Onium Ions. 20.[1] Ambident Reactivity of the Nitronium Ion. Nitration vs. Oxidation of Heteroorganic (S, Se, P, As, Sb) Compounds. Preparation and NMR Spectroscopic (^{13}C, ^{15}N, ^{31}P) Study of Nitro and Nitrito Onium Ions

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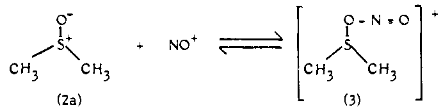
Abstract: The reaction of nitronium salts with sulfides, selenides, phosphines, arsines, and stibines has been investigated. Nitronium hexafluorophosphate (tetrafluoroborate) reacts rapidly at −78 °C with diaryl, aryl alkyl, and dialkyl sulfides, affording sulfoxides as the major products. Selenides, phosphines, arsines, and stibines react equally readily, giving the corresponding oxygenated products. In the case of diphenyl sulfide, less than 5% of competing ring *C*-nitro products were obtained. These observations suggest the intermediacy of nitrito onium ions ($>X^+$–ONO) being in equilibrium with the related nitro onium ions ($>X^+–NO_2$). The present study represents the first demonstration of the ambident reactivity of the nitronium ion in solution chemistry (i.e., competing attack on oxygen vs. nitrogen of NO_2^+). The equilibrium was confirmed by carrying out trans nitrosation of *N*,*N*-dimethylaniline in the presence of these onium salts. ^{13}C, ^{15}N, and ^{31}P NMR studies of the onium salts are also reported, showing that nitro onium salts are irreversibly transformed into nitrito onium salts either upon raising the temperature or during prolonged reaction times.

Introduction

Over the years, we have pursued the reactions of nitronium and nitrosonium ion salts.[2] In the course of our studies, we have also prepared *N*- and *S*-nitrito onium ion salts and found them to be electrophilic nitrating agents in their own right. The dimethylnitritosulfonium ion (**3**) and *N*-nitrito-4-nitropyridinium ion (**4**) were prepared from nitrosonium hexafluorophosphate and dimethyl sulfoxide or 4-nitropyridine *N*-oxide, respectively.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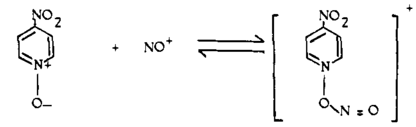
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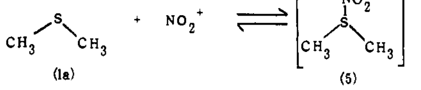
The isomeric nitro onium ions **5** and **6** were also prepared by reacting nitronium hexafluorophosphate with dimethyl sulfide and 4-nitropyridine, respectively.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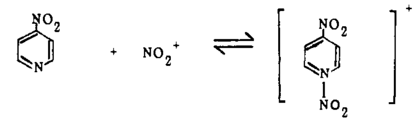
(6)

The nitrito onium ions **3** and **4** were found to possess significantly lesser nitrating ability than the corresponding nitro onium ions **5** and **6**.

The electrophilic nitrating ability of the nitrito compounds is somewhat surprising in view of the fact that nitrites are known to act mainly as nitrosating agents. To our knowledge, **3** and **4** are, so far, the only known examples of nitrito derivatives acting directly as nitrating agents in electrophilic aromatic nitrations (excluding nitrosative nitrations of highly activated aromatics, such as phenols and anilines). This interesting behavior of nitrito onium salts has led us to examine the nature of these intermediates in greater detail.

Results and Discussion

When diphenyl sulfide was reacted in methylene chloride solution with nitronium hexafluorophosphate under extremely mild conditions (−78 °C) in an inert, nitrogen atmosphere (so as to avoid moisture and any air oxidation), diphenyl sulfoxide was obtained in high yield accompanied by a very small amount of ring nitration giving *o*- and *p*-nitrophenyl phenyl sulfides. In other words, the reaction of diphenyl sulfide with the nitronium salt gave only limited ring nitration, the main product being that of oxidation, i.e., phenyl sulfoxide. We did not detect any diphenyl sulfone or nitrophenyl sulfoxides among the reaction products.

The observed oxidative ability of the nitronium ion is noteworthy in view of the apparent difficulty of its reduction under usual reductive conditions. Oxidation of sulfides with nitronium ion is, in fact, general for aryl, aryl alkyl, and alkyl sulfides and allowed the development of a preparative method for selective oxidation of sulfides to sulfoxides with nitronium salts, in which no sulfones are formed. The obtained results are summarized in Table I.

It should be noted that aryl sulfides have been previously oxidized by Campagnini et al.[3] using nitric acid in acetic anhydride, but in the reaction, the mechanism of which could involve radicals or radical ions, significant amounts of nitrated and other byproducts were also obtained. The reaction was further not suitable at all for aliphatic sulfoxides, because of the prevalence of rearrangements taking place under the reaction conditions. The authors themselves did not discuss any mechanistic aspects of their oxidation, which, obviously, are complex systems, compared with the presently studied, well-defined nitronium ions.

Dialkyl(aryl) selenides, trialkyl(aryl)phosphines, triaryl-

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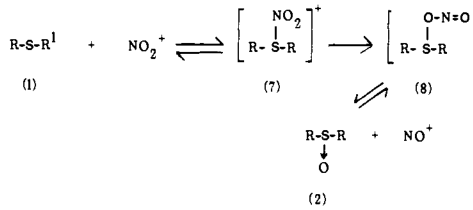
Table I. Oxidation of Sulfides, Selenides, Phosphines, Arsines, and Stibines Using Nitronium Hexafluorophosphate (or Tetrafluoroborate) at −78 °C

heteroorganic substrate (**1**)	oxidation product (**2**)	yield[b]	mp or bp (mm), °C obsd	mp or bp (mm), °C lit.[g]
a $(CH_3)_2S$	$(CH_3)_2SO$[a]	46[c]	189-190 (760)	189 (760)
b $(C_2H_5)_2S$	$(C_2H_5)_2SO$[a]	90	87-90 (15)	88-90 (15)
c $(n\text{-}C_3H_7)_2S$	$(n\text{-}C_3H_7)_2SO$[a]	95	80-84 (15)	82 (15)
d $(C_6H_5)_2S$	$(C_6H_5)_2SO$	62[d]	69[h]	69-71
e $C_6H_5SCH_3$	$C_6H_5SOCH_3$[a]	89[e]	102-106 (0.7)	104 (0.7)
f $(p\text{-}ClC_6H_4)_2S$	$(p\text{-}ClC_6H_4)_2SO$	90	142	141-144
g $(CH_3)_2Se$	$(CH_3)_2SeO$[a]	30	82.5[h]	83-85[i]
h $(C_6H_5)_2Se$	$(C_6H_5)_2SeO$	84	109[h]	110-112[i]
i $(C_6H_5)_3P$	$(C_6H_5)_3PO$	85	155.5[h]	156
j $(n\text{-}C_8H_{17})_3P$	$(n\text{-}C_8H_{17})_3PO$	95	51.5[h]	51.5[j]
k $(p\text{-}CH_3C_6H_4)_3P$	$(p\text{-}CH_3C_6H_4)_3PO$	*f*		
l $(C_6H_5)_3As$	$(C_6H_5)_3AsO$	87	187.7[h]	190-192[k]
m $(C_6H_5)_3Sb$	$(C_6H_5)_3SbO$	98	282.5[h]	280-285[l]

[a] Products isolated by nonaqueous workup (method B; see Experimental Section). [b] Yield of the isolated product. [c] A small amount of methanesulfonic acid ($\delta^{13}C$ (Me_4Si) 44.0 ppm) was also isolated (~5%). [d] Purified by column chromatography (see Experimental Section). A small amount of a mixture of *o*- and *p*-nitrophenyl phenyl sulfide was also separated from the column (~4%). The starting sulfide (10%) was also recovered. [e] Benzenesulfonic acid (5-8%) was also isolated in this case. [f] A complicated mixture of products was obtained. [g] "Dictionary of Organic Compounds", 4th ed.; Oxford University Press: New York, 1965. [h] Recrystallized from light petroleum-benzene mixture. [i] Ayrey, G.; Barnard, D.; Woodbridge, D. T. *J. Chem. Soc.* **1962,** 2089-2099. [j] White, J. C. 1956, AEC Report ORNL-2161, 24; *Chem. Abstr.* **1957,** *51,* 4205*c*. [k] "The Aldrich Library of Infrared Spectra", 1970; No. 1105A. [l] Wittig, G.; Hellwinkel, D. *Ber.* **1964,** *97,* 789.

Scheme I



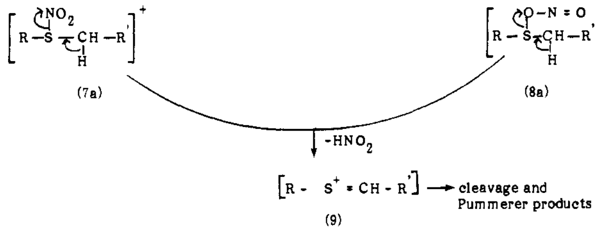
arsines, and triarylstibines also undergo similar oxidation with NO_2^+ to the corresponding selenoxides, phosphine oxides, arsine oxides, and stibine oxides in high yield (Table I). The oxidations are best carried out in methylene chloride solution at −78 °C to avoid the formation of any undesirable byproducts.[4] Thus, for example, oxidation of diethyl sulfide proceeds cleanly at −78 °C, but a more complex mixture of products is obtained at 0 °C. Dimethyl sulfoxide and dimethyl selenoxide were obtained in only relatively low yield (see subsequent discussion). Yields of oxidations with NO_2^+ can be significantly improved when products are isolated via nonaqueous instead of aqueous basic workup.

Based on the experimental observations, we propose the following mechanism for the NO_2^+ oxidation of sulfides (Scheme I).

A similar mechanism is indicated for the oxidation of selenides, phosphines, arsines, and stibines as well. The initially formed *S*-nitro onium ion (**7**) rearranges into the *S*-nitrito onium ion (**8**), which then cleaves by loss of NO^+ to yield the corresponding sulfoxides. The suggested mechanism is in accord with the lower yields of sulfoxides at higher temperatures, as both ions **7** and **8** are capable of 1,2 elimination, which becomes more significant at higher temperatures. Thus, both **7** and **8** could lead to **9**, which can undergo further cleavage or undergo nucleophilic addition to give Pummerer-type products in the case of aliphatic sulfides, whose onium ions (**7a** and **8a**) can readily undergo elimination of HNO_2 to give sulfenium ion **9** as shown in Scheme II.[5]

To substantiate the suggested mechanism in control experiments, it was shown that sulfoxides, indeed, undergo cleavage and Pummerer-type rearrangement reactions when treated with nitrosonium hexafluorophosphate, followed by quenching with water, thus, the necessity that in oxidation of sulfides with NO_2^+ the product sulfoxides should be isolated under nonaqueous conditions.

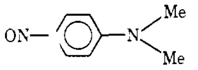
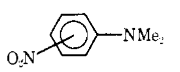
Scheme II



To further prove the mechanism of the oxidation of sulfides, selenides, phosphines, arsines, and stibines, we also carried out experiments to trap the NO^+ postulated to be formed in the reactions. When phenyl sulfide was reacted with nitronium hexafluorophosphate at −78 °C and after 40 min *N*,*N*-dimethylaniline was added, a mixture of phenyl sulfide, phenyl sulfoxide, *p*-nitroso-*N*,*N*-dimethylaniline, and *o*- and *p*-nitro-*N*,*N*-dimethylanilines was obtained. The nitrosoaniline can be formed via nitrosation with NO^+ or by intermediate **8**. Since nitrito onium compounds have been used previously in our work for the preparation of nitrosamines, both reaction pathways are equally likely.[6] Nitroanilines could be formed by nitration via intermediates **7** and **8** since, as mentioned previously, both kinds of onium salts are capable of effecting electrophilic aromatic nitration. Nitration of anilines via nitrosation is, however, also well-known. The amount of "unreacted" sulfide always corresponded to the amount of *o*- and *p*-nitro-*N*,*N*-dimethylanilines obtained from the reaction mixture.

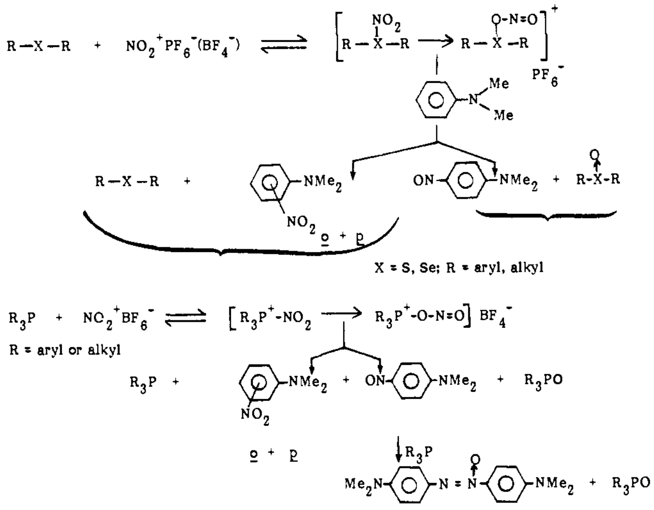
Although the NO^+ trapping reactions in the case of sulfides and selenides gave similar results, the data obtained from NO^+ trapping experiments with phosphines were different. Whereas we observed a relatively higher ratio of nitro-/nitroso-*N*,*N*-dimethylanilines, the phosphine/phosphine oxide ratio was the opposite of what was expected. Instead of obtaining predominantly phosphine and only about 15% of phosphine oxide, we have obtained mostly phosphine oxide. In the acidic extract 4,4′-bis(*N*,*N*-dimethylamino)azoxybenzene was also identified. This suggests that *p*-nitroso-*N*,*N*-dimethylaniline itself is further reacting under the reaction conditions to give the corresponding azoxybenzene. Indeed, *p*-nitroso-*N*,*N*-dimethylaniline was found to react with triphenylphosphine affording phosphine oxide and 4,4-bis(*N*,*N*-dimethylamino)azoxybenzene in excellent yield.[7] The results of the trapping

Table II. Trans Nitrosation and Nitration of *N,N*-Dimethylaniline at −78 °C with Nitro Onium Ions [$R_2S + NO_2PF_6$], [$R_2Se + NO_2PF_6$], and [$R_3P + NO_2PF_6$]

	% nitroso- and *o*- and *p*-nitro-*N,N*-dimethylaniline	
substrate (**1**)	 i	 ii
a $(CH_3)_2S$	66	34
b $(C_2H_5)_2S$	63	37
c $(C_6H_5)_2S$	30	70
d $C_6H_5SCH_3$	60	40
e $(p\text{-}ClC_6H_4)_2S$	30	70
f $(CH_3)_2Se$	55	45
g $(C_6H_5)_2Se$	64	36
h $(C_6H_5)_3P$	14	56[a]
i $(n\text{-}C_8H_{17})_3P$	19	51[a]

[a] In these experiments, 30% of 4,4′-bis(*N,N*-dimethylamino)azoxybenzene was also identified by ^1H NMR.

Scheme III



experiments of NO^+ liberated in the reactions of sulfides, selenides, and phosphines with NO_2^+ are summarized in Scheme III.

As the data in Table II shows, varying amounts of nitroso- and nitro-*N,N*-dimethylanilines were obtained from different reactions. This indicates some sort of equilibrium between the intermediate nitro onium and nitrito onium ions. Because of the various possibilities of obtaining nitration of aniline by both intermediates **7** and **8** and any free nitronium ion present, it is not possible to make any conclusions as to the position of the equilibrium between the two species, which could further be in equilibrium with the starting sulfide and the product sulfoxide. Thus, we decided to study the onium ions spectroscopically.

^{13}C, ^{15}N, and ^{31}P Nuclear Magnetic Resonance Spectroscopic Study of Nitro and Nitrito Onium Ions. The oxidizing ability of the nitronium ion, as discussed previously, reflects its ambident nature. In order to confirm the proposed mechanisms, we also undertook a low-temperature NMR spectroscopic study of the intermediate onium ions formed. NMR studies of onium ions obtained from dimethyl sulfide, dimethyl selenide, triphenylphosphine, and trioctylphosphine with nitronium ion, indeed, show the existence of equilibria between nitro and nitrito onium ions.

^{13}C NMR Studies. When a solution of dimethyl sulfide in SO_2 was added to a solution of nitronium hexafluorophosphate in SO_2, a green-colored solution was obtained, which showed three absorptions in the proton-decoupled ^{13}C NMR spectrum at $\delta^{13}C$ (Me_4Si) 25.2, 34.6 and 35.8, suggesting the formation of possibly three different species. Proton-coupled ^{13}C NMR spectra showed that all these peaks are quartets indicating that these absorptions are due to methyl groups. After the sample was kept for 48 h in a dry ice-acetone bath, the peak at $\delta^{13}C$ (Me_4Si) 25.2 completely disappeared while the peaks at $\delta^{13}C$ (Me_4Si) 34.6 and 35.8 became more intense. When dimethyl sulfoxide in SO_2 was treated with nitrosonium hexafluorophosphate, it gave two absorptions in the ^{13}C NMR spectrum at $\delta^{13}C$ (Me_4Si) 34.5 and 36.1, which could be resulting from the same species, as in the case of the dimethyl sulfide system. Indeed, when we mixed these two solutions, still only three absorptions were observed with slight variations (in the order of 0.3 ppm) in the chemical shifts (Table III), thus suggesting that the same species were formed in the case of dimethyl sulfide and dimethyl sulfoxide, which will be discussed later. The slight variations in the chemical shifts could be attributed to change in concentration of the solution.

Table III. ^{13}C NMR Chemical Shifts of Nitro and Nitrito Onium Ions in Sulfur Dioxide Solution at −60 °C

compd	^{13}C shifts **1**[a]	^{13}C shifts **2**	$\Delta\delta$ ($Me_2X^+NO_2$−Me_2X^+ONO)
$(CH_3)_2S$ (**1a**)	17.4		
$(CH_3)_2SO$ (**2a**)	37.9		
$(CH_3)_2S^+NO_2$ (**5**)	25.2		9.3
$(CH_3)_2S{=}O^+NO$ (**3**)	34.5		
$(CH_3)_3S^+$ (**11**)	27.1		
$(CH_3)_2S{=}O^{2+}CH_3$ (**12**)	33.0	61.2	
$(CH_3)_3S^+{=}O$ (**13**)	40.6		
$(CH_3)_2Se$ (**1g**)	10.4		
$(CH_3)_2SeO$ (**2g**)	35.0[b]		
$(CH_3)_2Se^+NO_2$	22.6		9.0
$(CH_3)_2Se^+ONO$	31.6		

[a] All the ^{13}C NMR chemical shifts are referenced from external Me_4Si. [b] This chemical shift was measured in dichloromethane as solvent.

Dimethyl selenide also showed similar behavior as that of dimethyl sulfide when treated with nitronium hexafluorophosphate in SO_2 at −78 °C. However, it showed only two absorptions at $\delta^{13}C$ (Me_4Si) 22.6 and 31.6. After the sample was kept for 24 h at dry ice-acetone temperature, it decomposed. Attempts to prepare nitrito onium ion from dimethyl selenoxide and nitrosonium hexafluorophosphate were unsuccessful. These results were not unexpected since dimethyl selenoxide can readily undergo fragmentations with nitrosonium ion in a Pummerer type of reaction as it is very unstable under these conditions (Scheme II). Aliphatic selenoxides are in general fairly reactive compounds and undergo fragmentations very readily.[8]

Two absorptions at $\delta^{13}C$ (Me_4Si) 25.2 and 34.5 observed in the product of dimethyl sulfide with nitronium hexafluorophosphate are considered to be due to onium ions **5** and **3**, as depicted in Scheme IV. In our preceding work,[9] we have reported ^{13}C NMR studies of various onium ions, allowing us to compare the chemical shifts of the presently observed ions with those of closely related nature. Comparison of **5** could be

Scheme IV

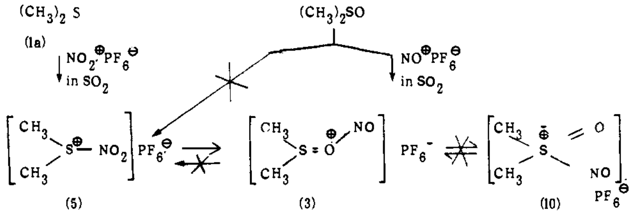


Table IV. ^{15}N NMR Chemical Shifts of Nitro and Nitrito Onium Ions in Sulfur Dioxide Solution at −60 °C

compd	^{15}N shifts[a]
$^{15}NO^+BF_4^-(PF_6^-)$	−0.4
$^{15}NO_2^+BF_4^-(FSO_3^-)$[b]	+127.8
$(CH_3)_2S^{+15}NO_2BF_4^-$	−261.5
$(CH_3)_2S^+O^{15}NOBF_4^-$	−620.5

[a] Shifts in parts per million from external 2 M solution of $Na^{15}NO_3$ in H_2O; positive values correspond to upfield shifts. [b] Fluorosulfonic acid was used to solubilize nitronium ion in this measurement.

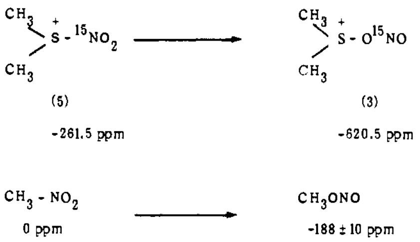
made with trimethylsulfonium ion as the hexafluoroantimonate **11**, which shows its methyl absorption at $\delta^{13}C$ (Me_4Si) 27.1. Since the nitro group is both inductively and conjugatively electron withdrawing, the methyl groups in **5** are expected to be more deshielded than in **11**. On the other hand, ion **5** can also be in rapid equilibrium with the starting materials. Thus, the ^{13}C NMR absorption might be appearing slightly shielded from that of **11**.

Ions **3** and **10** can be compared with O-methylated dimethyl sulfoxide (**12**) and S-methylated dimethyl sulfoxide (**13**), respectively (Table III). Since the nitroso group is inductively electron withdrawing and conjugatively electron donating, its effect on the chemical shift of the methyl group should be similar, as in either **12** or **13**. Based on these considerations, the methyl absorption in **10** is expected to be fairly deshielded and should appear at lower field to that of dimethyl sulfoxide itself. In addition, the chemical shift difference between the methyl absorption of **3** and **10** should be approximately similar to the chemical shift difference between **12** and **13** (i.e., 7 ppm) since similar electronic factors are operating in both **3** and **10**. This clearly excludes the possibility of the presence of onium ion **10**.

It may also be significant to note that the chemical shift differences between nitro onium and nitrito onium ion obtained from dimethyl sulfide (δ $Me_2S^+NO_2$-Me_2S^+ONO 9.3 ppm) and dimethyl selenide (δ $Me_2Se^+NO_2$-Me_2Se^+ONO 9.0 ppm) are quite comparable. This clearly suggests that similar types of ions are formed in both cases. Also, there is a considerable shielding in the case of selenium analogues compared with the corresponding sulfur analogues. This is consistent with the expected trend of increasing shielding going from related oxonium to sulfonium to selenonium ions. The increasing shielding effect arises due to the greater charge delocalization in the heavier atoms.[10]

^{15}N NMR Studies. Study of nitro and nitrito onium ions was also carried out by ^{15}N NMR. The results obtained are tabulated in Table IV. ^{15}N-enriched nitronium tetrafluoroborate and nitrosonium tetrafluoroborate, needed in preparing ions for ^{15}N NMR studies, were prepared by reacting $Na^{15}NO_3$ (95% atom enriched) and $Na^{15}NO_2$ (95% atom enriched), respectively, with anhydrous fluoroboric acid in sulfur dioxide solution at −78 °C. Labeled onium ions were prepared in the usual manner, as described previously, using enriched $^{15}NO_2^+$ diluted for convenience with a fivefold excess of the nonlabeled ion. The presence of a slight excess of acid in the solutions did not seem to affect the onium ions since their ^{13}C NMR spectra remained the same.

When dimethyl sulfide was reacted with ^{15}N-enriched nitronium tetrafluoroborate at −78 °C, in the ^{15}N NMR spectrum of the resulting solution at −60 °C two peaks were observed at δ ^{15}N ($Na^{15}NO_3$) −261.6 and −620.5 ppm, respectively, indicative of the presence of two different ions corresponding to nitro onium **5** and nitrito onium **3** ions. Furthermore, when dimethyl sulfoxide was reacted with ^{15}N-enriched nitrosonium tetrafluoroborate, the ^{15}N NMR at −60 °C showed a single resonance at δ ^{15}N ($Na^{15}NO_3$) −620.5 ppm due to the nitrito onium ion **3**. The 359-ppm chemical shift difference between ions **3** and **5** is quite striking and is much larger than the shift difference of 188 ± 10 ppm between isomeric nitromethane and methyl nitrite.[11] This can be readily accounted for considering that the ^{15}N chemical shift in **5** is shielded considerably due to charge-charge repulsion.



^{31}P NMR Studies. When triphenylphosphine was reacted with nitronium tetrafluoroborate in methylene chloride at −78 °C and the solution temperature was allowed consequently to rise to −20 °C, it showed two absorptions in ^{31}P NMR spectra at $\delta^{31}P$ [H_3PO_4 (85%)] −43.7 and −21.4. After the solution was brought to room temperature, the peak at −21.4 ppm disappeared. Similarly, when triphenylphosphine oxide was reacted with nitrosonium tetrafluorborate in methylene chloride, the resulting solution showed a single absorption in the ^{31}P NMR spectrum at $\delta^{31}P$ [H_3PO_4 (85%)] −42.9. Mixing the two solutions at room temperature resulted again in single absorption in the ^{31}P NMR spectrum at $\delta^{31}P$ [H_3PO_4 (85%)] −42.4. The slight variations observed in the chemical shifts can again be attributed to the variations in the medium and concentrations of the solutions. Trioctylphosphine also behaved similarly, although the disappearance of the peak at $\delta^{31}P$ [H_3PO_4 (85%)] −33.6 was rather slower than in the previous case. The complete results are tabulated in Table V.

The ^{31}P NMR results are also in agreement with the observations made in ^{13}C NMR studies. The phosphorus atom in nitro onium ions is expected to be less deshielded than in nitrito onium ions owing to the greater electronegativity of oxygen than nitrogen. In fact, our observations are in accordance with the expected chemical shifts. The disappearance of the peak at −21.4 ppm in the case of the complex obtained from triphenylphosphine-nitronium ion and the peak at −33.6 ppm in the case of the complex obtained from trioctylphosphine-nitronium ion clearly shows that the equilibrium is shifting toward more stable nitrito phosphonium ions (Scheme III).

Conclusions

The ambident nature of the nitronium ion was demonstrated by its oxidizing vs. nitrating ability (O vs. N reactivity) in sulfides, selenides, phosphines, arsines, and stibines. The discovered new oxidations with NO_2^+ represent one of the mildest and most selective methods for such conversions, particularly in the preparation of selenoxides. To our knowledge, these reactions are the first known examples showing the ambident reactivity of nitronium ion in solution chemistry.[12,13] The suggested mechanisms involving the formation of the corresponding nitro and nitrito onium ions were proven by the trans-nitrosating ability of the involved nitrito onium ions and also by ^{13}C, ^{15}N, and ^{31}P NMR spectroscopic studies.

Experimental Section

Starting Materials. All sulfides and phosphines used in this work were commercially available materials of highest purity (Aldrich Chemical Co.) as were dimethyl selenide and diphenyl selenide (Alfa Inorganics). $Na^{15}NO_3$ (95% atom enriched) and $Na^{15}NO_2$ (95% atom enriched) were obtained from Merck Sharp and Dohme.

Tri-*n*-octylphosphine oxide and tri-*p*-tolylphosphine were prepared by literature procedures. Dimethyl sulfoxide and methylene chloride were purified by the usual methods. Nitronium hexafluorophosphate

Table V. ^{31}P NMR Chemical Shifts of Nitro and Nitrito Phosphonium Ions in Methylene Chloride Solution[a]

	R_3P (**1**)	R_3PO (**2**)	$R_3P + NO_2BF_4$		$R_3PO + NOBF_4$		mixture[b]	
			−20 °C	room temp	−20 °C	room temp	−20 °C	room temp
i ($R = C_6H_5$)	7.5	−24.9	−43.7, −21.4	−41.0	−42.9	−44.9	−45.0, −21.5	−42.4
j ($R = n\text{-}C_8H_{17}$)	32.1	−47.7	−33.6, −75.4	−73.7	−75.4	−74.6	−75.4, −34.0	−74.5

[a] All the ^{31}P NMR chemical shifts are referenced from external 85% H_3PO_4; positive values correspond to upfield shifts. [b] Mixing of the corresponding onium ions was performed either at −78 °C or at room temperature as desired.

was purified by the method of Yoshida and Ridd.[14] All operations involving purification of nitronium salts were carried out under nitrogen atmosphere in a drybox. The reactions with selenides were carried out with specific care and precautions in a hood rated for toxic substances. The vessels used in all reactions were carefully cleansed with chromic acid and dried subsequently.

General Procedure for the Oxidation of Sulfides, Selenides, Phosphines, Arsines, and Stibines Using Nitronium Hexafluorophosphate (Tetrafluoroborate). The reactions were usually carried out on a 10-mmol scale in a 25-mL flask purged continuously with dry nitrogen. The following general procedure was used. To a slurry of nitronium hexafluorophosphate (or tetrafluoroborate) (1.6 g, 12 mmol) in dry methylene chloride (10 mL) cooled in a dry ice-acetone bath under nitrogen atmosphere was slowly added a solution of corresponding substrate (10 mmol) in methylene chloride (5 mL) with continuous good stirring. Soon the reaction started to take place as indicated by the formation of a pale yellow to dark brown colored reaction mixture. The temperature was maintained at −78 °C throughout the addition of substrate. After the addition was complete (usually in 5-10 min), the reaction mixture was stirred for another 5-10 min, and then the product isolated by aqueous or nonaqueous workup (method A or B).

Method A. Aqueous Workup. The reaction mixture was quenched with 10% solution of aqueous sodium bicarbonate (10 mL) and then allowed to warm up to room temperature, resulting in a clear solution. It was taken up in ether (50 mL), washed with aqueous bicarbonate solution (25 mL × 2), water, and brine, and dried over $MgSO_4$. Removal of ether gave the oxidized product, which was purified either by column chromatography or by recrystallization from a mixture of benzene-petroleum ether (Table I).

Method B. Nonaqueous Workup. Solid sodium carbonate (5 g) was added to the reaction mixture, and then it was allowed to warm to room temperature, resulting in a clear solution. Stirring for an additional 0.5-1 h completely removed all the acidic impurities in the reaction mixture. The solution was then filtered and dried over $MgSO_4$. Distilling off the volatile material under reduced pressure gave the oxidized products, which were purified, if necessary, as mentioned previously (Table I).

The following are specific examples.

Diphenyl Sulfoxide. To a slurry of $NO_2{}^+BF_4{}^-$ (1.6 g, 12 mmol) in methylene chloride (10 mL) kept at −78 °C (dry ice-acetone bath) was slowly added a solution of diphenyl sulfide (1.80 g, 10 mmol) in methylene chloride (5 mL) with good stirring (10 min). After stirring for another 10 min, the reaction mixture was quenched with aqueous $NaHCO_3$ solution (10 mL) and then brought to room temperature (40 min). It was then taken up in ether (50 mL) and washed successively with aqueous $NaHCO_3$ solution (25 mL × 2), H_2O, and brine. The ethereal extract was dried over $MgSO_4$ and volatile materials were distilled off under reduced pressure, leaving the crude oxidized product. The crude product was purified by column chromatography. Elution initially with hexane gave some unreacted starting material (200 mg, 10%) and a mixture of ring-nitrated products, *o*- and *p*-nitrophenyl phenyl sulfide (100 mg, 4%). Diphenyl sulfoxide was subsequently eluted with chloroform, yield 1.25 g (62%). All products showed correct physical and spectral characteristics.

Diethyl Sulfoxide. To a slurry of nitronium tetrafluoroborate (1.6 g, 12 mmol) in dry methylene chloride (10 mL) kept at −78 °C (dry ice-acetone bath) was slowly added (10 min) a solution of diethyl sulfide (0.9 g, 10 mmol) in methylene chloride (5 mL) with good stirring in a nitrogen atmosphere. The stirring was continued for another 10 min. Anhydrous Na_2CO_3 (5 g) was then cautiously added. Vigorous reaction took place, and the solution became colorless. The reaction mixture was allowed to warm to room temperature (60 min) and filtered to remove all inorganic materials. It was then dried over $MgSO_4$, and the solvent was removed to give crude diethyl sulfoxide, which was purified by distillation under vacuum, bp 87-90 °C (15 mm), yield 0.95 g (90%).

General Procedure for Trans Nitrosation and Trans Nitration of *N,N*-Dimethylaniline. To a slurry of purified nitrosonium-free nitronium hexafluorophosphate (1.91 g, 10 mmol) in methylene chloride (10 mL) cooled in a dry ice-acetone bath (−78 °C) under nitrogen atmosphere was added a solution (12 mmol) of the corresponding substrate (sulfide, selenide, or phosphine) in methylene chloride in a procedure similar to that used in the previous reaction, and the mixture was stirred for 40 min. A solution of *N,N*-dimethylaniline (1.21 g, 10 mmol) in methylene chloride (2 mL) was then added to the reaction mixture with good stirring (10 min). The temperature was maintained at −78 °C throughout the addition and the mixture stirred for an additional 10 min. The dark reddish brown reaction mixture was then quenched with aqueous sodium bicarbonate solution (10 mL); the solution turned dark green indicating the formation of a nitroso compound. It was then warmed up to room temperature (40 min) and subsequently extracted with benzene. The benzene layer was thoroughly shaken with sodium hydroxide to convert *N,N*-dimethylanilinium salts to the free bases. Subsequent washing with 3 N HCl solution removed all basic products. The benzene layer was then washed with water and brine and dried over $MgSO_4$. Distilling off the solvent gave a mixture of sulfides and sulfoxides or selenides and selenoxides, respectively, but only phosphine oxides were found in the case of the reaction of phosphines (see text). Neutralization of the aqueous layer with 10% NaOH solution and extraction with benzene gave a mixture of *p*-nitroso-*N,N*-dimethylaniline and isomeric nitro-*N,N*-dimethylanilines, whose compositions were analyzed by ^1H NMR via integration of the respective peak areas due to the dimethylamino group (Table II).

The nitroso to nitro product ratio was measured by the peak intensity of the methyl groups due to nitroso and nitro product in ^1H NMR. *p*-Nitroso-*N,N*-dimethylaniline gives a singlet at δ 3.65 (external Me_4Si) in ^1H NMR due to the methyl protons. *o*-Nitro-*N,N*-dimethylaniline gives a singlet at δ 3.32, *p*-nitro-*N,N*-dimethylaniline at δ 3.6, and *m*-nitro-*N,N*-dimethylaniline at δ 3.47 ppm in ^1H NMR due to the methyl protons. The singlet assigned to nitroso product was confirmed by addition of some authentic sample of nitroso compound to the mixture.

Preparation of Solutions for NMR Studies. In all NMR studies, freshly purified nitronium and nitrosonium hexafluorophosphate were used. In the case of ^{31}P NMR studies, the corresponding tetrafluoroborates were employed. For ^{13}C NMR studies, the solutions were prepared at −78 °C, cooling in a dry ice-acetone bath. Dimethyl sulfide or dimethyl selenide (0.2 g) was dissolved in SO_2 (2 mL) and carefully added in a ^{13}C NMR tube with good stirring to a solution of nitronium salt (0.7 g) in SO_2 (2 mL) taken up in a ^{13}C NMR tube. Upon addition, reddish-colored solutions were formed, which changed to green after stirring for a few minutes. Onium ions from dimethyl sulfoxide and dimethyl selenoxide were obtained by a similar procedure using nitrosonium hexafluorophosphate. The solutions (approximately 10%) for ^{31}P measurements were also prepared in a similar fashion reacting $NO_2{}^+BF_4{}^-$ or $NO^+BF_4{}^-$ and the appropriate precursor in methylene chloride solution. All the solutions were kept in a dry ice-acetone bath unless otherwise specified.

Preparation of ^{15}N-Enriched Nitronium and Nitrosonium Tetrafluoroborate. $^{15}NO_2{}^+BF_4{}^-$. To a suspension of $Na^{15}NO_3$ (87 mg, 1 mmol) in liquid sulfur dioxide (1 mL) in a quartz NMR tube was added dropwise anhydrous fluoroboric acid (360 mg, 4 mmol) from a Teflon dropper, the solution being stirred with a vortex stirrer. Stirring was continued for 10 min, during which time all $Na^{15}NO_3$

reacted to give a white, amorphous precipitate of the nitronium salt.

$^{15}NO^+BF_4^-$. A similar procedure to that described for $^{15}NO_2{}^+BF_4$ was used by starting with $Na^{15}NO_2$ resulting in a clear solution of ^{15}N-enriched nitrosonium tetrafluoroborate.

Nuclear Magnetic Resonance Studies. ^{31}P NMR studies were performed using a Varian XL-100 NMR spectrometer equipped with a heteronuclear decoupler, a variable-temperature probe, and a 620L computer with 32K memory capacity. The spectrometer was run in the Fourier transform pulse mode with proton decoupling. The total number of transients for suitable S/N for individual absorption varied from 200 to 500. The radio frequency was 39.80 MHz with the resonances referenced from external 85% phosphoric acid.

^{13}C NMR studies were performed using a Varian FT-80 NMR spectrometer equipped with a heteronuclear decoupler, variable-temperature probe, and 32K memory capacity computer. The spectrometer operated in the Fourier transform pulse mode with either proton decoupling or in the case of a proton-coupled experment with some nuclear Overhauser effect. The total number of transients for suitable S/N for individual absorption varied from 1000 to 3000. The radio frequency used was 20.00 MHz with the resonances referenced from external Me_4Si.

^{15}N NMR spectra were obtained using an FT-80 spectrometer operating at 8.059 MHz, using a broad-band variable-temperature probe. No heteronuclear decoupling was used during these experiments. Pyridine-^{15}N (150 mg) in 1 mL of methylene chloride contained in a 5-mm NMR tube served as external reference. The reference tube was centered in the 10-mm sample tube held by a Teflon plug. This reference resonance was found to be at $\delta^{15}N$ −65.2, i.e., 1.3 ppm downfield from that of an external solution of pyridine-^{15}N in methylene chloride, whose resonance was at $\delta^{15}N$ 63.9 (upfield from an external 2 M solution of $Na^{15}NO_3$ in H_2O). The reported chemical shifts are corrected with respect to the external 2 M $Na^{15}NO_3$ reference in H_2O (Table IV).

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References and Notes

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Structure and Stability of Radical Cations from Cyclic and Open-Chain Dithia Compounds in Aqueous Solutions

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Abstract: The formation of *intra-* and some *inter*molecular radical cation complexes has been observed during the oxidation of cyclic and open-chain organic dithia compounds (the two S atoms not adjacent) by hydroxyl radicals in aqueous solutions. These species are characterized by a new sulfur–sulfur bond established by interaction of the unpaired p electron from the oxidized sulfur atom with the free p-electron pair of a second sulfur atom. Two of these electrons form a σ bond while the third is promoted to an antibonding σ^* level. At low solute concentration (typically around 10^{-4} M) *Intra*molecular complex formation predominates. The radical cation complexes show characteristic broad optical absorptions which are attributable to a $\sigma \rightarrow \sigma^*$ transition. The position of the absorption maximum (reflecting the σ/σ^* energy difference) and the extinction coefficients are related to the p-orbital overlap between the two interacting sulfur atoms. The extent of overlap depends on the internuclear distance, $r(S\therefore S)$, and particularly on the angular relationship between the interacting orbitals. Other structural parameters influencing λ_{max} are the flexibility of the species formed and possible interactions between the $\sigma(S,S)$ bond with $\sigma(C,C)$ bonds. λ_{max} is found to range from 400 to 650 nm, these particular values referring to the *intra*molecular radical cation complexes from 1,5-dithiacyclooctane and 1,4-dithiacyclohexane, respectively. ϵ values are found up to 7×10^3 M^{-1} cm^{-1}. The lifetimes of the radical cation complexes depend on the stability of the new sulfur–sulfur bond and may well extend into the millisecond range in aqueous solutions.

Introduction

The one-electron oxidation of organic sulfides formally leads to a molecular radical cation, $R_2S^{+}\cdot$, which shows a strong tendency to stabilize by coordination with a free electron pair from another sulfur atom[1-4] in an equilibrium (eq 1).

Equilibrium constants of the order of 10^3–10^4 M^{-1} in favor of II for simple aliphatic thioethers indicate the relative stability of the complex radical cation.[4] Species II is characterized by a newly established sulfur–sulfur bond involving three electrons; two electrons form a σ bond and the third electron is located in an antibonding σ^* orbital.[2,3]

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