The common ion effect in sulfenylhalogenation of alkenes in formic acid

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The reactions of 2,4-dinitrobenzenesulfenyl chloride with cyclohexene and allylbenzene in formic acid were studied. In this solvent, the reaction yields solvo-adducts and the products of addition of the reagent to the double bond. The reaction follows kinetics of the second order, first order with respect to each reagent. The hydrogen chloride evolved in the reaction has no effect on the overall rate of the process but sharply decreases the rate of accumulation of solvo-adducts due to the common ion effect. In the reaction with allylbenzene, the yield of the solvo-adduct can vary under the action of HCl from 88% at low degrees of reagent conversion to 30% when the reaction is complete.

Key word: alkenes, sulfenylhalogenation, formic acid, kinetics; common ion effect; ion pairs, episulfonium ion; reaction mechanism.

It was shown previously 1-3 that the use of formic acid as the solvent in reactions with alkenes favors an increase in the effective electrophilicity of sulfenyl halide. For example, the reactions of sulfenyl halides with cyclooctene result in the formation of products of transannular rearrangement¹ along with the product of normal trans-addition, while the Wagner-Meerwein rearrangement occurs with such reagents as norbornene,² 3,6-dimethoxynorbornadiene,³ and tetrafluorobenzobarrelene.³ It is important that the formation of products of addition to the double bond in formic acid occurs to a considerable extent with the participation of a solvent. In particular, the reaction of cyclohexene with 2,4-dinitrobenzenesulfenyl chloride (DNBSC) in HCOOH results in the formation of the product of solvo-addition, formate 2 (50%),¹ along with chlorosulfide 1 (40%), unlike the reaction in acetic acid, where solvo-addition does not occur.4



involve a free episulfonium ion, which is in equilibrium with the solvate-separated ion pair. The ion pair is transformed to chlorosulfides, and the episulfonium ion is transformed to the products of solvo-addition.

In light of these concepts, the substantial effect of addition of a common ion on the product distribution should be expected. In fact, addition of lithium chloride for a ratio of LiCl : DNBSC = 5 : 1 and concentration of LiCl of 1-3 mol L⁻¹ results in the almost complete suppression of solvo-addition.^{1,2} However, for such high concentrations of the additive and taking into account the low nucleophilicity of formic acid,⁶ this result can be due to the reaction of lithium chloride directly with the ion pair.

Taking into account the facts presented above, we studied the reaction of DNBSC with cyclohexene under kinetically controlled conditions and at lower concentrations of LiCl, as well as the reaction of DNBSC with allylbenzene (3). As in the case of cyclohexene, the reaction of DNBSC with allylbenzene in formic acid gives the solvo-adduct (Scheme 1). The products of addition of the reagent form against (4a) and according to the Markovnikov rule (4b) in the ratio of 1 : 1, while solvo-adduct 5 only forms according to the Markovnikov rule. It is noteworthy that the similar reaction in acetic acid results only in adducts 4a, b.⁷

Experimental

¹H NMR spectra were recorded on a Tesla B3-487C instrument with a working frequency of 80 MHz using HMDS

and dissociating solvent⁵ as formic acid the reaction can ins

It was supposed 1-3 that in such a strongly ionizing

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as the internal standard. IR spectra were recorded on a Perkin-Elmer 180 instrument.

Anhydrous acetic acid and LiClO₄ were prepared as described previously.⁸ Commercial formic acid was dried for several days over B_2O_3 , distilled over anhydrous CuSO₄, and fractionally recrystallized three times.⁹ The purity of reagents was controlled by GLC on a Tsvet-530 instrument (column 3 m long, katharometer as the detector, He as the carrier-gas, 10% SKTF-50 on Chromaton as the stationary phase, T = 105 °C). 2,4-Dinitrobenzenesulfenyl chloride was prepared by a procedure described previously.¹⁰

The kinetic measurements were carried out at 25 °C with initial concentrations of reagents equal to 0.02-0.04 mol L⁻¹. The reaction rate was monitored by the consumption of DNBSC, and the ratio of products was determined from the evolution of HCI.

Since the reaction with cyclohexene lasts for 5-10 min, the kinetic experiments were carried out in a λ -like reactor. Thermostatted 0.04 *M* solutions of olefin and DNBSC (2 mL of each solution) were placed in different bends of the reactor, the bends were closed with a ground plug, and the solutions were mixed by vigorous shaking. This method ensured mixing of the reagents for 1-2 s. After the necessary time (from 30 s to 10 min), a 5-10% solution (10 mL) of KI was added to the reaction mixture, the solution obtained was quantitatively transferred to a titration flask, and the content of DNBSC was determined by titration with a 0.005 *M* solution of Na₂S₂O₃.

When the reaction with allylbenzene was studied, solutions of sulfenyl halide and allylbenzene of specified concentrations in the acid were prepared in volumetric 50-mL flasks. Additives of LiCl or LiClO₄ were placed in the flask containing a solution of olefin. The solutions prepared were thermostated for 10-15 min at 25 °C, then a sample (2 mL) was taken from a solution of DNBSC, the initial concentration of DNBSC was determined, the remaining portion was mixed rapidly with a solution of olefin in the thermostated reactor, and some later the samples were taken for determination of the content of DNBSC and HCl evolved. For analysis of HCl, an aliquot (5-10 mL) was added to anhydrous AcOH (20-25 mL), and the solution was titrated with a 0.01 M solution of potassium biphthalate in anhydrous AcOH. The equivalence point was determined on an EV-74 universal ionometer using glass and Ag/AgCl electrodes. The error of the analysis for [HCl] = 0.10-0.01 mol L⁻¹ was 5-7%. The presence of DNBSC and reaction products did not change the results of the analysis.

To isolate the reaction products, a 0.12 M solution of DNBSC in HCOOH (25 mL) was mixed with a solution of allylbenzene (25 mL) of the same concentration, and the resulting solution was left for 2 h at 25 °C. The reaction mixture was poured in water and extracted with chloroform. The organic layer was separated and dried over MgSO4. The solvent was removed under low pressure, and a mixture of products (0.73 g, 71%) was obtained. TLC showed a spot with $R_{\rm f}$ 0.27 assigned to compound 5 and two spots of equal intensities with $R_f 0.73$ and 0.78 assigned to adducts 4a,b, which were isolated as a mixture (0.36 g, 49%). The ¹H NMR spectra of compounds 4a,b are identical to those described previously.7 1-(2,4-Dinitrophenylthio)-2-formyloxy-3-phenylpropane (5) was isolated as an oil (0.14 g, 19%), which was crystallized by treatment with cold hexane. The crystals were washed on a glass filter with cold chloroform, and a sample with m.p. 165.0-166.5 °C was obtained. Found (%): N, 7.69; S, 8.78. C₁₆H₁₃N₂O₆S. Calculated (%): N, 7.76; S, 8.86. IR (CCl₄), v/cm^{-1} : 1725 (C=O). ¹H NMR (CDCl₃), δ : 3.2-3.3 (m, 4 H, 2 CH₂); 5.3 (m, 1 H, CH).

Results and Discussion

We established that in the reaction of DNBSC $(0.015-0.300 \text{ mol } L^{-1})$ with a two-threefold excess of cyclohexene, for 100% conversion of the reagent the yield of formate is equal to 51-53%. The addition of LiCl $(0.02-0.04 \text{ mol } L^{-1})$ exerts a very slight effect on the ratio of the products (47-50% yield of 2).

The following facts should be taken into account in the study of the kinetics and composition of the products of the reaction of DNBSC with alkenes in formic acid. It was repeatedly mentioned that sulfenyl halides decompose in formic acid, 1-3,11 Nevertheless, this solvent can be used for sulfenylhalogenation of alkenes, because the rate of decomposition of the reagent is substantially lower than the rate of its reaction with unsaturated compounds.1-3 This circumstance becomes important for quantitative studies. The statistical data on the results of 100 experiments showed that when DNBSC is dissolved (during 15-20 min) in a calculated concentration equal to 0.02-0.04 mol L⁻¹, its content decreases to 90-93% of the initial content. After holding the solution for 2 h at 25 °C, the concentration of DNBSC decreases approximately to 80% of the initial concentration (Fig. 1). Therefore, all experiments were carried out immediately after dissolution of DNBSC with simultaneous control of its content, which was taken as the initial concentration.

It was also necessary to reveal whether HCI is formed in decomposition of DNBSC. Potentiometric titration of the products of decomposition of DNBSC (at initial concentrations from 0.02 to 0.10 mol L^{-1}) in formic acid with potassium biphthalate showed a smooth, without jumps, change in the potential, and the titration curve had the same shape as in the absence of these products. It follows that HCI is not a product of decomposition of DNBSC in formic acid, and its content in 92



Fig. 1. Curves of the change in the concentration of DNBSC in HCOOH (1) and in the reaction with allylbenzene (2) at the initial concentration of 3 equal to 0.046 mol L^{-1} .

the reaction mixture makes it possible to estimate the relative yield of the solvo-adduct.

The rate of the reaction of DNBSC with cyclohexene is described by a second-order equation (by a first-order equation with respect to each reagent) with a rate constant of $k = 0.98\pm0.11$ L mol⁻¹ s⁻¹. The addition of LiClO₄ or LiCl does not change the reaction rate constant within the experimental error: $k = 1.06\pm0.13$ and 1.03 ± 0.12 L mol⁻¹ s⁻¹, respectively. This indicates, on one hand, that salts have no effect like Lewis acids on the limiting stage of the reaction (unlike, *e.g.*, the reaction in acetic acid^{8,12}), and on the other hand, the common ion added does not slow the reaction rate. The latter indicates that the first limiting stage of the reaction is irreversible and unambiguously rules out the mechanism with preliminary dissociation of DNBSC, which was suggested previously as highly improbable.^{1,2}

A question arises: what is a reason for the absence of a noticeable effect of LiC1 on the relative yields of products 1 and 2? We supposed that the reason for this is the more pronounced effect of the HCl evolved on the ratio of products. In formic acid, HCl is a strong acid with pK 0.89¹³ (in water pK_{HCl} 0.80¹³). When the concentration is equal to 0.01 mol L^{-1} , 97% of the hydrogen chloride in formic acid is dissociated. Therefore, the CI⁻ anions formed by the reaction of formation of the solvo-adduct can already have the common ion effect for low degrees of conversion of the reagents, and this effect should increase as conversion of the latter increases. Since the reaction of cyclohexene with DNBSC occurs very rapidly even for concentrations of the reagent equal to 0.005-0.01 mol L⁻¹, we checked this assumption using the reaction of DNBSC with allylbenzene as an example. It was established that the concentration of HCl increases during the reaction, however its relative content in the products (equal to the content of formate 5) decreases (Table 1).

 Table 1. Dependence of the concentration of HCl and relative yield of formate 5 on conversion of reagents in the reaction of

$C_0^* = 0.02 \text{ mol } L^{-1}$			$C_0^* = 0.04 \text{ mol } L^{-1}$		
Con- version (%)	[HCI] · 10 ² /mol L ⁻¹	Yield of HCl and 5 (mol.%)	Con- version (%)	[HCI] · 10 ² /mol L ⁻¹	Yield of HCl and 5 (mol.%)
24.5	4.3	88	13.2	4.6	87
25.0	4.3	86	17.5	5.6	80
44.1	6.8	77	19.3	5.5	71
53.3	7.0	66	36.8	8.6	58
59.3	8.6	72	47.4	7.7	41
67.7	8.3	61	59.9	11.0	46
78.6	10.2	65	65.8	9.8	37
97.8	12.2	62	75.0	13.5	45
100.0	13.0	65	81.0	9.9	31
			100.0	12.4	31

Initial concentrations of reagents.

allylbenzene with DNBSC in formic acid



Fig. 2. Dependence of the yield of formate 5 on conversion of DNBSC in the reaction with allylbenzene in HCOOH at different initial concentrations of reagents: $[DNBSC]_0 = [3]_0 = 0.02$ (*I*) and 0.04 mol L⁻¹ (2).

It can also be seen from the data in Table 1 that for high degrees of conversion, the relative content of formate 5 formed depends on the initial concentrations of the reagents. For example, for 100% conversion, the content of formate is equal to 31 and 65% for initial concentrations of the reagents equal to 0.04 and 0.02 mol L^{-1} , respectively. This fact is additional evidence of a decrease in the rate of formation of formate 5 due to the HCl evolved. The dependence of the yield of products of solvo-addition on the initial concentrations of the reagents in sulfenylhalogenation of alkenes in formic acid was observed previously.¹⁻³

The curves of the change in the yield of solvo-adduct 5 at different degrees of conversion of the reagents for initial concentrations equal to 0.02 and 0.04 mol L^{-1} are presented in Fig. 2. When the conversion decreases,



Table 2. Kinetics of consumption of DNBSC and secondorder rate constant in the reaction with allylbenzene ($\{DNBSC\}_0 = 0.018 \text{ mol } L^{-1}, \{3\}_0 = 0.021 \text{ mol } L^{-1}\}$

t/s	[DNBSC] · 10 ² /mol L ⁻¹	k · 10 ² /L mol ⁻¹ s ⁻¹	
490	1.56	1.33	
1308	1.27	1.42	
1920	1.09	1.48	
2250	1.01	1.49	
3195	0.83	1.54	
4254	0.74	1.40	
5400	0.61	1.43	
7200	0.50	1.39	
10800	0.31	1.52	

Note: $k_{av} = (1.44 \pm 0.02) \cdot 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$.

the curves converge, and their extrapolation to zero gives compound 5 in a $\sim 97\%$ yield. Thus, the assumption that the HCl evolved has an effect on the ratio of the products of the reaction of DNBSC with allylbenzene is experimentally confirmed.

The rate of the reaction of DNBSC with allylbenzene obeys a second-order equation and a first-order equation with respect to each reagent. The results of a typical experiment, which show that the observed rate constant is unchanged during the experiment, are presented in Table 2. This is also seen in the experiments performed for different ratios of reagents (Table 3), although decomposition of DNBSC should make the kinetics of the process more complicated. The kinetic curve of consumption of DNBSC in the reaction with allylbenzene is also presented in Fig. 1 for comparison. The rate of decomposition of DNBSC is approximately the same, and its contribution to the overall rate of consumption of DNBSC is low. Probably, this circumstance introduces an error only in the determination of the numerical value of the reaction rate constant but exerts almost no effect on the character of the kinetic regularity.

As in the reaction with cyclohexene, addition of LiCl or $LiClO_4$ has no effect on the overall rate of the process (see Table 3). Thus, in this case, replacement of the substrate does not change the kinetic regularities of the reaction.

Additional evidence of the irreversibility of the first, limiting, stage is the retention of second-order kinetics up to high degrees of conversion of the reagents under the conditions of accumulation of Cl⁻. Thus, the common ion effect occurs in fast stages that determine the distribution of the products. Taking into account the strongly ionizing properties of the solvent, which favor dissociation, it can be assumed that the reaction proceeds through formation of episulfonium ion 8, which is in equilibrium with ion pairs 6 and 7 (Scheme 2). As a result, the ion pairs are transformed to chlorosulfides, and episulfonium ion 8 is transformed to the products of solvo-addition.

The kinetic analysis of Scheme 2 under the steadystate approximation leads to Eq. (1), according to which the ratio of the yield of chlorosulfides ([Cl-S]) to the yield of formates ([Form]) linearly depends on the concentration of Cl^- ions.

Table 3. Kinetic data for the reaction of allylbenzene with DNBSC in formic acid

[DNBSC] ₀ +10	$(3 _0 \cdot 10^2)$	[3]0	[LiCI]	[LiClO ₄]	$k \cdot 10^{2}$
mol L-	1	[DNBSC]0	mol L ⁻¹		/L mol ⁻¹ s ⁻¹
1.80	2.08	1.16			1.50
1.51	3.47	2.30			1.57
0.87	2.10	2.4!			1.47
1.99	4.57	2.30		0.1	1.62
1.72	4.05	2.35	-	0.2	1.64
1.79	3.95	2.21	0.1		1.61
1.82	4.21	2.31	0.2		1.42

Note: $k_{av} = (1.55 \pm 0.04) \cdot 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$.

$$[CI-S]/[Form] = a[CI^-] + b.$$
(1)

$$a = \frac{k_{-1}}{k_3} \frac{(k_4 k_{-2} + k_4 k_5 + k_5 k_2)}{k_6 k_2 [\text{HCOOH}]}; \quad b = \frac{k_4 (k_3 + k_{-2}) + k_5 (k_4 + k_2)}{k_3 k_2}$$

Coefficients a and b in Eq. (1) are a rather complicated combination of the constants of the elementary stages. The interpretation of the parameters of the linear dependence becomes simpler and more evident if ion pairs 6 and 7 are replaced by common intermediate (A), which leads to the formation of chlorosulfides (Scheme 3). This method is standard for the kinetic analysis of schemes involving different ion pairs.¹⁴

Scheme 3



In this case, the rates of accumulation of chlorosulfides and formates are described by Eqs. (2) and (3), respectively, and the ratio of their yields is described by Eq. (4).

$$\frac{d[CI-S]}{dt} = \frac{k_{1}[RSCI][aik] k_{3}(k_{-2}[CI^{-}] + k_{4}[HCOOH])}{(k_{4}[HCOOH]k_{2} + k_{3}(k_{-2}[CI^{-}] + k_{4}[HCOOH]))} .(2)$$

$$\frac{d[\text{Form}]}{dt} = \frac{k_1[\text{RSCI}][a]k]k_2k_4[\text{HCOOH}]}{\{k_4[\text{HCOOH}]k_2 + k_3(k_{-2}[\text{CI}^-] + k_4[\text{HCOOH}])\}},(3)$$

where [alk] is the concentration of alkene,

$$\frac{[\text{CI-S}]}{[\text{Form}]} = \frac{k_3}{k_2 k_4 [\text{HCOOH}]} (k_2 [\text{CI}^-] + k_4 [\text{HCOOH}]) = \frac{k_3 k_2 [\text{CI}^-]}{k_2 k_4 [\text{HCOOH}]} + \frac{k_3}{k_2}.$$
(4)

Let us analyze the experimental data on the ratio of products of the reaction of DNBSC with allylbenzene using Eq. (4). The main complication is that the concentration of Cl⁻ ions is unknown for each ratio (4a + 4b)/5 determined during the reaction. The concentration of HCl determined at a given moment is the final result of participation of the Cl⁻ ion in the reversible stage A \implies 8 (see Scheme 3). Nevertheless, we succeeded in performing this analysis. Statistical processing of the dependence of (4a + 4b)/5 on [HCl] by Skorobogatova et al.

the equation for a straight line y = ax + b gave the following results:

$$a = k_3 k_{-2} / (k_2 k_4 [\text{HCOOH}]) = 63, S_a = 16;$$

 $b = k_1 / k_2 = 0.034, S_b = 0.14 (n = 18).$

Using this dependence, we established that when the concentration of HCl is equal to 0.03 mol L^{-1} , the (4a + 4b)/5 ratio should be equal to -2 and -10 for [HCl] = 0.1 mol L^{-1} . In the experiments with $[DNBSC]_0 = 0.02$ mol L^{-1} , when 0.03 mol L^{-1} HCl is added, the yield of formate 5 for 100% conversion of the reagent decreased to 30%, and when [HCl] = 0.1 mol L^{-1} , according to the TLC data, a negligible amount of compound 5 forms. The results of the analysis performed make it possible to conclude that Scheme 3 corresponds to the experimental data observed.

In this connection, let us analyze the parameters of the linear dependence obtained. Taking into account the above, high values of S_a and S_b are expected. However, the value of the $b = k_1/k_2$ parameter is remarkable. Even taking into account a high error of determination, it indicates that the rate of transformation of intermediate A into the episulfonium ion is considerably higher than that of its transformation into the adduct. At the same time, it follows from the value of parameter a that the $k_{2}/(k_{4}[HCOOH])$ ratio is equal to 1853, *i.e.*, the rate of the reverse reaction in the A 🛥 8 stage is much higher than the rate of transformation of ion 8 into the solvoadduct. Thus, the ratio of products in the reactions studied is determined by the equilibrium constant of the stage that is not rate-limiting, and the shift of this equilibrium is due to the HCl evolved. It is likely that the absence of the effect of LiCl additives, unlike additives of HCl, at concentrations of 0.02-0.04 mol L⁻¹ on the ratio of products at 100% conversion of the reagents is related to the fact that LiCl dissociates in formic acid to a smaller extent than HCl. This follows from the comparison of the total free energy of solvation of these compounds in HCOOH, which is equal to 323.55 kcal g-ion⁻¹ for HCl and 194 kcal g-ion⁻¹ for LiCl (see Ref. 13).

The kinetic results obtained can also be explained in terms of simpler Scheme 4, according to which a free episulfonium ion is formed in the limiting stage.



However, this scheme is less probable due to the following reasons. Since in this case chlorosulfides should be formed due to the reaction of ion 8 with Cl⁻, it should be assumed that Cl⁻ anions are capable of efficient competition with the solvent for trapping the episulfonium ion even at very low concentrations (~0.005 mol L⁻¹, see Table 1). The assumption that the Cl⁻ anion affects the yields of the products due to shifting of the A \implies 8 equilibrium seems to be preferable also due to the regiochemistry observed in the reaction of allylbenzene with DNBSC. The formation of adducts 4a and 4b against and according to the Markovnikov rule can be considered as one more piece of evidence in favor of the fact that products 4a,b and 5 are formed from different intermediate species.

Independently of the choice of alternative schemes discussed, the results obtained, in our opinion, prove the participation of the free episulfonium ion in the reaction of sulfenylhalogenation of alkenes in formic acid.

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