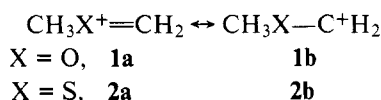# On the Electron-Donating Properties of Oxygen vs. Sulfur. A Study of the Gas-Phase Ion Chemistry of Methoxymethylthioalkanes

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Abstract: The gas-phase ion–molecule reactions of compounds of structure $CH_3O(CH_2)_nSCH_3$, $n = 1$–3, have been investigated by the method of pulsed ion cyclotron resonance spectroscopy. The results show that when there is a choice of forming either a sulfur-containing ion or its oxygen analogue, the sulfur ion is formed preferentially. The major reactions that lead to sulfur-stabilized product ions are regioselective hydride abstractions from carbon next to sulfur to give $(M - 1)^+$ ions and ionization of the parent neutral to give product ions of composition $CH_3S^+(CH_2)_n$. In a related study, chloride abstraction from CH_3SCH_2Cl to give $CH_3SCH_2^+$ was found to be much preferred over chloride abstraction from CH_3OCH_2Cl to give $CH_3OCH_2^+$. These results imply that sulfur is better than oxygen at stabilizing a neighboring positive carbon by electron donation. The fact that $CH_3OCH_2^+$ is reported to be formed more rapidly than $CH_3SCH_2^+$ from their respective chlorides *in solution* is attributed to external solvation effects rather than internal electronic effects.

The abilities of oxygen and sulfur to stabilize adjacent cation, radical, and carbanion centers is well documented.[1] There is little doubt that carbanions and radicals prefer to be adjacent to sulfur rather than to oxygen, but the situation with respect to positive carbon is not so clear. If stabilization of methoxymethyl and methylthiomethyl cations **1** and **2** is achieved mainly through π-electron donation from the heteroatom to carbon, then the better stabilized cation is expected to be the ion with the largest contribution from the π-bonded form, **1a** or **2a**.

$$CH_3X^+\!\!=\!\!CH_2 \leftrightarrow CH_3X\!\!-\!\!C^+H_2$$

$$\begin{array}{lll} X = O, & \textbf{1a} & \textbf{1b} \\ X = S, & \textbf{2a} & \textbf{2b} \end{array}$$

For many years it has been argued that sulfur is a poorer π donor than oxygen because the degree of bonding with carbon 2p orbitals achieved by π overlap with sulfur 3p orbitals is less than with oxygen 2p orbitals.[1a] The properties of thiocarbonyl compounds (low C=S bond strengths, high polarity, instability, reactivity[2]) certainly confirm that sulfur is reluctant to form stable double bonds to carbon. This being so, $CH_3O^+\!\!=\!\!CH_2$ ought to be better stabilized than $CH_3S^+\!\!=\!\!CH_2$. However, recent theoretical calculations on the comparative properties of related ions, $HO^+\!\!=\!\!CH_2$ and $HS^+\!\!=\!\!CH_2$, reveal that *sulfur* should form the stronger π bond to an adjacent *positive* carbon.[3] Sulfur also is estimated to be a σ donor whereas oxygen is a σ acceptor. Overall then, theory predicts that the sulfur ion **2** is better stabilized by electron donation than the oxygen ion **1**.

Conclusions regarding the stabilities of **1** and **2** based on experimental evidence are conflicting. In solution, oxygen is regarded as the better π donor from σ_p^+ values of CH_3O and CH_3S substituents,[4] from equilibrium data on the effects of these substituents on the pK_as of benzoic acids,[5] and from kinetic data on the solvolysis of 1-chloroalkyl ethers and thioethers.[6,7] In contrast, gas-phase kinetic data from chemical ionization studies on the dissociation of protonated esters $(RCO_2CH_2XCH_3)H^+$ to give $CH_3XCH_2^+$ where X = O or S strongly favor formation of the sulfur ion.[8] However, thermochemical data on the heats of formation of **1** and **2** from appearance potential data give ΔH_f $(CH_3XCH_2^+)$ values of 170 kcal for X = O[9,10] and 203 kcal for X = S,[11] implying that the oxygen ion has the greater stability with respect to its elements. The *difference* in appearance potentials of $CH_3OCH_2^+$ and $CH_3SCH_2^+$ from various neutrals is small but slightly favors formation of the sulfur ion, and Taft and co-workers

have concluded from this that stabilization of positive carbon by sulfur is more significant than by oxygen.[10,12]

The problem of arriving at a definitive conclusion as to which is the better electron donor, sulfur or oxygen, arises because "stability" is necessarily a relative quantity, and will vary according to what it is being measured relative to. That is to say, a scale of stabilities measured by heats of ion formation will not necessarily correlate with stabilities measured by appearance potentials because one measurement is with reference to the elementary state and the other to the molecular state. Furthermore, we are comparing apples and oranges by making quantitative comparisons between oxygen and sulfur. Some of these difficulties are removed when ions are derived competitively from the *same* neutral substrate, as in the α-cleavage of bifunctional molecules XCH_2CH_2Y on electron impact. In a thoughtful study, Harrison[13] has concluded that the most abundant ion (XCH_2^+ or YCH_2^+ correlates with the radical of lowest ionization potential (IP) ($XCH_2\cdot$ or $YCH_2\cdot$). In the specific case of $HOCH_2CH_2SH$, both ions are produced at low electron energies in approximately equal abundance, indicating that the IPs of CH_2X and hence the stabilizing effects of sulfur and oxygen on positive carbon are roughly equal.

In principle, a scale of gaseous carbocation stabilities could be derived from the energetics of hydride transfer equilibria (reaction 1) in the same way that scales of gas-phase acidities and basicities have been established from proton transfer equilibria[14] (reaction 2).

$$RH + R'^+ \rightleftarrows R^+ + HR' \tag{1}$$

$$AH^+ + :B \rightleftarrows A: + HB^+ \tag{2}$$
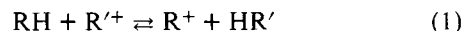
Unfortunately, hydride transfer is slower than proton transfer and equilibria of reaction 1 are not rapidly established in the gas phase at low pressures.[15] For example, we attempted to measure the equilibrium between methyl sulfide, methyl ether, and their respective $(M - 1)^+$ ions by ICR methods[14,16,17] (reaction 3) but the reaction proved to be too slow in both directions under the low-pressure conditions (10^{-6} Torr).

$$CH_3OCH_2^+ + CH_3SCH_3 \underset{}{\overset{slow}{\rightleftarrows}} CH_3OCH_3 + {}^+CH_2SCH_3$$

$$\tag{3}$$
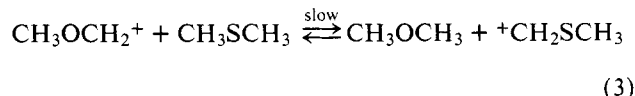
Another reaction that we hoped would provide relative stabilities of **1** and **2** was the condensation equilibrium of reaction 4. Although related condensations have been observed,[18]

reaction 4 was *not* observed in either the forward or backward direction.

$$CH_3O=^+CH_2 + CH_3SH \overset{slow}{\rightleftarrows} CH_3S=^+CH_2 + CH_3OH$$

$$(4)$$
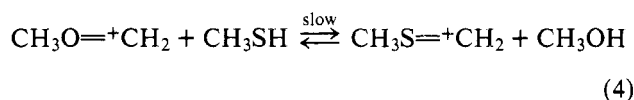
We were more successful with related but more rapid chloride transfer reactions involving chloromethyl ethers and thioethers CH_3XCH_2Cl, and with the ion chemistry of mixed ethers of the type $CH_3O(CH_2)_nSCH_3$, $n = 1$-3. The results of these investigations are interesting and informative as to the relative electron-donating abilities of oxygen and sulfur in gaseous ions, and are described in detail in the following section.

Results and Discussion

Instrumentation. The reactions of gaseous ions with neutral molecules were investigated by the method of pulsed ion cyclotron resonance spectroscopy at sample pressures of 10^{-6}-10^{-5} Torr in a trapped-ion analyzer cell.[16] The instrument was equipped with a dual inlet system to permit mixtures of neutral reactants to be introduced into the analyzer system at various partial pressures. Reactions were routinely followed over 5-200 ms reaction time, and the precursor ions in each reaction were identified through double resonance experiments and by plots of ion abundance as a function of time. Details of ion cyclotron resonance spectroscopy as a technique for studying ion-molecule reactions have been described elsewhere.[17]

Chloride Transfer Reactions. Alkoxymethyl cations $ROCH_2^+$ and alkylthio cations $RSCH_2^+$ can be formed by ionization of the corresponding chlorides $RSCH_2Cl$ under *solvolytic* conditions, and the fact that $ROCH_2^+$ is formed more rapidly than $RSCH_2^+$ is generally quoted to mean that the oxygen ion is more stable.[6,7] Similar ions can be generated in the *gas phase* by reaction of the neutral chlorides with positive ions of higher chloride affinity. Using a mixture of chloromethyl methyl ether and thioether at pressures of 1.9×10^{-6} and 1.7×10^{-6} Torr, respectively, the major fragment ion produced on electron impact at 19 eV in a trapped-ion ICR cell was $CH_3OCH_2^+$ (m/e 45). The abundance of this ion decayed rapidly as the major product ion $CH_3SCH_2^+$ (m/e 61) was formed (see Figure 1a). Double resonance experiments confirmed that the reaction that led to m/e 61 used m/e 45 as the reactant ion, and that m/e 45 was in turn produced from m/e 61 (see Figure 1b). The reaction

$$CH_3OCH_2^+ + ClCH_2SCH_3 \rightleftarrows CH_3OCH_2Cl$$
$$+ {}^+CH_2SCH_3 \quad (5)$$
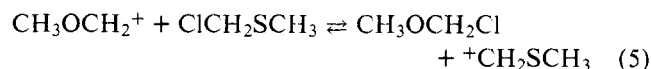
describes these results, and while both the forward and backward reactions can be observed, the position of equilibrium lies far to the right. This is very clear from the time plot in Figure 1a, which shows that after 75 ms the abundance of m/e 45 has decayed almost to zero. Because of the low equilibrium abundance of the methoxymethyl ion we were unable to obtain a reliable estimate of the equilibrium constant for reaction 5,[19] but the position of equilibrium unquestionably favors the sulfur cation. We conclude that the order of chloride affinity of the ions is $CH_3OCH_2^+ > CH_3SCH_2^+$ and, with reference to their respective neutral chlorides, the order of ion stability is $CH_3SCH_2^+ > CH_3OCH_2^+$. Insofar as reaction 5 is an elementary or one-step reaction, the conclusion is valid that the sulfur ion is formed more rapidly than the oxygen ion. This result is consistent with related gas-phase data of Field and Weeks[8] but inconsistent with solvolytic data on the rates of ionization of $RXCH_2Cl$.[6,7]

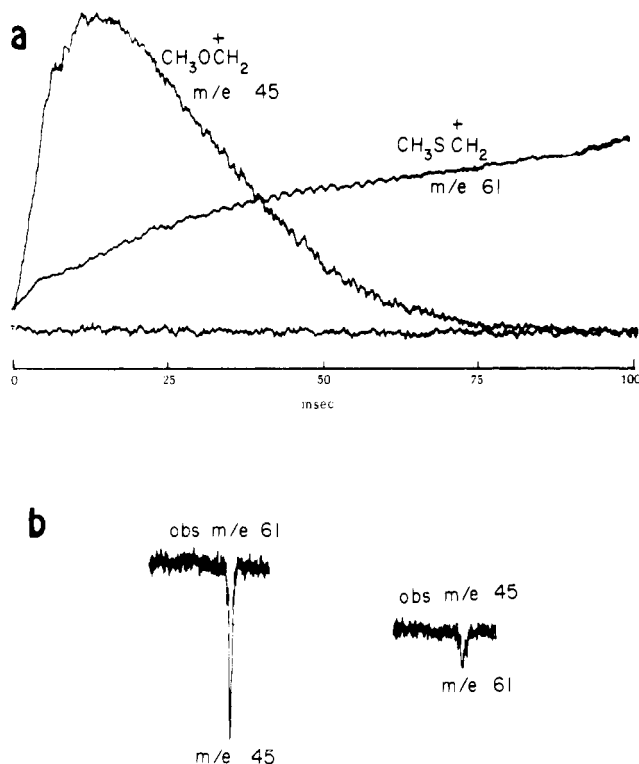**Methoxymethylthioalkanes.** One reason for investigating the ion chemistry of mixed ethers of the type CH_3O-

Figure 1. (a) Plot of ion abundance vs. time in the 19-eV ICR spectrum of a 4:3 mixture of CH_3OCH_2Cl and CH_3SCH_2Cl at a pressure of 3.5×10^{-6} Torr. (The slight rise in intensity of m/e 61 at 90 ms is an artifact.) (b) Double resonance spectrum at 60 ms indicating that m/e 61 is formed from m/e 45, and vice versa.

$(CH_2)_nSCH_3$ was in anticipation of reaction 6 in which the protonated parent ion could dissociate by loss of either methanol or methanethiol. Previous studies on related dissociations of MH^+ ions revealed that the partitioning between competing reaction channels (as in 6a or 6b) favors the more exothermic

$$CH_3O(CH_2)_nSCH_3$$

$$(6)$$
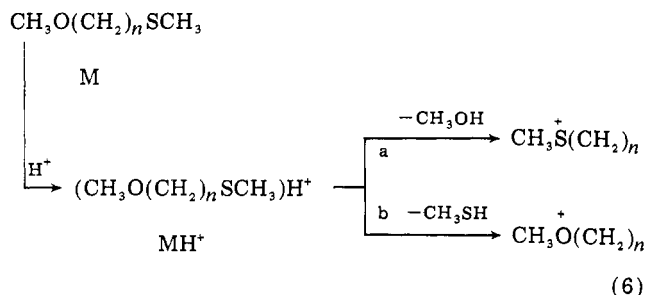
route,[20] but in actuality reaction 6 turned out to be a relatively minor route to ions of structure $CH_3S^+(CH_2)_n$. Precursor MH^+ ions were of minor abundance, except for $n = 3$, but to the extent that reaction 6 was observed, it led *only* to $CH_3S^+(CH_2)_n$ ions ($n = 2, 3$).

A more important pathway to product ions of composition $CH_3S^+(CH_2)_n$ utilized methoxymethyl cations as the reactant ions (reaction 7). This reaction is described here in detail for each of the ethers under investigation.

$$CH_3OCH_2^+ + CH_3O(CH_2)_nSCH_3 \overset{-C_3H_8O_2}{\longrightarrow} CH_3S^+(CH_2)_n$$

$$m/e \ 45 \qquad\qquad (M - OCH_3)^+ \quad (7)$$
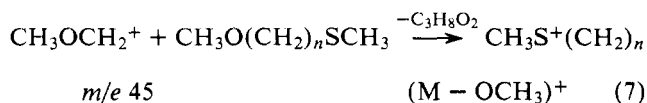
A third reaction observed between certain fragment ions and the neutral ethers was hydride abstraction to give $(M - 1)^+$ product ions (reaction 8, X = O or S).

$$CH_3O(CH_2)_nSCH_3 \overset{CH_3XCH_2^+}{\underset{-CH_3XCH_3}{\longrightarrow}} (M - 1)^+ \quad (8)$$
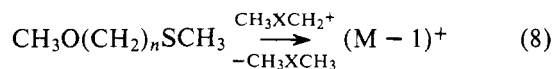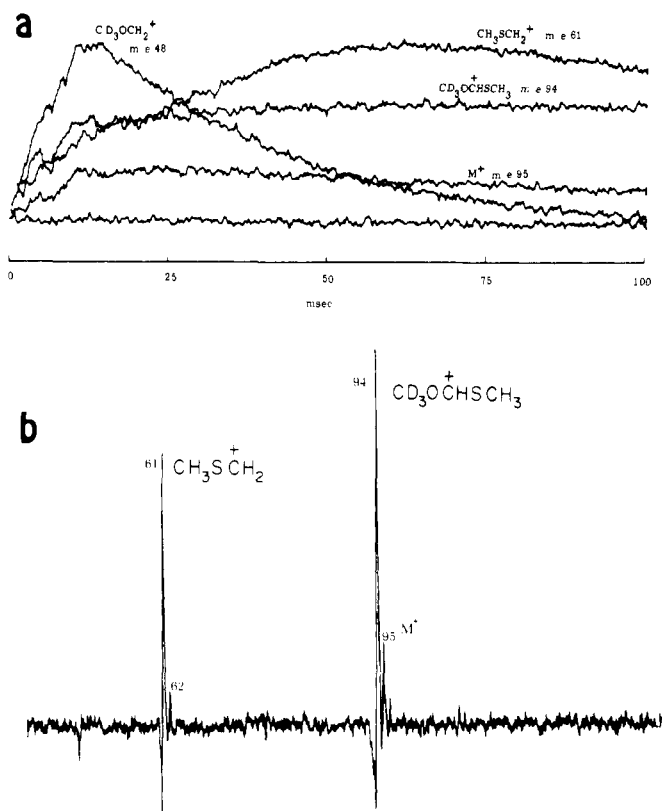
Figure 2. (a) Plot of ion abundance vs. time in the 20-eV ICR spectrum of $CD_3OCH_2SCH_3$ at 1.2×10^{-6} Torr showing that m/e 61 and 94 are formed from m/e 48. The molecular ion m/e 95 is unreactive. Kinetic analysis of the data shows that the sum of the rates of formation of m/e 61 and 94 equals the rate of disappearance of m/e 48. The specific rate constant is $k = 1.16 \times 10^{-9}$ mL mol^{-1} s^{-1} obtained from the time plot after appropriate mass corrections of measured intensity and baratron correction (0.8) of pressure. (b) Single resonance spectrum of $CD_3OCH_2SCH_3$ at 1.3×10^{-6} Torr and 100 ms.

The site of hydride abstraction in reaction 8 was of considerable interest as an indication of where a positive charge on carbon is best stabilized. A major objective of the work to be described here was to elucidate this point.

**Methoxymethylthiomethane.** The 20-eV ICR mass spectrum of $CH_3OCH_2SCH_3$ at 1.2×10^{-6} Torr showed only two primary ions—the molecular ion (m/e 92) and the fragment ion $CH_3OCH_2^+$ (m/e 45). Although $CH_3SCH_2^+$ (m/e 61) was

not evident as a fragment ion, it was a major product ion of reaction of m/e 45 with methoxymethylthiomethane. The appearance of m/e 61 at the expense of m/e 45 can be seen from the time plot of Figure 2, and double resonance confirmed that m/e 45 was the precursor ion to m/e 61. The nature of this reaction is not totally clear because the identity of the neutral products cannot easily be determined by the ICR method. One possible pathway (reaction 9, $n = 1$) involves hydride abstraction from the methoxy group followed by dissociation of formaldehyde. This route predicts the intermediate formation of an (M − 1) ion, and indeed a second major product ion was observed corresponding to $(M - 1)^+$ m/e 91. Moreover, ions of structure $^+CH_2O(CH_2)_nSCH_3$ are known to dissociate readily in the gas phase by elimination of neutral formaldehyde.[18] However, the deuterium-labeled compound $CD_3OCH_2SCH_3$ showed *no* $(M - 2)^+$ corresponding to abstraction of deuteride, which means that m/e 91 in the spectrum of the unlabeled material cannot be $^+CH_2OCH_2SCH_3$ (see Figure 2). Route 9 is therefore suspect as the source of m/e 61, but we cannot exclude it completely because hydride abstraction could be concurrent with dissociation of CH_2O. An alternative pathway is shown in reaction 10 and amounts to O-methylation and dissociation by loss of CH_3OCH_3. Productwise, this route is indistinguishable from 9, but there is precedent for the methylation step since $CH_3OCH_2^+$ (m/e 45) with methoxyethane gives dimethylethyloxonium ions in low abundance.[21] In the present case, an intermediate oxonium ion $(M + 15)^+$ was not observed, but is likely to dissociate readily by participation of the neighboring sulfur.[20] A third possible route to m/e 61, shown as reaction 11, involves a related O-alkylation–elimination sequence by way of an association complex $(M + 45)$. We have no experimental data from which to infer whether 10 or 11 is the preferred route, and since both reactions are calculated to be almost equally exothermic[22] both appear to be equally probable. However, it is intuitively more reasonable that the reactant ion should form a bond to oxygen at the positive methylene (reaction 11) rather than at the neutral methyl (reaction 10).

A fourth possible route to m/e 61 involves rearrangement of a transient $(M - 1)^+$ ion. If hydride is removed from the S-methyl group, an ion of structure $CH_3OCH_2SCH_2^+$ would presumably be formed, and ions of homologous structure $CH_3O(CH_2)_nSC^+H_2$, $n = 2-4$, have been observed to rearrange by hydride transfer from the O-methyl group to give ions corresponding to $^+CH_2O(CH_2)_nSCH_3$ which dissociate by loss of CH_2O.[23] If this route (reaction 12) prevails in the present case, then $CD_3OCH_2SCH_3$ would give m/e 62,

$$\xrightarrow{-CH_3OCH_3} [\dot{C}H_2O(CH_2)_nSCH_3] \xrightarrow{-CH_2O} (\dot{C}H_2)_nSCH_3 \tag{9}$$
$$(M - 1) \qquad\qquad (M - CH_3O)$$

$$n = 1, m/e\ 61$$
$$n = 2, m/e\ 75$$
$$n = 3, m/e\ 89$$

$$\begin{array}{c} CH_3O(CH_2)_nSCH_3 \\ + \\ CH_3OCH_2^+ \\ (m/e\ 45) \end{array} \xrightarrow{-CH_2O} \left[\begin{array}{c} CH_3 \\ \diagdown \\ O^+{-}(CH_2)_nSCH_3 \\ \diagup \\ CH_3 \end{array} \right] \xrightarrow{-CH_3OCH_3} (\dot{C}H_2)_nSCH_3 \tag{10}$$
$$(M + 15) \qquad\qquad (M - CH_3O)$$

$$\xrightarrow{} \left[\begin{array}{c} CH_3 \\ | \\ O \\ +\diagup \diagdown \\ CH_3OCH_2\quad (CH_2)_n \\ \diagdown \cdots \diagup \\ S \\ | \\ CH_3 \end{array} \right] \xrightarrow{-CH_3O(CH_2)OCH_3} (\dot{C}H_2)_nSCH_3 \tag{11}$$
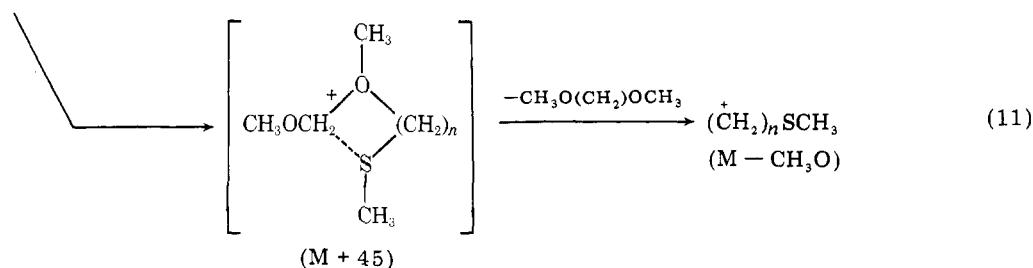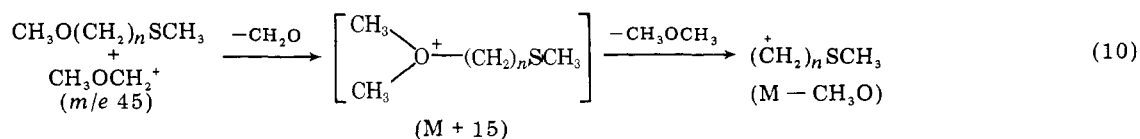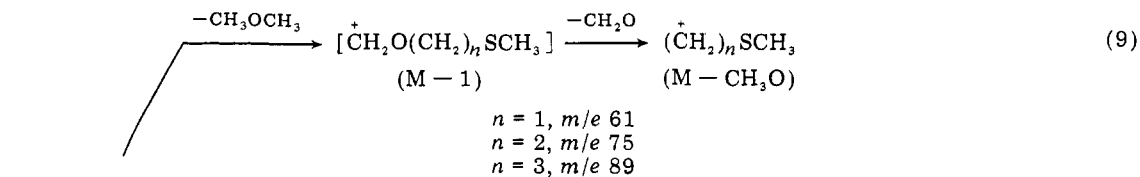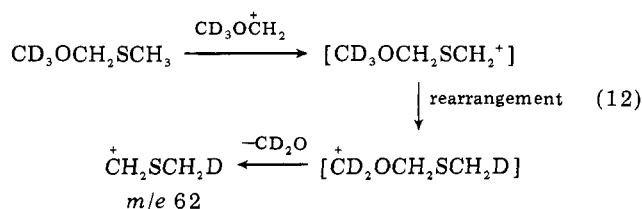$$(M + 45) \qquad\qquad (M - CH_3O)$$

Table I. Primary and Product Ions in the ICR Mass Spectrum of Labeled 1-Methoxy-2-methylthioethane

Neutrals	$CH_3OCH_2CH_2SCH_3$	$CD_3OCH_2CH_2SCH_3$	$CH_3OCH_2CH_2SCD_3$	$CH_3OCD_2CH_2SCH_3$	$CH_3OCH_2CD_2SCH_3$
Primary					
ions (m/e)[a]	$CH_3OC^+H_2$ (45)	$CD_3OC^+H_2$ (48)	$CH_3OC^+H_2$ (45)	$CH_3OC^+D_3$ (47)	$CH_3OC^+H_2$ (45)
$(M - CH_3SH)^{+\cdot}$	$CH_3O^{+\cdot}CH{=}CH_2$ (58)	$CD_3O^{+\cdot}CH{=}CH_2$ (61)	$CH_3O^{+\cdot}CH{=}CH_2$ (58)	$CH_3O^{+\cdot}CD{=}CH_2$ (59)	$CH_3O^{+\cdot}CH{=}CD_2$ (60)
$(M - CH_3S\cdot)^+$	$CH_3O^+C_2H_4$ (59)	$CD_3O^+C_2H_4$ (62)	$CH_3O^+C_2H_4$ (59)	$CH_3O^+C_2H_2D_2$ (61)	$CH_3O^+C_2H_2D_2$ (61)
	$CH_3SC^+H_2$ (61)	$CD_3SCH_2^+$ (61)	$CD_3SC^+H_2$ (64)	$CH_3SC^+H_2$ (61)	$CH_3SC^+D_2$ (63)
$(M - CH_3O\cdot)^+$	$CH_3S^+C_2H_4$ (75)	$CH_3S^+C_2H_4$ (75)	$CD_3S^+C_2H_4$ (78)	$CH_3S^+C_2H_2D_2$ (77)	$CH_3S^{+\cdot}C_2H_2D_2$ (77)
$(M - CH_3OH)^{+\cdot}$	$CH_3S^{+\cdot}CH{=}CH_2$ (74)	$CH_3S^{+\cdot}CH{=}CH_2$ (74)	$CD_3S^{+\cdot}CH{=}CH_2$ (77)	$CH_3S^{+\cdot}CH{=}CD_2$ (76)	$CH_3S^{+\cdot}CD{=}CH_2$ (75)
$M^{+\cdot}$	(106)	(109)	(109)	(108)	(108)
Product					
ions (m/e)[b,c]					
$(M - CH_3O)^+$	$CH_3S^+C_2H_4$ (75) [45, 107[d]]	$CH_3S^+C_2H_4$ (75) [48, 110[d]]	$CD_3S^+C_2H_4$ (78) [45, 110[d]]	$CH_3S^+C_2H_2D_2$ (77) [47, 109[d]]	$CH_3S^+C_2H_2D_2$ (77) [45, 109[d]]
$(M - H)^+$	$CH_3OCH_2C^+HSCH_3$ (105) [61]	$CD_3OCH_2C^+HSCH_3$ (108) [61]	$CH_3OCH_2C^+HSCD_3$ (108) [64]	$CH_3OCD_2^+CHSCH_3$ (107) [61]	$CH_3OCH_2C^+DSCH_3$ (106) [63]
$(M + H)^+$	MH^+ (107) [59]	MH^+ (110) [62]	MH^+ (110) [59]	MH^+ (109) [61]	MH^+ (109) [61]

[a] Ions produced on electron impact. [b] Ions produced on reaction of primary ions with neutrals at pressures around 10^{-6} Torr. [c] Numbers in brackets are m/e of precursor ions. [d] Endothermic double-resonance response.

$^+CH_2SCH_2D$. A minor amount of m/e 62 is indeed present in the 100-ms mass spectrum of $CD_3OCH_2SCH_3$ (Figure 2b) and we attribute this to the hydride transfer rearrangement sequence of reaction 12.

$$CD_3OCH_2SCH_3 \xrightarrow{\overset{+}{CD_3OCH_2}} [CD_3OCH_2SCH_2^+]$$

$$\downarrow \text{rearrangement} \quad (12)$$

$$\overset{+}{CH_2SCH_2D} \xleftarrow{-CD_2O} [\overset{+}{CD_2OCH_2SCH_2D}]$$
$$m/e\ 62$$

However, the most abundant methylthiomethyl cation from $CD_3OCH_2SCH_3$ has m/e 61. Rearrangement cannot then be the dominant pathway, and routes 10 or 11 are evidently preferred.

We anticipated that product ions $CH_3SCH_2^+$ or $CH_3OCH_2^+$ would be formed by the dissociation of the protonated parent MH^+, according to reaction 6a or 6b, but MH^+ ions were not observed even when methane was intentionally added as a reagent gas to provide a source of acidic fragment ions (CH_5^+) from which to produce MH^+. Essentially, the spectrum of methoxymethylthiomethane was the same with added methane as without.

As already mentioned, the spectrum of Figure 2b shows an abundant product $(M - 1)^+$ ion. This ion is almost certainly formed by hydride abstraction from the methylene group of the neutral as this reaction would give a product ion that is stabilized by electron donation from both sulfur and oxygen. Double resonance confirmed that the precursor ions are methoxymethyl $(m/e$ 45) and methylthiomethyl $(m/e$ 61).
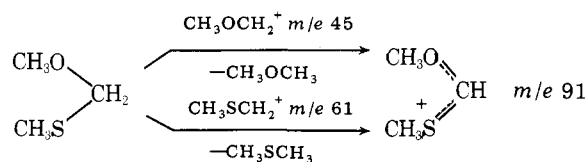
1-Methoxy-2-methylthioethane. The ion–molecule chemistry of $CH_3OCH_2CH_2SCH_3$ and its deuterium-labeled analogues was studied in detail in order to elucidate the nature of the observed reactions. A summary of the primary and product ions derived from labeled and unlabeled neutrals is given in Table I. The primary ions observed in the 19-eV mass spectrum were the molecular ion, *both* α-cleavage ions,

$CH_3OCH_2^+$ $(m/e$ 45) and $CH_3SCH_2^+$ $(m/e$ 61), and ions corresponding to $(M - CH_3SH)^{+\cdot}$, $(M - CH_3S)^+$, $(M - CH_3OH)^{+\cdot}$, and $(M - CH_3O)^+$. Each of the labeled compounds was 99% isotopically pure and gave primary fragment ions with no significant label scrambling. It is worth noting that $(M - CH_3SH)^{+\cdot}$ $(m/e$ 58) and $(M - CH_3OH)^{+\cdot}$ $(m/e$ 74) arise by a 1,2-elimination from the molecular ion judging from the m/e values of the labeled fragment ions (Table I and reactions 13 and 14).
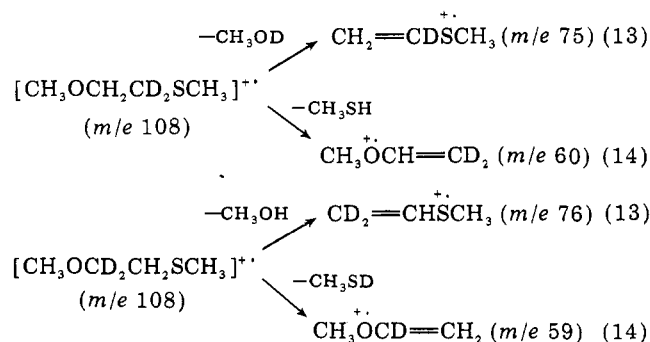
The most abundant product ion corresponds to $(M - CH_3O)^+$, or $CH_3S^+(CH_2)_2$ $(m/e$ 75). Previous discussion has described four possible routes to the formation of $(M - CH_3O)^+$ ions They are dissociation of the protonated parent ion (reaction 6a), hydride abstraction and CH_2O elimination (reaction 9), and alkylation–elimination (reaction 10 or 11). In the case of 1-methoxy-2-methylthioethane, double resonance confirms that reaction 6a does contribute to the formation of $(M - CH_3O)^+$. The intensity of the MH^+ ions is significant (Figure 3) and on irradiation at the resonance cyclotron frequency of MH^+ they dissociate by loss of methanol to give m/e 75. We conclude, therefore, that of the two elimination routes available to MH^+, 6a or 6b, the kinetically and energetically preferred route (6a) leads to a sulfonium ion and methanol. The alternative reaction involving loss of methanethiol to give m/e 59 was insignificant as m/e 59 appeared as a fragment ion, not a product ion.

However, the major route to m/e 75 utilizes $CH_3OCH_2^+$ $(m/e$ 45) as the reactant ion. If the hydride abstraction–elimination of reaction 9 is a significant route to m/e 75, then the labeled neutral $CD_3OCH_2CH_2SCH_3$ should lead to an $(M - 2)$ ion, but none was observed (see Table I). If hydride ab-

Figure 3. Single resonance 19-eV ICR mass spectrum at ~1.3 × 10⁻⁶ Torr and 50 ms of CH₃O(CH₂)₂SCH₃.

straction occurred at the thiomethyl group, the resultant ion $CD_3OCH_2CH_2SCH_2^+$ would not be stable as previous work has demonstrated that ions of this structure rearrange by a 1,6-hydride transfer and dissociate by loss of formaldehyde.[23] In the case of $CD_3OCH_2CH_2SCH_3$, this would lead to deuteride transfer and formation of m/e 76 (reaction 15). A minor

amount of m/e 76 appeared in the spectrum of $CD_3OCH_2CH_2SCH_3$ but the *major* product ion had m/e 75 (m/e 75: m/e 76 = 100:18), which means that if reaction 15 is a valid route to (M − CH₃O)⁺, it is by no means the major route. The same conclusion was arrived at in the related reaction (12) of the lower homologue $CH_3OCH_2SCH_3$.

The most interesting product ion in the spectrum of $CH_3OCH_2CH_2SCH_3$ is the (M − 1)⁺ ion formed by abstraction of hydride from the neutral by $CH_3SCH_2^+$ (m/e 61). There are four positions in the neutral from which hydride could be abstracted—two of which would lead to positive charge next to oxygen, and two next to sulfur. In order to determine the regiospecificity of hydride transfer to m/e 61, each of the four labeled compounds having deuterium at different locations along the chain was prepared. As may be ascertained from the data in Table I, the *only* compound that gave an (M − 2)⁺ ion was $CH_3OCH_2CD_2SCH_3$. There was no significant abundance of (M − [(⁺. The other three labeled compounds,

$CD_3OCH_2CH_2OCH_3$, $CH_3OCH_2CH_2SCD_3$, and $CH_3OCD_2CH_2SCH_3$, gave only (M − 1)⁺ ions. We conclude from these results that abstraction of hydride occurs selectively at the methylene group next to sulfur (reaction 16a).

Related hydride transfer from methoxyethane has been shown to occur at the methylene position rather than from the *O*-methyl group.[21] Therefore it is not surprising that hydride transfer is selective for methylene over methyl in the present case. The important point is that reaction is selective for *S*-methylene over *O*-methylene. This result establishes that *there is a kinetic preference in the gas phase for the formation of the sulfur-stabilized ion $CH_3OCH_2C^+HSCH_3$ over the oxygen-stabilized ion $CH_3OC^+HCH_2SCH_3$*.

1-Methoxy-2-methylthiopropane. The pattern of fragmentation and ion chemistry changes somewhat for the propane compound, $CH_3OCH_2CH_2CH_2SCH_3$. The major fragment ions are the molecular ion and $CH_3OCH_2^+$ (m/e 45). The sulfur analogue, $CH_3SCH_2^+$ (m/e 61), is neither a fragment ion nor a product ion. The major product ions are $CH_3S^+(CH_2)_n$ (m/e 89) and MH⁺ (m/e 121); a product ion of hydride abstraction (M − 1)⁺ (m/e 119) was not observed.

The abundance of the protonated parent ion increases in the series $CH_3O(CH_2)_nSCH_3$ from $n = 1$ (unobserved) to $n = 3$ (major product ion), and this observation parallels that of Beauchamp and Morton[24] that MH⁺ ions derived from dimethoxyalkanes are most abundant when the chain length permits a cyclic structure for MH⁺ such that that proton is bound to both heteroatoms in a five- or six-membered ring. In the present case, MH⁺ for the methoxymethylthiopropane could have a six-membered ring **1**.

Double resonance indicates that **1** dissociates by loss of methanol (not methanethiol) to give $CH_3S^+(CH_2)_3$ (m/e 89), but the main route to m/e 89 is by way of m/e 45 ($CH_3OCH_2^+$). For the same reasons given to explain the formation of (M − CH₃O)⁺ ions from $CH_3OCH_2SCH_3$ and $CH_3OCH_2CH_2SCH_3$, the most plausible pathway to m/e 89 is by alkylation--elimination according to reaction 10 or 11.

The absence of an (M − 1)⁺ ion appears a little surprising. However, there is no precursor ion of structure $CH_3SCH_2^+$ (m/e 61), which may be the reason why there is no apparent (M − 1)⁺ ion. Only m/e 61 gave an (M − 1)⁺ ion in the ethane derivative, which raises the question as to why $CH_3OCH_2^+$ (m/e 45) does not similarly abstract hydride. A possible reason is that the reaction of m/e 45 with the parent to produce $CH_3S^+(CH_2)_n$, $n = 2$ and 3, is so rapid that it is totally diverted into this reaction channel. Both (M − 1) and (M − OCH₃) ions were observed only in the reaction of m/e 45 with $CH_3SCH_2OCH_3$. In this case the (M − 1) ion presumably is stabilized by both sulfur and oxygen and therefore its formation is sufficiently exothermic to compete successfully with formation of (M − OCH₃). Thus, it appears that variable partitioning between reaction channels depends critically on their exothermicities.

Conclusions

The gas-phase ion–molecule reactions of mixed ethers of the type $CH_3O(CH_2)_nSCH_3$, where $n = 1-3$, show a strong preference for formation of sulfonium ions over similarly constituted oxonium ions. This result is not unexpected of reactions leading to tricoordinate sulfonium ions, R_3S^+, which are well known to be stable ions. In contrast, oxonium ions R_3O^+ are less common and considerably more reactive.[25] The two routes to $CH_3S^+(CH_2)_n$ according to reactions 6a, and 10 or 11 for $n = 2$ and 3, both lead to stable neutral products and involve dissociation of an intermediate ion $CH_3S-(CH_2)_n-Z^+$ where expulsion of the leaving group ($Z = CH_3OH$, CH_3OCH_3, or $CH_3OCH_2OCH_3$) is assisted by neighboring sulfur, which is notably better as a neighboring group than oxygen.[26] Accordingly, we presume that the sulfonium ions formed are cyclic tricoordinate species. Although there is no direct evidence from the current ICR study as to ion structure, a recent study on the gas-phase structure of $CH_3X^+(CH_2)_n$ has revealed a cyclic structure for the sulfur ion ($n = 2$) and an acyclic structure for the oxonium ion.[27]

A significant finding is that dicoordinate sulfonium ions $CH_3S^+=CH_2 \leftrightarrow CH_3S-CH_2^+$ are also formed in preference to oxonium ions $CH_3O^+=CH_2 \leftrightarrow CH_3O-CH_2^+$. The supporting evidence includes the observation that hydride transfer from $CH_3OCH_2CH_2SCH_3$ is selective for the methylene hydrogens next to sulfur; that oxonium ions $CH_3OCH_2^+$ induce the decomposition of $CH_3OCH_2SCH_3$ to give sulfonium ions $CH_3SCH_2^+$; and that ion stability as measured by relative chloride affinity favors $CH_3S^+CH_2$ over $CH_3O^+CH_2$.

A seeming contradiction to the finding that $CH_3SCH_2^+$ is formed in preference to $CH_3OCH_2^+$ is the fact that the major fragment ion in the 20-eV mass spectrum of $CH_2OCH_2SCH_3$ is $CH_3OCH_2^+$, not $CH_3SCH_2^+$. However, Harrison and coworkers have carefully considered the factors that determine relative ion abundance in competing fragmentation reactions.[13] They point out that relative ion abundance is not a direct measure of relative ion stability but depends on the ionization potentials of the neutral radicals and on the strength of the bonds cleaved. Thus, a lower ionization potential of the methoxymethyl radical relative to methylthiomethyl,[13] and a lower C–S vs. C–O bond[11] strength, favor fragmentation of $CH_3OCH_2SCH_3$ to give $CH_3OCH_2^+$.

Another apparent inconsistency is that the neutral reactants $CH_3O(CH_2)_nSCH_3$ react with $CH_3OCH_2^+$ by O-alkylation (reaction 10 or 11) rather than by S-alkylation. If sulfonium ions are preferred over oxonium ions, a route by way of S-alkylation might be expected. However, the actual route is dictated more by the stability of the final products than by the stability of the ion–molecule complex, and the products are indeed sulfonium ions rather than oxonium ions.

Our results are mainly descriptive and give no quantitative estimate of the preference of sulfonium over oxonium. However, they clearly establish that in competing modes of reaction, as in reactions 16a and 16b, the *kinetically* preferred product ion places the positively charged carbon adjacent to *sulfur*. Barring some unprecedented entropy effect, the kinetic products in a low-pressure ion–molecule reaction generally are the thermodynamic products,[31,20] which means that reaction to give the sulfur ion $CH_3OCH_2C^+HSCH_3$ is more exothermic than reaction to give $CH_3OC^+HCH_2SCH_3$. Because the reactants and the neutral product are *identical* for both reactions, 16a and 16b, the difference in enthalpy between the two reactions is the difference between the heats of formation of the two product ions. And for 16a to be more exothermic than 16b the heat of formation of $CH_3OCH_2C^+HSCH_3$ must be less (more stable) than $CH_3OC^+HCH_2SCH_3$. This result agrees well with the conclusions of Field,[8] Taft,[12] and Wolfe[3] that, in the gas phase, sulfur is better able to stabilize adjacent

positive carbon than oxygen, but it is contrary to the published heats of formation for 1 and 2.[9-11]

In the particular case of reaction between $CH_3OCH_2^+$ and $CH_3OCH_2SCH_3$, there are two competing reactions (7 and 8) which lead respectively to $CH_3SCH_2^+$ and $(M - 1)^+$. From the time plot of Figure 2a it can be determined that the specific rate of disappearance of m/e 45 is 1.16×10^{-9} mL mol^{-1} s^{-1}, which is close to the maximum rate of 1.2×10^{-9} mL mol^{-1} s^{-1} calculated from the Langevin–Gioumousis–Stevensen formulation of ion–molecule reaction rates.[32] This means that the collision complex is formed almost as rapidly as it dissociates to the product ions m/e 61 and $(M - 1)$, and reversion to m/e 45 is slow. That is to say, $CH_3SCH_2^+$ is kinetically preferred over $CH_3OCH_2^+$ in the dissociation of the ion–molecule complex $(M + 45)$. Accepting that the kinetic preference is a manifestation of thermodynamic preference,[31] then reaction 7 to give $CH_3SCH_2^+$ is more exothermic than the reverse process to give $CH_3OCH_2^+$.

In solution phase, the oxonium ion RO^+CH_2 is kinetically preferred over the sulfonium ion RS^+CH_2 when derived from the corresponding chlorides, which is *opposite* to their gas-phase reactivities. If we accept that the gas-phase results reflect the intrinsic properties of the ions, then it follows that inversion of reactivity in the ionization of $RXCH_2Cl$ in condensed phase is a manifestation of solvation and counterion effects.[28] Solvation energies of substituted carbocations, $CH_3XCH_2^+$, are not available, but it is well established that smaller ions are more strongly solvated than larger ions. Thus, the solvation energy gained on forming $CH_3OCH_2^+$ may be sufficiently larger than for the sulfur ion to cause the chloromethyl ether to ionize in a suitable solvent more rapidly than the chloromethyl sulfide.

The overall implications of the present work underscore the importance of solvation effects in reactions of organic ions and raise doubts about the validity of correlating relative reactivities exclusively with relative ion stabilities in solvolytic ionization reactions.

Experimental Section

Methoxymethylthiomethane was prepared from methyl chloromethyl ether and sodium methiolate in pentane and had bp 97–100 °C (lit.[29] 95–99 °C) and ^1H NMR (CCl$_4$) δ 2.05 (singlet, SCH$_3$), 3.25 (singlet, OCH$_3$), 4.50 (singlet CH$_2$). The labeled compound $CD_3OCH_2SCH_3$ was obtained from the reaction of chloromethyl methyl thioether with sodium methoxide-d_3 in dimethylformamide.[29]

1-Methoxy-2-methylthioethane was prepared in 35% yield overall from 2-chloroethanol by methylation with trimethyloxonium fluoroborate in dichloromethane to give 2-chloroethyl methyl ether (bp 91–95 °C) followed by displacement of chloride by sodium methiolate in tetrahydrofuran. The product had bp 132–133 °C (lit.[30] 131–132 °C) and ^1H NMR (CCl$_4$) δ 2.13 (singlet, SCH$_3$), 2.23 (triplet, SCH$_2$), 3.50 (triplet, OCH$_2$), 3.34 (singlet, OCH$_3$).

1-Methoxy-3-methylthiopropane was prepared from 3-chloropropanol by a similar route used in the synthesis of the ethane analogue. The product had bp 142–144 °C and ^1H NMR (CCl$_4$) δ 1.83 (multiplet, β-CH$_2$), 2.00 (singlet, SCH$_3$), 2.14 (triplet, $J = 7$ Hz, SCH$_2$), 3.20 (singlet, OCH$_3$), 3.34 (triplet, $J = 6$ Hz, OCH$_2$).

Anal. Calcd for $C_5H_{12}OS$: C, 49.95; H, 10.07. Found: C, 50.08; H, 10.10. Mol wt by MS, 120.

1-(Methoxy-d_3)-2-methylthioethane was obtained in 65% yield from 2-methylthioethanol, methyl-d_3 iodide, and silver oxide in dimethylformamide.

1-Methoxy-2-methylthio-d_3-ethane was obtained similarly from 2-methoxyethanethiol by reaction with methyl-d_3 iodide and silver oxide in dimethylformamide. The yield was 45%. **1-Methoxy-2-methylthioethane-2,2-d_2** was prepared in 56% yield from $CH_3OCH_2CD_2Cl$ and sodium methiolate in dimethylformamide. The starting labeled 2-chloroethyl methyl ether was prepared by reduction of methyl methoxyacetate with lithium aluminum deuteride (86% yield) followed by conversion of the product $CH_3OCH_2CD_2OH$ to

the chloride using thionyl chloride in ether and 1 equiv of tri-*n*-butylamine (78.5% yield).

1-Methoxy-2-methylthioethane-*1,1-d₂* was prepared from ethyl methylthioacetate by reduction with lithium aluminum deuteride to give 2-methylthioethanol-*1,1-d₂* (67% yield) followed by methylation of the alcohol with methyl iodide and silver oxide in dimethylformamide (62% yield). All samples were purified by preparative gas chromatography prior to analysis of their ICR spectra.

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Electron Transfer to and from Molecules Containing Multiple, Noninteracting Redox Centers. Electrochemical Oxidation of Poly(vinylferrocene)

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Abstract: A general analysis is presented of the behavior to be expected in voltammetric experiments with molecules containing a number of identical, noninteracting centers that accept or give up electrons. It is shown that all such molecules will exhibit current–potential responses having the same shape as that obtained with the corresponding molecule containing a single center. Only the magnitude of the current is enhanced by the presence of additional electroactive centers. As an experimental example of the predicted behavior, the electrooxidations of vinylferrocene and two poly(vinylferrocenes) in nonaqueous media are described. A comparison of the behavior predicted in the present work with several previous studies of molecules with multiple redox centers is also presented.

The electrochemical behavior of molecules which contain several electroactive sites has been the subject of a number of studies.[2,3] The differences in potential between the half-reactions of the successive electron transfers to such molecules can depend upon the extent of interaction between the sites, solvation changes, ion pairing, and structural changes of the molecule, but for molecules containing identical, *noninteracting* centers, the successive electron transfers will follow simple statistics. In the absence of significant molecular reorganization or solvation changes, the separations between successive formal potentials (as defined below) will depend only on the number of centers present. For example, with two centers present the separation is equal to $(RT/F) \ln 4$.[4a] This situation is analogous to that of the separation in p*K*s of a molecule with noninteracting acidic groups.[5] As Ammar and Savéant have pointed out,[4a] the Nernstian voltammetric wave which results from such a situation has the shape of a one-electron transfer reaction, although more than one electron is