sulfoxide ([4]) this reaction proceeds by the S_E1 mechanism; in 80% aqueous alcohol, by the S_E2 mechanism ([5]). Nevertheless, the character of the substituent effect in all cases proved to be the same: the nitro group and halogens accelerated, while alkyl substituents slowed the process.

At the same time, in the study of the isotope-exchange reaction of benzylmercuric bromide with bromomercury labeled with Hg^{203}, an order of substituent effects was obtained that corresponds to the usual ideas concerning the influence of substituents in S_E2 reactions:

$$\text{Alk} > \text{H} > \text{Hal}.$$

A substituent effect corresponding to the S_E2 mechanism was also found by us in studying the reaction of phenylmercuric bromide with bromine in the presence of ammonium bromide in dimethylformamide.

In connection with the foregoing, the question arose whether the order of substituent effects obtained in the study of the symmetrization reaction is not determined by the specificity of the reaction itself, since it was shown ([1,7]) that the reaction

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* Subsequently, in studying the protolysis of fatty organomercury salts, M. Kreevoy expressed the supposition that formation of the new C–H bond may lag behind cleavage of the old C–Hg bond ([2]).

proceeds through a transition state of the type

in which the breaking of the old C–Hg and Hg–Br bonds and the formation of new C–Hg and Hg–Br bonds take place.

The fact that the ease of cleavage of the Hg–Br bond affects the reaction rate was proved by us using as an example the cosymmetrization reaction ([7]) of differently substituted esters $XC_6H_4CH(HgBr)CO_2C_2H_5$ and $YC_6H_4CH(HgBr)CO_2C_2H_5$ with substituents X and Y opposite in polar effect. The rate of the cosymmetrization reaction for any pair of compounds

reaction scheme: cosymmetrization of substituted arylmercury bromides with radioactive Hg and NH3 workup to mixed organomercury product

Figure 3: reaction scheme: cosymmetrization of substituted arylmercury bromides with radioactive Hg and NH3 workup to mixed organomercury product

reaction scheme: substituted arylmercury bromide reacts with I2(CdI2) via cyclic iodine/mercury intermediate to give aryl iodide product and HgBrI(CdI2)4

Figure 4: reaction scheme: substituted arylmercury bromide reacts with I2(CdI2) via cyclic iodine/mercury intermediate to give aryl iodide product and HgBrI(CdI2)4

always exceeds the rate of symmetrization of even the most rapidly reacting component; moreover, the mercury atom entering the organomercury compound formed comes from the initial molecule containing the electron-donating substituent Y (shown using radioactive mercury Hg^{207} (^{7})):

Thus, the case of symmetrization of organomercury compounds proved insufficiently simple for drawing, on its basis alone, a conclusion that the series of effects of substituents X on the reaction rate is inconsistent with Ingold' s classical ideas about the S_E2 mechanism.

Naturally, it was desirable to study the influence of substituents on some S_E2 reaction of ethyl esters of α-bromomercuriarylacetic acids in which cleavage of only the C–Hg bond occurs.

As such a reaction, the reaction with iodine was chosen; it had already been studied using benzylmercury chloride (^{8}) and β-chlorovinylmercury chloride (^{9}) as examples. In these works it was shown that, in the presence of cadmium iodide, the reaction proceeds only by an electrophilic mechanism. The mechanism of the reaction studied may be represented by the following scheme:

The kinetics of the reaction of ethyl α-bromomercuriphenylacetate was studied in absolute toluene with an addition of absolute methanol (1.5 vol. %) at equimolar ratios of iodine and the organomercury salt ((0.5—0.25) $\times 10^{-3}$ mol/l) and a tenfold excess of cadmium iodide.

The choice of solvent proved to be limited by the fact that in polar solvents* the reaction proceeds instantaneously, while in nonpolar solvents cadmium iodide dissolves poorly; in this connection the addition of methanol was required. The kinetics was studied spectrophotometrically from the change in the optical density of iodine. It was shown beforehand that, in the concentration ranges employed, the solution of iodine with cadmium iodide obeys the Lambert–Beer law (Fig. 1). The linear dependence of $\frac{d_0}{d} - 1$ on t indicates that the reaction is of second order (Figs. 2, 3). The values of the second-order rate constants, given in Table 1, show that the substituent-effect series is analogous to that

Fig. 2

Figure 5: Fig. 2

Fig. 3

Figure 6: Fig. 3

found earlier for the symmetrization reaction.

Fig. 2. Dependence of $\left(\frac{d_0}{d}-1\right)$ on t for various halogen-substituted mercurated esters $XC_6H_4CH(HgBr)CO_2C_2H_5$ ($C_0 = 0.25 \cdot 10^{-3}$ mol/l).
1—$X = m$-Br;
2—$X = n$-J;
3—$X = n$-Cl;
4—$X = n$-F;
5—$X = H$

Fig. 3. Dependence of $\left(\frac{d_0}{d}-1\right) - t$ for various alkyl-substituted mercurated esters $XC_6H_4CH(HgBr)CO_2C_2H_5$ ($C_0 = 0.5 \cdot 10^{-3}$ mol/l).
1—$X = H$;
2—$X = m$-CH_3;
3—$X = n$-iso-C_3H_7;
4—$X = n$-tert-C_4H_9

Fig. 4. Dependence $\lg(K/K_0)$—σ

The Hammett equation is applicable to the obtained series with good agreement (Fig. 4). The somewhat lower sensitivity of this reaction to the influence of substituents ($\rho = 2.3$), in comparison with the symmetrization reaction, is seen from a comparison of the relative constants for various substituted ethyl α-bromomercuriphenylacetates in the reaction with iodine and in the symmetrization reaction (K_2 for ethyl α-bromomercuriphenylacetate is taken as 1). The corresponding data are given in Table 2.

The results of the present work show that the conclusion concerning the determining character of the rupture of the old C–Hg bond in the symmetrization reaction is also applicable to other reactions of electrophilic bimolecular substitution (more precisely S_{Ei}) of ethyl esters of α-bromomercurarylacetic acids.

* It was shown earlier that the reaction of ethyl α-bromomercuriphenylacetate with iodine in the presence of cadmium iodide in aqueous dioxane proceeds instantaneously ([10]).

Table 1

Fig. 4

Figure 7: Fig. 4

X	*p*-NO_2*	*p*-Br	*p*-I	*p*-Cl	*p*-F	H	*m*-CH_3	*p*-iso-C_3H_7	*p*-tert.-C_4H_9
$C_0 \cdot 10^3$, mol/l	0.5	0.25	0.25	0.25	0.5	0.5	0.5	0.5	0.5
$C_0 \cdot 10^3$, mol/l		0.25	0.25	0.25	0.25	0.25	0.5	0.5	0.5
K_2, l/msec	615	78.8	43.5	33.1	13.97	10.05	6.96	4.55	3.56
K_2, l/msec		79.8	43.76	33.8	14.16	10.14	7.04	4.59	3.5

* The constant was calculated on the assumption that the Hammett equation is applicable to this series.

Table 2

X	*p*-NO_2	*m*-Br	*p*-I	*p*-Cl	*p*-F	H	*m*-CH_3	*p*-iso-C_3H_7	*p*-tert.-C_4H_9
K_X/K_H for the reaction with iodine	61.5	7.98	4.36	3.34	1.4	1	0.7	0.457	0.353
K_X/K_H for the symmetrization reaction	161	13.1	6.08	4.27	1.34	1	0.645	0.382	0.254

This conclusion, although quite unexpected, can be explained if one takes into account that there should be no sharp boundary between the mechanisms of S_E2

and S_E1 reactions, and that the reactions we have studied most likely belong to the borderline region between these mechanisms.

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