유기 황화합물의 친핵성 치환반응(제 7 보).
염화벤젠술페닐의 형태와 가에탄올 분해

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Nucleophilic Displacement at Sulfur Center(VII).
Conformation and Ethanolysis of Benzenesulfenyl Chloride

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요 약. 염화벤젠술페닐의 바람직한 형태를 EHMO 법으로 구하였다. 이 형태의 안정도는 황원자와 벤젠고리 사이의 n-π 콘쥬게이션에 따른다는 것을 알았다. 또 염화벤젠술페닐의 가에탄올 분해반응을 연구하여 얻은 반응속도상수를 치환기 효과와 황원자의 d-궤도함수 기여로 논의하였다.

비선형 Hammett 그래프로 부터 쌍뿔형의 중간체를 제안할 수 있었다.

ABSTRACT. The preferred conformation of benzenesulfenyl chloride was determined by EHMO calculation. It was found that the stability was dictated by the n-π conjugation of S atom with the benzene ring.

The ethanolysis reaction of benzenesulfenyl chlorides has been studied. The rate constants obtained have been discussed in terms of substituent effects and d-orbital participation of sulfur atom. From a non-linear Hammett plot, bipyramid type of intermediate has been suggested.

INTRODUCTION

Nucleophilic displacement at carbon center has been investigated extensively. Recently, however, the industrial as well as biochemical importance prompted studies on the reactivities of the 3rd row elements.[1] These elements possess vacant d-orbitals adjacent to p-orbitals and participation of these d-orbitals in the nucleophilic substitution (S_N) reaction have been attracting considerable interests of both theoretical and experimental investigators. In general, the mechanism of the S_N reaction at these elements is interpreted with S_N2[2] or S_AN[3] mechanism, analogously with those at carbon center.

Divalent sulfur is reported to behave similarly with methylene carbon in the nucleophilic displacement reaction[2], proceeding via S_N2 or S_AN. Electrostatic repulsion between the incoming anion nucleophile and the leaving group favors back site attack and it is therefore likely to proceed via S_N2 mechanism for anion nucleophiles. On the other hand, there will be no such repulsion in the case of neutral nucleophile and trigonal bipyramid type of intermediate,

(A), is highly conceivable especially in view of the low lying vacant d-orbitals available. [1]
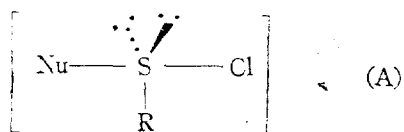

In this type of intermediate, sulfur will have valence state of sp^2d hybridization, while MO theoretical studies seem to support sp^3 hybridized state for the ground state. [4]

In the present study molecular orbital calculations on the molecular conformation of benzenesulfenyl chloride were carried out using the Extended Hückel Theory (EHT), [5] and the ethanolysis rate constants were determined for some substituted benzenesulfenyl chlorides in order to investigate the S_N mechanism of divalent sulfur center. Results of onr study seem to support the trigonal bipyramid type (A) mechanism (S_AN). Our literatnre survey shows that there is no previous report on kinetic studies of ethanolysis of benzenesulfenyl chloride.

EXPERIMENTAL

MO Calculation. Method and program used in the EHT calculation were the same as described before. [6] Bond length and bond angles used in the calcnlation of molecular geometry were the standard values obtained from the literature. [7] Numbering scheme used is shown below.
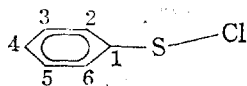
Conformation was varied by using different bond angles of α (bond angle, C_1—S—Cl) and β (dihedral angle, C_6—C_1—S—Cl).

The atomic orbitals of sulfur atom were employed up to its $3p$ orbitals, since it has been shown that the inclusion of $3d$ orbitals resulted in unreasonable aspects from experimental fact. [4]

Ethanolysis Ethanol used was 99.8 % G. R.

grade (E. Merck). Carbon tetrachloride (G. R. of E. Merck) was dried over calcium chloride overnight and then dried over P_2O_5 again, after which it was distilled in a Todd Column.

p-NO_2-, p-Cl-, p-CH_3- and p-H-benzenesulfenyl chlorides were obtained by chlorinating corresponding thiols or disulfides in anhydrous CCl_4. These compounds were analysed by the method of Kharash and Wald. [8] p-$NO_2C_6H_4SCl$, m. p 50~51°C. [9] p-ClC_6-H_4SCl, b. p 83~85°C/ 2 mm. [10] p-$CH_3C_6H_4SCl$, b. p 68~70°C/2 mm. [11] C_6H_5SCl, b. p 48~50 °C/0. 8 mm. [12]

Rates were followed by conductivity method using Beckman RC–18A type conductivity bridge. Cells used had cell constants of 0. 1~0. 5 cm^{-1} and temperature control was better than to ±0. 005 °C. Reaction solution consisted of about 0. 4−4×10^{-4} M benzenesulfenyl chlorides in the excess ethanol. Pseudo–first order rate constants were obtained from Guggenheim plot. [13]

RESULTS and DISCUSSION

Conformation. Results of the EHT calculations are summarized in *Table* 1. Two features of interest are readily recognized. Firstly, the preferred conformation is the coplanar form (I), and secondly the sulfur atom has sp^3 hybridized valence state. This latter is shown by the higher energies of the forms (IV) and (V) which have deviations of bond angle, α, from the sp^3 state. These are in good agreement with the CNDO/2 result of Fukui *et al.* [4] In their paper Fukui and coworkers[4] suggested that the stabilization of (I) may be attributed to the π-conjugation effect between the lone pair (nonbonding, n) electrons on the sulfur atom and the π-electrons on the benzene ring (n-π conjugation). This suggestion is nicely confirmed in a quantitative and concrete manner in *Table* 1, where we can see that the order of increasing stability for sp^3 hybridized conformations, i. e., (III), (II)

Table 1. EHT analysis of conformation of benzenesulfenyl chloride.

Conformation		E_T(kcal/mol) (Total energy)	Net formal atomic charge		Overlap population	
$\alpha(°)$	$\beta(°)$		S	Cl	ClS	SCl
I 109.5,	0	—16740.0893	+0.1356	—0.2466	0.7312 (0.0386)*	0.4906
II 109.5,	30	—16739.4193	+0.1206	—0.2472	0.7232 (0.0341)	0.4879
III 109.5,	90	—16736.2543	+0.0714	—0.2447	0.6967 (0.0220)	0.4807
IV 90	90	—16730.1599				
V 90	0	—16716.2155				

*Values in ( ) is contribution of the π bond to the overlap population.

Table 2. Rate constants for ethanolysis of benzenesulfenyl chlorides. ($k \times 10^4$ sec^{-1}).

Substituent	25°	35°
p-CH$_3$	1.51	2.77
p-H	2.11	3.16
p-Cl	1.67	3.08
p-NO$_2$	0.37	0.87

and (I), is in the order of increasing overlap population of C_1S bond. Furthermore, the π-overlap contribution for the C_1S bond which is the measure of n–π conjugation suggested is also in the order of stabilities of these conformations.

Thus we can also conclude that the preferred conformation of benzenesulfenyl chloride is the coplanar form and the stability is dictated by the degree of n–π conjugation.

Ethanolysis. Pseudo-first order rate constants obtained are summarized in Table 2. These rate constants were found consistent within experimental error of $\sim\pm3$ % upon changes in substrate concentrations. The reaction was normally followed up to$\sim$90 % completion with average of 20 points in the Guggenheim plot. Good linearities obtained for the Guggenheim plot constituted strong evidence that the first step in the ethanolysis is rate determining.

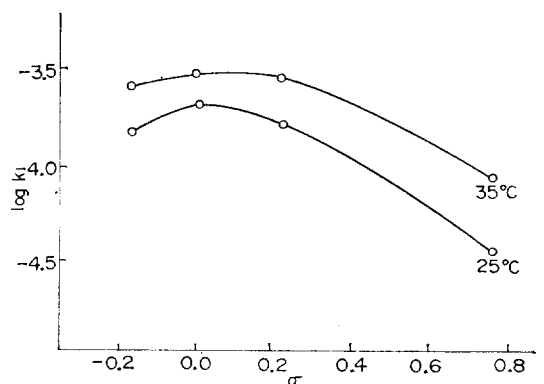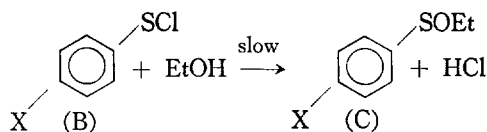It has been reported that the product(C) seem to transform in subsequent fast steps to

Fig. 1. Hammett plot for ethanolysis benzenesulfenyl chloride.

give disulfides, disulfoxide or thiosulfonic ester. [14] If any of these subsequent steps were the rate-determining, the kinetics would have been extremely complicated and the Guggenheim plot would have been non-linear. [15]

Table 2 also shows that both electron donating (p-CH$_3$-) and electron withdrawing (p-Cl and p-NO$_2$) groups retard the reaction rate, although the effect upon rate is not large. Thus we obtain a non-linear Hammett plot, Fig. 1, where the curve is slightly convex. The convex Hammett plot was obtained also in the reaction of benzaldehyde with n-butyl amine. [16] This was inter-

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Table 3. Activation parameters for ethanolysis of benzenesulfenyl chlorides (ΔH^*(kcal/mol) and $-\Delta S^*$(e. u.))

Substituent	ΔH^*	$-\Delta S^*$
p-CH$_3$	10. 5	23
p-H	6. 8	34
p-Cl	10. 6	22
p-NO$_2$	14. 9	24

preted as the possible change in rate controlling step from the reversible addition of amine to aldehyde, which is favored by electron withdrawing substituents, to the subsequent dehydrationstep which is accelerated by electron donating substituents. Analogous change in the rate controlling step may occur in the ethanoltysis of benzenesulfenyl chloride although the effect is very small. In this case the electron-donating group stabilizes the ground state by enhanced n–π conjugation and therefore extra activation energy is required to break this conjugation in the formation of the bipyramid intermediate, i. e., in the process of rehybridization from sp^3 to sp^2d, while the leaving of Cl$^-$ ion is made difficult by the electron withdrawing group since partial breaking of S—Cl bond of bipyramid may now be the rate determining and this will require extra energy for the substrate with electron withdrawing group resulting in the rate decrease.

In Table 3, activation parameters based on rate constants at two temperatures are summarized. We do not attach much mechanistic significance to these results since they are not precise enough. However, general trend in activation parameters are in accord with our mechanistic interpretations of MO theoretical and rate results described above.

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