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INVERSION OF THE SUBSTITUENT EFFECTS ON THE RATES OF ArSCl Ad_E-REACTIONS WITH STYRENES

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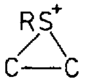
Summary: The inversion of the reactivity order of $R^2C_6H_4SCl$ in Ad_E-reactions with $R^1C_6H_4CH{=}CH_2$ owing to the variations in R^1 and R^2 has been found and interpreted in terms of two kinetically distinguishable Ad_E-2 mechanisms.

Recent investigations of RSHal additions to olefins have shown that generally accepted [1] episulphonium mechanism could be realized only with the use of strongly polarized complexes of $RS^+BF_4^-$ type [2]. Actually the addition of covalent RSHal under usually adopted non-polar condition occurs without the intervention of the species with complete dissociation of S-Cl bond(such as 1)but via less polar intermediates of ion pair type(such as 2) or even via non-ionic σ-sulphurane type(such as 3).

These conclusions were drawn both from the data on the reactivity of episulphonium ions as stable species [2] and the studies on the variations of the cour-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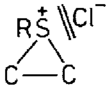
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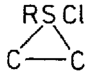
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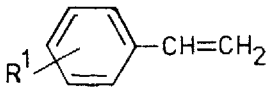
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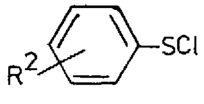
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se of RSHal addition under the conditions of increased polarity ("doping-addition" [2,3]). At the same time the kinetic criteria substantiating the multiplicity of mechanisms operating in this reaction thus far were lacking. Up to the present all available kinetic data were universally interpreted in terms of the formation of bridged ionic intermediate **1** at the rate determining step[1,4,5]. However in the vast majority of these studies only the effects of the substituents in olefins on the reaction rates were investigated[1,4]. The substituent effects in ArSHal have been studied only for the addition of the series of 4-X substituted 2-$NO_2C_6H_4SHal$ to cyclohexene [5] and satisfactory correlation with σ^+ was found ($\rho^+=-0.715$ and -0.667 for chloride and bromide respectively).

Here we present the result of the studies of structural effects of the substituents in both olefine and ArSCl on the rates of their reactions in AcOH at 25°C. Under these conditions the reaction yields mainly β-chlorosulphides accompanied by the formation of varying amounts of solvoadducts (IR and NMR). The rates were determined by the measurement of ArSCl consumption either by stop-flow method or with the use of conventional titrimetric technique. The initial concentrations of the reagents were in the range of 0.005-0.05 mol/l. In all cases the reactions were found to proceed as the second order processes, first order in each of reagents. For the variously substituted styrenes, **4**, excellent correlation of log k with Brown-Okamoto σ^+ constants for substituents R^1 was observed in agreement with literature data [4]. The data given in Table show that the reaction rate increases monotonously with the increase of electron-releasing ability of R^1 in styrenes **4**. The absolute values of ρ_1 decrease with the increase of electron-releasing properties of R^2 in ArSCl, **5**.

However the consideration of the structural effects of the substituents R^2 in reagents **5** reveals rather peculiar pattern of $\delta\rho$-type of correlation. The respective data are exhibited at Fig where the values of log k_{R^1}/k_H are plotted vs. σ^+ for R^1 in olefins **4**. The Fig evidences that for electron-withdrawing substituents R^1 in styrenes **4** the rate of addition increases with the increase of electron-donating ability of R^2 group in reagent **5** ($\rho_2 < 0$) [6]. In other words the effects similar to those described earlier [5] are observed. On the contrary in the region of electron-releasing substituents R^1 in styrenes the reaction rate increases with the growth of electron-withdrawing properties of R^2 substituents in 5 ($\rho_2 > 0$) [6]. To the best of our knowledge such dual effects R^2 substituents on the rate of ArSCl addition have never been observed [7].

Table. Rate constants, k(l/mol·sec), and parameters of correlation

R^1 \ R^2	p-NO_2	H	p-CH_3
m-NO_2	0.16±0.01	0.75±0.04	1.3±0.2
H	6.9±0.3	10.2±0.2	11.2±0.4
p-CH_3	16.4±0.5	23±2	15.6±0.1
p-OCH_3	279±6	76±9	50±6
ρ_1	-2.15	-1.37	-1.06
r	0.996	0.995	0.991
s	0.1473	0.1022	0.1063

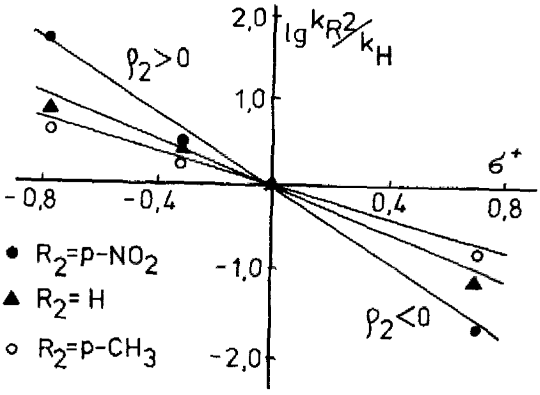

Fig. Dependence of $\lg \frac{k_{R^1}}{k_H}$ vs. σ^+.

The discovered phenomena clearly indicates the existence of two regions of mechanisms for the reaction under study the rate of addition in these regions being controlled by the opposite electronic effects.

We suggest the following interpretation of these data. Since the negative sign of ρ_1 was found for all the reaction series the process should be universally considered as the electrophilic addition. In terms of frontier orbital description the Ad_E-reactions are interpreted as electron transfer from HOMO of the donor(π-orbital of olefine) to LUMO of the acceptor(σ^*-orbital of S-Cl bond)[8,9]. The net result of this charge transfer must be the polarization of S-Cl bond leading to the formation of ion pair intermediates and(as extreme) episulphonium ion (2 and 1 respectively). This process should be generally facilitated by the increase of electron-donating ability of substituents in alkenes. However, the transient charge on the sulphur atom is the subject to the competition between two opposite processes: the charge transfer from olefin to reagent(bond-making process) generating the transient negative charge on the sulphur atom and the dissociation of S-Cl bond(bond-breaking process).

The experimental data presented in this paper on the inversion of ArSCl reactivity order clearly indicate that these electron transfer processes, namely from olefine to reagent and from sulphur to chlorine, could proceed in non-synchronous manner. Thus, for olefins bearing strongly donating substituents the former process takes place more readily than the latter one($\rho_2>0$) and *vice versa*. The presented data disclose the realization of two kinetically discernable mechanisms for Ad_E-2 general process.

References and Notes.

1 G.Schmid and D.Garratt, in "*The Chemistry of Double Bonded Functional Groups*", S.Patai, Ed., Wiley, New York, 1977, Chapter 9 and references therein.

2 W.A.Smit, N.S.Zefirov, I.V.Bodrikov and M.Z.Krimer, *Acc.Chem.Res.*, **12**, 282(1979); *Dokl.Akad.Nauk SSSR*, **240**, 859(1978).

3 See the works of Zefirov's and Bodrikov's groups: *Tetrahedron Letters*, 2617 (1978); 1547(1979); *Tetrahedron*, **31**, 2948(1975); **34**, 1373(1978); *Zhur.Org.Khim.*, **13**, 245, 2093(1977); **14**, 463, 1224, 1806(1978); **15**, 223, 1361(1979).

4 W.L.Orr and N.Kharasch, *J.Am.Chem.Soc.*, **78**, 1201(1956); I.V.Bodrikov, T.I.Ganzhenko, N.S.Zefirov and V.R.Kartashov, *Dokl.Akad.Nauk SSSR*, **226**, 831(1976).

5 C.Brown and D.R.Hogg, *J.Chem.Soc.*, (B), 1262(1968); 1059(1969).

6 At present we prefer not to give accurate values for ρ_2 since only three experimental series differing by R^2 in ArSCl are available. However the sign of this parameter is determined unequivocally.

7 (a) Analogous order of reactivity has been observed in the reaction of ArSCl with amines [7b]; (b) V.A.Ignatov, L.S.Degtjar'ov and co-workers, *Izv.VUZ.SSSR, khim.and khim.technol.*, **20**, 337(1977).

8 (a) G.Klopman, "*Chemical Reactivity and Reaction Paths*", Wiley, 1974; (b) M.J.S. Dewar and J.R.Ford, *J.Am.Chem.Soc.*, **101**, 783(1979).

9 Back-donation process($n \rightarrow \pi^*$) could be also important [8]. This problem has been clearly exposed by Dewar and Ford [8b].

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