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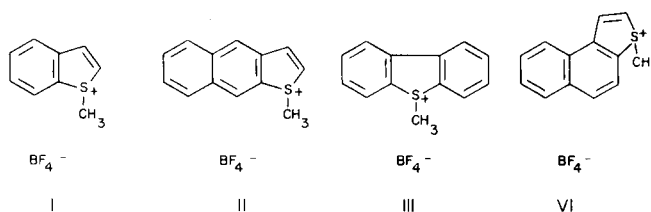
The polarographic behavior of four *S*-methylthiophenium tetrafluoroborates, I-IV, has been investigated in Britton-Robinson aqueous buffers. The compounds under study were the *S*-methylbenzo[*b*]thiophenium (I), *S*-methylnaphtho[2,3-*b*]thiophenium (II), *S*-methyl dibenzothiophenium (III), and *S*-methylnaphtho[2,1-*b*]thiophenium (IV) tetrafluoroborates which were obtained from the parent sulfur heterocycles by their reaction with methyl iodide and silver tetrafluoroborate in 1,2-dichloroethane, II and IV being new compounds. Compounds I-IV give two one-electron reduction waves and the more positive wave appears to be associated with an electron transfer from the electrode to the LUMO of the substrate as indicated by the experimental $E_{1/2}$ vs calculated LUMO values plot (Figure 2). The rates of demethylation of the ions I-IV with the iodide ion acting as the nucleophile have been determined in the Britton-Robinson buffer (pH 6)-acetonitrile solution at 24°. The results of the polarographic study and of the kinetic studies with the iodide ion confirm the high reactivity of *S*-methylthiophenium ions which originates in the antiaromatic destabilization of these structures.

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A detailed knowledge of the role of the heteroatom is essential for a satisfactory understanding of the physical and chemical properties of heteroaromatic compounds. Bonding of heteroatoms in these molecules differs from their bonding in nonaromatic species and their reactivities differ as well. In thiophenes the reactivity of the sulfur atom is drastically reduced compared to the sulfur atom in sulfides. Thus, *e.g.*, the rate of oxidation to the respective sulfoxide is a hundred times slower in dibenzothiophene than in diphenyl sulfide (1). Furthermore, in contrast with sulfides which are readily methylated with methyl iodide to the respective sulfonium iodides, *S*-alkylthiophenium ions can be obtained only by using strong alkylating reagents which provide nonnucleophilic counterions, such as the methyl iodide-silver tetrafluoroborate reagent (2). This is because *S*-alkylthiophenium ions themselves are strong alkylating reagents and react, *e.g.*, very quickly, with iodide ions producing the respective thiophene and methyl iodide (2,3). These observations can be summarized as follows. The more difficult it is to alter the sulfur atom in the thiophenes, the more easily are these compounds recovered from their *S*-derivatives. A possible explanation of this phenomenon can be found in detailed nmr studies of thiophene *S*-oxides (4) and *S*-alkylthiophenium salts (2) according to which the bonds in these compounds at the sulfur atom are not in one plane. In such structures, the formal lone electron pair (involving the trigonal pyramidal sulfur) is incapable of an efficient overlap with the *p_z* orbitals of the adjacent carbon atoms as is the case in the thiophene. Based on this information, the molecules of thiophene *S*-oxides and *S*-alkylthiophenium

ions are considered as nonaromatic structures (2,4). By accepting this interpretation, the sulfur reactions in thiophenes are represented as nonregenerative processes (5) in which the molecular π -electron system of the heterocyclic moiety loses its "aromatic" (or more specifically thiophene-like) character. Using the same argument, the reverse reactions should be characterized as aromatization processes. Parameters of reactions of the latter type in which the activation energies would parallel the delocalization energies should make it possible to compare the "aromaticity" in a series of structurally related compounds.

The study presented in this paper involves the investigation of a series of *S*-methylthiophenium tetrafluoroborates I-IV and was aimed toward extending the knowledge of the nature of the sulfur atoms in *S*-substituted thiophenes (Table I).



Acheson's general method (2) was used for preparation of the above compounds I-IV among which II and IV are new compounds. The application of the same procedure in the case of *S*-methylthiophenium tetrafluoroborate was unsuccessful. The tendency of the thiophenium ions I-IV to form the respective thiophenes was examined in two different

TABLE I
Yields and Physical Data of *S*-Methylthiophenium/Tetrafluoroborates

Compound	Name	Yield %	M.p., °C Lit. (2)	Uv Spectra in Dichloromethane λ max, Nm ($\log \epsilon$)	Nmr Spectra in Dichloromethane δ (vs. TMS)	
					S-CH ₃	Other Protons
I	<i>S</i> -Methylbenzo[<i>b</i>]thiophenium tetrafluoroborate	57%	72-73	230 (4.32) 270 (3.40) 300 (3.43)	3.5	8.3-7.5
II	<i>S</i> -Methylnaphtho[2,3- <i>b</i>]thiophenium tetrafluoroborate	89%	160-161 (a)	240 (4.36) 263 (4.49) 298 (4.00) 310 (4.00) 348 (3.59) 363 (3.63)	3.4	8.5-7.5
III	<i>S</i> -Methyldibenzothiophenium tetrafluoroborate	89%	149-150	232 (4.41) 239 (4.42) 272 (4.00) 380 (3.16)	3.4	8.5-7.5
IV	<i>S</i> -Methylnaphtho[2,1- <i>b</i>]thiophenium tetrafluoroborate	36%	150-151 (b)	254 (4.56) 292 (4.20) 303 (4.20) 315 sh (3.67) 329 (3.38)	3.3	8.4-7.5

(a) Anal. Calcd. for C₁₃H₁₁BF₄S (286.38); C, 54.55, H, 3.85; F, 26.57, S, 11.19. Found: C, 54.33; H, 4.04; F, 26.13; S, 11.01. (b) Unstable, not analyzed. New compound.

reactions: the cathodic reduction using dc-polarography and a nucleophilic reaction in which the iodide ion acted as a nucleophile and the thiophene molecule as a leaving group. Cathodic cleavage of the triphenylsulfonium ion (V) which has been investigated in detail (6) served as a model for the polarographic study. The preparative dealkylation of *S*-alkylthiophenium ions with the iodide and hydroxide ions has been documented in the literature (2).

Results and Discussion

Polarographic behavior of 5-methyldibenzothiophenium tetrafluoroborate (III) (see Figure 1), is very similar to that of the triphenylsulfonium bromide (V) (6). Cathodic scans involving either of the cations are characterized by large maxima which are successfully suppressed with Triton X-100. In the presence of the surfactant the polarograms show two one-electron waves, the second wave being rather indistinctive for compound III. The more positive waves (III, $E_{1/2} = 0.70$ vs SCE; V, $E_{1/2} = -1.10$ V vs SCE) which are unusually steep for a single-electron step are diffusion controlled (for compound III the limiting current is linearly dependent on concentration and on the square root of the mercury column height and its temperature coefficient is 2%). For compound III the logarithmic analysis of the first wave recorded in the presence of 0.001% Triton X-100 is linear with a slope of 0.062 V in the range from 10 to 90% of the limiting current. The dependence of the $E_{1/2}$ potential of the first wave on concentration of the substrate and the surfactant has been documented for compound V (6). The $E_{1/2}$ potentials of the first wave for both III and V are pH-independent (for compound III in the range between pH 2 and 12). Controlled-potential coulometry at the limiting current of the first

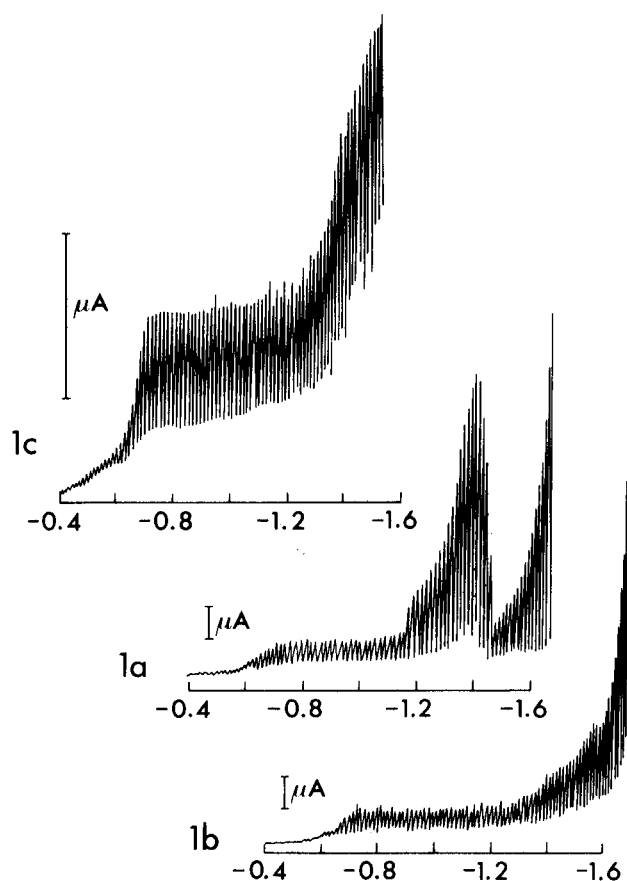


Figure 1.

Polarograms of 5-methyldibenzothiophenium tetrafluoroborate ($1.3 \times 10^{-4}M$) in phosphate buffer (pH 5.8) without surfactant (center) and with 0.01% of Triton X-100 at the same sensitivity (bottom) and with sensitivity increased five times (top). Voltage scale refers to saturated calomel electrode.

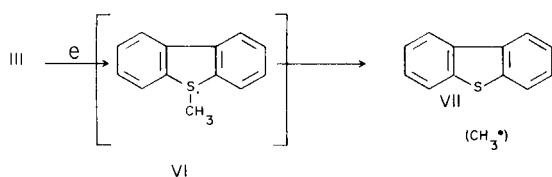
TABLE II

Experimental $E_{1/2}$ (the more positive wave) and $\log k_2$ Data for Compounds I-IV and Calculated Total π -Electron and LUMO Energies of Respective Thiophenes (PPP method).

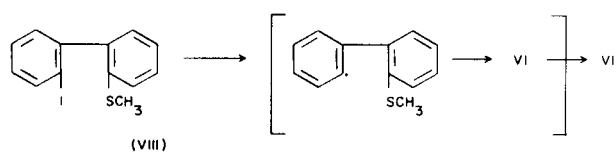
Compound (V vs. $E_{1/2}$ SCE)	$\log k_2$	Total π -Electron Energy (eV)	LUMO Energy (eV)
I	-0.73	-303.9	-1.78
II	-0.63	-491.0	-2.55
III	-0.70	-496.2	-2.01
IV	-0.62	-0.115	-494.6

wave suggests a one-electron process for either of the compounds. Dibenzothiophene was the product of electrolysis of compound III. Thus, the polarography of 5-methyl-dibenzothiophenium and triphenylsulfonium ions is characterized by a two-step electrode process (each step involving one electron) which is also observed for the triphenylselenium and triphenyltellurium ions (7). The course of electrolysis of the above compounds differs from a single two-electron electrode process characterizing bond cleavage in dialkylphenacylsulfonium (8,9,10), tetraphenylarsonium, and tetraphenylphosphonium (7) ions. The close parallel between the polarographic behavior of III and V indicates a structural similarity for the two ionic types. Such a similarity is in accord with the nonaromatic character postulated for *S*-alkylthiophenium ions (2).

The more positive waves represent a process in which a single electron is accommodated in the lowest unoccupied molecular orbital of the ion III and V, respectively. The radicals formed in this process undergo spontaneous chemical changes. For compound III this sequence of steps can be represented by the following diagram.



Support for the proposed *ec*-mechanism for the single-electron cathodic demethylation of III comes not only from the experimental results and the analogy with the polarography of V, but also from observations of non-electrochemical processes involving 2-iodo-2'-methylmercaptobiphenyl (VIII). The latter compound is converted photochemically, using tri-*n*-butyltin hydride or in a phenyl-radical induced reaction (12) into dibenzothiophene (VII). In all these processes the radical VI is postulated as an intermediate.



In order to determine the relationship between the polarographic data and the structure of the respective compounds, $E_{1/2}$ potentials for the more positive wave for compounds I-IV were measured under the same experimental conditions. These and the calculated MO data are presented in Table II. The total π -electron and LUMO energies for thiophenes structurally related to *S*-methylthiophenium ions I-IV were calculated using the PPP (LCI-SCF-MO) method. The electrode mechanism discussed above fully excludes any direct relationship between the $E_{1/2}$ potentials and the delocalization energies of the respective thiophenes. However, the ability to accommodate the electron should be reflected in the LUMO energies. Testing the $E_{1/2}$ potentials against these energies (see Figure 2) may indicate such relationship even if the MO data are calculated for parent thiophenes only (parameters for thiophenium sulfur are not available). The relatively narrow range of $E_{1/2}$ values (110 mV) for significantly altered structures I-IV indicates that the an-related rings do not exert any significant effect upon the polarographic electron affinity in *S*-methylthiophenium ions.

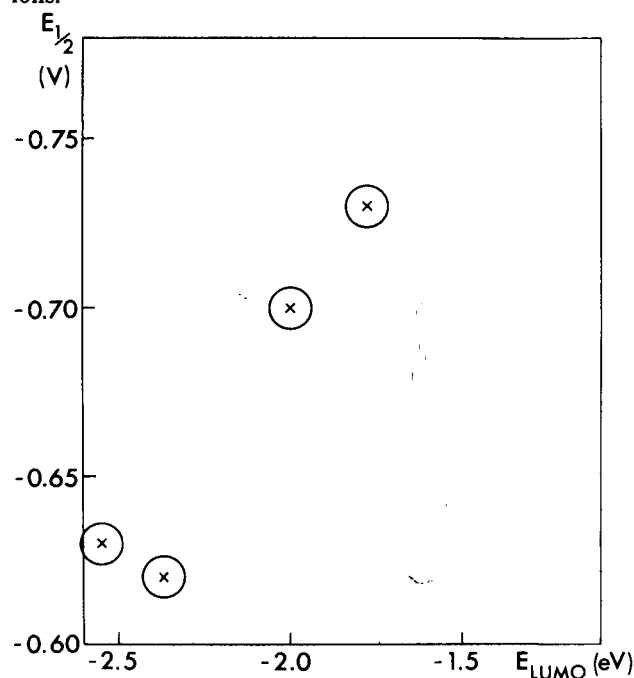


Figure 2.

The experimental polarographic half-wave potentials, $E_{1/2}$ (V), for compounds I-IV plotted against the calculated LUMO energies (eV). For numbering compounds, see Table I.

TABLE III
Data from Kinetic Studies of the Reaction of I-IV with Iodide

Compound	Initial Concentration of Sodium Iodide ($\times 10^{-2}M$)	Initial Concentration of Substrate ($\times 10^{-3}M$)	Correlation Coefficient r	Intercept	Slope ($\times 10^{-2}M$)	k_2 ($\ell. \text{ mole}^{-1} \text{ sec}^{-1}$)	k_2 ($\ell. \text{ mole}^{-1} \text{ sec}^{-1}$)
I	1.23	1.24	1.00	1.96 ± 0.12	-6.27 ± 0.11	1.96×10^{-1}	$1.96 \pm 0.03 \times 10^{-1}$
			1.00	1.96 ± 0.01	-6.27 ± 0.14	1.94×10^{-1}	
			1.00	2.11 ± 0.02	-6.38 ± 0.15	1.99×10^{-1}	
II	1.23	1.28	1.00	2.15 ± 0.01	-1.84 ± 0.05	5.74×10^{-2}	$5.59 \pm 0.16 \times 10^{-1}$
			0.99	2.19 ± 0.02	-1.74 ± 0.06	5.43×10^{-2}	
			0.99	2.10 ± 0.02	-1.79 ± 0.06	5.60×10^{-2}	
III	1.64	0.93	1.00	2.14 ± 0.01	-5.20 ± 0.14	1.22×10^{-1}	$1.15 \pm 0.06 \times 10^{-1}$
			1.00	2.10 ± 0.01	-4.71 ± 0.09	1.10×10^{-1}	
			1.00	2.11 ± 0.01	-4.87 ± 0.10	1.14×10^{-1}	
IV	0.42	0.31	0.99	1.92 ± 0.13	-8.34 ± 0.19	7.59×10^{-1}	$7.67 \pm 0.16 \times 10^{-1}$
			0.99	2.22 ± 0.02	-8.32 ± 0.20	7.57×10^{-1}	
			0.99	2.06 ± 0.02	-8.64 ± 0.28	7.86×10^{-1}	

The measurements of the rates of demethylation of *S*-methylthiophenium ions I-IV with the iodide ion acting as the nucleophile were executed under the pseudo-first order conditions in the Britton-Robinson buffer (pH 6.0)-acetonitrile mixture at $24.00 \pm 0.01^\circ$. The k_2 values calculated from the log substrate concentration *vs.* time plots are reported in Table III, the log k_2 values in Table II. For kinetic measurements the concentration of the particular *S*-methylthiophenium ion I-IV was monitored by polarography using calibration graphs which were linear and passed through the origin. Examination of Table II shows that simple relationship exists neither between log k_2 and $E_{1/2}$ values nor between log k_2 and total π -electron energies (the latter by considering isomeric compounds II, III, and IV only).

Studies of demethylation using a mercury cathode and with a nucleophile certainly document the high reactivity of *S* methylthiophenium ions. It was the anti-aromaticity of thiophene *S*-oxides which was suggested to explain the high reactivity and instability of these compounds (4). The application of this concept would explain similar behavior of *S*-alkylthiophenium ions as well. However, within the investigated series of compounds the activation energy differences (measured by $E_{1/2}$ potentials and log k_2 , respectively) of the two kinetically controlled reactions do not parallel the differences in the resonance energies of the reaction products, the respective thiophene-like compounds.

EXPERIMENTAL

LCI-SCF-MO (PPP) Treatment.

The calculations were carried out on an IBM 360/65 computer. The usual version of the PPP method was used. The parameterization and the method have been described elsewhere (13). Interactions between mono-excited configurations formed by promotion of one electron from one of

the four highest occupied MO's to one of the four lowest vacant MO's were considered. The systems studied were assumed to be planar and to have idealized geometry. All C-C and C-S bond lengths were assigned to be 1.40 Å. The rings were assumed to be regular hexagons and pentagons. SCF MO's served as the basis for CI calculations. Only resonance integrals between nearest neighbors were considered. The following parameters were used (values in eV) (14-16).

Atom	I_μ	A_μ	$\gamma_{\mu\mu}$	Z_μ	$\beta_{C-\mu}$
μ					
C	11.22	0.69	10.53	1	-2.318
S	20.27	10.47	9.80	2	-1.623

I_μ and $\gamma_{A\mu}$ are the ionization potential and electron affinity of atom μ in the atomic valence state, respectively. The monocentric repulsion integrals and core integrals between nearest neighbors are represented by $\gamma_{\mu\mu}$ and $\beta_{C-\mu}$, respectively, and Z_μ is the core charge at atom μ . The bicentric electronic repulsion integrals have been calculated using the Mataga-Nishimoto formula (17),

$$\gamma_{\mu\nu} = \frac{14.399}{R_{\mu\nu} + 1.328} \text{ eV}$$

Apparatus.

Melting points were determined on a Kofler hot stage. Electronic spectra were measured with a Cary 15 spectrophotometer using 1-cm optical path quartz cells. Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrophotometer with tetramethylsilane as the internal standard. A Corning pH-meter Model 10 was used to determine pH. Polarograms were recorded on a Sargent Recording Polarograph Model XV and Heath Polarograph Model EVW-401. Kaloušek's cell equipped with a 1M calomel electrode was used for polarographic experiments. The characteristics of the dropping mercury electrode were the following: at mercury column height $h = 74.5$ cm the drop time was 8.6 seconds and outflow velocity was 0.045 g/minute. A controlled potential coulometer (*c.F.*, Beadel and co-workers (18)) was used for *n*-value determinations and the preparation of the product of electrolysis for identification. An electrolytic cell (*c.F.*, Schultz (19)) with mercury pool (5 cm in diameter) and a stirrer at the mercury-electrolyte interface (1500 rpm

using a synchronous motor) was used in controlled potential coulometry experiments. The auxiliary electrode was a coiled platinum wire housed in a 10-20 μ pore glass-frit-bottomed tube while the reference electrode was a 0.1M mercurousulfate type.

Solvents and Buffers.

Methylene chloride, 1,2-dichloroethane, acetonitrile, and ether were Baker Analyzed Reagents and were freshly distilled. Distilled deionized water was used for preparation of Britton-Robinson buffers from Baker Analyzed grade phosphoric acid, boric acid, acetic acid, and sodium hydroxide. The resulting buffers were 0.04M with respect to each acid and 0.02M sodium hydroxide was added to obtain the desired pH. A phosphate buffer (pH 5.8) was prepared in an analogous manner.

Chemicals.

Methyl iodide, benzo[b]thiophene, and dibenzothiophene were Aldrich Chemical Co. products. Benzo[b]thiophene (m.p. 31-32°) was purified by distillation; dibenzothiophene (m.p. 98-99°) was recrystallized from ethanol. Silver tetrafluoroborate (Ventron Corp. Alfa Products) was recrystallized from ethanol. Naphtho[2,3-b]thiophene (m.p. 191-193°) (20) and naphtho[2,1-b]thiophene (m.p. 111-113°) (21) were prepared according to the literature.

General Procedure for the Preparation and Characterization of S-Methylthiophenium Salts.

Following Acheson's general procedure, methyl iodide was added dropwise to a stirred solution of an S-heterocyclic compound and silver tetrafluoroborate in 1,2-dichloroethane (2). The mixture was stirred at room temperature for an additional 24-30 hours with the exclusion of moisture. The resulting silver iodide precipitate was removed by filtration and washed with a small amount of acetonitrile (5-10 ml.). A large excess of reagent grade ether was added to the combined filtrates producing cloudiness. The mixture was cooled in dry ice-acetone and scratched until crystallization began. If an oil was formed, the supernatant liquid was decanted, and the oil dissolved in acetonitrile at room temperature. Ether was added to this solution to the cloud point. On cooling, this mixture usually yielded a precipitate. The yields and physical and spectroscopic data for S-methylthiophenium salts I-IV are shown in Table I.

Polarographic Measurements.

To a deaerated buffer (15 ml.) in a Kalousek cell, 1.5 ml. of 0.001M stock solution of the S-methylthiophenium salt in acetonitrile was added and the solution was further deaerated under stirring for 30 seconds before the current-voltage curve was recorded. In some instances 0.15 ml. of 0.1% solution of the surfactant Triton X-100 was added to the electrolyzed solution.

Controlled Potential Coulometry of S-Methyldibenzothiophenium Tetrafluoroborate (IV).

Compound IV was electrolyzed under a nitrogen atmosphere at a constant potential of -1.2 V vs. 0.1M mercurousulfate electrode using a modified potentiostat (cF., Beadel and coworkers (18)).

Experiment 1.

With 0.0377 g. of IV in 100 ml. of Britton-Robinson buffer (pH 6.0) and 20 ml. of acetonitrile, the original current dropped below 1% after 2.25 hours of electrolysis. The charge output corresponded to 15.0 coulombs and the calculated n-value was 1.18 electrons. After evaporation of the solvent, the benzene extract of the electrolyte yielded a solid which was identified as dibenzothiophene by its m.p. (98-100°), mixed m.p., uv spectrum and thin-layer chromatography using authentic sample as standard.

Experiment 2.

Similarly as in the previous experiment, 0.0466 g. of IV after 2 hours of electrolysis gave a charge output 15.0 coulombs corresponding to an n-number of 0.95 electrons.

Kinetics of Demethylation of S-Methylthiophenium Ions with Iodide Ion.

The kinetics were studied in a jacketed polarographic vessel with mercury pool anode and dropping mercury cathode. The calibration graphs for S-methylthiophenium ions I-IV resulted in straight lines which passed through the origin in all cases. In the kinetic experiment 5 ml. of Britton-Robinson buffer (pH 6) thermostatted at 24.00 \pm 0.01° was deaerated and 1 ml. of a stock solution of S-methylthiophenium tetrafluoroborate in acetonitrile and 1 ml. of sodium iodide in water were added while deaeration was continued. The limiting current (i_l) of the Salkylthiophenium ion was recorded at -0.9 V (vs. mercury pool) at known time intervals. The linear plots of ($i_l - i_\infty$) vs. time were calculated by the least squares method. Experimental data from kinetic measurements are given in Table III and log k_1 values in Table II.

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