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NMR Study of Protonated Halothiophenes. I.
^{1}H NMR Study of Chlorothiophenium Ions[1)]

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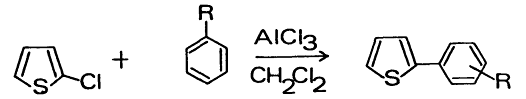
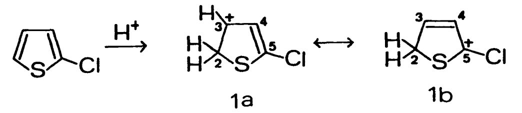
Well-resolved ^{1}H NMR signals of the cations formed from chlorothiophenes were observed in the HSO_3F or $AlCl_3$–HCl–CH_2Cl_2 system. Chlorothiophenes are protonated exclusively at the position adjacent to sulfur, either with or without substituents. The protonation of 2-chloro-5-methylthiophene occurs at the 5-position, and, in the HSO_3F system, the cation 5*H*-2-chloro-5-methylthiophenium ion thus formed undergoes an irreversible 2,5-hydrogen shift.

It was recently reported that 2-chlorothiophene reacted with active benzene derivatives such as aromatic ethers in the presence of aluminum chloride to give 2-arylthiophenes.[2)] In this reaction, the existence of a protonated intermediate (**1**) was assumed because a proton was presumably derived from the contact of aluminum chloride with water in the moist air.



Scheme 1.



Scheme 2.

Studies of various kinds of arenium ions in the super acids have been energetically performed by many researchers.[3)] These studies are important and interesting in connection with the direct observation of the protonation of aromatic rings and the kinetics of arenium-ion rearrangement. However, the cations in the super acids are not necessarily the same as the species produced in ordinary cationic reaction processes, *e.g.*, in the $AlCl_3$–HCl–solvent system. In general, it is difficult to observe such species directly during the reaction process.

This study was undertaken to get proof of the formation of chlorothiophenium ions involving **1** in the $AlCl_3$–HCl–CH_2Cl_2 system as well as in the HSO_3F system, and, in addition, to obtain information about the structures of the chlorothiophenium ions. A few works have been carried out so far by Okami *et al.*[4)] and Belen'kii *et al.*[5)] aimed at the direct NMR spectroscopic observation of some protonated benzenes and thiophenes in the $AlCl_3$–HCl–solvent system, but they were concerned with compounds having active substituents such as alkyl groups. There has not yet been reported any work concerning thiophenes having inactive substituents such as halogens. Our preliminary results have previously been reported.[6)]

Experimental

All the compounds studied were synthesized by one of the present authors (T.S.). The reagents used were commercial ones and were used without further purification.

The ^{1}H NMR measurements were carried out by means of a Hitachi R-20B spectrometer at 60 MHz with a variable-temperature controller (R-202-VTC). The ^{1}H chemical shifts are referred to the signal of tetramethylsilane in a sealed Pyrex capillary inserted into each sample tube.

The cations studied were prepared by the following general procedures.

Preparation of the Cations in HCl–$AlCl_3$–Solvent Systems. In the reaction of 2-chlorothiophene with active benzene derivatives, once a small amount of the products has been formed, it can provide HCl, which in turn can prompt a further reaction. However, for the ^{1}H NMR measurements of the cation, the second material (benzene derivative) is not brought into the system; therefore, the addition of HCl gas is necessary.

A hand-made Pyrex container (*ca.* 10 ml) is filled with *ca.* 1 g of $AlCl_3$ powder. The container has an inlet for HCl gas, and the gas is blown into the container from a HCl-generator for about 5 min. The container is then immersed in a low-temperature bath (methanol–Dry Ice), which is kept at about −40 °C, and *ca.* 5 ml of solvent is introduced. Further HCl gas is then blown into the container for about 90 min or more. The solvent in the container is thus thoroughly saturated with HCl and $AlCl_3$. A small reactor, connected to an NMR sample tube, is first filled with $AlCl_3$ in an amount corresponding to the 1 : 1 mole ratio of the sample (chlorothiophene) used, and then kept at −40 °C. About 1 ml of the previously prepared solvent is then added into the reactor, and the mixture is stirred by means of a magnetic stirrer. The starting material, chlorothiophene, is then added into the reactor. A suitable reaction time is about 2—6 min depending upon the reactivity of the material. When enough time has passed, the material seems to be polymerized. When the amount of the material is in excess of that of HCl or $AlCl_3$ in the solvent, a polymerization of the material occurs. The NMR spectra of the polymerized products give broad signals. When the protonation is considered to have progressed to a desired extent, the mixture is transferred into the connected NMR tube and kept at −40 °C in the bath. Then the NMR tube is moved into another Dry Ice–methanol bath at *ca.* −80 °C, cut off from the reactor, and sealed by means of a Teflon cap. The sample is then used for the NMR measurements. When it is kept at −80 °C, the reaction seems to be frozed, showing no progress for several hours.

Preparation of the Cations in Fluorosulfonic Acid or in the Magic Acid. The magic acid used in this study contains 7.7 mol/l of SbF_5 in HSO_3F, which has been prepared by mixing the two reagents in a stream of nitrogen in a dry box. The acid is kept in several sealed Pyrex glass tubes until it is used. The

NMR samples of the cations are prepared by the following procedure. An ordinary NMR sample tube is filled with about 0.5 g of the magic acid or HSO_3F, and then kept in a Dry Ice–methanol bath at −80 °C. The starting material (*ca.* 0.05—0.10 g) is then added to the tube. The material ordinarily keeps in the solid state on the wall of the tube and does not react with the acid under these conditions. The tube is then pulled out from the bath, shaken in the air for a few seconds, and again put into the bath. The shaking is repeated several times until the solution in the tube shows a homogeneous coloration. In this instance, when the shaking in the air has continued long enough, the reaction products are too complex to be analyzed by means of the ^{1}H NMR. However, when the shaking time is too short, the reaction will not start at all. The coloration of the solution is a most suitable indication of the reaction progress. When the sample exhibits a suitable and characteristic coloration, it is kept in the bath at −80 °C until it is used for the NMR measurements.

Results and Discussion

The ^{1}H NMR data of the eight cations produced are given in Table 1. The site of the protonation is taken to be the 2-position to make clear the comparison of the species.[7)]

A typical ^{1}H NMR spectrum of protonated 2-chlorothiophene (**1**) in HSO_3F and an $AlCl_3$–HCl–solvent system is given in Figs. 1a and 1b respectively. It is shown that the two cations produced under the two different circumstances are of the same kind, although the chemical shifts of the signals of the cation (**1**) are

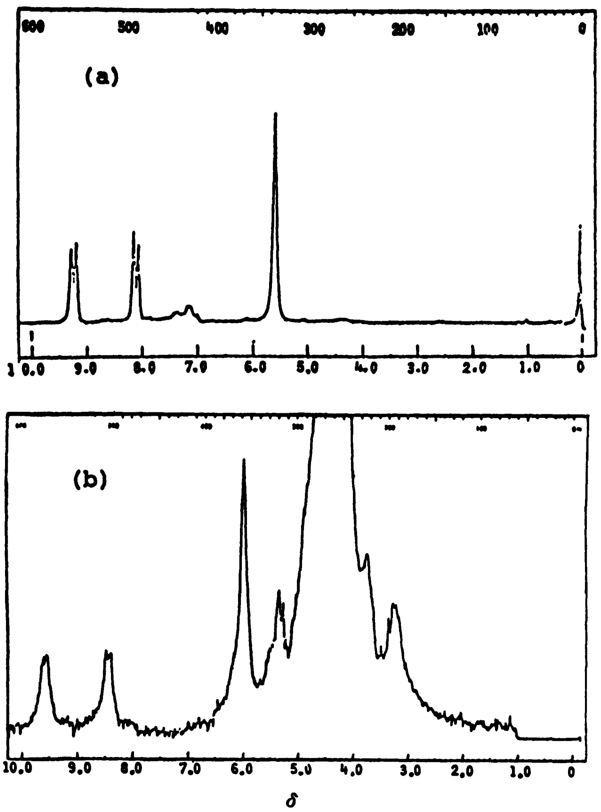


Fig. 1. ^{1}H NMR spectra of protonated 2-chlorothiophene (**1**) at 60 MHz. (a) In HSO_3F at −50 °C, (b) in $AlCl_3$–HCl–dichloroethane at −30 °C.

Table 1. ^{1}H NMR data of protonated chlorothiophenes[a)]

No.	Substituent	Solvent	Temp / °C	Chemical shift/ppm[b)] 2-H	3-H	4-H	5-H
1	5-Cl	A[c]	−50	5.50 (1.3)[d]	9.15(5.5,1.3)	8.03(5.5)	—
		C	−70	[e]	9.69	8.51	—
		D	−40	6.19	9.78	8.65	—
2	2-CH_3, 5-Cl	A	−70	2.13(CH_3,7.$_5$) 5.75(7.$_5$)	9.07(5.$_5$)	7.92(5.$_5$)	—
		B	−50	2.22(CH_3) 5.83	9.14	8.00	—
		C	−70	2.61(CH_3) [e]	9.60	8.42	—
3	2-Cl, 5-CH_3	A	−70	6.92	8.64(5.$_5$)	7.84(5.$_5$)	3.51(CH_3)
		B	−50	7.00	8.70	7.92	3.59(CH_3)
4	3-Cl	A	−50	5.39(2.0)	—	8.09(4.5)	11.00(4.5, 2.0)
5	4,5-Cl_2	A	−50	5.45(2.0)	9.07(2.0)	—	—
6	2,5-Cl_2	A	−70	7.10(1.5)	8.83(5.6,1.5)	7.89(5.6)	—
		B	−70	7.18	8.90	7.96	—
		C	−70	7.78	9.41	8.43	—
		D	−40	7.80	9.47	8.51	—
7	2,5-Cl_2, 3-CH_3	A	−50	6.82	2.99(CH_3)	7.79	—
		B	−50	6.90	3.03(CH_3)	7.84	—
		C	−50	7.38	3.44(CH_3)	8.27	—
		D	−40	7.39	[e]	8.29	—
8	2, 3, 5-Cl_3	B	−50	6.89	—	7.99	—

a) As stated in the text, the site of the protonation is taken to be the 2-position. b) ^{1}H chemical shifts are referred to an external neat TMS contained in a capillary. c) Abbreviations: A, HSO_3F; B, HSO_3F–SbF_5; C, $AlCl_3$–HCl–dichloromethane; D, $AlCl_3$–HCl–1,2-dichloroethane. d) The values in parentheses are the coupling constants between protons in Hz; they are given only for the first example of each starting material. e) Not available because of the large solvent peaks.

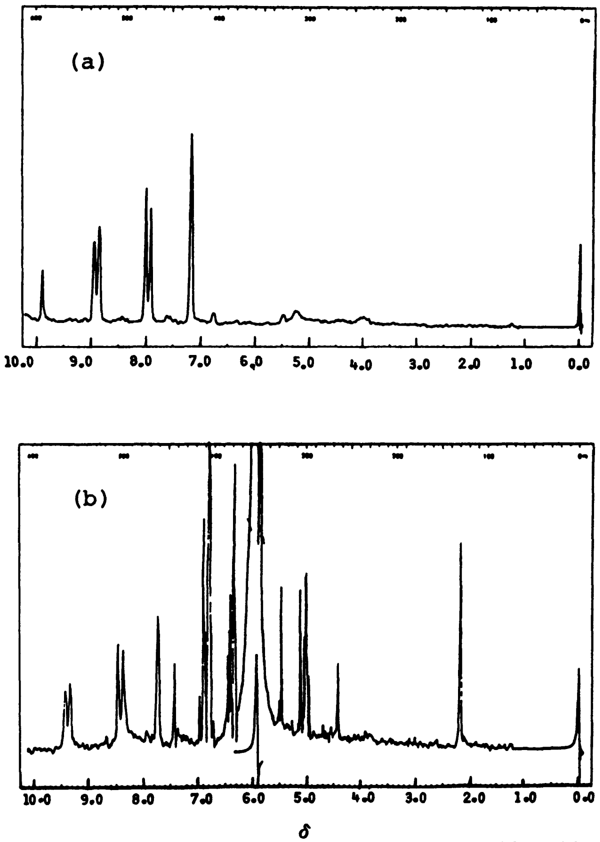
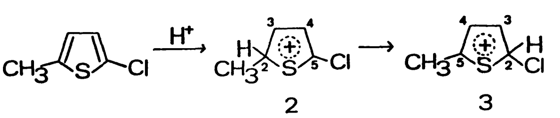


Fig. 2. ^{1}H NMR spectra of protonated 2,5-dichlorothiophene (**6**) at 60 MHz. (a) In the magic acid (see text) at −50 °C and the signal at near 10.0 ppm is due to the sideband of the acid proton, (b) in $AlCl_3$–HCl–dichloromethane at −50 °C and a signal at 2.17 ppm is unknown.

larger by about 0.5 ppm in the latter than those in the former system. The chemical shifts are quite apart from each other, so the signals can easily be assigned. The intensity ratio of the three peaks is 1 : 1 : 2 from low to high field in Fig. 1a, as would be expected for the cation (**1**). The protonation of 2-chlorothiophene at the 5-position is consistent with the ordinary concept of thiophene chemistry. The protonation of 2,3-dichlorothiophene also occurs at the 5-positioned carbon atom not carrying the substituent.

In the cases where the two α-positions have already been substituted, the protonations still occur at the α-position. Thus, the protonation of 2,5-dichlorothiophene has occurred at the chlorine-bearing α-position and produced the cation (**6**), as is shown in Fig. 2, in sharp contrast to those of chlorobenzenes, which occur at the unsubstituted ring position;[8] although Olah *et al.* have reported that the protonation of the halogen-bearing carbon can be assumed in explaining a Friedel-Crafts-type isomerization.[9]



2 3

Scheme 3.

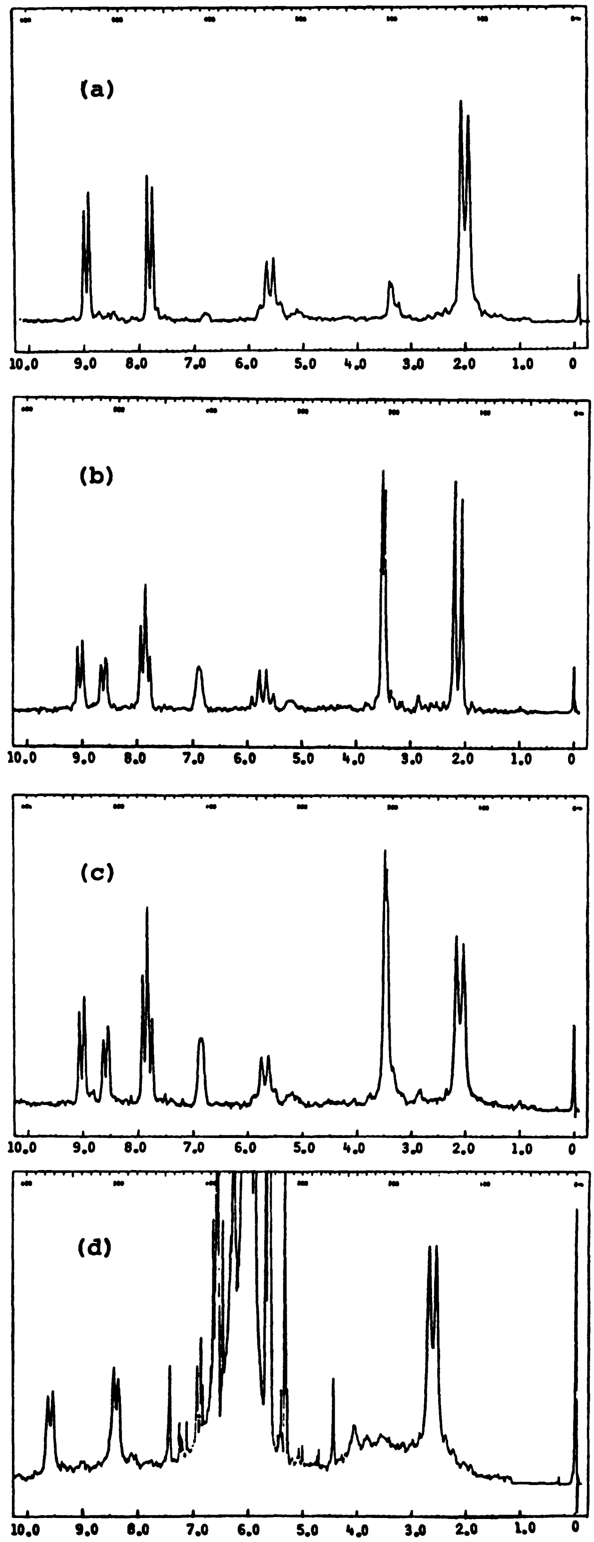


Fig. 3. ^{1}H NMR spectra of protonated 2-chloro-5-methylthiophene (**2** and **3**) at 60 MHz. (a) In HSO_3F at −70 °C, (b) at −30 °C, (c) again at −70 °C after observing the spectrum b, (d) in $AlCl_3$–HCl–dichloromethane at −70 °C.

The protonation of 2-chloro-5-methylthiophene has produced two cations, (**2**) and (**3**), in HSO_3F in ratios from 3 : 1 to 10 : 1, depending on the shaking time described in the Experimental part. The signals of **2**

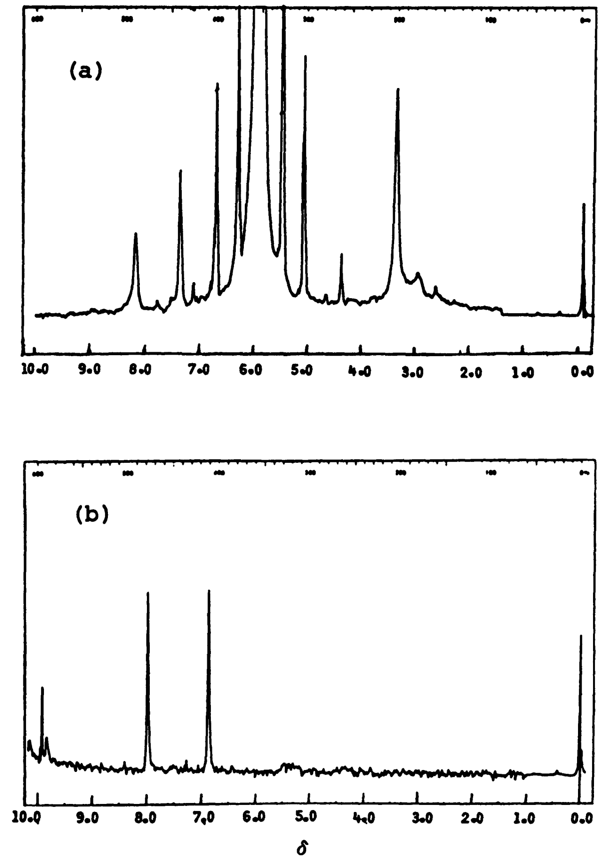


Fig. 4. ^{1}H NMR spectra of (a) protonated 2,5-dichloro-3-methylthiophene (**7**) in $AlCl_3$–HCl–dichloromethane at −70 °C, (b) protonated 2,3,5-trichlorothiophene (**8**) in the magic acid at −30 °C.

are considerably stronger than those of **3** at low temperatures, as is shown in Fig. 3a. When the temperature is carefully raised from −70 °C to −30 °C, the signals of **3** increase in intensity to the same extent as those of **2** (Fig. 3b). When the temperature is again lowered, the signals of **3** do not show any decrease (Fig. 3c). The conversion from **2** to **3** is not reversible. These results clearly indicate that the protonation occurs at the 5-position to give the cation (**2**), which later rearranges to the thermodynamically stable cation (**3**).[10] In the $AlCl_3$–HCl–CH_2Cl_2 system, the cation (**2**) is produced exclusively, as is shown in Fig. 3d.

The protonation of the compounds having one β- and two α-substituents occurred at the α-position neighbouring the β-substituent. This was the case with the cations (**7** and **8**), whose spectra are given in Fig. 4. In such cases, the electron-donating ability of the β-substituent seems to play a role.

The cations produced in this study are stable until the temperature reaches about −30 °C. Above −30 °C, the spectra gradually become complex, probably because of the rearrangement and/or polymerization of the molecule.

The data given in Table 1 are those obtained at the lower temperature rather than at the higher, because the proton-exchange effects are then suppressed and so are small. However, the resolution of the absorption lines is ordinarily better at a higher temperature than at a lower one.

A characteristic point of the couplings in thiophenium ions appears in the values of J_{23} and J_{34}. The J_{34} values of the thiophenium ions are larger than those of thiophenes. The J_{23} and the J_{34} of **1** are 1.3 and 5.5 Hz, while the corresponding values of 2-chlorothiophene are 6.1 and 4.0 Hz respectively. The change in these coupling constants shows the change in the system caused by protonation. It means that the distance between C_2 and C_3 increases, while that between C_3 and C_4 decreases, upon the protonation at the 2-position. The structural change in the system is clearly expressed by the change in the interproton couplings. The J_{24} of **1** is about 0.5 Hz, as estimated from the line broadening of the H_4 signal. The same is true for that of **6**. This may be compared with the J_{35} of 2-chlorothiophene (1.1 Hz).

The chemical shifts of the H_3 are always larger than those of the H_4 in thiophenium ions. Two limiting resonance structures of the ions are shown in Scheme 2. The positive charge is localized at C_3, but not at C_4, in the Scheme. This fact is consistent with the chemical-shift difference between H_3 and H_4 in Table 1.

This study provides a proof of the formation of the 2-chlorothiophenium ion (**1**) as a key intermediate in the reaction shown in Scheme 1. The cations observed here become reaction intermediates in similar acid-catalyzed reactions, one example of which is given in the case of 2,5-dichlorothiophene.[11] The study is now being extended to other halothiophenes; the synthetic use of halothiophenium ions is also under investigation.

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