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OBSERVATION OF THE CATIONS PRODUCED FROM CHLOROTHIOPHENES

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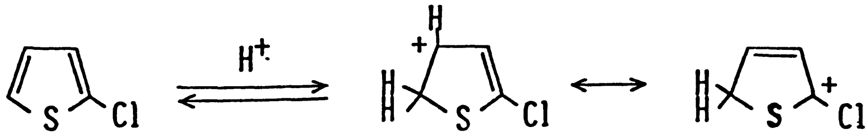
Well-resolved ^{1}H NMR signals of the title cations were observed in HSO_3F and $AlCl_3$-HCl-CH_2Cl_2 systems. Chlorothiophenes are protonated exclusively at the positions adjacent to sulfur with or without substituents.

Sone, Yokoyama, and Okuyama reported that 2-chlorothiophene reacted with active benzene derivatives such as aromatic ethers in the presence of aluminium chloride to give corresponding 2-arylthiophenes.$^{1)}$ In the reaction the existence of the protonated intermediates was assumed as follows.



This study provides a proof of the existence of such protonated species in fluorosulfonic acid system as well as in the $AlCl_3$-HCl-CH_2Cl_2 system similar to that reported by Sone et al.$^{1)}$ A typical ^{1}H NMR spectrum of protonated 2-chlorothiophene is shown in Fig. 1. In the figure, three signals appear at 9.22, 8.05, and 5.55 ppm with the intensity ratio of 1:1:2. Small signals at 7.2 ppm are ascribed to the starting material. The spectra of five other related protonated-chlorothiophenes were observed in similar manners. Some ^{1}H NMR data are presented in Table 1. The chemical shifts are quite apart from each other, so the signals are easily assigned. In Table 1, the site of the protonation is taken to be the 5-position to make clear the comparison of each species.

First, chlorothiophenes are found to be protonated at the α-position in the thiophene ring regardless of whether both α-positions have already been substituted or not. Thus, protonation of 2,5-dichlorothiophene occurs at the chlorine-bearing carbon, while chlorobenzenes are protonated at the unsubstituted ring positions.$^{2)}$ Second, it is of particular interest to know that protonation of 2-chloro-5-methylthiophene occurs at the 5-position as well as at the 2-position to give two cations, II and III, with the ratio of 3:1 at -70°C in the HSO_3F system. However, II was found selectively in the $AlCl_3$-HCl-CH_2Cl_2 system.[3)] Details will be reported elsewhere.

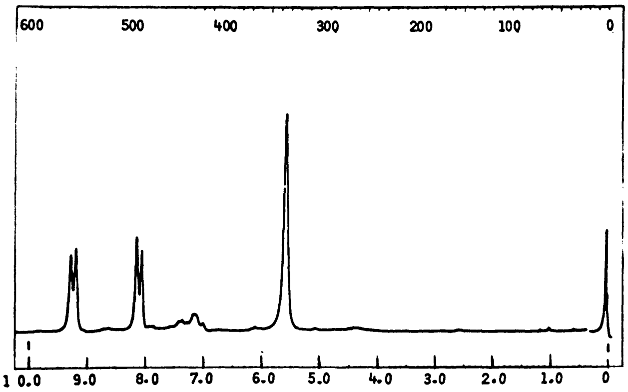


Fig.1. ^{1}H NMR spectrum of 2-chlorothiophene in HSO_3F at -50°C (60 MHz)

Table 1. ^{1}H Chemical Shifts of Protonated Chlorothiophenes

Cation	Substituents	Solvent	Temp. °C	Chemical Shift, ppm[+] 2-H	3-H	4-H	5-H
I	2-Cl	A[++]	-50	---	8.05(5.$_5$)	9.22(5.$_5$)[+++]	5.55
		B	-70	---	8.51(5.$_5$)	9.69(5.$_5$)	++++
		C	-40	---	8.65	9.78	6.19
II	2-Cl,5-CH_3	A	-70	---	7.92(5.$_5$)	9.07(5.$_5$)	2.13(CH_3,7.$_5$) 5.75(7.$_5$)
		B	-70	---	8.42(5.$_5$)	9.60(5.$_5$)	2.61(CH_3,7.$_5$) ++++
III	2-CH_3,5-Cl	A	-70	3.51(CH_3)	7.84(5.$_5$)	8.64(5.$_5$)	6.92
IV	2,5-Cl_2	A	-70	---	7.89(5.$_5$)	8.83(5.$_5$)	7.10
		B	-70	---	8.43(5.$_5$)	9.41(5.$_5$)	7.78

[+] ^{1}H chemical shifts are referred to an external neat TMS contained in a capillary. [++] Abbreviation: A, HSO_3F; B, $AlCl_3$-HCl-dichloromethane; C, $AlCl_3$-HCl-1,2-dichloroethane. [+++] The values in parentheses are the coupling constants between protons in Hz. [++++] Not available because of the large solvent peaks.

References

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3) The experimental procedures are similar to those described in (a)L.I.Belen'kii, A.P.Yakubov,and Ya.L.Gol'dfarb, Zhur. Org. Khim., 11, 424(1975) and (b) N. Nambu, K. Yamamoto, S. Hamanaka, and M. Ogawa, Nippon Kagaku Kaishi, 1979, 925.

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