J. Org. Chem. **1996,** *61,* 929−934

Ion−Radical Complexes and $S_{RN}1$-like Reactions in the Gas-Phase. A Negative-Ion Mass Spectrometric Investigation of Arylazo Sulfides[‡]

Carlo Dell'Erba,[1a] Abdelaziz Houmam,[1b] Nicole Morin,[1c] Marino Novi,[1a,*] Giovanni Petrillo,[1a]
Jean Pinson,[1b,*] and Christian Rolando[1c,*]

Istituto di Chimica Organica dell'Università, C.N.R., Centro di Studio per la Chimica dei Composti
Cicloalifatici e Aromatici, Corso Europa 26, 16132 Genova, Italy, Laboratoire de l'Activation Moléculaire,
Ecole Normale Supérieure, Département de Chimie, Unité de Recherche Associée au CNRS No. 1679,
Laboratoire Associé à l'Université Pierre et Marie Curie, 24 Rue Lhomond, 75231 Paris Cedex 05, France,
and Laboratoire d'Electrochimie Moléculaire de l'Université Denis Diderot-Paris 7, Unité de Recherche
Associée au CNRS No. 438, 2 Place Jussieu, 75251 Paris Cedex 05, France

Received July 21, 1995[⊗]

The negative-ion mass spectra of arylazo sulfides ArN═NSR (**1**) show that their radical anions ($\mathbf{1}^{\bullet-}$), in competition with the fragmentation to aryl radicals, nitrogen, and thiolate anions, generate the radical anions of the corresponding sulfides ($ArSR^{\bullet-}$) and/or fragments therefrom. The competition between the two pathways above depends on the nature of the aryl moiety (possible presence and strength of electron-withdrawing substituents), on the nucleophilicity of the thiolate fragment, and on the stereochemistry [(*E*)- or (*Z*)-configuration] of the starting arylazo sulfide. The results are best interpreted through the possibility that $\mathbf{1}^{\bullet-}$ leads to $ArSR^{\bullet-}$ through an electrostatically bonded thiolate ion−aryldiazenyl radical complex, in competition with dissociation of such a complex into separated species. A comparison with previous results on electrochemically induced reactions of **1** suggests that ion−radical pairs are key intermediates both in gas-phase and in solution.

Introduction

The $S_{RN}1$ reaction[2,3] of arylazo sulfides **1** with suitable anionic nucleophiles (Nu^-) has been recently exploited for the synthesis of a number of variously functionalized aromatic compounds.[4] The $\mathbf{1}^{\bullet-}$ radical anion, obtained via cathodic or homogeneous reduction (*e.g.* by the nucleophile itself, sometimes under photostimulation) (reaction 1), has been proposed to cleave (reaction 2) to give an aryl radical; coupling between $Ar^\bullet$ and the nucleophile produces (reaction 3) the radical anion of the substitution product, which effectively closes the propagation cycle by means of an electron exchange with the substrate (reaction 4). Anyway, the "external" nucleophile (Nu^-) always suffers competition by RS^- (*i.e.* the "internal" nucleophile, formed along the fragmentation step 2), whose coupling with $Ar^\bullet$ (reaction 3′) triggers an alternative propagation cycle leading to the ArSR sulfide **2**.

$$\underset{\mathbf{1}}{ArN{=}NSR} + \text{electron donor} \rightleftharpoons \underset{\mathbf{1}^{\bullet-}}{ArN{=}NSR^{\bullet-}} \qquad [1]$$

$$\underset{\mathbf{1}^{\bullet-}}{ArN{=}NSR^{\bullet-}} \xrightarrow{k_2} Ar^{\bullet} + N_2 + {}^{-}SR \qquad [2]$$

$$Ar^{\bullet} + Nu^{-} \xrightarrow{k_3} ArNu^{\bullet-} \qquad [3]$$

$$ArNu^{\bullet-} + ArN{=}NSR \rightleftharpoons ArNu + ArN{=}NSR^{\bullet-} \qquad [4]$$

$$Ar^{\bullet} + {}^{-}SR \xrightarrow{k_{3'}} ArSR^{\bullet-} \qquad [3']$$

$$ArSR^{\bullet-} + ArN{=}NSR \rightleftharpoons \underset{\mathbf{2}}{ArSR} + ArN{=}NSR^{\bullet-} \qquad [4']$$

Hints[4b] that reaction 3′ could take place in a solvent cage[5] have been more recently supported[6] by means of electrochemistry, which has proved to be a very efficient way of initiating and analyzing $S_{RN}1$ processes.[7] As a matter of fact, analysis by cyclic voltammetry of the behavior of arylazo sulfides upon cathodic reduction in the presence of increasing amounts of cyanide as the "external" nucleophile has revealed, at least in some cases, the existence, in the plot of ArCN percent *vs* [CN^-], of a plateau region at high [CN^-] values which is significantly less than 100%: this clearly indicates that a fraction of aryl radicals cannot be trapped by the "external" nucleophile. Actually, it was found that the trapping of the 4-cyanophenyl radical (at CN^-/azo sulfide molar ratios higher than 200) was more efficient starting from the (*E*)-(4-cyanophenyl)azo *tert*-butyl sulfide (96% of "external" trapping) than from the (*Z*)-isomer (65% of trapping) although these two compounds present, in the

---

[‡] Dedicated to Professor Giorgo Modena on the occasion of his 70th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

[1] (a) Università di Genova. (b) Université Denis Diderot. (c) Ecole Normale Supérieure.

[2] Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11,* 413.

[3] Rossi, R. A.; Rossi, R. H. *Aromatic Nucleophilic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178, American Chemical Society: Washington, D.C., 1983.

[4] (a) Petrillo, G.; Novi, M.; Garbarino, G.; Dell'Erba, C. *Tetrahedron* **1986**, *42*, 4007. (b) Petrillo, G.; Novi, M.; Garbarino, G.; Dell'Erba, C. *Tetrahedron* **1987**, *43*, 4625. (c) Petrillo, G.; Novi, M.; Dell'Erba, C.; Tavani, C.; Berta, G. *Tetrahedron* **1990**, *46*, 7977. (d) Dell'Erba, C.; Novi, M.; Petrillo, G.; Tavani, C.; Bellandi, P. *Tetrahedron* **1991**, *47,* 333. (e) Dell'Erba, C.; Novi, M.; Petrillo, G.; Tavani, C. *Tetrahedron* **1992**, *48,* 325. (f) Dell'Erba, C.; Novi, M.; Petrillo, G.; Tavani, C. *Tetrahedron* **1993**, *49,* 235. (g) Dell'Erba, C.; Novi, M.; Petrillo, G.; Tavani, C. *Tetrahedron* **1994**, *50,* 3529.

[5] (a) Koenig, T.; Fisher, H. Cage Effects. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol I, p 157. (b) Frank, J.; Rabinowitch, E. *Trans. Faraday Soc.* **1934**, *30,* 120. (c) Calverts, J.; Pitts, J. *Photochemistry;* Wiley: New York, 1966; p 226. (d) Noyes, R. M. *Z. Electrochem.* **1960**, *69,* 153. (e) Strong, R. L. *J. Am. Chem. Soc.* **1965**, *87,* 3563.

[6] Dell'Erba, C.; Houmam, A.; Novi, M.; Petrillo, G.; Pinson, J. *J. Org. Chem.* **1993**, *58,* 2670.

[7] (a) Pinson, J.; Savéant, J.-M. *J. Chem. Soc., Chem. Commun.* **1974**, 933. (b) Savéant, J-M. *Acc. Chem. Res.* **1980**, *13,* 123. (c) Savéant, J.-M. *Adv. Phys. Org. Chem.* **1990,** *26,* 1. (d) Pinson, J.; Savéant, J.-M. In *Electroorganic Synthesis, Festschrift for Manuel Baizer*; Little, R. D., Weinberg, N. L., Eds.; Marcel Dekker: New York, 1991; p 29.

0022-3263/96/1961-0929$12.00/0

absence of CN^-, the same cyclic voltammetry. Two explanations were envisaged[6] in order to rationalize the different behavior of the two isomers. The first possibility is that, while the radical anion of the (*E*)-isomer does actually fragment (reaction 2) to give the 4-cyanophenyl radical (which would then couple with the different nucleophiles present in the bulk solution), the radical anion of the (*Z*)-isomer undergoes, in competition with fragmentation, an intramolecular formation of the carbon−sulfur bond simultaneously with the cleavage of the aryl−nitrogen and of the sulfur−nitrogen bonds; for stereochemical reasons this intramolecular component would not be as efficient in the case of the (*E*)-isomer. The second possible explanation would take into account that the radical anions of both (*E*)- and (*Z*)-azo sulfides fragment into $Ar^•$ and RS^-, which are separated by a nitrogen molecule for the (*E*)-isomer, but proximal (and thus ready for in-cage coupling) for the (*Z*)-isomer.

A possible way to gain a deeper insight into the mechanism of formation of the sulfide radical anion $\mathbf{2}^{•-}$ from $\mathbf{1}^{•-}$ would be to suppress any solvent-cage or out-of-cage coupling of the aryl radical with the nucleophile.[5] In principle, this goal can be achieved by producing $\mathbf{1}^{•-}$ in the gas phase where, because of the low-pressure conditions, the probability of recombination of separated fragments therefrom (*i.e.* $Ar^•$ and RS^-) should be lowered.[5] As a matter of fact, it would be very interesting, and indeed unprecedented, to ascertain whether $S_{RN}1$-like reactions exist in the gas phase, and azo sulfides, which provide upon cleavage both the radical and the nucleophile, are suitable candidates for such a test.

For these reasons, we decided to analyze by negative-ion mass spectrometry the behavior of some representative azo sulfides (**1a**−**h**)[8,9] and, for comparison, of sulfides **2a**−**e**, the relevant radical anions being produced by chemical ionization.

	ArN=NSR **1**	ArSR **2**
(*E*)-**1a**, **2a**	Ar = 4-CNC_6H_4	R = C_6H_5
(*E*)-**1b**, **2b**	Ar = 4-$NO_2C_6H_4$	R = C_6H_5
(*E*)- and (*Z*)-**1c**, **2c**	Ar = 4-CNC_6H_4	R = Bu^t
(*E*)- and (*Z*)-**1d**, **2d**	Ar = 4-$NO_2C_6H_4$	R = Bu^t
(*Z*)-**1e**, **2e**	Ar = C_6H_5	R = Bu^t
(*Z*)-**1f**	Ar = 2-$NO_2C_6H_4$	R = Bu^t
(*Z*)-**1g**	Ar = 4-$CH_3C_6H_4$	R = Bu^t
(*Z*)-**1h**	Ar = 2,4,6-$(CH_3)_3C_6H_2$	R = Bu^t

Results

The relative intensities of the peaks corresponding to the main fragments in the negative-ion mass spectra of the compounds examined are summarized in Table 1, and a complete description of the spectra is given in the Experimental Section. The spectra were obtained with ammonia as the ionizing gas: identical or very similar results can be obtained with methane, as ascertained for compounds **1a**−**d**.

Table 1. Relative Intensities[a] of the Most Significant Peaks in the Chemical-Ionization (NH_3) Negative-Ion Mass Spectra of Azo Sulfides ArN═NSR (1) and Sulfides ArSR (2)[b,c]

compd	Ar	R	$ArSR^{•-}$	ArS^-	RS^-
(*E*)-**1a**	4-CNC_6H_4	C_6H_5	7	17	100
2a			100	62	2
(*E*)-**1b**	4-$NO_2C_6H_4$	C_6H_5	100	18	18
2b			100	2	<1
(*E*)-**1c**	4-CNC_6H_4	Bu^t	<1	100	9
(*Z*)-**1c**			<1	100	2
2c			<1	100	
(*E*)-**1d**	4-$NO_2C_6H_4$	Bu^t	<1	100	5
(*Z*)-**1d**			<1	100	<1
2d				100	<1
(*Z*)-**1e**	C_6H_5	Bu^t		3	100
2e			45	100	<1
(*Z*)-**1f**	2-$NO_2C_6H_4$	Bu^t	4	100	4
(*Z*)-**1g**	4-MeC_6H_4	Bu^t		9	100
(*Z*)-**1h**	2,4,6-$Me_3C_6H_2$	Bu^t		5	100

[a] Relative intensities calculated for a base peak of 100%, taking into account, for each species, the contribution both of the whole isotopic cluster and, when detected, of the (M − 1) peak. [b] Relative intensity < 1 means observed but not quantified. [c] All the spectra were recorded consecutively, and self-consistent data are always obtained when samples are run under identical conditions.

The most interesting feature of the data reported in Table 1 is represented by the observation, for almost all the azo sulfides investigated, of peaks of anionic species deriving from the corresponding sulfides ArSR and of arenethiolate anions (ArS^-), whose presence calls, of course, for an effective formation, along the decay of azo sulfide radical anions, of an Ar−S bond. The sulfide radical anion ($ArSR^{•-}$) corresponds to the base peak in the spectrum of *(E)*-**1b** and it can be observed as a minor peak in the case of *(E)*-**1a**, *(E)*- and *(Z)*-**1d**, and *(Z)*-**1f**, while is completely absent for *(Z)*-**1e** and *(Z)*-**1h**; minor peaks corresponding to $m/z = [ArSR\text{-}1]^-$ are observed for (*E*)- and (*Z*)-**1c** and (*Z*)-**1g**. On the other hand, the ArS^- peak can be observed for all the compounds, being the base peak in the spectra of (*E*)- and (*Z*)-**1c**, (*E*)- and (*Z*)-**1d**, and (*Z*)-**1f**: as a matter of fact, except for the case of (*E*)-**1b**, the intensity of the ArS^- peak is larger than that corresponding to $ArSR^{•-}$ or $[ArSR\text{-}1]^-$.

Another product constantly present in the decay of azo sulfide radical anions is represented by RS^- [observed as the base peak for *(E)*-**1a**, *(Z)*-**1e**, *(Z)*-**1g**, and *(Z)*-**1h**]. Minor, though quite widespread, fragmentation pathways involve the formation: of the following $ArN{=}NS^-$ [for *(E)*- and *(Z)*-**1c**, *(E)*- and *(Z)*-**1d**, *(Z)*-**1e**, *(Z)*-**1g**, and *(Z)*-**1h**)];[10] Ar^- and in some cases also of $ArH^{•-}$ [for *(E)*-**1a**, *(E)*-**1b**, *(E)*-**1c**, *(E)*- and *(Z)*-**1d**, and *(Z)*-**1f**−**h**]; $ArNH_2^{•-}$ and/or $ArNH^-$ species [for *(E)*-**1a**, *(E)*- and *(Z)*-**1c**, *(E)*- and *(Z)*-**1d** and *(Z)*-**1e**].

As expected for charged species, the radical anions of azo sulfides appear to be shorter lived in the gas phase than in solution. In ACN at 20 °C the following lifetimes have been measured: 2.6×10^{-5} s for *(E)*-**1a**,[6] 9.2×10^{-3} s for *(E)*-**1b**,[6] 6.9×10^{-4} s for *(E)*-**1c**,[6] 1.7×10^{-3} s for *(Z)*-**1c**,[11] and ca. 170 s for *(E)*-**1d**;[11] herein, the detectable $\mathbf{1}^{•-}$ mass peaks [*(E)*-**1c** and *(E)*-**1d**] are always smaller

---

(8) The voltammograms at 0.2 V s^{-1} in ACN + 0.1 M NBu_4BF_4 are similar to those of the substrates described in reference 6: (*Z*)-**1e** ($E_p = -1.65$ V/SCE, irreversible, $n = 0.64$ F/mol); (*Z*)-**1f** ($E_p = -1.15$ V/SCE, reversible, $n = 0.90$ F/mol); (*Z*)-**1g** ($E_p = -1.70$ V/SCE, irreversible, $n = 0.62$ F/mol) ; (*Z*)-**1h** ($E_p = -1.95$ V/SCE, irreversible, $n = 0.78$ F/mol).

(9) Mass spectrometry of (*E*)- and (*Z*)-**1d** with different ionization methods (electron impact, fast bombardment, positive-ion chemical ionization) and collision experiments has been already reported. Sottani, C.; Mele, A.; Favretto, D.; Traldi, P. *Org. Mass Spectrom.* **1992**, *27*, 169.

(10) The cleavage of ArN═NSBu^t radical-anion at the level of the S−Bu^t bond to give arenediazothiolate anion was never observed[4] in solution, and no product reasonably ensuing from it was ever isolated in the course of the reactions carried out on such kind of azo sulfides.

(11) Dell'Erba, C.; Novi M.; Neudeck, A.; Petrillo, G.; Pinson, J. Preliminary results.

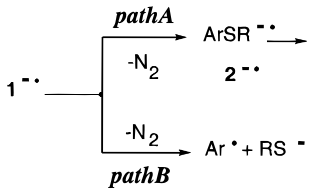
than 1%, indicating that their gas-phase lifetime is smaller than 1 μs.

The gas-phase cleavage of the ArSR$^{\bullet-}$ radical anions from sulfides **2a**−**e** mainly gives ArS$^-$, together with at most meager quantities of RS$^-$: for **2a** and **2b** the intensity ratio of the peaks relevant to ArS$^-$ and RS$^-$ (R = Ph) is 31 and ca. 2, respectively, while for **2c**, **2d**, and **2e**, RS$^-$ (R = Bu^t) is hardly detectable, indicating that herein, for **2a**−**e**$^{\bullet-}$, the fragmentation of the S−R bond to ArS$^-$ and R$^\bullet$ is in general much faster than that of the Ar−S bond to Ar$^\bullet$ and RS$^-$, for both R = Ph and Bu^t. The same type of fragmentation has already been observed for other sulfide radical anions obtained by electron impact,[12−14] and the results herein well match those obtained in aprotic solvents by either electrochemistry, solution electron transfer, or alkali-metal reduction. Thus, the electrochemically generated diphenyl sulfide radical anion cleaves[15,16] to give a phenyl radical and a benzenethiolate anion while diphenylmethyl 4-nitrophenyl sulfide radical anion[17] fragments to a diphenylmethyl radical and a 4-nitrobenzenethiolate anion. Alkyl aryl sulfide radical anions[18] produced by photochemically induced electron transfer or by alkali or alkali-earth metal reduction[19−22] cleave consistently and selectively the alkyl−sulfur bond regardless of the identity of the aryl moiety. This experimentally observed mode of cleavage is furthermore in agreement with the results of calculations indicating that, on purely thermodynamic grounds, the radical anion of ethyl phenyl sulfide should cleave to give a benzenethiolate anion.[18]

Discussion

The negative-ion MS data reported in Table 1 provide, at least in some cases [*(E)*- and *(Z)*-**1c**, *(E)*- and *(Z)*-**1d**], clear-cut evidence that the gas-phase decay of ArN=NSR$^{\bullet-}$ (**1**$^{\bullet-}$) effectively goes through the relevant ArSR radical-anions (**2**$^{\bullet-}$): as a matter of fact, the fragmentation patterns of **1c**$^{\bullet-}$ and **1d**$^{\bullet-}$, which experience formation of ArS$^-$ as the base peak, very well match those of the radical anions obtained by ionization of the corresponding sulfides (little differences being only connected with the relative abundance of RS$^-$ which appears hardly formed, if any, when starting from **2c** and **2d**). Unlike **1c** and **1d**, in the negative-ion mass spectra of *(E)*-**1a** and *(E)*-**1b** (R = Ph) as well as of *(Z)*-**1e** (R = Bu^t) the difference in the relative abundance of the species ensuing from the fragmentation of **1**$^{\bullet-}$ and **2**$^{\bullet-}$ is substantial. Thus, the ArS$^-$/ArSR$^{\bullet-}$ and RS$^-$/ArSR$^{\bullet-}$ ratios of relative abundance are always much larger for the azo sulfides than for the corresponding sulfides. Overall, considering the experimental data, ArN=NSR with electron-withdrawing groups (CN, NO$_2$) in Ar exhibits a behavior which is different from that of the corresponding sulfides when R = Ph, but similar when R = Bu^t. With less electrophilic aryl moieties (*i.e.* for the phenyl compounds **e**) the behavior of **1** and **2** is dissimilar, notwithstanding R = Bu^t: the former fragments mainly to Bu^{t}S$^-$, the latter to ArS$^-$. In agreement with the main fragmentation pattern of the phenyl derivative *(Z)*-**1e** are also those of the p-tolyl [*(Z)*-**1g**] and mesityl [*(Z)*-**1h**] derivatives, while the 2-nitro derivative *(Z)*-**1f** gives results consistent with those of the 4-nitro analogue *(Z)*-**1d**. Thus, introduction in the aryl ring of substituents *ortho* to the azothio group [2-nitro in *(Z)*-**1f** and 2,4,6-trimethyl in *(Z)*-**1h**] does not completely prevent the formation of an aryl−sulfur bond (the intensities of the peaks of ArSR$^{\bullet-}$ and ArS$^-$ being, respectively, 4% and 100% for **1f**, 0% and 5% for **1h**).

Scheme 1



In principle, the two sets of results of Table 1 (i.e. azo sulfide behavioral similarity or dissimilarity with **2**) could be reconciled within the same framework of a common intermediate (ArSR$^{\bullet-}$) for the negative ion-induced fragmentation of **1** and **2** by admitting that **2**$^{\bullet-}$, when formed from **1**, possesses an excess of internal energy and thus undergoes a faster cleavage. A similar observation has been actually reported[23] for the decomposition, for instance, of diaryl ether radical cations generated either by electron-impact ionization of the neutral precursor or via carbon dioxide elimination from diaryl carbonate radical cations. In accordance with its higher energy content,[24] the diaryl ether radical cation fragments more intensively when formed by internal ion-radical reaction from diaryl carbonates. Nonetheless, while the hypothesis above cannot easily be dismissed for the enhanced cleavage of the ArS−R bond from **1** [(ArS$^-$/ArSR$^{\bullet-}$)$_1$ ≥ (ArS$^-$/ArSR$^{\bullet-}$)$_2$], since a source for ArS$^-$ alternative to ArSR$^{\bullet-}$ is hardly conceivable, the extention of the same hypothesis to the Ar−SR fragmentation does not seem likely to hold for the whole of the results obtained: *e.g.* while there is no variation of the RS$^-$/ArS$^-$ abundance ratio from **2d** to (*Z*)-**1d** (<0.01 in both cases), the same value increases more than three thousand times on going from **2e** to **1e**.

Thus, in our opinion, a more comprehensive logical basis of the results obtained is that the fragmentation of azo sulfide radical anions (**1**$^{\bullet-}$) proceeds through two different competitive pathways (Scheme 1). The first one should involve the formation of ArSR radical anions **2**$^{\bullet-}$ and of fragments ensuing from their successive cleavage (mainly ArS$^-$); the second route should give RS$^-$ together with Ar$^\bullet$ as separated species, the fragmentation of **2**$^{\bullet-}$ into RS$^-$ and Ar$^\bullet$ being negligible. Moreover, the hypothetical formation of ArSR$^{\bullet-}$ by coupling between an Ar$^\bullet$ radical and a RS$^-$ anion as separated species ensuing from (i) unimolecular fragmentation of ArN=NSR$^{\bullet-}$ or (ii) two different molecules of azo sulfide, is very unlikely

---

[12] Bowie, J. H. *Mass Spectrom. Rev.* **1984**, *3*, 161.

[13] Nolde, C.; Madsen, J. O.; Lawesson, S. O.; Bowie, J. H. *Arkiv Kemi* **1969**, *31*, 481.

[14] Bowie, J. H., Duss, F.; Lawesson, S. O.; Larsson, F. C. V.; Madsen, J. O. *Aust. J. Chem.* **1969**, *22*, 153.

[15] Amatore, C.; Combellas, C.; Pinson, J.; Oturan, M. A.; Robveille, S.; Savéant, J.-M.; Thiébault, A. *J. Am. Chem. Soc.* **1985**, *107*, 4846.

[16] Gerdil R. *J. Chem. Soc.* **1966**, 1071.

[17] Farnia, G.; Severin, M. G.; Capobianco, G.; Vianello, E. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1.

[18] Cheng, C.; Stock, L. M. *J. Org. Chem.* **1991**, *56*, 1436.

[19] Van Schooten, J.; Knoterus, J.; Boer, H.; Duinker, Ph. *Recl. Trav. Chim. Pays-Bas* **1958**, *77*, 935.

[20] Adams, R.; Ferretti, A. *J. Am. Chem. Soc.* **1959**, *81*, 4939.

[21] Truce, W. E.; Breiter, J. J. *J. Am. Chem. Soc.* **1960**, *82*, 2872.

[22] Ferretti, A. *Org. Synth.* **1962**, *42*, 54.

[23] Williams, D. H.; Cooks, R. G.; Hove I. *J. Am. Chem. Soc.* **1968**, *90*, 6759.

[24] Fragmentation of arylazo sulfides is generally so fast that no molecular radical anion is detected; therefore it was not possible to perform MS/MS experiments in order to investigate the dependence of fragmentation on internal ion energy.

Table 2. Ratios of the Relative Intensities of the Sum ($ArSR^{\bullet-}$ + ArS^-) to RS^-: k_A/k_B Values

compd	Ar	R	k_A/k_B
(*E*)-**1a**	$4\text{-}CNC_6H_4$	C_6H_5	0.24
(*E*)-**1b**	$4\text{-}NO_2C_6H_4$	C_6H_5	6.55
(*E*)-**1c**	$4\text{-}CNC_6H_4$	Bu^t	11.1
(*Z*)-**1c**	$4\text{-}CNC_6H_4$		50.0
(*E*)-**1d**	$4\text{-}NO_2C_6H_4$	Bu^t	20.0
(*Z*)-**1d**	$4\text{-}NO_2C_6H_4$		>100
(*Z*)-**1e**	C_6H_5	Bu^t	0.03
(*Z*)-**1f**	$2\text{-}NO_2C_6H_4$	Bu^t	26.0
(*Z*)-**1g**	$4\text{-}MeC_6H_4$	Bu^t	0.09
(*Z*)-**1h**	$2,4,6\text{-}Me_3C_6H_2$	Bu^t	0.05

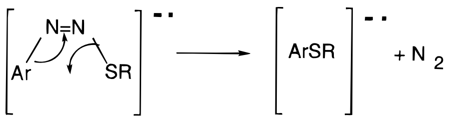
in the ion source of a mass spectrometer. Actually, only few reactions of this kind between ions and radicals have been reported;[25−29] furthermore, such a reaction should be very sensitive to the concentration of substrate in the ion source, while the fragmentation described here shows no dependence upon the quantity of sample introduced.[30]

Therefore, being plausible that paths A and B of Scheme 1 are independent, an estimation of the relative rates of the two competitive routes (k_A/k_B, Table 2) can be obtained from the ratio of the relative intensities of the sum of $ArSR^{\bullet-}$ + ArS^- to RS^-. The k_A/k_B values reported in Table 2 clearly show that the competition between paths A and B depends on the nature of both the aryl moiety (possible presence and strength of electron-withdrawing substituents) and R (Ph or Bu^t) as well as on the stereochemistry in the starting azo sulfide.

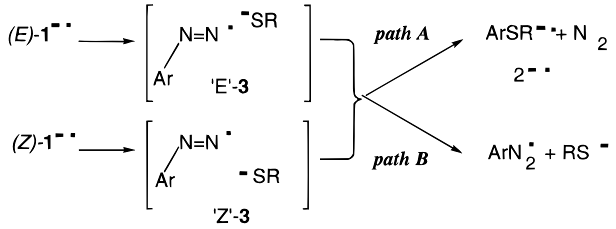
On this last point, in particular, the comparison of the values k_A/k_B for the pairs of stereoisomers of **1c** and **1d** shows that such ratio is about five times larger for the *(Z)*- than for the *(E)*-isomers. The different k_A/k_B values indicate that complete equilibration between the radical anions of the two *(E)*- and *(Z)*-isomers does not take place before any subsequent reaction in the gas phase.[31]

As already anticipated, the hypothesis of a competition similar to that depicted in Scheme 1, *i.e.* an intramolecular process, leading from $\mathbf{1}^{\bullet-}$ to $\mathbf{2}^{\bullet-}$, which competes with fragmentation of $\mathbf{1}^{\bullet-}$ into $Ar^\bullet$ and RS^-, has been previously advanced[6] also in solution in order to explain the results obtained from the electrochemically induced reactions of *(E)*- and *(Z)*-**1c** with tetraethylammonium cyanide in ACN. When large concentrations of cyanide are present in the solution containing (*E*)-**1c** or (*Z*)-**1c**, 96% and 65%, respectively, of the 4-cyanophenyl radicals are trapped by the cyanide ion to give eventually terephthalonitrile. With the assumption that all the aryl radicals coming from a process assimilable to path B of Scheme 1 are trapped by the excess cyanide,[32] the results obtained indicate that the contribution of the reaction leading to $ArSR^{\bullet-}$ (a process assimilable to path A of Scheme 1) is at most 4% for *(E)*-**1c** and 35% for *(Z)*-**1c**. Therefore, for such reactions in solution an estimation of the k_A/k_B values gives 35/65 = 0.53 for *(Z)*-**1c** and 4/96 = 0.04 for *(E)*-**1c**. Thus, the same relative order $k_A/k_{B[(Z)\text{-}\mathbf{1c}]} > k_A/k_{B[(E)\text{-}\mathbf{1c}]}$ is found in the gas phase and in solution.

Scheme 2



Scheme 3



On the grounds of the discussion above, the following two mechanistic possibilities can, in principle, account for the formation of $\mathbf{2}^{\bullet-}$ from $\mathbf{1}^{\bullet-}$ along path A: (a) a concerted process, within the radical anion of the azo sulfide, involving cleavage of the Ar−N and S−N bonds and formation of the Ar−S bond; (b) reaction between a radical ($Ar^\bullet$ or $Ar\text{-}N{=}N^\bullet$) and the RS^- anion which have never become completely separated.

Actually, the first of the two mechanistic hypotheses above, which could be sketched as in Scheme 2, appears to be less likely as (i) such a process should be possible only for radical anions of azo sulfides in *(Z)*-configuration. Accordingly, as we believe that no significant *(E)* to *(Z)* stereomutation occurs at the level of $\mathbf{1}^{\bullet-}$ due to its very fast decay, the sulfide formed from the *(E)*-isomer cannot originate from the pathway in Scheme 2; (ii) the concerted mechanism should involve a strained four-center cyclic transition state, which would supposedly be of high energy[33] and thus make path A slow and kinetically disfavored with respect to the competing path B (what would make k_A/k_B < 1 in every case).

As concerns the second mechanistic possibility advanced above to account for the formation of $\mathbf{2}^{\bullet-}$ from $\mathbf{1}^{\bullet-}$, it should involve (Scheme 3) an initial cleavage of the N−S bond[4] at the level of the azo sulfide radical anion to form an intermediate complex "*E*"- or "*Z*"-**3** between the aryldiazenyl radical and the thiolate anion. The previously cited paths A and B originate from these intermediate complexes. Path A leads to $ArSR^{\bullet-}$ within the complex itself. Path B corresponds to the dissociation of the complex to $ArN_2^\bullet$ and RS^- as separated species. Path B can well account for the observed formation of RS^- and of minor species ($ArH^{\bullet-}$, Ar^-, $ArNH^-$) conceivably ensuing from subsequent reactions (electron and proton transfers, coupling with NH_2^- from the ionizing gas) of aryl radicals formed by fragmentation of aryldiazenyl radicals escaping from the complex. Within com-

---

[25] Callery, P. S.; Garland, W. A.; Fukuda, E. K. *Org. Mass Spectrom.* **1989**, *24*, 385.

[26] Radical molecule reactions have been observed for example between 7,7,8,8-tetracyanoquinodimethane and the $CH_3\cdot$ radicals obtained from the reagent gas[27,28] and between benzoyl radicals and benzene-1,4-diol.[29] However in this last case, the radicals are produced by thermal decomposition of benzoyl peroxide during the coevaporation of both reagents.

[27] McEwen, C. N.; Rudat, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 6470.

[28] McEwen, C. N.; Rudat, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 4343. *Ibid. Idem.* 4349. *Ibid. Idem.* 4355.

[29] Tu, Y-P.; Liu, Y-Q. *Org. Mass Spectrom.* **1992**, *27*, 313.

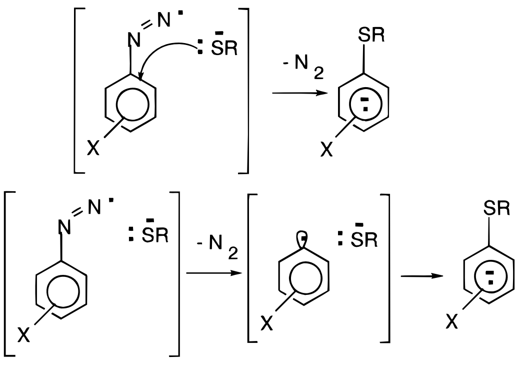
[30] The spectrum of *(E)*-**1a** was investigated as a function of concentration; no significant change could be observed upon a hundred fold increase of the concentration.

[31] Preliminary results[11] indicate that, in solution, the slow-cleaving radical anion $\mathbf{1d}^{\bullet-}$ undergoes stereomutation. The difference with the gas-phase behavior observed herein is related to the difference of the lifetimes (170 s in solution compared to less than 1 μs in gas phase).

[32] The contribution of $Ar^\bullet$ to Ar^- at the electrode is very low and can be neglected without affecting the the estimation of the k_A/k_B values.

[33] As suggested by a referee, twisting of the aryl moiety in order to accomplish the Ar−S bond formation would further increase the barrier to a four-center reaction.

Scheme 4



plexes “*E*”- and “*Z*”-**3**, in turn, the formation of $ArSR^{\bullet -}$ (path A) can be best envisaged to occur, as depicted in Scheme 4, via a nucleophilic attack of RS^- on the aryl carbon bearing the diazenyl nitrogen with detachment of a nitrogen molecule. This possibility implies that diazenyl radical intermediates survive[34] long enough to undergo nucleophilic attack; however, a fragmentation of the aryldiazenyl radical (with extrusion of nitrogen) followed by coupling of the resulting aryl radical with the thiolate anion (always within a complex) cannot be excluded at least as a contributing reaction channel to $ArSR^{\bullet -}$.

The formation of complexes between ions and neutral species, held together by electrostatic forces arising from ion-dipole or ion-induced dipole interactions, is well documented in the gas phase[36-38] including examples with anions.[39,40] The stabilization energy (V_r) of such complexes is approximately given by:

$$V_r = -q\mu_D \frac{\cos \Theta}{r^2} - \frac{\alpha q^2}{2r^4}$$

The first term represents the contribution of the permanent dipole of the neutral (q is the electronic charge of the ion, μ_D is the dipole moment, *r* is the ion neutral distance, and Θ is the angle between the direction of the dipole and the axis charge−dipole); the second term represents the contribution of the induced dipole moment of the neutral (α being molecular polarizability); the short range repulsive forces are neglected.

Reactions mediated by ion-neutral complexes “are prominent only around the threshold of associated simple dissociation, the energy range being largely determined by the strength of the attraction between the ion and the neutral”.[37] As the internal energy content of the species in the complex increases, the electrostatic attractive forces are more rapidly overcome so that the partners will simply part company before they react with each other: the ion−neutral complex-mediated reactions are indeed especially important in the low energy fragments formed by chemical ionization[37] and are also favored with larger species because of an increasing number of degrees of freedom which determines a profitable energy distribution.

One can confidently assume that both of these conditions are fulfilled in the examples described in this paper. In particular, with reference to the ion−radical complexes reported in Scheme 3, it is worth stressing that, in view of the expected low critical energy for the initial cleavage of $\mathbf{1}^{\bullet -}$, there is a reliable possibility that the low-energy incipient species may retain (at least for relatively short times) a mutual position related to the stereochemistry of the fragmenting $\mathbf{1}^{\bullet -}$ as in the “*E*”- and “*Z*”-**3** complexes. Thus, the expected greater distance between the reacting centers in the “*E*”- with respect to the “*Z*”-**3** complex, besides likely decreasing the stabilization energy V_r in the former, can be responsible for the different k_A/k_B values observed in going from the *(E)*- to the *(Z)*-stereoisomer of the same azo sulfide. As a matter of fact, the observation that the k_A/k_B values increase from 11.1 to 50.0 and from 20.0 to >100, in going, respectively, from *(E)*- to *(Z)*-**1c** and from *(E)*- to *(Z)*-**1d**, corroborates some retention of the geometry of the starting azo sulfides in the intermediate complexes. In other words in the “*Z*”-**3** complexes the two reacting centers (the aryl carbon bearing the diazenyl nitrogen and the negatively charged sulfur of the thiolate) remain proximal and ready for coupling (higher k_A/k_B value) while in the “*E*”-**3** complexes a more substantial reorganization within the complex is needed before reaction to occur. Thus, in the latter case, though path A is still the favored reaction channel, the dissociation route B can play a more important role than in the “*Z*”-**3** complexes: as a consequence lower k_A/k_B values are observed.

In the light of the mechanistic approach above, it should be stressed that the competition between paths A and B should be also influenced (a) by the substituent effect in the aryl moiety, as electron-withdrawing substituents are expected to favor both routes of Scheme 4, and (b) by the nucleophilicity of the thiolate anion. In regard of the latter point, for the well known basicity/nucleophilicity relationship, on the grounds of the relevant proton affinity (PA) values in the gas phase,[41] Bu^tS^- (PA 353 kcal mol^{-1}) is expected to be a by far stronger nucleophile than PhS^- (PA 339 kcal mol^{-1}). This has been found to be indeed the case, as an increase of the k_A/k_B value from 0.24 to 11.1 and from 6.55 to 20.0 has been observed in going, respectively, from (*E*)-**1a** to (*E*)-**1c** and from (*E*)-**1b** to (*E*)-**1d**: i.e. in going from PhS^- to Bu^tS^- as nucleophile in pairs which involve the same aryldiazenyl radical and the same initial mutual position of the reacting species in the intermediate complex. As far as point (a) above is concerned, there is the expectation that, in analogous complexes (“*E*” or “*Z*”) with the same thiolate as nucleophile, the decrease in the k_A/k_B

---

[34] Actually, aryldiazenyl radicals (ensuing also from photolysis of azo sulfides) have been reported[35] to be relatively persistent species even in solution (the lifetime[35a] of the phenyl diazenyl d_5 radical is 3.4 μs at 25 °C), where collision with a solvent molecule can activate their following fragmentation to $Ar^\bullet$ and nitrogen.[35a] In such fragmentation, on the other hand, the intermediacy of a complex between diazenyl radicals and olefinic solvents, under charge transfer from the olefinic double bond to diazenyl nitrogen, has been shown to be most likely involved.[35a]

(35) (a) Suehiro, T.; Masuda, S.; Nakausa, R.; Taguchi, M.; Mori, A.; Koike, A.; Date, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3321. (b) Engel, P. S.; Gerth, D. B. *J. Am. Chem. Soc.* **1983**, *105*, 6849.

(36) Longevialle, P. *Mass Spectrometry Rev.* **1992**, *11*, 157.

(37) McAdoo, D. J. *Mass Spectrometry Rev.* **1988**, *7*, 363.

(38) (a) Longevialle, P.; Botter, R. *J. Chem. Soc., Chem. Commun.* **1980**, 823. (b) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195. (c) Hammerun, S. *J. Chem. Soc., Chem. Commun.* **1988**, 858. (d) Hammerun, S.; Audier, H. E. *J. Chem. Soc., Chem. Commun.* **1988**, 860. (e) Audier, H. E.; Morton, T. H. *J. Am. Chem. Soc.* **1991**, *113*, 9001.

(39) Bowie, J. H. *Mass Spectrometry Rev.* **1990**, *9*, 349.

(40) (a) Tumas, W.; Foster, R. F.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 7464. (b) Froelicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 6863. (c) Tumas, W ; Foster, R. F.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 961.

(41) Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 87. Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046. Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109.

values parallels that of the electron-withdrawing power of the 4-substituent in the aryl moiety. Consistently, in going from (*Z*)-**1d** to (*Z*)-**1c** and to (*Z*)-**1e** the k_A/k_B values decrease (from >100, to 50 down to 0.03) indicating a substantial substituent effect in the order 4-NO_2 > 4-CN > H.

Does the same scenario hold also for the reactions of azo sulfide radical anions in solution? Actually, as previously stressed, the same relative order $k_A/k_{B[(Z)\text{-}\mathbf{1c}]} > k_A/k_{B[(E)\text{-}\mathbf{1c}]}$ has been evidenced both in gas-phase and in solution. Thus, one can confidently assume that also in solution the fragmentation of (*E*)- and (*Z*)-$\mathbf{1}^{\bullet -}$ results in the formation of diazenyl radical/thiolate complexes in a solvent cage, which, at least initially, retain a mutual position related to the stereochemistry of the fragmenting $\mathbf{1}^{\bullet -}$. Therefore, the possibility of synthetic exploitation[4] of the azo sulfides in solution as substrates in $S_{RN}1$ reactions with "external" nucleophiles (in competition with the thiolate, the "internal" nucleophile) is substantially affected by the ability of the complex to dissociate into separated species.

Conclusion

This paper describes an unprecedented example of a gas-phase $S_{RN}1$-like reaction, insofar as the chemically-induced negative-ion mass spectra of arylazo sulfides **1** give evidence, among the fragments of the decay of $\mathbf{1}^{\bullet -}$, of the corresponding sulfide radical anions (ArSR$^{\bullet -}$) and/or of products therefrom. The outstanding feature herein is that, in the low-pressure gas-phase conditions employed, the Ar and SR moieties which concur to the eventual formation of ArSR$^{\bullet -}$ must originate from the same azo sulfide molecule. The results are best rationalized through the initial formation of the ion−radical complexes **3** (Scheme 3), the lifetime of which depends on electrostatic forces arising from ion−dipole or ion-induced dipole interactions. From **3**, coupling (path A) and fragment separation (path B) competitively lead to ArSR$^{\bullet -}$ and RS$^-$, respectively. A substantial difference between the $S_{RN}1$-like reaction herein and the usual $S_{RN}1$ in solution is that the last step of the propagation cycle, *i.e.* electron transfer from the sulfide radical anion to the starting azo sulfide, cannot occur under the gas phase conditions used. It should also be noted that the reaction above is a clear cut example of recombination of an anion and a radical arising from the unimolecular fragmentation of radical anions and that the original *(E)* or *(Z)* stereochemistry is to some extent preserved in the ion−radical complex **3**, leading to different branching ratios (k_A/k_B) for the *(E)*- and the *(Z)*-isomers.

Furthermore, a comparison between the present results and previous ones, on electrochemically induced reactions of the same arylazo sulfides in the presence of "external" nucleophiles, strongly suggests that a relatively persistent complex between a diazenyl radical and thiolate anion could be the key intermediate also in solution. Accordingly, in the overall mechanism for the reaction of arylazo sulfides with nucleophiles such a complex must be duly taken into account. It must be stressed that, should ArSR$^{\bullet -}$ actually derive from substitution of N_2 by RS$^-$ on the diazenyl radical (ArN=N$^\bullet$) (in the gas phase and/or in solution), this would represent yet a further difference with classical $S_{RN}1$ processes on *e.g.* aryl halides, where a coupling between the nucleophile and an aryl radical (Ar$^\bullet$) is involved.

Experimental Section

Arylazo sulfides [(*E*)-**1a**,[4c] (*E*)-**1b**,[4c] (*E*)-**1c**,[4d] (*Z*)-**1c**,[4c] (*E*)- and (*Z*)-**1d**,[42] (*Z*)-**1e**,[43] (*Z*)-**1f**,[4d] (*Z*)-**1g**,[4e]], aryl phenyl sulfides (**2a**,[4b] **2b**[4a]), and aryl *tert*-butyl sulfides (**2c**,[4c] **2e**[44]) were analytically pure samples prepared as reported. *tert*-Butyl 4-nitrophenyl sulfide (**2d**) was an authentic sample from our laboratory, isolated in the reactions on the corresponding arylazo sulfide (*Z*)-**1d** with nucleophiles:[4g] mp 37.1−38.0 °C (petroleum ether); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.35 (9H, s), 7.66 and 8.16 (2H each, AA′BB′, *J* 8.6 Hz). Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63. Found: C, 56.76; H, 6.31; N, 6.70.

The purity of the compounds was always checked by ^{1}H NMR before recording the mass spectra. The mass spectra were obtained with a Nermag R 10-10-C mass spectrometer operated in the negative ion mode (EI 70 eV) using NH_3 or CH_4 as ionization reagent. The pressure of the gas was 1.6 Torr; the emission current was 0.2 mA. The temperature of the chamber was about 80 °C. The compounds (approximately 1 mg) were introduced into the ionization chamber by the direct inlet probe without heating.[45] The mass spectrometer was scanned every 2 s over the mass range 70−300. Most often it was possible to record only one spectrum immediately after the introduction of the probe due to the high volatility of the products. The mass spectra have been recorded several times on different days, the same fragments and relative intensities being always observed. The absolute accuracy is of the order of 20%. The observed mass spectra are described below [*m/z* (relative intensity)]:

(*E*)-**1a**: 212 (1), 211 (4), 210 (3), 135 (2), 134 (18), 131 (3), 117 (<1), 116 (1), 111(6), 110 (9), 109 (100), 108 (2), 102 (2).

2a: 214 (1), 213 (6), 212 (20), 211 (100), 210 (17), 136 (3, 135 (8), 134 (79), 118 (2), 109 (3).

(*E*)-**1b:** 233 (6), 232 (14), 231 (100), 230 (6), 155 (1), 154 (22), 123 (1), 122 (<1), 110 (1), 109 (22).

2b: 234 (1), 233 (7), 232 (16), 231 (100), 230 (4), 154 (3), 109 (<1).

(*E*)-**1c**: 219 (1), 190 (<1), 162 (3), 136 (4), 135 (12), 134 (100), 133 (4), 117 (2), 116 (1), 102 (2), 89 (11).

(*Z*)-**1c**: 218 (<1), 190 (<1), 162 (2), 136 (4), 135 (8), 134 (100), 133 (5), 89 (2).

2c: 191 (1), 190 (1), 136 (4), 135 (10), 134 (100), 133 (2).

(*E*)-**1d**: 239 (1), 211 (1), 182 (1), 156 (5), 155 (9), 154 (100), 153 (6), 138 (1), 137 (1), 123 (1), 122 (1), 89 (6).

(*Z*)-**1d**: 211 (<1), 156 (4), 155 (9), 154 (100), 153 (13), 138 (1), 137 (<1), 123 (<1), 122 (<1), 89 (<1).

2d: 156 (6), 155 (11), 154 (100), 153 (12), 138 (1), 89 (<1).

(*Z*)-**1e:** 137 (1), 109 (2), 108 (1), 91 (3), 90 (4), 89 (100), 88 (6).

2e: 167 (6), 166 (4), 165 (42), 111 (6), 110 (9), 109 (100), 108 (1), 89 (<1).

(*Z*)-**1f**: 238 (1), 211 (5), 156 (4), 155 (9), 154 (100), 153 (4), 138 (1), 123 (3), 122 (2), 118 (2), 89 (5).

(*Z*)-**1g**: 196 (3), 123 (9), 91 (6), 90 (7), 89 (100).

(*Z*)-**1h**: 179 (3), 151 (6), 145 (2), 119 (4), 91 (7), 90 (10), 89 (100), 88 (4).

Acknowledgment. M.N. and J.P. gratefully acknowledge CNR and CNRS for contributions within the frame of International Cooperation Projects. This work is partially supported by MURST (60% funds) (Italy). We are indebted to Dr. H. E. Audier for helpful scientific discussion.

JO9513368

---

[42] van Beek, L. K. H.; van Beek, J. R. G. C. M.; Boven, J.; Schoot, C. J. *J. Org. Chem.* **1971**, *36*, 3194.

[43] van Zwet, H.; Kooyman, E. C. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 993.

[44] De la Mare, P. B. D.; Vernon, C. A. *J. Chem. Soc.* **1956**, 41.

[45] Harisson, A. G., *Chemical Ionization Mass Spectrometry*, CRC Press: Boca Raton, FL, 1983; Ch. 4, p 75.