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KINETICS AND MECHANISM OF THE DOPING-ADDITION OF ArSCl TO OLEFINS

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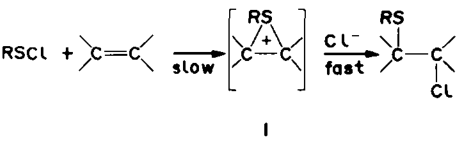
Abstract—A lithium percholate effect on the rate and product ratio of 2,4-dinitrobenzenesulfenyl chloride doping-addition to 1-methylcyclopropene (**5**) and tetrafluorobenzobarrelene (**10**) in acetic acid has been examined. The rates of both doping-addition reactions follow the normal salt effect dependence. However, the yields of doping-addition products is much higher than expected from the term $k_0 \cdot b \cdot [\text{LiClO}_4]$ at low concentrations of the salt added and, hence, the catalytic influence of LiClO_4 on product formation is much more pronounced than expected from normal salt effect dependence. The mechanism of doping-addition is analyzed in detail.

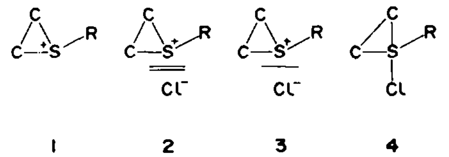
The Ad_E reaction of sulfenyl chlorides to olefins appears to be a synthetically useful process and it has been studied and reviewed extensively.[1-3] The classical mechanistic description of this reaction, developed by Kharasch and co-workers[4] and accepted in many publications,[1] suggests a rate-determining formation of the episulfonium ion **1** (Scheme 1), which undergoes nucleophilic attack by chloride ion at the second and fast step.



Scheme 1.

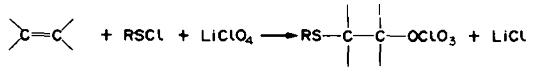
In contrast with that general belief, however, recent investigations have shown that "pure" episulfonium ions **1** are certainly *not* the intermediates under normal conditions and *ion-pairs* are involved in this addition reaction.[2,3,5] This conclusion was derived from the following arguments. Firstly, the observed chemical behavior of specially prepared episulfonium ion salts has been in striking contrast with the regularities of RSCl addition.[2,6] Secondly, it was demonstrated that one can change the "effective electrophilicity"[7] of RSCl by an appropriate change of the reaction conditions,[2,3,5,8,9] changes which led to the discovery of the "doping-effect" in addition of RSCl to olefins.[2,3,5,8,10-13]

Consider the latter in more detail. If the addition of RSCl could proceed via a number of intermediates of varying polarity, the episulfonium ion **1** and the sulfurane **4** (Scheme 2) must be the limiting cases for the structures with complete dissociation vs complete covalent bonding of the S—Cl bond, respectively. Hence, the increase of the effective electrophilicity of RSCl by an increase in the polarity of the reaction media proves the involvement of intermediates less polar than ions **1** in less polar media.[2,3,9]



Scheme 2.

In a series of papers[2,3,5,8-13] we have disclosed the occurrence of the "doping-effect": the substantial increase in the effective electrophilicity[7] of RSCl when the addition is carried out in the presence of strong electrolytes (usually LiClO_4).[14] The synthetic potential of the doping-addition is unquestioned: the net result of such salt addition is a change in the structure of the intermediate(s) to such an extent that it becomes possible to obtain the 1,2-solvoadducts,[3,5,8,10-13] and products of hydride shift,[2a,6b] of participation of a remote double bond,[3,10] of skeletal rearrangements,[3,5,8,10,11] of a series of rearrangements,[3] of cyclopropane ring opening,[13] etc. One of the most remarkable results of the doping-addition studies is the discovery of the incorporation of the ClO_4^- ion in the final step of the additions in accordance with Eq. (1).[3,15]



$$\text{>C=C<} + \text{RSCl} + \text{LiClO}_4 \longrightarrow \text{RS—}\overset{|}{\underset{|}{\text{C}}}\text{—}\overset{|}{\underset{|}{\text{C}}}\text{—OClO}_3 + \text{LiCl}$$

In turn, this finding led us to the discovery of the novel general phenomenon of competitive covalent binding of nucleofugic (i.e. super-weak nucleophilic) anions in carbocationic processes.[16-21]

Exploration of the doping-addition principle has led also to important mechanistic results, because the question of ion-pair intermediates in RSCl addition could now be treated on an experimental basis[22] (see, for example, the concept of stereo-control of the addition by ion-pair structure[3,10a,24] and the attempt to elaborate the criteria to distinguish the different types of ion-pair intermediates).[5] The first version of the mechanism of the doping-addition was suggested by us in 1975[8] (*vide infra*) and has been further generally supported.[2,3,5,11,14b]

However, there still remain many unanswered mechanistic questions in the doping-addition study. As a part of our mechanistic investigations[11,14b,25] we have performed a kinetic study of the doping-addition of 2,4-dinitrobenzenesulfenyl chloride (DNBSC) to methylcyclopropene (**5**) and tetrafluorobenzobarrelene (**10**). The novelty of this study is the following: we have performed both the usual measurements of total rates and the determination of the product distribution as a function of the salt concentration. This permits one to extract important mechanistic conclusions and the goal of this paper is to present these kinetic data and to discuss the general mechanism of the doping-addition.

RESULTS

Model reactions

We have chosen the addition of DNBSC to olefins **5** and **10** for the following reasons: (i) the addition of DNBSC to both olefins has been previously studied[13,26] and these reactions were found to be sensitive to the doping-effect; (ii) the rates of these additions under doping conditions are convenient for kinetic measurements. The reaction of cyclopropene **5** in AcOH proceeds to give the normal adduct **6** (74% yield) and the product of the ring-opening, namely chloride **7** (11% yield). Under doping conditions the addition proceeds to give the acetate **8** (<2%) and acetate **9** together with chlorides **6** and **7** (cf. ref. 13), the product ratio being dependent of $LiClO_4$ concentration. At high concentrations of $LiClO_4$ the rearranged chloride **7** and the acetate **9** become the predominant products. The dependence of the yields of the addition products vs $[LiClO_4]$ is shown in Fig. 1 and Table 1.

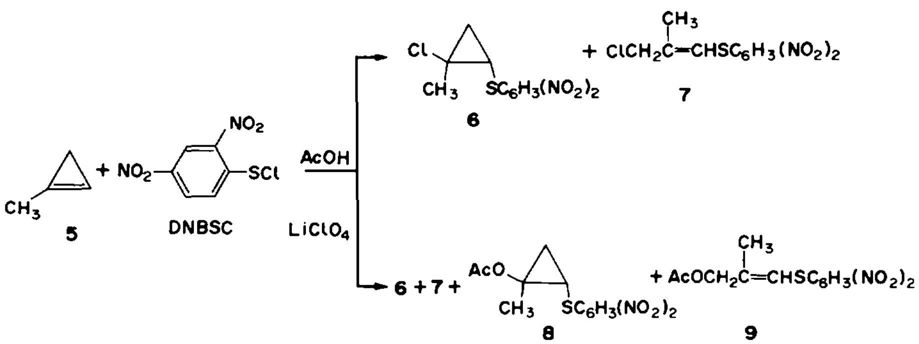
Table 1. A dependence of the yields of **7** and **9** on $LiClO_4$ for the addition of DNBSC to the olefin **5**

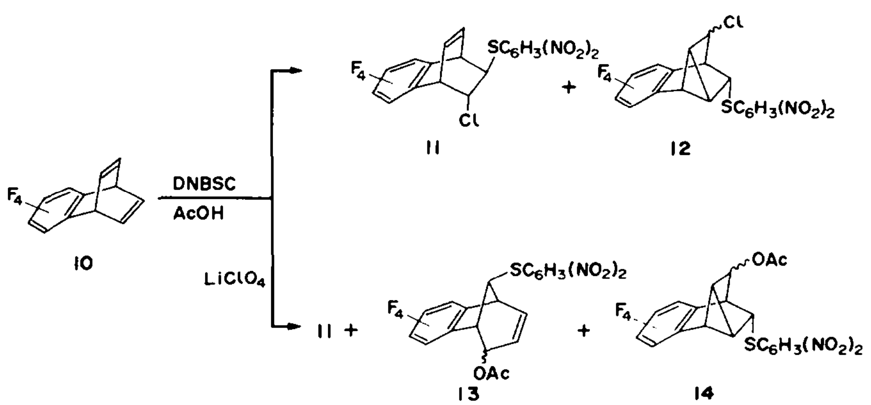
$[LiClO_4]$ M	Total yield of **7**+**9** (mol %±5%)[a]	Yield of **7** (^{1}H-NMR)	Yield expected in accordance with Eq[b] 100% $(k-k_0)/k$
0	13	13	0
0.0025	21	16	1.3
0.005	35	22	2.6
0.01	40	25	5.1
0.02	43	29	10
0.03	44	33	14
0.04	46	34	18
0.05	55	38	21
0.06	55	38	25
0.08	62	41	30
0.09		43	33
0.1		44	35

[a] By bromide–bromate method.

[b] See text for explanation; *k*-values were calculated using Eq. (2) and data of Table 3.

The addition of DNBSC to the tetrafluorobarrelene, **10**, in AcOH proceeds to give the adduct **11** together with tricyclic chloride **12** (<2% yield). In the presence of $LiClO_4$ the products are the chloride **11**, a mixture of the two epimeric acetates **13** and the epimeric tricyclic acetates **14** (<7% yield). At high concentrations of the





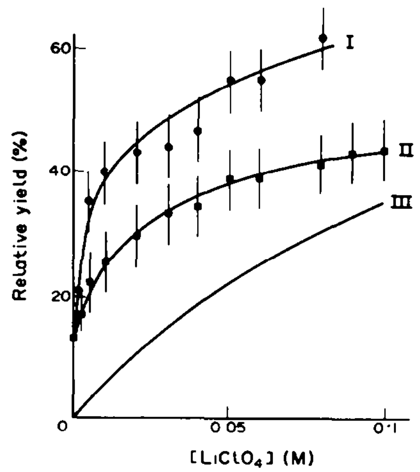


Fig. 1.

added salt (0.2–0.25 M) the formation of acetates **13** is the dominating process; the dependence of the yields of the doping-addition products on $[LiClO_4]$ is shown in Table 2.

In both cases (Tables 1 and 2) we have observed a sharp increase in the content of doping-addition products (as well as the rearranged chloride **7**) at low concentrations of the salt, which was followed by a moderate increase at higher concentrations.

Table 2. A dependence of the yield of acetates **13**+**14** on $[LiClO_4]$ for the addition of DNBSC to the olefin **10**

$[LiClO_4]$ M	Relative yield of acetates **13**+**14** (±5%)	Yield expected in accordance with eq[a] $100\% \cdot (k-k_0)/k$
0	0	0
0.01	14	7
0.015	19	10
0.02	25	13
0.04	31	24
0.075	40	37
0.15	46	54
0.20	57	61
0.25	62	66

[a] See text for explanation; k-values were calculated using Eq. (2) and data of Table 4.

Kinetic data

The rates of the addition were measured in AcOH by the standard titrimetric method.[4a] The additions were found to exhibit normal second-order kinetics, first order in both olefin and DNBSC. We have studied the dependence of the rate of the addition reactions on the $[LiClO_4]$ over a wide range of salt concentrations; the data for olefin **5** are shown in Table 3 and in Table 4 for olefin **10**.

The treatment of these data in accordance with the equation for the normal salt effect (Eq. 2)[27] gives nice linear correlations (Tables 3 and 4), the parameter b being 5.4 for addition to **5** and 7.7 for addition to **10**. We should like especially to emphasize the absence of a special salt effect[28–30] for the studied reactions, an observation that is in agreement with previous kinetic data[14b] (*vide infra*).

$$k = k_0(1 + b[LiClO_4]) \quad (2)$$

It is important that the relative increase in the

Table 3. Second-order rate constants for the addition of DNBSC to olefin **5** in acetic acid at 20° in presence of varying amounts of $LiClO_4$

[olefin **5**] × 10^2 M	[DNBSC] × 10^2 M	$[LiClO_4]$ M	$k \times 10$ ($M^{-1}\,s^{-1}$)	$k_{av} \times 10^a$
0.73	0.73	0	1.71±0.02	1.71±0.05
1.48	0.53	0	1.71±0.02	
0.53	0.53	0	1.74±0.02	
0.56	0.56	0	1.67±0.01	
0.93	0.93	0.02	1.85±0.02	1.84±0.05
0.85	0.85	0.02	1.86±0.02	
0.53	0.53	0.02	1.82±0.01	
0.93	0.93	0.04	2.08±0.02	2.08±0.11
0.73	0.73	0.04	2.13±0.02	
1.17	0.59	0.04	2.02±0.03	
1.27	0.50	0.04	2.07±0.01	
0.93	0.93	0.06	2.17±0.02	2.13±0.09
0.66	0.50	0.06	2.11±0.04	
1.82	0.62	0.06	2.11±0.02	
2.00	0.62	0.08	2.00±0.03	2.37±0.82
1.02	0.50	0.08	2.62±0.04	
1.40	0.76	0.08	2.50±0.02	
1.07	0.62	0.10	2.69±0.07	2.64±0.2
1.00	0.50	0.10	2.55±0.08	
1.40	0.76	0.10	2.69±0.05	

Calculated for Eq. (2): $k_0 = 0.168$; $b = 5.4$; $r = 0.987$.
[a] Error is found using Student criterium ($\alpha = 0.95$).

Table 4. Second-order rate constants for the addition of DNBSC to olefin **10** in acetic acid at 30° in presence of varying amounts of $LiClO_4$

[olefin **10**] × 10^2 M	[DNBSC] × 10^2 M	[$LiClO_4$] M	$k \times 10^3$ ($M^{-1}\,s^{-1}$)	$k_{av} \times 10^{3}$ [a]
4.99	4.16	0	1.25±0.10	1.24±0.08
4.98	9.84	0	1.27±0.08	
4.15	6.34	0	1.13±0.06	
2.50	2.84	0	1.30±0.10	
5.00	9.84	0.04	1.35±0.13	1.44±0.11
4.08	5.72	0.04	1.39±0.16	
1.83	1.83	0.04	1.41±0.19	
2.05	2.05	0.04	1.60±0.04	
2.43	4.39	0.06	1.40±0.08	1.60±0.13
1.79	3.30	0.06	1.60±0.14	
2.42	2.42	0.06	1.58±0.17	
1.83	1.83	0.06	1.66±0.12	
2.05	2.05	0.06	1.76±0.01	
2.67	2.84	0.08	1.97±0.14	1.78±0.13
2.97	4.39	0.08	1.69±0.16	
4.00	5.72	0.08	1.68±0.18	
1.88	1.88	0.08	1.79±0.06	
4.18	4.39	0.10	2.09±0.08	1.95±0.18
3.29	3.30	0.10	1.96±0.13	
4.23	5.72	0.10	1.70±0.15	
1.33	1.87	0.10	1.85±0.12	
2.05	2.05	0.10	2.17±0.06	
1.73	1.73	0.12	2.20±0.25	2.21±0.02
1.83	1.83	0.12	2.23±0.06	
1.73	1.73	0.15	2.47+0.21	2.38±0.13
1.83	1.83	0.15	2.29±0.35	
1.73	1.73	0.20	2.93±0.27	2.93±0.01
1.85	1.85	0.20	2.93±0.07	
1.85	1.85	0.25	3.25±0.06	3.31±0.08
1.73	1.73	0.25	3.36±0.09	

Calculated for Eq. (2): $k_0 = 1.13 \times 10^{-3}$; $b = 7.7$; $r = 0.996$.

[a] Least-square error.

doping-addition products is much ahead of the enhancement of the rate due to the normal salt effect dependence. For both additions we have calculated the possible yield of product for catalytic flow, determined by the term $k_0 \cdot b \cdot [LiClO_4]$ (we have used the expression $100 \times (k_{obs} - k_0)/k_{obs}$).[28] These data are presented in Fig. 1 and Tables 1 and 2, and clearly demonstrate this point. If the doping-addition products for **5** were formed in an independent catalytic flow in accordance with the increase in the rate due to the term $k_0 \cdot b \cdot [LiClO_4]$, their yield should be represented by curve III in Fig. 1. Thus, the catalytic influence of $LiClO_4$ on product formation is much more pronounced than expected from the normal salt effect dependence.

DISCUSSION

The most important results of the present study are the following: (1) the addition of lithium perchlorate leads to an increase in the rate (i.e. in the reagent electrophilicity[7,14a]) in accordance with the equation of the normal salt effect; (2) both reactions studied show the doping-effect (i.e. increase in the effective electrophilicity[7] of the reagent); (3) the dependence of the yields of the doping-addition products exhibits a strikingly rapid non-linear rise with the addition of small concentrations of the salt followed by a more modest increase (Tables 1 and 2); (4) the addition reaction to cyclopropene **5** gives an appreciable yield of the rearranged chloride **7**, a content that is also increased with an increase in [$LiClO_4$]. These facts lead to several important mechanistic conclusions that are developed below.

Before proceeding further, it is expedient to summarize briefly those mechanistic points extracted from the kinetic data which proved the two-step mechanism of RSCl addition to olefins. The uniformity and simplicity of the kinetic description of this addition, namely clear second-order kinetics, first order in both sulfenyl chloride and alkene, has been definitely documented.[1,23,25a,c] The electrophilic character of these additions has been supported with a number of Hammett type correlations with the corresponding ρ (or ρ^+) values being negative.[1,4,25] It should be recognized, however, that these kinetic data for the RSCl additions leading to 1,2-chlorosulfides as a single reaction product do not prove the suggested two-step mechanism;[22] even the one-step concerted mechanism (e.g. the one with orthogonal approach of the RSCl to olefin moiety)[31] is consistent with these kinetic data.

Thus, the most significant observation is the existence of good second-order kinetics (and Hammett correlation) for the olefins in reactions that give a mixture of solvoadducts,[25c] rearranged and non-rearranged products,[11,14b] and stereoisomers.[32] These data definitely support every two-stage mechanism (including the one originally proposed by Kharasch; Scheme 1) with the first step being rate determining. In other words, these data do not show any indication of a change in the structure of the rate determining transition state while product structure/s is changed rather drastically.

Let us consider now the influence of perchlorate and the mechanism of the doping-addition. The first interpretation of this phenomenon was suggested by us in 1975:[8] "... the action of the salt added is not connected with an increase of the RS—Cl bond polarity in the initial reagent ... The salt participation is effective at some intermediate step of the reaction. In the absence of a special investigation we can only assume that the mechanism operating here resembles the one proposed for the special salt effect in solvolysis. The addition of $LiClO_4$ suppresses internal return in the solvent separated ion-pair (**2**) due to the exchange reaction between the **2** and $LiClO_4$". A shortened version of this mechanism[8] is presented in Scheme 3.[33]

Thus the suggested version of the mechanism of doping-addition[8] included principally two points. Firstly, it is the acceptance of ion-pair intermediate/s (of type **2** and **3**) but not a pure episulfonium ion **1** for the rate limiting step.[34] Secondly, it is the assumption that the *fast* exchange between ion-pair **2** and lithium perchlorate produces a more electrophilic and hence more reactive perchlorate ion-pair **15** in accordance with the Winstein concept of "the special salt effect".[29] This general picture has been explained further.[2,3,5,11,14b]

The particulars included the elaboration of the experimental criteria for recognizing ion-pair intermediacy and for differentiating their types.[3,5] In principle, these criteria take into account the more manifested participation of the counter ion (e.g. Cl^-) in the final step of the reaction in competition with external nucleophiles (e.g. nucleophilic solvent) as compared with the purely ionic mechanism (Scheme 1). Recognition of these aspects offers an explanation for the (i) formation of rearranged chlorides (but not acetates!) and (iii) stereoselectivity of the addition pathways (for a detailed discussion, see refs 3 and 5).

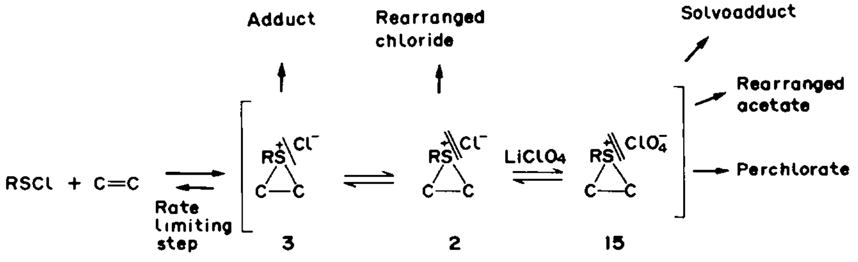
The addition reactions to **5** and **10** in AcOH in the absence of $LiClO_4$ proceed to give the chlorides (**6**+**7** and **11**+**12**, respectively) with the absence of a noticeable amount of acetates, which means the intermediacy of some sort of "tight" intermediate in accordance with earlier suggestions.[3,5] Moreover, the addition to cyclopropene **5** proceeds to give an appreciable amount of the rearranged chloride **7** in the nucleophilic media which, as stated previously,[3,5] may also be regarded as evidence for the involvement of an ion-pair intermediate which bears a positive charge on the carbon at least sufficiently developed for the rearrangement into the allylic structure **7**, but without the full separation of the chlorine anion. Thus, one is faced with the decision to accept either one ion-pair intermediate reacting in two directions to give normal and rearranged products, or two different ion-pair intermediates of different polarity, each giving its own product. To simplify the pictorial representation of the mechanism, we shall accept the second point of view, interpreting the data in terms of the tight ion-pair **3** for the formation of the normal adduct and of solvent separated ion-pair **2** for the formation of the rearranged adduct (chloride!) as it is shown in Scheme 3.[35]

It has been suggested previously[2a,5] that one of the mechanisms of $LiClO_4$ influence on the effective electrophilicity of ArSCl may be due to the shift of the intermediate structure toward a more polar one. The observation of an increase in the chloride **7** yield with an increase in $LiClO_4$ concentration (Fig. 1) may be regarded as support for this mechanistic statement, being interpreted as the shift of **3** → **2** in presence of the added salt (*vide infra*).

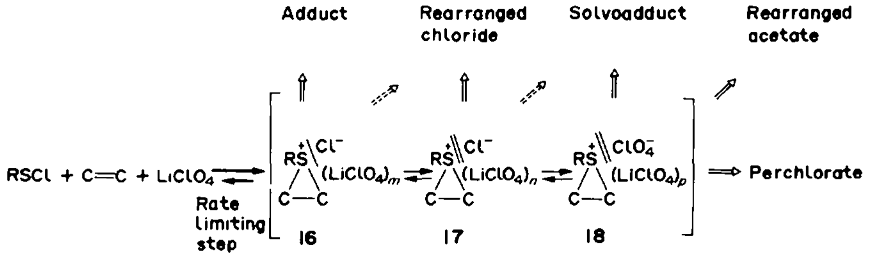
Consider now the kinetic arguments. We have found earlier[14b] that the addition of DNBSC to a series of allylbenzenes follows the Hammett equation with and without added $LiClO_4$ with approximately equal ρ values ($\rho = 2.34$; ρ $LiClO_4 = 2.59$) which seems to suggest that added $LiClO_4$ does not influence significantly the polarization of RSCl. It was also found that the increase in rate follows the equation of the normal salt effect (Eq. 2).[14b,36]

In the present paper we provide additional proof for the significant acceleration of the reaction by $LiClO_4$ in accordance with equation of the normal salt effect. The observed values of parameter b, 5.4 and 7.7 for the reactions of **5** and **10**, respectively, correlate quite well with the previous value $b = 7$ for the addition to allylbenzene.[14b] Thus, the presence of added $LiClO_4$ *does* increase the electrophilicity of RSCl (despite claims to the contrary)[37] in accordance with normal salt effect dependence (Eq. 2).

From the formal kinetic point of view, the normal salt effect can be regarded as one example of a homogenic catalytic reaction, the value $k_0 \cdot b$ being the rate constant of the catalytic flow. While the mechanism of this effect is still unknown, one may suppose the



Scheme 3.



Scheme 4.

existence of an interaction between the molecule/s of $LiClO_4$ and the organic matrix in the transition state for the rate limiting step.

The question which immediately arises is how to accommodate the involvement of the salt in the rate determining step with the mechanism of Scheme 3. Indeed, the structure of a transition state as well as of an intermediate of type **3** should also include the involvement of molecules of the salt as a cluster complex (cf. ref. 38). We depict the structure of such a multiplet complex in the most deliberate manner by the inclusion of an indefinite number of molecules of the salt in the ion-pair brackets. The mechanism of catalytic flow is represented by Scheme 4, which includes the clusters of ion-pair type **16** and **17**. Indeed, we do not know the exact structure of these intermediates **16** and **17**, i.e. the type of bonding between the salt matrix and organic framework or, for that matter, even the stoichiometry for that interaction (cf. ref. 38). However, the change in the reactivity of ion-pair clusters **16** and **17** as compared with the parent ion-pairs **3** and **2**, respectively, is quite clear: one may expect an increase in rearranged and solvent-incorporated products for the processes proceeding via clusters **16** and **17**.

Thus, the addition of the salt leads to the appearance of new kinetic flow in accordance with Eq. (2) due to the inclusion of the molecule/s of the salt added into the inner shell of the transition state leading to the new ion-pair clusters (**16** and **17**), the type and concentration of which are proportional to the concentration of $LiClO_4$. The reactivity of these species **2**, **3**, **16** and **17**, as well as the balance between them, is subject to the effects of the medium and the nature of olefins and hence the relationship to the observed product ratio.

Consider now the product-determining steps of the reaction. Our mechanism of doping addition (Scheme 3) explained the effect of the added $LiClO_4$ on the product composition *via* an exchange of chloride ion by perchlorate ion in solvent separated ion-pairs, **2**, **15**. Obviously, the mechanism of such a process is identical to the one accepted for the special salt effect.[29]

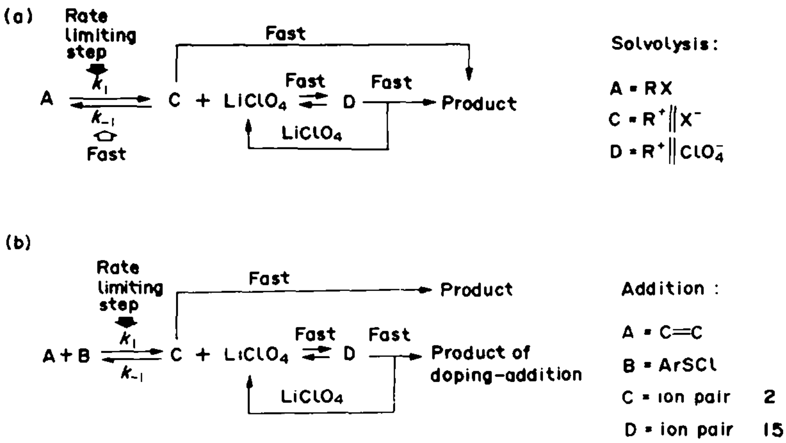
Previous studies have revealed the dependence of the yield of doping-addition products on the $LiClO_4$/DNBSC and $Et_4N^+ClO_4^-$/DNBSC ratio.[11,14b,25c] Unfortunately, these data have not been correlated with rate measurements. The study of product compositions performed in the present paper (Tables 1 and 2) reveals a remarkable result: we have found a rapid *increase in the yields* of the doping-addition products at low concentrations (up to 0.01–0.02 M) of the added salt. What is more, the observed increase in yield significantly exceeds the one expected from the *increase in the rate* due to the second term, $k_0 \cdot b \cdot [LiClO_4]$, Eq. (2) (Fig. 1). In other words, at low concentrations of $LiClO_4$ the doping-addition pathway surpasses catalytic flow as predicted by the equation of the normal salt effect. This sharp increase is followed by much less pronounced rise in the yields of doping-addition products with $[LiClO_4]$ for higher concentrations of the salt (Tables 1 and 2).

These data reveal the complex mechanism of the $LiClO_4$ influence and at the same time they can be regarded as evidence for the previously suggested idea regarding the "specific" influence of the salt via its catalytic participation due to the exchange of type **2**, **15** (Scheme 3) or of type **17**, **18** (Scheme 4). Indeed, low concentrations of $LiClO_4$ only slightly promoted the formations of clusters of type **16** and **17** as compared with chloride ion-pairs **2** and **3** and the rise in the total rate is small (in accordance with Eq. 2). At the same time, the salt is actively included into the catalytic cycle (Chart 1) for the fast steps of the process due to the rapid exchange of type **2**, **15** (and **17**, **18**) and hence sharply influences the yield of doping-addition products. At concentrations of 0.01–0.02 M, the added salt provides a completion of the catalytic flow **2**, **15** (and **17**, **18**) and the "specific" influence of $LiClO_4$ achieves its maximal value. Thus, additional amounts of the salt change the rate by changing the properties of media under a constant contribution of the "specific" influence.

The slow increase in the yield of the doping-addition products at higher concentrations of the added salt is consistent with the increase in the rate (Eq. 2) due to the incorporation of the term $k_0 \cdot b \cdot [LiClO_4]$ (Fig. 1). In this case, the influence of the $LiClO_4$ should be connected with the increase in the pathway *via* the clusters **16** and **17** as compared with the ion-pairs **3** and **2** as well as with the change in their reactivity with the change in the number of the salt molecules associated within the brackets. In other words, this process may be regarded as a competition of the kinetic flow *via* **3** and **2** with the one *via* **16** and **17**, and an increase in $[LiClO_4]$ favors the latter flow. It is reasonable to accept that the $S \cdots Cl$ bonding in ion-pairs **3** and **2** is tighter than in clusters **16** and **17** respectively (cf. ref. 38), and hence the exchange process $\mathbf{16} \rightarrow \mathbf{17} \rightarrow \mathbf{18}$ is faster than the process $\mathbf{3} \rightarrow \mathbf{2} \rightarrow \mathbf{15}$. This consideration permits one to explain the increase in the yield of both the doping-addition products with the incorporation of external nucleophile and the rearranged chlorides (chloride **7** in the present paper).

In conclusion, it is worthy to consider the kinetic schemes of the special salt effect[29] and the doping-effect[2,3,5,8,12] to evaluate the difference and relationship of these phenomena. The algebraic notions of the

Chart I



kinetic schemes are shown in Chart 1. Obviously, the doping-addition puts the emphasis on the product ratios and operates for Ad$_E$ reactions, while the "special salt effect" is kinetic in nature and is related to solvolyses. However, the kinetic schemes of these processes are reasonably similar (Chart 1) and one may question why the specific influence of LiClO$_4$ on the rate is absent in the case of the addition.

It is usually agreed that the occurrence of a special salt effect indicates the fast formation of intermediate **D** (Chart 1(a)) which prevents the return to the starting material **A**. Hence the existence of reversibility (k_{-1}) kinetic flow as well as the relative magnitude of k_{-1} is important for the appearance of the specific salt effect as a kinetic phenomenon. This is the direct consequence of the kinetic equations for this salt effect.[28,29] The application of this logic to the addition process of Chart 1(b) shows that kinetic special salt effect could also be observed if the rate-limiting step were reversible and k_{-1} had the proper magnitude, comparable with the rate constants of the fast steps.[39]

In the case of RSCl addition, the Cl$^-$ of the ion-pairs **2** and **3** (Scheme 3) may attack the carbon atom to give adducts, but it may also attack the sulfur and return to starting material. The reversibility of the rate limiting step has been accepted from the observation of an exchange of the ArSCl moiety between adducts and olefins.[40] For example, the addition product of ClC_6H_4SCl to cyclooctene readily exchanges ClC_6H_4SCl with 1-octene.[40] An alternative explanation involving attack of 1-octene at the sulfur atom of intermediate ion-pairs has been considered as unlikely.

However, the absence of the "special" increase in the rate forces us to the conclusion that the reverse process, measured by k_{-1}, is relatively unimportant, and the **A** + **B** → **C** transformation (Chart 1(b)) may be regarded as a non-reversible rate-limiting step for the whole process. In this case, the subsequent trapping of **C** by the salt influences the product distribution, but does not influence the total rate.[39]

While it is impossible to generalize this statement at present, it may be used as a guideline in the search for cases of the specific salt influence on the rate. The likelihood of finding this phenomenon is more probable for those olefins (i) where the double bond is less prone to be transformed into a three-membered ring[41] and (ii) which provide a steric hindrance to attack from the backside of ion-pairs **2** and **3**. Our investigation of the addition of the 2-nitrobenzenesulfenyl chloride to dimethyl[4,2,2,0^{2,5}]-deca-3,7,9-triene-9,10-dicarboxylate[36b] may satisfy these requirements but the detailed discussion of this problem is beyond the scope of the present paper and will be presented in a special publication.

EXPERIMENTAL

Materials

5 was synthesized by a previously reported method.[42] The samples of **5** for kinetic studies were purified by a twofold low temperature distillation. The olefin **10**[43] was recrystallized twice from EtOH. DNBSC was purified by crystallization from CCl_4 to 100 + 1% (by iodometric titration). AcOH was dried over phosphorous pentoxide and carefully distilled $LiClO_4$ was carefully dried *in vacuo*.

Product determination

The content of the reaction mixtures and the product ratios were determined by ^{1}H-NMR (and ^{19}F-NMR in the case of **10**). For the addition to **5** the content of rearranged products (**7** + **9**) was examined further by the bromide–bromate method as follows: a sample (0.02–0.1 g) of the reaction mixture after evaporation of the solvent was dissolved in 10 ml of AcOH and 5 ml of 0.1 N standard bromide–bromate solution was added. Then 5 ml of conc HCl was added via a specially closed funnel, the mixture was allowed to stand for 5–8 min, 10 ml of 10% KI was added, and after 5 min iodine was determined by titration with 0.01 N thiosulfate. A blank was performed simultaneously. The error was ±2% in the case of specially prepared mixtures, but was only ±5% in the case of actual reaction mixtures.

Kinetics

The kinetics for the reactions of DNBSC with olefins **5** and **10** were performed in AcOH (at 20° for **5** and at 30° for **10**) by reported methods.[44] $LiClO_4$ and the olefin were dissolved and the resulting solution was rapidly mixed with the solution of DNBSC in AcOH. A pre-cooled (−40°) calibrated syringe was used to measure the desired amounts of cyclopropene **5**. Aliquots were removed at appropriate intervals and analyzed for remaining sulfenyl chloride.[44] Good second-order plots (followed to 55–80%) were obtained in all cases. The data are shown in Tables 3 and 4.

Reaction of DNBSC with cyclopropene **5**

The appropriate amount of $LiClO_4$ was added to a solution of **5** in AcOH (25 ml; 0.03–0.11 M) and then a solution of DNBSC in AcOH (0.025–0.1 M) was added in the dark at room temperature. The usual work up[3,5,13] gave the residue which was analyzed by ^{1}H-NMR and the bromide–bromate method. Preparative TLC chromatography (Al_2O_3; ether : hexane = 7 : 3 or SiO_2; ether : hexane = 1 : 1) was used to isolate the products. The compounds **6**, **7** and **9** have been described previously.[13] The acetate **8** was obtained by chromatography as an enriched fraction (mixture with **9**) and its actual content (< 2%) and structure were determined by ^{1}H-NMR (ppm, TMS): 1.1–1.3 (m, 2H, CH_2), 1.6 (s, 3H, CH_3), 2.04 (s, 3H, $COCH_3$), 2.3–2.6 (m, 1H, CH).

Reaction of DNBSC with olefin **10**

(a) 3.11 g of DNBSC in 15 ml of AcOH was added to 3 g of **10** in 15 ml of AcOH and after a week, solid crystals of the adduct **11** were removed by filtration (4.95 g), dried, and recrystallized from EtOH–AcOEt, m.p. 185° (cf. ref. 26). The residue was chromatographed on silica gel (ether : hexane : acetone = 1 : 3 : 1) and 0.41 g of the crude chloride **12** was obtained. Analytical sample had m.p. 173–175°.[26]

(b) 20 ml of a 0.1 M solution of DNBSC in AcOH was added to 20 ml of 0.1 M **10** in AcOH containing 0.05 mol of $LiClO_4$ and the resulting solution was left in the dark for 60 hr. The usual work up and chromatography (TLC, silica gel, ether : hexane : acetone = 1 : 3 : 1) gave (i) the adduct **11**; $R_f \sim 0.6$ (25%), (ii) a mixture of epimeric acetates **13**; $R_f \sim 0.68$ (35%), *endo* : *exo* ratio 1 : 3 : (by ^{19}F-NMR), m.p. 175–177°, (iii) a mixture of epimeric acetates **14** (5–7%), as an oil which crystallized upon treatment with ether; m.p. 88–90°. The mixture of epimeric acetates **13** was resolved by chromatography (TLC, silica gel, benzene) to give the *exo*-isomer, m.p. 178° and the *endo*-isomer, m.p. 208°.[26]

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[7a] To escape misunderstanding this term[3,5,7c,8–10] needs to be clarified further. For simple substitution reactions the terms "nucleophilicity" and "electrophilicity" are used in a kinetic sense and reflect the relative rates of the processes. In other words, a "strong nucleophile" reacts faster than a "weak nucleophile" with the same electrophile and *vice versa*. However, for multistage reactions these notions must be applied exclusively to the rate-limiting step. For example, in the case of electrophilic additions to olefins only the comparison of total rates can be performed in terms of "electrophilicities" of reagents. It is quite evident that this notation does not permit one to describe the changes in characteristics of intermediates for the fast product-determining step.

Indeed, the addition of electrophilic reagents to double bonds can provide at least three types of reactivity including (i) normal 1,2-addition of the reagent, (ii) 1,2-addition with incorporation of the external nucleophile at the final step, and (iii) skeletal rearrangement/s of the carbocation type. Hence, the ratio of pathways (ii)/(i) and (iii)/(i) are valuable characteristics of the addition process, but which are ignored by a pure kinetic description in terms of electrophilicity of reagents.

It was found empirically that "strong electrophiles" often give an increase in the content of rearranged product/s and vice versa. Moreover, the "electrophilicity" of the reagent in addition reactions was often accepted as a measure of the positive charge generated at the carbon atom.[7b] At first we also suggested the use of the ratio of the pathways (iii)/(i) as a measure of the electrophilicity of reagents.[8] However, this "rearrangement ability" of reagents, namely (iii)/(i) product ratio, has to be labelled more adequately by a special term, and we have used the notion "effective electrophilicity" for this purpose.[3,5,7c,9,10] In accordance with that definition an "effectively strong electrophile" generates an intermediate which is more capable of skeletal carbocationic-like rearrangement than the "effectively weak" one.

The term "effective electrophilicity" is probably not perfect and can be even misleading. What is definite is that there exists a need of special terms to label those properties of electrophilic reagents which are measured by (ii)/(i) and (iii)/(i) ratios, because they permit one to gain an insight into fast and preparatively valuable step/s of Ad_E processes. [b] K. E. Green and L. A. Paquette, *J. Org. Chem.* **48**, 1849 (1983); L. A. Paquette, L. W. Hertel, R. Gleiter, M. C. Bohm, M. A. Beno and G. G. Christoph, *J. Am. Chem. Soc.* **103**, 7106 (1981) and refs therein; [c] N. S. Zefirov, N. V. Zyk, A. A. Borisenko, M. Yu. Kreysin and T. G. Shestakova, *Tetrahedron* **39**, 3145 (1982).

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[36a] Literature data pertaining to the salt effect on the rate of RSCl addition to olefins are scarce. The normal salt effect for LiCl + NaClO$_4$ with $b = 3.25$ was reported[4a] and our recent data[36b] describe the normal salt effect of LiClO$_4$ at large concentrations with $b = 5.52$. Kwart *et al.*[36c,37b,c] found a normal salt effect for LiClO$_4$ in the chlorination of ArSCl with *b* being in the range 5–25. [b] R. Caple, I. S. Kislina, A. S. Koz'min, A. B. Nikitin, M. I. Vinnik and N. S. Zefirov, submitted for publication; [c] E. N. Givens and H. Kwart, *J. Am. Chem. Soc.* **90**, 386 (1968).

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