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Selective Catalysis of Thioether Oxidations with Dioxygen. Critical Role of Nitrosonium EDA Complexes in the Thermal and Photochemical Transfer of Oxygen Atom from Nitrogen Oxides to Sulfur Centers

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Various alkyl and aryl thioethers (R_2S) are readily converted in high yields to sulfoxides in the presence of dioxygen and catalytic amounts of nitrogen dioxide. Separate experiments with stoichiometric amounts of reagents (under anaerobic conditions) establish the nitrosonium EDA complex [R_2S, NO^+] NO_3^- as the critical intermediate formed from the thioether-induced disproportionation of NO_2. Low-temperature photoactivation by the deliberate irradiation of the charge-transfer absorption band of [R_2S, NO^+] NO_3^- leads to sulfoxide *via* the thioether cation radical. Electron transfer is also a viable route to the thermal (stoichiometric) oxidation of thioethers with NO_2 *via* the same nitrosonium EDA complex. As such, Scheme 4 presents the complete sequence of redox changes of the nitrogen oxides in the catalytic conversion of thioether to sulfoxide *via* the cation radical.

Introduction

Preparative conversions of thioethers to the corresponding sulfoxides commonly suffer from competitive over-oxidation to sulfones.[1−3] As a result, new selective methods for sulfoxide preparation are highly desirable—especially those that employ readily available reagents, mild reaction conditions, and convenient work-up procedures.

The use of nitric acid in the oxidation of dibenzyl sulfide is among the earliest reports on the selective transformation of thioethers to sulfoxides.[4] It is noteworthy that this procedure, as well as that utilizing other nitrogen oxides,[5−7] gave no evidence for sulfone formation. Although there are limited examples of the varied use of nitrogen dioxide as an oxidative reagent,[8] its application to organic synthesis has been largely ignored. However, we recently demonstrated that the oxidative versatility of nitrogen dioxide can be considerably enhanced by the presence of dioxygen as a co-oxidant.[9] In order to exploit this new methodology, we describe the facile and selective oxidation of various aliphatic and aromatic sulfides by the combination of NO_2 and dioxygen at room temperature and below. Moreover, the use of such gaseous reagents allows a trivial workup procedure (merely by removing the solvent *in vacuo*) for the ready isolation of sulfoxides in high yields.

Results

The series of alkyl, aryl, and aromatic sulfides included in Table 1 were arbitrarily chosen to illustrate the high efficiencies with which oxidative conversions to various sulfoxides could be carried out with the NO_2/O_2 combination. In each case, the solutions of thioether persisted unchanged for indefinite periods when exposed only to dioxygen at atmospheric pressure. After nitrogen dioxide was introduced, the colorless solution immediately turned bright orange; and sulfoxide was isolated upon the removal of solvent. In order to establish the oxidant requirements under these aerobic conditions, the conversion of the prototypical dibutyl sulfide to its sulfoxide was examined in more detail as follows.

I. Oxidation of Dibutyl Sulfide with NO_2/O_2. The Catalytic Nature of Sulfoxide Formation. A solution of di-*n*-butyl sulfide (0.1 M) in dichloromethane was stable even after exposure to an atmosphere of pure dioxygen for weeks (in the dark) at room temperatures. Nitrogen dioxide (0.2 equiv) was added, and the mixture was stirred overnight and then concentrated *in vacuo*. The residue consisted of essentially pure dibutyl sulfoxide (with the sulfone below the detectable limits of < 0.1%).[10] Spectral analysis of the solvent mixture in the cold trap indicated the presence of unchanged nitrogen dioxide by its diagnostic IR stretching bands at $\nu_{NO} = 1600$ and 1620 cm^{-1}.[11] Coupled with the oxygen consumption determined volumetrically (see Experimental Section), the stoichiometry for the thioether oxidation was established as

$$n\text{-Bu}_2\text{S} + {}^1/_2\text{O}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{[\text{NO}_2]} n\text{-Bu}_2\text{SO} \qquad (1)$$

where the brackets enclose the unconsumed nitrogen dioxide. Although a detailed kinetics examination was not carried out, the increased rates of oxidation resulting from the addition of 0.15, 0.20, and 0.25 equiv of NO_2 to 0.1 M *n*-Bu_2S and 1 atm of dioxygen in dichloromethane

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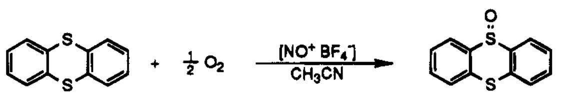
Table 1. Catalytic Autoxidation of Thioethers with NO_2[a]

thioether	(mmol)	nitrogen oxide	(mmol)	sulfoxide yield[b] (%)
dimethyl sulfide	79.10	NO_2	4.4	93
dibutyl sulfide	17.60	NO_2	1.76	91
tetrahydrothiophene	33.40	NO_2	2.64	87
phenyl ethyl sulfide	9.00	NO_2	1.76	97
phenyl benzyl sulfide	17.50	NO_2	2.60	92
diphenyl sulfide	4.76	NO_2	0.85	90[d]
dibenzothiophene	4.20	NO_2	1.50	87[d]
thianthrene	4.29	NO_2	0.20	99
phenoxathiin	5.00	NO_2	0.18	99
dibutyl sulfide	17.60	NO	3.40	97
tetrahydrothiophene	14.20	$NO^+BF_4^-$	0.47	95
dibutyl sulfide	6.85	$NO^+BF_4^-$	0.47	93
thioanisole[c]	23.10	$NO^+BF_4^-$	0.45	94
diphenyl sulfide	4.76	$NO^+BF_4^-$	0.85	92[d]
thianthrene[c]	5.56	$NO^+BF_4^-$	0.08	97
phenoxathiin[c]	1.60	$NO^+BF_4^-$	0.02	93
N-phenylphenothiazine[c]	3.18	$NO^+BF_4^-$	0.10	98

[a] In dichloromethane solution under 1 atm of dioxygen at -50 to 25 °C, unless indicated otherwise (see Experimental Section). The corresponding sulfoxide was the exclusive product. [b] Yield of pure (distilled/recrystallized) sulfoxide. [c] In acetonitrile. [d] Nitroarene also formed (see Experimental Section).

at 0 °C was evident from the increasing conversions of 67, 87, and 100%, respectively, to dibutyl sulfoxide after 100 min.

The catalysis of thioether autoxidation was also effected by small amounts of other nitrogen oxides, such as nitric oxide and nitrosonium salts. For example, the addition of 1 mol% of either NO or $NO^+BF_4^-$ was sufficient to effect the quantitative conversion of thianthrene within an hour at −10 °C under a dioxygen atmosphere.



(2)

II. Catalytic Autoxidation of Various Alkyl and Aryl Sulfides.

The uniformly high sulfoxide yields in Table 1 (last column) establish the synthetic versatility of the NO_x/O_2 system for the efficient catalytic oxidation of structurally diverse aliphatic and aromatic sulfides. These autoxidations were carried out under standard conditions in which the solution of thioether (~100 mmol) in dichloromethane at −50 °C was flushed with dioxygen for several minutes, and the excess O_2 was diverted to a rubber balloon (reservoir). A cold dichloromethane solution of nitrogen dioxide (4.4 mmol) was added with the aid of an all-glass hypodermic syringe. After the orange solution was allowed to stir at ambient temperatures overnight, the balloon deflated, and the solvent and NO_2 were removed *in vacuo*. The sulfoxide residue was purified by either distillation or recrystallization to afford the isolated yields in Table 1 (last column). The same catalytic results were obtained when nitrogen dioxide was replaced with small amounts of nitric oxide (compare entries 2 and 10) or the crystalline nitrosonium salt $NO^+BF_4^-$ (see last seven entries).

Catalytic turnover numbers in excess of 75 were apparent by the small amounts of nitrogen oxide used for the uniformly high sulfoxide conversions in Table 1 (column 4). However, among the various thioethers, the autoxidation of diphenyl sulfide and dibenzothiophene were rather inefficient, as judged by the somewhat low turnover numbers and the formation of minor amounts of nitro byproducts.

Table 2. Stoichiometric Oxidation of Thioethers with NO_2[a]

thioether	(E_p[b])	additive (equiv)	conv[c] (%)	sulfoxide yield[d] (%)
tetrahydrothiophene			100	100
dibutyl sulfide			100	100
phenyl ethyl sulfide	1.16		55	100
p-methylthioanisole	1.05		75	100
p-methoxythioanisole	0.86		100	100
diphenyl sulfide	1.24		40 (95[f])	94[e] (91[e])
diphenyl sulfide	1.24	NO (0.4)	17	94[e]
diphenyl sulfide	1.24	NO_3^- (1.0)	1	95[e]
diphenyl sulfide	1.24	$SbCl_5$ (0.25)	70	93[e]

[a] All reactions with 1.25 equiv of NO_2 at 0.3 M in dichloromethane under an argon atmosphere at 0 °C for 1 h. [b] In V vs Ag/Ag^+ at CV scan rate of 500 mV s^{-1} in acetonitrile solution. Data from ref 16. [c] Based on recovered thioether determined by quantitative GC-MS. [d] Based on consumed thioether determined after aqueous workup. [e] Nitroarenes formed in 6−7% yield. [f] Reaction carried out for 36 h.

III. Stoichiometric Oxidation of Thioethers with NO_2 under Anaerobic Conditions.

When dibutyl sulfide (3 mmol) in dichloromethane was directly treated with 1 equiv of nitrogen dioxide (NO_2, 3 mmol) under an argon atmosphere, a vigorous reaction was accompanied by the copious evolution of nitric oxide that was spectrally identified by its characteristic IR stretching bands at 1906, 1876, and 1852 cm^{-1}.[12,13] Quantitative analysis of dibutyl sulfoxide and nitric oxide established the 1:1 stoichiometry under anaerobic conditions,[14] *i.e.*

$$n\text{-}Bu_2S + NO_2 \xrightarrow[CH_2Cl_2]{} n\text{-}Bu_2SO + NO \qquad (3)$$

Quantitative yields of sulfoxide were also obtained according to eq 3 when less than 1 equiv of nitrogen dioxide was charged.

The relative reactivity of alkyl and aryl sulfides toward nitrogen dioxide under an argon atmosphere generally followed the trend observed in the catalytic autoxidation under a dioxygen atmosphere (*vide supra*). For example, the treatment of dibutyl and diphenyl sulfides with 1 equiv of NO_2 (each for an hour at 0 °C) led to the sulfoxides Bu_2SO and Ph_2SO in 100% and 40% conversions, respectively, as described in Table 2, entries 2 and 6. [The prolonged treatment of diphenyl sulfide with NO_2 ultimately led to a 91% yield of isolated sulfoxide.[15]] Among a series of aryl sulfides, the analogues, *p*-methoxythioanisole, *p*-methylthioanisole, phenyl ethyl sulfide, and diphenyl sulfide, represent increasingly weaker donors as judged by the progressively positive potentials for anodic oxidation with E_p = 0.85, 1.05, 1.16, and 1.24 V vs Ag/Ag^+, respectively.[16] As such, their reactivity toward NO_2 decreased in the same qualitative order, as given by the decreasing sulfoxide conversions of 100, 75, 55, and 40%, respectively, in Table 2 (see entries 3−6). Otherwise, the direct comparison of the results in Tables 1 and 2 indicates that the stoichiometric

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(13) Nitric oxide was observed in combination with NO_2 at intermediate stages of thioether oxidation as the green dinitrogen trioxide (λ_{max} = 690 nm). See: Bosch, E. *et al.* in ref 9a.

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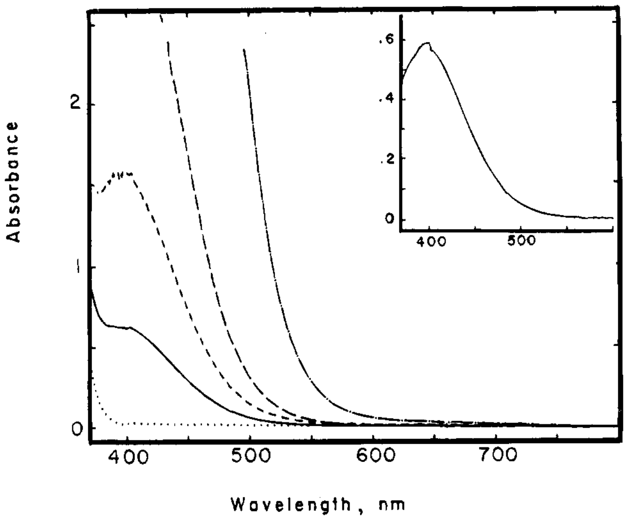

Figure 1. Charge-transfer absorption spectra from 1.3×10^{-2} M NO_2 (···) and (bottom-to-top) 0.0002, 0.0023, or 0.023 M dibutyl sulfide in dichloromethane at −78 °C. Inset: Charge-transfer absorption spectrum from 1.3×10^{-2} M NO_2 and 2×10^{-4} M Bu_2S obtained by subtraction of the absorbance due to NO_2 alone (···).

oxidations of the various thioethers could not be distinguished from those carried out catalytically with dioxygen.

The reactivity of thioethers to NO_2 in eq 3 was not amenable to direct kinetics study, owing to the strong retarding effect of the gaseous product (NO). For example, the deliberate addition of nitric oxide (0.4 equiv) to a mixture of diphenyl sulfide and nitrogen dioxide (1.2 equiv) in dichloromethane led to a markedly diminished conversion to Ph_2SO (see Table 2, entry 7).[17] Likewise, the presence of nitrate induced an even more pronounced retardation of sulfide oxidation by nitrogen dioxide (entry 8).[18] Interestingly, small amounts of antimony pentachloride (entry 9) caused a marked improvement in sulfoxide conversion.

IV. Visual and Spectral Changes Accompanying Oxidations with NO_2 under Catalytic and Stoichiometric Conditions. The Formation of Thioether EDA Complexes of NO^+. The efficient oxidations of various thioethers with the NO_2/O_2 combination and by NO_2 alone, as described in Tables 1 and 2, respectively, share in common a strong and distinctive coloration of the reaction mixture immediately attendant upon the introduction of nitrogen dioxide. Since the visual changes were particular to each thioether, a common origin of the colors to NO_2 was indicated. As such, the quantitative effects of the color change arising from the interaction of thioether with NO_2 was monitored by UV−vis spectroscopy at low temperatures where the thermal oxidation in eq 3 was too slow to compete. Thus Figure 1 shows the well-resolved absorption band with $\lambda_{max} = 400$ nm of the bright orange solution resulting from the addition of NO_2 to a solution of dibutyl sulfide in dichloromethane at −78 °C. At this temperature, the absorption band was persistent over the course of several hours (when protected from adventitious room light); and dibutyl sulfide could be recovered intact when the cold solution was quenched rapidly.

Table 3. Charge-Transfer Spectra of Thioether EDA Complexes Prepared from Nitrogen Dioxide and Nitrosonium Salt[a]

		NO_2		$NO^+BF_4^-$	
thioether donor	(IP^b) (eV)	λ_{CT},[c] nm	fwhm,[d] 10^{-2} cm^{-1}	λ_{CT},[c] nm	fwhm,[a] 10^{-2} cm^{-1}
methyl sulfide	8.68	393	54	390	60
butyl sulfide	8.22	400	56	400	52
benzyl methyl sulfide	8.42	406	61	406	62
tert-butyl methyl sulfide		400	59	396	63
tert-butyl octadecyl sulfide		408	61		
tetrahydrothiophene	8.42	386	61	387	57
thioanisole	8.07	500	55	502	53
phenyl ethyl sulfide	8.00	500	61	500	53
isopropyl phenyl sulfide	8.46	494	51	494	55
p-chlorothioanisole		512	59	510	52
p-methylthioanisole		514	63	514	58
p-methoxythioanisole		542	55	542	57
p-*tert*-butylthioanisole		516	58	514	55
benzyl phenyl sulfide				506	57
diphenyl sulfide	7.90	563	50	558	54

[a] In dichloromethane solution at −78 °C with 10^{-4} M thioether and 2×10^{-4} M nitrogen oxide. [b] Ionization potential from ref 78. [c] Maximum of the CT absorption band (±3 nm). [d] Full width at half maximum.

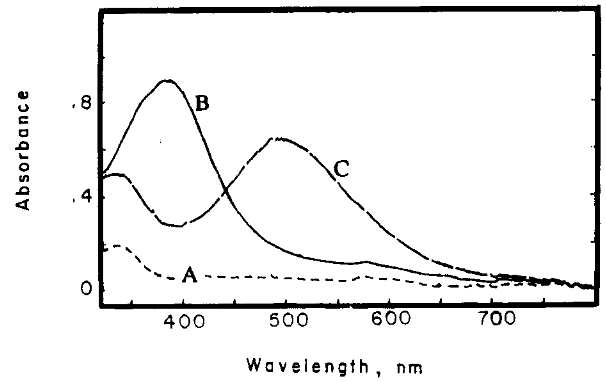

Figure 2. Comparison of the charge-transfer colorations in dichloromethane solution at −78 °C with (A) 2×10^{-4} M nitrogen dioxide and (B) tetrahydrothiophene, 1.4×10^{-4} M, (C) phenyl ethyl sulfide, 2.9×10^{-2} M, or diphenyl sulfide, 0.1 M (same as A).

The various thioethers in Table 3 produced similar distinctive colorations upon their treatment with NO_2 at −78 °C—the dilute solutions of dialkyl sulfides generally turning yellow with spectral absorptions in the range $390 < \lambda_{max} < 410$ nm, whereas aryl sulfides produced red solutions with $\lambda_{max} > 500$ nm, as listed in Table 3. Moreover, dialkyl sulfides produced significantly stronger colorations than mixed alkyl aryl sulfides at the same concentrations (and diaryl sulfides evoked the weakest colorations). The quantitative aspects of these visual differences are typified by the spectral changes illustrated in Figure 2.

Since the positions of the new absorption bands in Table 3 (column 3) underwent progressive bathochromic shifts to lower energies with increasing donor strengths of the thioether (as measured by the ionization potential tabulated in column 2), they were spectrally assigned to charge-transfer (CT) absorption bands in the manner described earlier by Addison and Sheldon.[14] Although these workers ascribed the colors to the presence of molecular (addition) complexes (but of unspecified structure), we find that they bear a striking resemblance to the colors of the electron donor−acceptor or EDA complexes derived from the cationic nitrosonium acceptor (NO^+).[20] For example, the color changes attendant upon

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[17] In the absence of dioxygen, diphenyl and dibutyl sulfides were recovered intact after exposure to NO over prolonged periods.

[18] Introduced as the PPN^+ salt where PPN^+ = bis(triphenylphosphoranylidene)-ammonium.[19]

the mixing of the crystalline nitrosonium salt ($NO^+BF_4^-$) with various thioethers at −78 °C were the same as those obtained from nitrogen dioxide, and Table 3 establishes the direct correspondence of the charge-transfer absorption maxima (λ_{CT}) and transition probabilities (fwhm) of the various thioether complexes with NO_2 (columns 3 and 4) and those derived from NO^+ (columns 5 and 6). The latter were obtained simply by the addition of the crystalline $NO^+BF_4^-$ to a solution of the thioether in dichloromethane under an argon atmosphere at −78 °C. On stirring at this temperature for a few minutes, the mixture increasingly took on a bright (yellow/red) coloration as the nitrosonium salt dissolved. Equation 4 describes the resultant formation of the EDA complex[21] where R_2S is the generic representation of thioethers. As

$$R_2S + NO^+BF_4^- \overset{K_4}{\rightleftharpoons} [R_2S, NO^+]BF_4^- \qquad (4)$$

expected, the rapid workup of the cold solution (see Experimental Section) led to the quantitative recovery of thioether.

The chemical reversibility and the quantitative aspects of the equilibrium in eq 4 could not be evaluated by direct methods (such as the Benesi−Hildebrand method[22]) owing to the instability of the EDA complex at ambient temperatures and the limited solubility of nitrosonium salts in dichloromethane (or nitroethane) at −78 °C. Accordingly, an indirect approach was based on our previous study of the reversible interaction of NO^+ with aromatic donors (ArH), as established in eq 5.[23]

$$ArH + NO^+BF_4^- \overset{K_5}{\rightleftharpoons} [ArH, NO^+]BF_4^- \qquad (5)$$

As such, we reasoned that the reversible character of the thioether equilibrium in eq 4 could be verified by a ready exchange process with aromatic donors, such as the competitive CT equilibrium in eq 6 for which $K_6 = K_4/K_5$.

$$[ArH, NO^+]BF_4^- + R_2S \overset{K_6}{\rightleftharpoons} [R_2S, NO^+]BF_4^- + ArH \qquad (6)$$

Experimentally, the red EDA complex of hexamethylbenzene (ArH) and $NO^+BF_4^-$ (with its diagnostic charge-transfer absorption at λ_{CT} = 335, 500 nm[23]) was treated with incremental amounts of Bu_2S, and the accompanying spectral changes were found to be the same as those obtained from the reverse treatment of the yellow EDA complex of Bu_2S and $NO^+BF_4^-$ (λ_{CT} = 400 nm) with incremental amounts of hexamethylbenzene. Moreover, the presence of two well-defined isosbestic points at λ = 364 and 482 nm, as typically illustrated in Figure 3, established the facile (quantitative) interchange of NO^+ between the R_2S/ArH donor pairs in accord with eq 6. The digital deconvolution of the composite charge-transfer spectrum obtained at various donor concentrations provided an estimate for the equilibrium constant of $K_6 \sim 1$ and the value of unity indicated that $K_4 \sim 3 \times 10^4$ M^{-1} for dibutyl sulfide in eq 4 (see Experimental Section for details). By an analogous procedure, the equilibrium constant K_6 for phenyl ethyl sulfide of <0.1 indicated $K_4 \leqslant 3 \times 10^3$ M^{-1} for the formation of its nitrosonium complex in eq 4. Such a sharply diminished value of K_4 for PhSEt relative to Bu_2S, accorded with the qualitative results of the direct competition for NO^+. Thus, the treatment of [PhSEt, NO^+] with only 1 equiv of Bu_2S was sufficient for its immediate conversion at −78 °C, *i.e.*

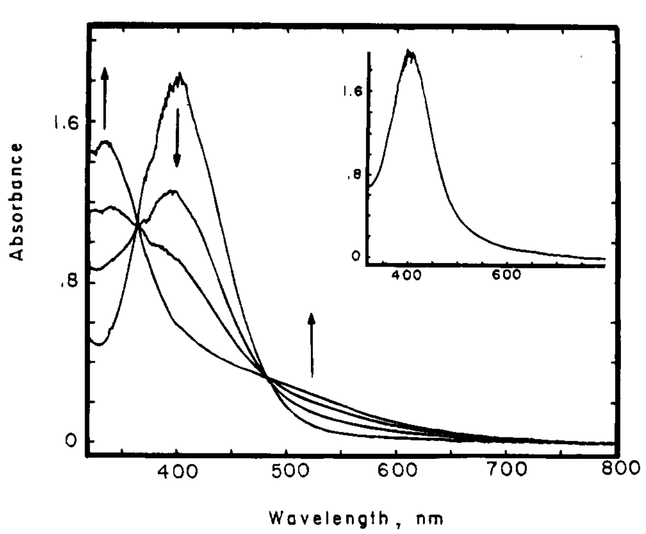

Figure 3. UV−vis spectral changes upon the stepwise addition of hexamethylbenzene (final concentration = 3.0×10^{-2} M) to a cold (−78 °C) dichloromethane solution containing [Bu_2S, NO^+] BF_4^- at an initial concentration of 5.0×10^{-4} M. Inset: The spectrum obtained after the addition of 10 mL of dibutyl sulfide (1.1×10^{-2} M) to the final solution.

$$[PhSEt, NO^+] + Bu_2S \rightleftharpoons [Bu_2S, NO^+] + PhSEt \qquad (7)$$

as indicated by the dramatic color change from red (see λ_{CT} = 500 nm in Table 3) to yellow (λ_{CT} = 400 nm). Conversely, a large excess (>10 fold) PhSEt was required in order to completely convert the yellow solution of [Bu_2S, NO^+] to the bright red solution of [PhSEt, NO^+].

The color (spectral) changes associated with the competitive equilibria in eqs 6 and 7 were reproduced when the crystalline $NO^+BF_4^-$ was replaced with the gaseous NO_2. This observation, coupled with the essential identity of the two series of CT absorption bands in Table 3, lead to the inescapable conclusion that the distinctive colorations of thioether solutions with nitrogen dioxide involve the same nitrosonium moiety. Since the latter is known to derive from the reversible disproportionation of NO_2,[24-27] the most convenient formulation for the relevant charge-transfer interaction of thioethers with nitrogen dioxide is

$$2NO_2 \rightleftharpoons NO^+NO_3^- \overset{R_2S}{\rightleftharpoons} [R_2S, NO^+] + NO_3^- \qquad (8)$$

In accord with this formulation, orange (1:1) microcrystals of a nitrosonium complex were collected from con-

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centrated solutions of dibutyl sulfide and nitrogen dioxide at −78 °C, but their extreme lability precluded handling for either an X-ray crystallographic or infrared analysis.[28] Indirect evidence for the ionic disproportionation in eq 8 was obtained by readily shifting the equilibrium (a) to the right via the *complexation* of nitrate with $SbCl_5$ as a Lewis acid,[29] *i.e.*

$$2NO_2 + R_2S \xrightarrow{SbCl_5} [R_2S, NO^+] + Cl_5SbNO_3^- \qquad (9)$$

and (b) to the left by the addition of nitrate as the PPN^+ salt,[18] *i.e.*

$$2NO_2 + R_2S \xleftarrow[\text{(excess)}]{NO_3^-} [R_2S, NO^+] \qquad (10)$$

(see Experimental Section for details.).

V. Charge-Transfer Oxidation of Thioethers with NO_2 by Selective Activation of the EDA Complex. The critical role of the nitrosonium complex (eq 8) in thioether oxidations with NO_2 was probed by its selective activation (*via* its charge-transfer absorption band) at −78 °C, where the thermal process (Table 2) was too slow to compete. Experimentally, the brightly colored solutions were held at this low temperature and continuously exposed to actinic radiation from a 250-W mercury lamp equipped with a sharp cutoff filter so that only light with $\lambda_{exc} > 410$ nm was transmitted. Under these controlled conditions, the results in Figure 1 ensured the selective excitation of the charge-transfer absorption band of the EDA complex and precluded any adventitious activation of either the uncomplexed thioether or nitrogen dioxide.

Photoactivaction of the EDA complex of thioanisole and nitrogen dioxide in dichloromethane solution at −78 °C resulted in the monotonic bleaching of the CT color, as depicted in Figure 4. Interruption after 10 min,[30] followed by the rapid workup of the partially bleached solution, indicated the formation of methyl phenyl sulfoxide that was uncontaminated by its sulfone below detection limits (< 0.1%), i.e.

$$[PhSMe, NO^+]NO_3^- \xrightarrow[-78\ °C]{[h\nu_{CT}]} PhS(O)Me, \mathit{etc.} \qquad (11)$$

Control experiments with an identical solution (but protected from light and placed alongside the irradiated solution at the same temperature) showed no change, and simultaneous workup indicated the thioanisole recovery to be quantitative. However, the quantum efficiency for sulfoxide formation (determined by selective irradiation with monochromatic light at $\lambda_{exc} = 440$ nm) could only be estimated as $\phi = 0.5 \pm 0.3$, owing to the limited control of the low temperature over extended irradiation times[31] (see Experimental Section).

The charge-transfer oxidations of the various dialkyl and mixed alkyl aryl sulfides in Table 4 led to high yields of sulfoxides (column 6) by the same photochemical procedure. In each case, cognizance was always taken of the potential competition from the accompanying thermal process. Thus, the periods of irradiation in Table 4 were deliberately limited[32] to achieve rather low (unoptimized) conversions. Otherwise, the direct comparison of the results in Tables 2 and 4 indicates that the charge-transfer oxidations of the various thioethers could not be distinguished from those carried out with stoichiometric amounts of NO_2.

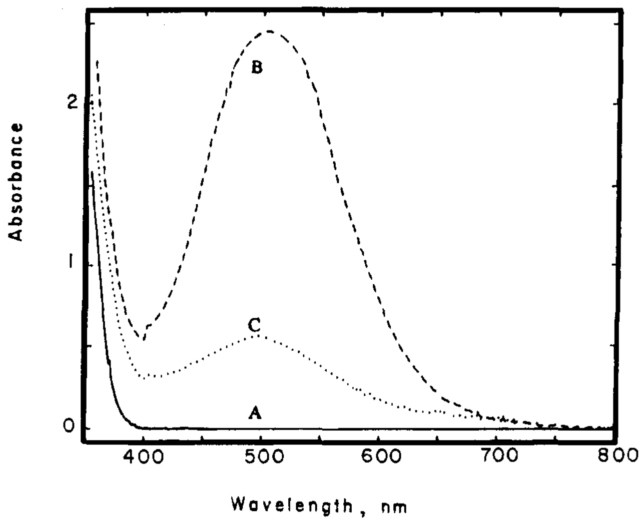

Figure 4. Photobleaching of the charge-transfer absorption band from 0.056 M NO_2 and 0.017 M thioanisole (in dichloromethane at −78 °C) upon actinic irradiation with $\lambda_{exc} > 410$ nm. (A) Spectrum of NO_2 alone, (B) spectrum obtained immediately after mixing NO_2 and thioanisole, and (C) spectrum after irradiation for 10 min.

Table 4. Charge-Transfer Oxidation of Thioethers with Nitrogen Dioxide at −78 °C[a]

thioether	(mmol)	NO_2 (mmol)	time (min)	conv[b] (%)	yield[c] (%)
dimethyl sulfide	0.20	0.70	40	27	100
dibutyl sulfide	0.06	0.70	70	51	93
tetrahydrothiophene	0.23	0.84	120	70	85
benzyl methyl sulfide	0.11	0.56	47	18	80
thioanisole	0.17	0.28	10	24	80
isopropyl phenyl sulfide	0.42	0.90	25	39	75
diphenyl sulfide	0.45	1.20	25	8	90[d]

[a] All oxidations performed in dichloromethane solution (cooled at −78 °C) by irradiating using a medium pressure Hg lamp with a 415 nm cutoff filter (see Experimental Section). In each reaction, the sole product was the corresponding sulfoxide. [b] Based on recovered thioether as determined by quantitative GC. [c] Yield of sulfoxide based on consumer thioether. [d] Traces of nitroarenes detected by GC-MS.

VI. Thioether Cation Radicals as the Reactive Intermediates in Photochemical and Thermal Oxidations with NO_2. Photochemical Oxidation. Intermediates formed in the charge-transfer activation of the thioether complexes (compare eq 11) were probed directly by time-resolved spectroscopy.[33] The laser pulse at $\lambda_{exc} = 355$ nm (corresponding to the third harmonic of the Q-switched Nd^{3+}:YAG laser) was well suited for the specific excitation of CT absorption bands derived from dialkyl sulfides and NO_2 (see Table 3), while the second harmonic at $\lambda_{exc} = 532$ nm was suited for the corresponding complexes from alkyl aryl sulfides. Most importantly, the time-resolved spectrum in Figure 5 graphically

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(28) The red microcrystals obtained from methyl *tert*-butyl sulfide and NO_2 at −78 °C, turned pale yellow upon warming and yielded equimolar amounts of methyl *tert*-butyl sulfoxide, nitric oxide, and nitrogen dioxide.

(29) Compare: Bosch, E.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 3314.

(30) Competition from the thermal reaction was difficult to control reliably when the irradiations were carried out over extended periods at −78 °C.

(31) The excitation light was weak since the relatively narrow band width (fwhm ± 5 nm) was achieved with a (low efficiency) interference filter.

(32) To obviate complications from the thermal process.[30]

(33) See: Bockman, T. M. *et al.* in ref 23 and Kochi, J. K. *Adv. Phys. Org. Chem.* **1993**, *29*, 185.

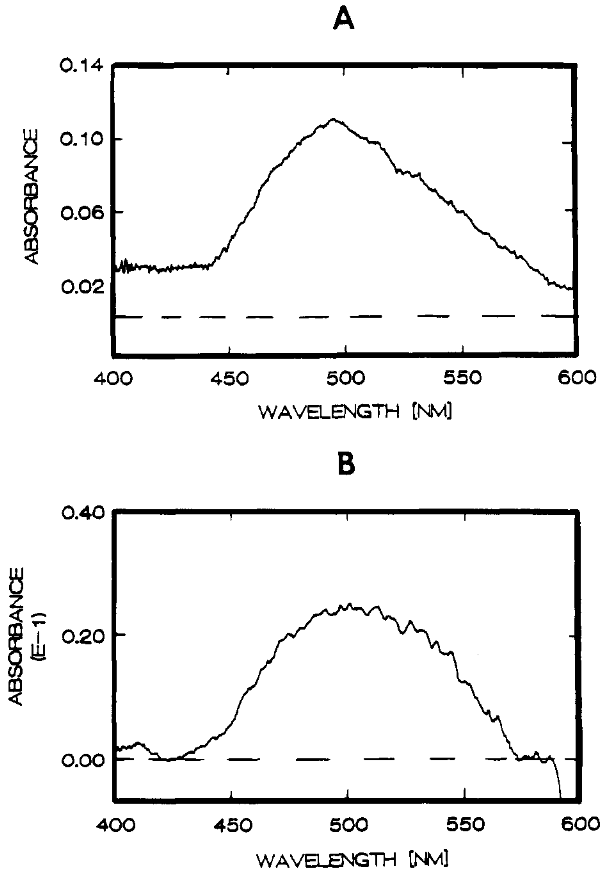


Figure 5. (A) Time-resolved (25 ps) absorption spectrum observed upon the CT excitation (λ_{exc} = 355 nm) of the tetrahydrothiophene EDA complex from $NO^+BF_4^-$ in dichloromethane at −78 °C. (B) As for A except the EDA complex was prepared from NO_2.

Table 5. Formation of Thioether Cation Radicals upon the Selective Charge-Transfer Excitation of Various Thioether EDA Complexes with Nitrogen Dioxide and Nitrosonium Cation[a]

thioether donor	NO_2[b] λ_{max}, nm	$NO^+BF_4^-$ [b] λ_{max}, nm
dimethyl sulfide[c]	500	500[e]
tetrahydrothiophene[c]	500	500[e]
thioanisole[d]	775	760
diphenyl sulfide[d]	780	775[f,g]

[a] With 10^{-4} M thioether and 10^{-4} M nitrogen oxide in dichloromethane solution cooled to −78 °C. [b] Absorption maximum of the cation radical (±10 nm). [c] Excitation wavelength, λ = 355 nm. [d] Excitation wavelength λ = 532 nm. [e] Maximum in frozen s-BuCl matrix at 465 nm.[35] [f] The same absorption maximum was obtained on the CT excitation of the diphenyl sulfide EDA complex with tetranitromethane. [g] Maximum in s-BuCl matrix at 790 nm.[35]

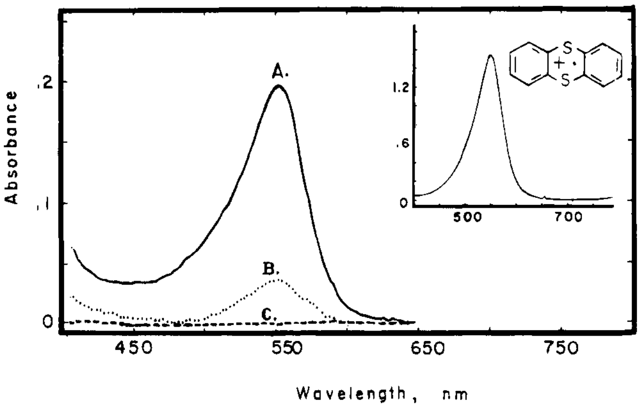
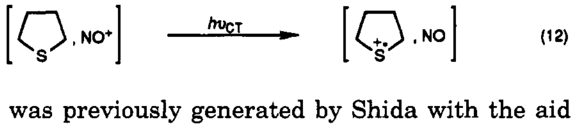


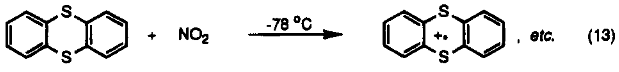
Figure 6. Spectral changes during the (nitrogen dioxide) catalyzed autoxidation of thianthrene (2.3 mmol) in dichloromethane at −45 °C. (A) Immediately after addition of nitrogen dioxide (0.3 mmol), (B) after 5 min, and (C) after 45 min (prior to workup). Inset: Spectrum of thianthrene cation radical in dichloromethane solution.

illustrates the earliest stages of the charge-transfer activation[34] of the EDA complex prepared from tetrahydrothiophene and NO^+, in which direct spectral comparison confirms the spectral transient with λ_{max} = 500 nm to coincide with that of tetrahydrothiophene cation radical, *i.e.*

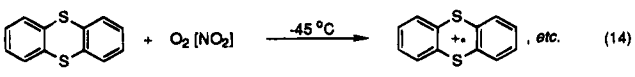


which was previously generated by Shida with the aid of pulse radiolytic techniques.[35,36] Furthermore, the appearance of the same species *via* the tetrahydrothiophene complex with NO_2 (see Figure 5B) provides further support that nitrosonium cation is the critical acceptor in the formation of thioether EDA complexes as described in eq 8. Moreover, the results in Table 5 show that thioethers as diverse as dimethyl sulfide, thioanisole, and diphenyl sulfide all afforded cation radicals from the CT excitation of the nitrosonium EDA complex that were spectrally indistinguishable from those prepared with nitrogen dioxide.

Thermal Oxidations. Intermediates in the thermal oxidations of thioethers with NO_2 (under either stoichiometric or catalytic [O_2] conditions in eqs 3 and 1, respectively) were generally difficult to detect owing to the limiting reaction rates.[37] The exceptions were the oxidations of strong sulfur-containing donors derived from dibenzothianes (thianthrene)[38] and dibenzothiazines (phenothiazine).[39] For example, the stoichiometric and catalytic (O_2) oxidation of thianthrene at −78 °C produced a spectral transient as a fleeting red (pink) solution that finally led to a pale yellow solution from which thianthrene 5-oxide was isolated in quantitative yields. Interruption of the oxidation at partial (pink) conversions with an aqueous quench afforded mixtures containing only thianthrene and its oxide.[40] Moreover, UV−vis spectral analysis of the transient pink-colored solutions at −78 °C afforded a well-resolved absorption spectrum with λ_{max} = 544 nm of the thianthrene cation radical,[41] *e.g.*



Thianthrene cation radical was also transiently observed (see Figure 6) in the catalytic autoxidation of thianthrene at −45 °C, *i.e.*



In the latter regard, it is noteworthy that dioxygen alone was incapable of the oxidation of thianthrene; but the nitrosonium cation added as the crystalline salt $NO^+BF_4^-$

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[34] Compare the time-resolved spectroscopic studies of the related aromatic EDA complexes with NO^+.[23]

[35] Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988.

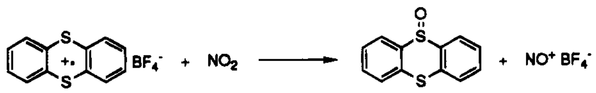
to a solution of thianthrene under an argon atmosphere resulted immediately in the purple solution of the cation radical, *i.e.*[42]

(15)

The reduced nitric oxide (eq 15) was identified in the head gas by its diagnostic IR and UV−vis spectra (ν_{NO} = 1876 cm^{-1};[12] λ_{max} = 204, 212, 224 nm[43]). Thianthrene cation radical in combination with NO (as prepared in eq 15) was immediately converted by dioxygen to thianthrene 5-oxide in quantitative yields. The cation radical was also observed as a spectral intermediate when the related polycyclic aromatic sulfides phenothiazine and phenoxathiin were treated with either $NO^+BF_4^-$, NO_2, or NO_2/O_2 in dichloromethane, as indicated by the formation of highly colored solutions of the cation radicals with λ_{max} = 514[44] and 584 nm,[45] respectively.[46]

VII. Thioether Cation Radicals as Intermediates in Sulfoxide Formation. Enhanced Reactivity toward NO_2 and NO_3^-. The ultimate step in the conversion of the thioether cation radical to its sulfoxide was examined directly by exposing an authentic sample to various nitrogen oxides extant in solution during oxidation, as described in eqs 1, 3, and 11. For these studies, we selected the thianthrene cation radical as the prototype owing to (a) the high purity in which it can be prepared as the crystalline tetrafluoroborate salt[47] and (b) its persistent character in solution.[42]

Nitrogen Dioxide. The addition of nitrogen dioxide (1 equiv) to a cold solution of thianthrene cation radical in dichloromethane under an argon atmosphere at −50 °C resulted in the immediate bleaching of the purple color, and thianthrene 5-oxide was readily isolated as colorless crystals in 94% yield. The concomitant separation of the nitrosonium salt $NO^+BF_4^-$ (identified by its diagnostic IR spectrum with ν_{NO} = 2341 cm^{-1} and ν_{BF} = 1054 cm^{-1})[48] as colorless crystals confirmed the transfer of oxygen atom as



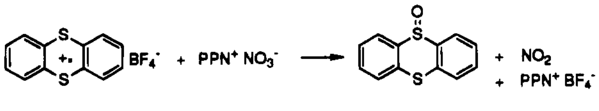
(16)

Even in the presence of NO_2 in excess, there was no evidence for the further oxidation or nitration of thianthrene sulfoxide (isolated in quantitative yield).

Nitric Oxide. Thianthrene cation radical did not react with NO in dichloromethane (saturated solution) at 25 °C, since no change of the UV−vis spectrum (λ_{max} = 544 nm) occurred if the system was protected from air.

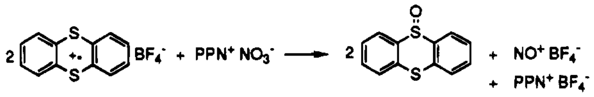
Dioxygen. The purple solution of thianthrene cation radical (as the tetrafluoroborate salt) and dioxygen (1 atm) persisted unchanged at 25 °C over the course of several hours.

Nitrate. The addition of nitrate (1 equiv as the PPN$^+$ salt[18]) to the deep purple thianthrene cation radical under an argon atmosphere at 25 °C resulted in the immediate bleaching of the dichloromethane solution and the spontaneous evolution of a brown gas. Isolation of thianthrene oxide in quantitative yield, coupled with the spectral analysis of the head gas as NO_2 (ν_{NO} = 1629 and 1601 cm^{-1}),[11] indicated the stoichiometry for oxygen transfer to be



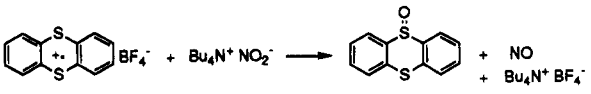
(17)

In a separate experiment, thianthrene cation radical was treated with only one-half of an equiv of nitrate salt. The deep purple solution bleached immediately, but no nitrogen oxide was detected by spectral analysis of the head gas. Careful addition of pentane to the colorless solution led to a white precipitate that was analyzed as the nitrosonium salt $NO^+BF_4^-$ (*vide supra*). A quantitative yield of thianthrene oxide was isolated from the reaction mixture according to 2:1 stiochiometry in eq 18.[49]



(18)

Nitrite. The addition of nitrite (as the tetra-*n*-butylammonium salt) to a dichloromethane solution of thianthrene cation radical at 0 °C led to an immediate bleaching of the purple color. Spectral (UV−vis, IR) analysis of the head gas revealed the characteristic absorptions of nitric oxide, which was the only gaseous nitrogen oxide formed. The nitric oxide was removed *in vacuo*, and thianthrene 5-oxide was isolated in quantitative yield after aqueous workup, *i.e.*



(19)

Discussion

Among the various methods available for thioether oxidation to sulfoxides,[1,2] nitrogen dioxide is unique in that it can be employed either as a *reagent* in stoichiometric amounts or as a *catalyst* for (O_2) autoxidation with equal efficacy, as described in Tables 2 and 1, respectively. Since dioxygen alone is incapable of oxidizing thioethers at ambient temperatures and atmospheric

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[36] We note that Asmus has presented evidence that the visible absorption maxima for dialkyl sulfide cation radicals correspond to the dimer cation radical, *i.e.* ($R_2SSR_2^{\bullet+}$). See: Asmus, K.-D. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus, K.-D., Eds.; Plenum Press: New York, 1990; p 155ff.

[37] In thermal (adiabatic) reactions, the slow rate-limiting activation process precludes the direct observation of reactive intermediates that react at diffusion controlled rates.

[38] Joule, J. A. *Adv. Heterocycl. Chem.* **1990**, *48*, 301.

[39] Compare: Bosch, E.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 1*, in press.

[40] The reaction of water with thianthrene cation radical yields a 1:1 mixture of thianthrene and thianthrene 5-oxide. Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

[41] Mao, Y.; Thomas, J. K. *J. Org. Chem.* **1993**, *58*, 6641.

[42] Boduszek, B.; Shine, H. J. *J. Org. Chem.* **1988**, *53*, 5142.

[43] Marmo, F. F. *J. Opt. Soc. Am.* **1953**, *43*, 1186.

[44] Hester, R. E.; Williams, K. P. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 852.

[45] Shine, H. J.; Small, R. J. *J. Org. Chem.* **1965**, *30*, 2140.

[46] It is noteworthy that NO alone afforded no coloration indicative of the polycyclic aromatic cation radical. However, immediately upon the introduction of dioxygen, the characteristic colors appeared, and the corresponding sulfoxides were isolated in quantitative yields.

[47] Bock, H.; Rauschenbach, A.; Nather, C.; Kleine M.; Havlas, Z. *Chem. Ber.* **1994**, *127*, 2043. See, also: Boduszek, B. *et al.* in ref 42.

[48] Evans, J. C.; Rinn, H. W.; Kuhn, S. J.; Olah, G. A. *Inorg. Chem.* **1964**, *3*, 857.

[49] Compare: Pemberton, J. E.; McIntire, G. L.; Blount, H. N.; Evans, J. F. *J. Phys. Chem.* **1979**, *83*, 2697.

pressures,[50,56] one of nitrogen oxide species must be the active agent in the catalytic oxidations.[58] As such, the most economical formulation of the catalytic oxidation in eq 1 (as presented in Table 1) is based on the stoichiometric oxidation of thioethers by NO_2 according to eq 3 (Table 2) that is coupled to the facile regeneration of NO_2 from NO *via* the well-known oxygen-atom transfer from dioxygen,[60] *i.e.*

Scheme 1

$$R_2S + NO_2 \rightarrow R_2SO + NO \qquad (20)$$

$$NO + {}^1/_2O_2 \xrightarrow{\text{fast}} NO_2 \qquad (21)$$

However, this simple scheme does not adequately account for the various facets of thioether oxidations—namely, (a) the marked color changes (Table 3) that accompany the stoichiometric and catalytic processes, (b) the replaceability of NO_2 with NO^+ in eq 2, (c) the deliberate retardation and promotion by added nitrate and Lewis acid in eqs 10 and 9, respectively, and (d) the spontaneous appearance of the cation radical as the reactive intermediate in thianthrene oxidation (Figure 6). Most importantly, any mechanistic formulation that can accommodate all these facets of thioether oxidations must be consistent with the results in Tables 1, 2, and 4 that show the thermal and charge-transfer oxidations with stoichiometric amounts of NO_2 to be equivalent to the catalytic oxidations with dioxygen. Accordingly, let us first focus on the mechanism of the stoichiometric oxidation of thioethers with NO_2 in eq 20 by considering the significance of the spectral (color) changes.

I. Spectral Changes Accompanying the Formation of Thioether Complexes of Nitrogen Dioxide. The UV–vis spectra in Figures 1 and 2, together with the spectral parameters in Table 3, provide definitive identification of the nitrosonium EDA complex as the first observable intermediate formed from thioethers and nitrogen dioxide. In order to understand how the chromophoric moiety $[R_2S, NO^+]$ is formed from NO_2, we recall the earlier dimerization studies[61] that identified the existence of small amounts of the O–N bonded (nitrito nitro) dimer in facile equilibrium with the prevalent N–N bonded (nitro nitro) dimer,[62] *i.e.*

$$O_2NNO_2 \rightleftharpoons 2NO_2 \rightleftharpoons ONONO_2 \qquad (22)$$

Although the heterolytic (disproportionation) cleavage of the nitrito-nitro dimer to the nitrosonium nitrate ion pair[24-26] is negligible in nonpolar solvents (such as dichloromethane), charge-transfer complexation of NO^- to strong electron donors such as thioethers can shift the equilibrium to the ionic EDA complex,[63] *i.e.*

$$O_2NNO_2 \rightleftharpoons NO^+NO_3^- \xrightleftharpoons{R_2S} [R_2S, NO^+]NO_3^- \qquad (23)$$

Indeed, the measured formation constant of $K_4 = 10^4\ M^{-1}$ for the nitrosonium EDA complex (eq 6) accounts for the strong charge-transfer coloration attendant upon the addition of dibutyl sulfide to nitrogen dioxide in Figure 1.

II. Nitrosonium EDA Complex as the Critical Intermediate in Thioether Oxidation with Nitrogen Dioxide. There are two principal lines of independent evidence that strongly support the nitrosonium EDA complex $[R_2S, NO^+]NO_3^-$ as the critical intermediate in thioether oxidation with nitrogen dioxide. These relate to the strong correlation between the oxidative conversion of thioethers to sulfoxides and (A) the concentration or (B) the direct activation of $[R_2S, NO^+]$ as follows.

A. Structure/Reactivity Relationship to the Concentration of $[R_2S, NO^+]$. The enhanced reactivity of an alkyl thioether such as dibutyl sulfide relative to diphenyl sulfide in Table 2 directly parallels the difference in the (steady-state) concentrations of the corresponding nitrosonium EDA complexes (*i.e.*, $[Bu_2S, NO^-]$ versus $[Ph_2S, NO^+]$), as indicated by the greater intensity of its charge-transfer absorbance in Figure 2.[64] The same trend in structure/reactivity relationships is more clearly shown in the oxidative conversion of the homologous thioethers in the order p-$MeOC_6H_4SMe > p$-$MeC_6H_4SMe > PhSEt$ in Table 2 that parallels the bathochromic shifts of the charge-transfer bands of the corresponding nitrosonium EDA complexes in Table 3.[67] Moreover, those additives such as antimony pentachloride that effectively enhance the ionic disproportionation of NO_2 (*via* the Lewis acid effect described in eq 9) also greatly promote the oxidative conversion of a given thioether. Conversely,

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(50) The selective autoxidation of thioethers to sulfoxides has been reported at high temperature and pressure.[51] However, at ambient temperatures and atmospheric pressure, the autoxidation has only been observed in the presence of metal-based catalysts[52-54] and radical initiators.[55]

(51) (a) Correa, P. E.; Riley, D. P. *J. Org. Chem.* **1985,** *50*, 1787. (b) Correa, P. E.; Hardy, G.; Riley, D. P. *J. Org. Chem.* **1988,** *53*, 1695.

(52) Riley, D. P.; Shumate, R. E. *J. Am. Chem. Soc.* **1984,** *106*, 3179.

(53) (a) Riley, D. P.; Correa, P. E. *J. Chem. Soc., Chem. Commun.* **1986,** 1097. (b) Riley, D. P.; Smith, M. R.; Correa, P. E. *J. Am. Chem. Soc.* **1988,** *110*, 177.

(54) Mashkina, A. V. *Catal. Rev., Sci. Eng.* **1990,** *31*, 105.

(55) Autoxidation of thioethers catalyzed by azobisisobutyronitrile affords low yields of sulfoxides. See: (a) Bateman, L.; Cunneen, J. I. *J. Chem. Soc.* **1955,** 1596. (b) Bateman, L.; Cunneen, J. I.; Ford, J. *J. Chem. Soc.* **1957,** 1539. (c) Bateman, L.; Cunneen, J. I.; Ford, J. *J. Chem. Soc.* **1956,** 3056.

(56) The photochemical oxidation of thioethers with dioxygen has been reported.[57]

(57) (a) Sinnreich, D.; Lind, H.; Batzer, H. *Tetrahedron Lett.* **1976,** 3541. (b) Tezuka, T.; Miyazaki, H.; Suzuki, H. *Tetrahedron Lett.* **1978,** 1959. (c) Akasaka, T.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1987,** *109*, 8085.

(58) The nitrogen oxide (NO, NO_2, and HNO_3) catalyzed gas-phase air oxidation of dimethyl sulfide to dimethyl sulfoxide has been patented.[59]

(59) (a) Smedslund, T. H. *Swed. Patent* 121, 576. (b) Smedslund, T. H. U.S. Patent 2,581, 050. (c) Wetterholm, G. A.; Fossan, K. R. Swedish Patent 151, 609. (d) Smedslund, T. H. U.S. Patent 2,825, 745. See, also: Luk'yanitsa, V. G.; Gal'pern, G. D. *Neftekhimiya* **1985,** *25*, 103.

(60) Smith, J. H. *J. Am. Chem. Soc.* **1943,** *65*, 74.

(61) Pinnick, D. A.; Agnew, S. F.; Swanson, B. I. *J. Phys. Chem.* **1992,** *96*, 7092.

(62) (a) Vosper, A. J. *J. Chem. Soc. (A)* **1970,** 2191. (b) Redmond, T. F.; Wayland, B. B. *J. Phys. Chem.* **1968,** *72*, 1626. (c) James, D. W.; Marshall, R. C. *J. Phys. Chem.* **1968,** *72*, 2963. (d) Brunning, J.; Frost, M. J.; Smith, I. W. M. *Int. J. Chem. Kinet.* **1988,** *20*, 957.

(63) Compare Bosch, E. *et al.*. in ref 27 and 29.

(64) The estimated formation constants for the thioether EDA complexes in eq 4 indicate that $K_4(Bu_2S)/K_4(Ph_2S) > 100$, despite the lower ionization potential of diphenyl sulfide (Table 3). The higher stability of the dialkyl sulfide EDA complex relative to the aryl sulfide analogue is, however, typical of the strong $n \rightarrow \sigma$ EDA complexes formed by thioethers.[65,66] This trend is ascribed to the reduced n-character of the HOMO of aryl sulfides due to $n \rightarrow \pi$ overlap with the aryl moiety.[65]

(65) Reichenbach, G.; Santini, S.; Mazzucato, U. *J. Chem. Soc., Faraday Trans. 1* **1973,** *69*, 143.

(66) Note that for $n \rightarrow \pi$ and $\pi \rightarrow \pi$ EDA complexes, the complex stability, K_{EDA}, increases with the donor strength. See: Foster, R. In *Organic Charge Transfer Complexes*; Academic Press: New York, 1969.

(67) Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988,** *27*, 1227.

the deliberate inhibition of the ionic disproportionation of NO_2 by added nitrate (*via* the mass action effects in eq 10) leads to a greatly diminished oxidative conversion of thioether. From these separate lines of evidence, we conclude that the nitrosonium EDA complex is the critical intermediate in the oxidative conversion of thioethers with nitrogen dioxide, *i.e.*

$$[R_2S, NO^+]NO_3^- \xrightarrow[-NO_2]{\Delta} R_2SO + NO \qquad (24)$$

Accordingly, let us now consider how the nitrosonium EDA complex of thioether is converted to the sulfoxide in eq 24.

B. Direct Activation of Nitrosonium EDA Complexes. Nitrosonium EDA complexes are directly activated by the selective irradiation of the charge-transfer absorption band ($h\nu_{CT}$) to afford high sulfoxide yields (Table 4) at temperatures too low (−78 °C) to effect thermal oxidation of thioethers. As such, the time-resolved spectra in Figure 5 and the spectral data in Table 5 establish the thioether cation radical as the reactive intermediate in charge-transfer activation in accord with Mulliken theory,[68] *i.e.*

$$[R_2S, NO^+]NO_3^- \xrightarrow{h\nu_{CT}} [R_2S^{\bullet+}, NO_3^-] + NO \qquad (25)$$

The further conversion of the thioether cation radical in eq 25 can then proceed *via* ion-pair collapse with the nitrate counterion. The validity of this formulation is established by the ready conversion of even the relatively stable thioether cation radical derived from thianthrene to its sulfoxide, as described by the rapid oxygen transfer in eq 17. The complete stepwise mechanism for the photoinduced oxidation of thioethers is summarized by the charge-transfer cycle in Scheme 2.[69]

Scheme 2

$$R_2S + 2NO_2 \rightleftharpoons [R_2S, NO^+]NO_3^- \qquad (26)$$

$$[R_2S, NO^+]NO_3^- \underset{k_{bet}}{\overset{h\nu_{CT}}{\rightleftharpoons}} [R_2S^{\bullet+}, NO]NO_3^- \qquad (27)$$

$$[R_2S^{\bullet+}, NO_3^-] \xrightarrow{k_{ip}} R_2SO + NO_2 \qquad (28)$$

According to Scheme 2, the measured quantum yield ϕ ~0.5 for the charge-transfer oxidation indicates that the thioether cation radical paired with NO in eq 27 suffers back electron transfer (k_{bet}) with essentially the same facility as it undergoes ion-pair collapse (k_{ip}) *via* oxygen transfer to yield sulfoxide in eq 28.[70]

III. Electron-Transfer Formulation of the Thermal Oxidation of Thioethers with Nitrogen Dioxide. The strong similarity of the CT spectral changes accompanying both the thermal and photochemical oxidation of thioethers with NO_2 (as described in Tables 2 and 4, respectively) suggests that both processes proceed via similar intermediates. If so, the formation of the thioether cation radical via an adiabatic activation of the nitrosonium EDA complex involving electron transfer (as given in eq 29) represents the thermal counterpart to the charge-transfer activation of thioethers with NO_2 in Scheme 2.

$$[R_2S, NO^+]NO_3^- \overset{k_{ET}}{\rightleftharpoons} [R_2S^{\bullet+}, NO] + NO_3^- \qquad (29)$$

Indeed, separate experiments with thianthrene, chlorpromazine, and related phenothiazines[71,72] establish the ease with which cation radicals are generated from NO^+ by electron transfer, especially with electron-rich heterocyclic sulfides (compare Figure 6). Moreover, it is expected that the redox equilibrium in eq 29 for the less endowed thioethers, such as dibutyl and diphenyl sulfides, may not yield thioether cation radicals in sufficient (steady-state) concentrations to be observed owing to the endergonic electron transfer.[73] Under these circumstances, a facile and irreversible followup reaction, such as oxygen transfer from nitrate in eq 32,[74] will be required to pull the redox equilibrium to completion, *i.e.*

Scheme 3

$$R_2S + 2NO_2 \rightleftharpoons [R_2S, NO^+]NO_3^- \qquad (30)$$

$$[R_2S, NO^+]NO_3^- \overset{k_{ET}}{\rightleftharpoons} [R_2S^{\bullet+}, NO] + NO_3^- \qquad (31)$$

$$R_2S^{\bullet+} + NO_3^- \xrightarrow{\text{fast}} R_2SO + NO_2 \qquad (32)$$

According to Scheme 3, the driving force for electron transfer, as given by $-\Delta G = F[E^\circ_{ox}(R_2S) + E^\circ_{red}(NO^+)]$ where F is the faraday constant and E° is the redox potential, becomes progressively exergonic with increasing strength of the thioether donor. As such, the reactivity of the graded series of aryl sulfide donors in the order PhSEt < p-MeC_6H_4SMe < p-$MeOC_6H_4SMe$ in Table 2 (entries 3−5) follows the trend in their oxidation potentials (column 2).[75] Furthermore, we believe that the highly effective use of NO^+ as the nitrogen oxide source in the catalytic autoxidation of thioether provides the best experimental support for electron transfer in Scheme 3 as elaborated in the following section.

IV. Mechanism of the Nitrogen Oxide Catalysis of Thioether Oxidation with Dioxygen. Catalytic amounts of different nitrogen oxides (including the gaseous NO_2 and the crystalline NO^+ salt) are equally effective in thioether oxidation with dioxygen, as described in Table 1. Thus, it follows from Scheme 1 that

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[68] (a) Mulliken, R. S.; Person, W. B. *Molecular Complexes. A Lecture and Reprint Volume*; Wiley: New York, 1969. (b) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600.

[69] Note that the diffusive separation of the triad is not included for the sake of clarity.

[70] Since nitrogen dioxide is present in the reaction mixture, some of the sulfoxide may also derive from reaction of the thioether cation radical with NO_2 as demonstrated in eq 16. The nitrosonium cation that is generated in eq 16 may react with the remaining nitrate to form N_2O_4 and thus leave the stoichiometry unchanged. The possible formation of traces of nitrite in the reaction mixture may also lead to sulfoxide by oxygen transfer to thioether cation radicals from NO_2^- (see eq 19). For the purposes of clarity, the possible intervention of these pathways is not included in the schemes.

[71] (a) Bandlish, B. K.; Shine, H. J. *J. Org. Chem.* **1977**, *42* 561. (b) Eberson, L.; Radner, F. *Acta Chem. Scand.* **1984**, *B 38*, 861. (c) Bosch, E. *et al.* in ref 39.

[72] Compare Musker, W. K. *Acc. Chem. Res.* **1980**, *13*, 200.

[73] Typically the oxidation potential for thianthrene (E_{ox}° = 1.21 V vs SCE) is less positive by roughly 400 mV than that of dibutyl and diphenyl sulfide.

[74] The possibility that some sulfoxide may be formed from the thioether cation radical and NO_2 or NO_2^- is not included.[70]

[75] Although diphenyl sulfide is a better donor than dibutyl sulfide, it exhibits lower reactivity toward NO_2 (see Table 2, entries 2 and 6). The apparently anomalous reactivity derives from the large difference in the concentrations of the thioether EDA complexes.[64] This difference is manifested in the observed rate of reaction since $k_{obs} \propto K_{EDA}\, k_{ET}$ and the large difference in K_{EDA} (> 10^2) dominates the observed rate of reaction.

NO_2 and NO^+ must be readily interconverted during the catalytic cycle. Although the disproportionations described in eqs 22 and 23 account for the reductive conversion: $NO_2 \rightarrow NO^+$; the reverse is clearly not possible in the absence of nitrate. Since NO^+ is not directly oxidized to NO_2 by dioxygen, an alternative pathway must be available for the oxidative conversion $NO^+ \rightarrow NO_2$. Indeed, the further consideration of Scheme 1 suggests the indirect route *via* the reduced NO which is readily oxidized to NO_2 by dioxygen (see eq 21). In this formulation, the reversible (electron-transfer) reduction of NO^+ by thioether (compare eq 31) is driven to completion by the facile oxidation of NO. As such, the initiation by $NO^+ BF_4^-$ of the catalytic autoxidation of thioethers can be described as[76]

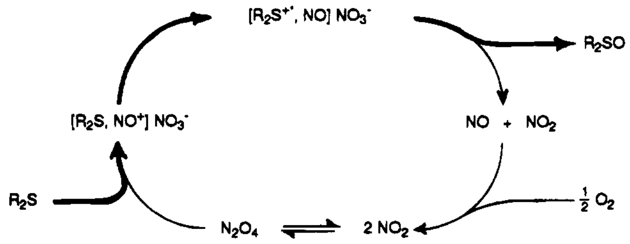
$$R_2S + NO^+BF_4^- \rightleftharpoons [R_2S, NO^+]BF_4^- \qquad (33)$$

$$[R_2S, NO^+] \overset{k_{ET}}{\rightleftharpoons} R_2S^{\cdot +} + NO \qquad (34)$$

$$NO + {}^1\!/_2O_2 \xrightarrow{\text{fast}} NO_2, \textit{etc.} \qquad (35)$$

Nitrogen dioxide that is either added directly or generated *in situ* from NO^+ (eqs 33–35) is responsible for the catalytic autoxidation of thioethers in Scheme 1. However, the identification of the disproportionation/electron-transfer equilibria in the charge-transfer activation (Scheme 2) provides the *mechanistic* basis for understanding how the various thioethers are actually transformed to sulfoxide *via* their cation radicals (Scheme 3). Accordingly, the catalytic cycle in Scheme 4 summarizes the multitude of nitrogen oxide intermediates derived from NO_2, the various thioether donors, and dioxygen.[74] In particular, the heavy (bold) lines in the top half of the catalytic cycle trace the oxidative conversion of the thioether to sulfoxide *via* the nitrosonium EDA complex and the cation radical. The lower half of the cycle represents the dimerization/disproportionation of nitrogen dioxide in association with its regeneration by dioxygen.

Scheme 4



Summary and Conclusions

The nitrogen oxide catalysis of thioether autoxidation produces the corresponding sulfoxide selectively and efficiently under mild conditions (Table 1). Based on the stoichiometric and photoinduced oxidation of thioethers (R_2S) with NO_2 in Tables 2 and 4, the catalytic process is shown to proceed *via* a series of equilibria in which the first critical intermediate is the nitrosonium EDA complex formed from the thioether-induced disproportionation of NO_2 to nitrosonium nitrate according to eq 23. According to Scheme 4, the adiabatic electron transfer within $[R_2S, NO^+]NO_3^-$ to generate the thioether cation radical and NO, followed by the facile oxygen transfer from nitrate, leads to sulfoxide. Aerobic oxidation of NO to NO_2 completes the catalytic cycle.

In a biological context, we note that the high formation constant ($K_4 > 10^4$ M^{-1}) for the nitrosonium EDA complex with dialkyl sulfides (eqs 4 and 5) provides a ready mechanism for the biochemical formation (and storage) of the powerful one-electron oxidant, NO^+, from nitric oxide in oxygenated media. Any further discussions of the biochemical aspects of nitrogen oxides[77] should take this process into account.

Experimental Section

Catalytic Oxidation of Thioethers with Dioxygen and Nitrogen Dioxide. Autoxidation of Sulfides Using Nitrogen Dioxide. General Procedure. A solution of dimethyl sulfide (5.8 mL, 79.1 mmol) in dichloromethane (50 mL) was prepared in a flask fitted with a sidearm. The solution was cooled to −50 °C and dry oxygen bubbled through the solution for several minutes. The flask was capped with a rubber septum and an oxygen-filled balloon fitted to the side arm to ensure an oxygen atmosphere. A cold dichloromethane solution of NO_2 (1 mL, 4.4 mmol) was added with an all-glass hypodermic syringe. The dark orange/brown mixture was allowed to warm to room temperature and stirred overnight. The solvent and nitrogen oxides were removed *in vacuo*, and the crude dimethyl sulfoxide was distilled at 70 °C/10 mmHg (5.74 g, 73.6 mmol). Autoxidations using nitrosonium salts were performed in a similar manner (the flask was initially charged with a weighed amount of nitrosonium salt in the drybox). Dichloromethane was added and oxygen bubbled through the slurry as described above. [Note that $NO^+BF_4^-$ is not soluble in dichloromethane.] The thioether was added to the vigorously stirred slurry at −50 °C, and the resultant orange mixture was allowed to warm slowly and stirred overnight. The solution was diluted with dichloromethane, washed with saturated aqueous $NaHCO_3$, and dried, and the solvent was removed *in vacuo*. The crude dimethyl sulfoxide was further purified by distillation.

The sulfoxides listed in Table 1 were purified by distillation or recrystallization and were found to be identical to authentic samples (mp/bp, IR, ^1H NMR, and GC-MS). The nitrogen oxide catalyzed autoxidations listed in Table 1 were performed in reagent grade solvents with the same results.

Measurement of the Oxygen Uptake. A solution of dibutyl sulfide (0.56 mL, 3.2 mmol) in dichloromethane (20 mL) was cooled to −10 °C in a salt/ice bath. The solution was saturated with oxygen, and the flask was sealed with a rubber septum. An O_2 filled gas buret was attached to the side arm, and a dichloromethane solution of NO_2 (1.0 mL, 0.2 mmol) was added with the aid of an all-glass syringe. The temperature of the solution was carefully controlled at −10 °C, and the uptake of oxygen was monitored. After 3 h, 33.5 mL (1.50 mmol) of oxygen was consumed, and the uptake of oxygen ceased. The reaction was worked up as described above, and dibutyl sulfoxide was isolated in quantitative yield (0.498 g, 3.07 mmol).

Spectral Characterization of the Precursor EDA Complex Formed from Thioether and Nitrogen Oxides. General Procedure (NO_2). A solution of NO_2 in dichloromethane (0.02 M) was cooled to −78 °C and (3 mL) transferred under a flow of argon into a quartz cuvette equipped with a Teflon stopcock. The cuvette was cooled in a dry ice/acetone bath and allowed to equilibrate for several minutes. The UV−vis absorption spectrum of the solution of NO_2 was recorded at −78 °C, and dibutyl sulfide (1.5 μL) was

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[76] Note that after the first cycle, NO^+ is effectively converted to NO_2 *via* eqs 34 and 35.

[77] (a) Janzen, E. G. *Chem. Eng. News* **1994**, *Mar. 14*, 4. (b) Butler, A. R.; Williams, D. L. H. *Chem. Soc. Rev.* **1993**, 233. (c) Feldman, P. L.; Griffith, O. W.; Stuehr, D. J. *Chem. Eng. News* **1993**, *Dec. 20*, 26. (d) Culotta, E.; Koshland, D. E., Jr. *Science* **1992**, *258*, 1862. (e) Stamler, J. S.; Loscalzo, J. *Science* **1992**, *258*, 1898.

[78] Gleiter, R.; Spanget-Larsen, J. *Top. Curr. Chem.* **1979**, *86*, 139.

added. After mixing thoroughly (while cold), the UV–vis absorption spectrum of the resultant bright yellow solution was recorded at −78 °C. The former spectrum was subtracted from the latter, and the difference was referred to as the *charge-transfer spectrum* with $\lambda_{max} = 400$ nm. [After recording the absorption spectra, the colored solution was rapidly transferred, with the aid of a Teflon cannula, into a vigorously stirred slurry of ether and saturated aqueous $NaHCO_3$. The organic layer was separated, dried, and analyzed by quantitative HPLC. After each measurement, the thioether was recovered quantitatively.] Typical concentrations to yield absorbances between 0.5 and 1 were [thioanisole] = 1.3×10^{-3} M, [NO_2] = 0.02 M; [phenyl sulfide] = 0.02 M, [NO_2] = 0.1 M.

Nitrosonium Cation. A Schlenk tube was charged with $NO^+BF_4^-$ (11.8 mg, 0.2 mmol) in the drybox. Dichloromethane (3 mL) was added, under a flow of argon, the heterogeneous mixture cooled to −78 °C, and the UV–vis absorption spectrum was recorded. Dibutyl sulfide (1 μL) was then added, and the slurry was stirred at −78 °C until a pale yellow colored solution formed. The UV–vis absorption spectrum was recorded at −78 °C. The difference spectrum was considered to be the *charge-transfer* absorption spectrum. In general, the aryl sulfides required higher concentrations to form highly colored solutions of the CT complexes in CH_2Cl_2 at −78 °C. The absorption maxima and the full width at half maximum of the *charge-transfer* bands with NO_2 and NO^+ are compared in Table 3.

Evaluation of the Formation Constants and Extinction Coefficients of Nitrosonium EDA Complexes with Thioethers. An excess of $NO^+BF_4^-$ (15 mg, 0.13 mmol) was added, under a flow of argon, to a dichloromethane solution of hexamethylbenzene (3.9 mg, 50 mL) in a Schlenk tube. The suspension was stirred for 30 min during which the solution rapidly became red brown. A 5 mL aliquot of this solution was transferred, under an argon atmosphere, to a 1-cm quartz cuvette fitted with a Teflon stopcock. Hexamethylbenzene (2.2 mg) dissolved to yield a total concentration of HMB = 2.9×10^{-3} M. The solution was cooled to −78 °C, and the UV–vis absorption spectrum was recorded. The concentration of [HMB, NO^+] was calculated to be 4.6×10^{-4} M (note that ϵ for [HMB, NO^+] is 3100 M^{-1} cm^{-1} at 336 nm). Increments of dibutyl sulfide were added to the solution at −78 °C, and the color changes were monitored by UV–vis spectroscopy. The characteristic spectrum of the [HMB, NO^+] complex with λ_{max} = 336 and 500 nm was gradually replaced by the charge-transfer (CT) band at λ_{max} = 400 nm assigned to the [Bu_2S, NO^+] complex. After the addition of 5 equiv of dibutyl sulfide, there was no further spectral change. Complete complexation of the nitrosonium cation to dibutyl sulfide was assumed, and the extinction coefficient was evaluated as $\epsilon = 4000 \pm 250$ M^{-1} cm^{-1}. Based on this value of the extinction coefficient, the concentrations of the respective nitrosonium EDA complexes with HMB and Bu_2S were extracted from the intermediate UV–vis absorption spectra by deconvolution. For example, the addition of Bu_2S (1.7×10^{-3} M) resulted in the following equilibrium concentrations: [HMB, NO^+] = 3.23×10^{-4} M; [Bu_2S, NO^+] = 1.37×10^{-4} M; [HMB] = 4.12×10^{-3} M; [Bu_2S] = 1.56×10^{-3}; thus the equilibrium constant for eq 6 was 1.1 ± 0.2, and the equilibrium constant for formation of the [R_2S, NO^+] complex in eq 4 was $K_5K_6 = 3.4 \times 10^4 \pm 600$ M^{-1}). The following extinction coefficients were estimated for the [R_2S, NO^+] complexes: [PhSEt, NO^+] = 4400 ± 250 M^{-1} cm^{-1}; [PhSMe, NO^+] = 4500 ± 250 M^{-1} cm^{-1}; [*p*-MeC_6H_4SMe, NO^+] > 2900 M^{-1} cm^{-1}. [In this experiment, there was a partial reaction to form the aryl sulfoxide and the value of 2900 was a lower limit.] The formation constant for [PhSEt, NO^+] in eq 4 was estimated to be $K_4 = K_5K_6 \sim 3 \times 10^3$ M^{-1}. In a second experiment, $NO^+BF_4^-$ (11.5 mg, 0.1 mmol) was added, under an argon atmosphere, to a cold (−78 °C), dilute solution of dibutyl sulfide (4.0×10^{-4} M) in dichloromethane. As the cold slurry was stirred, the solution took on a yellow color. After 30 min, the concentration of the [Bu_2S, NO^+]EDA complex was estimated by UV–vis spectral analysis at λ = 400 nm (assuming $\epsilon = 4000$ M^{-1} cm^{-1}) to be 4.1×10^{-4} M. This value confirms the high formation constant for the thioether EDA complex and the earlier estimate of the extinction coefficient. A 5 mL portion of the pale yellow solution of [Bu_2S, NO^+] complex was transferred at −78 °C to a quartz cuvette fitted with a Teflon stopcock. Dibutyl sulfide (1 μL) was added to the cold solution so that the total concentration of Bu_2S was 2.2×10^{-3} M. An excess of hexamethylbenzene (24 mg, 3×10^{-2} M) was added, and the crystals gradually dissolved in the cold solution. UV–vis absorption spectroscopy monitored the color changes from bright yellow to orange and finally red/brown. After there was no further spectral change, the concentration of the [HMB, NO^+]EDA complex was estimated to be 4.8×10^{-4} M (using ϵ = 3100 M^{-1} cm^{-1} at λ_{max} = 336) to indicate the quantitative complexation of the nitrosonium ion with HMB. Addition of 10 μL of Bu_2S to the final red/brown colored solution resulted in the regeneration of the yellow color. In a separate series of reactions, it was possible to transfer the nitrosonium cation between thioethers. Thus, the addition of PhSEt to 5 mL of the dilute (4×10^{-4} M) yellow solution of [Bu_2S, NO^+]BF_4^- resulted in the red solution (λ_{max} = 500 nm) characteristic of [PhSEt, NO^+]BF_4^-. A large excess of phenyl ethyl sulfide (100 μL, 0.1 M) was necessary to effect the complete disappearance of the absorption at 400 nm arising from [Bu_2S, NO^+]. At this point, complete nitrosonium transfer was assumed. The requirements of the large excess of phenyl ethyl sulfide provided a lower estimate for the formation of aryl sulfide EDA complexes as compared to alkyl sulfides. The addition of 10 μL of dibutyl sulfide to the final red solution resulted in the reformation of the yellow color.

Photochemical Oxidation of Thioethers with Nitrogen Dioxide *via* the Selective Activation of the EDA Complex. General Procedure. A solution of N_2O_4 (0.35 mmol) in dichloromethane (10 mL) was prepared under an argon atmosphere in a Schlenk tube fitted with a Teflon stopcock. The solution was cooled to −78 °C in dry ice/acetone bath, and dimethyl sulfide (20 μL, 0.203 mmol) was added to the cold colorless solution with the aid of a hypodermic syringe. The solution immediately became bright yellow. An identical cold yellow solution was prepared in a second Schlenk tube which was sealed with the aid of a Teflon stopcock and wrapped in aluminum foil to serve as the "dark" control. The two reaction tubes were then placed side-by-side in a transparent Dewar flask cooled to −78 °C with dry ice in acetone. The reaction tube was irradiated with a medium pressure 250-W Hg lamp fitted with an aqueous IR filter and a ESCO 410 nm cut-off filter. After 40 min, the bright yellow color was partially bleached (see Figure 4), and the photosylate was transferred with the aid of a cannula, under argon pressure, to a slurry of $NaHCO_3$ in ether containing thioanisole (15 μL) as internal standard for chromatographic analysis. Quantitative HPLC and GC-MS analyses indicated that the photosylate contained dimethyl sulfoxide (0.056 mmol) and dimethyl sulfide (0.148 mmol). Identical workup and analysis of the "dark" control indicated that the dimethyl sulfide was recovered intact. The other thioethers were irradiated at the concentrations indicated in Table 4. In all reactions the thioether was recovered quantitatively from the "dark" control solutions.

Reaction of Thianthrene Cation Radical with Various Nitrogen Oxides. Nitrogen Dioxide. Thianthrene cation radical tetrafluoroborate (114 mg, 0.38 mmol) was treated with one equiv of NO_2 in dichloromethane (75 mL) under an argon atmosphere at 25 °C. The deep purple color immediately bleached, concomitant with the formation of a white suspension. The suspension was allowed to separate, and the supernatant liquid was carefully removed with the aid of a Teflon cannula under argon pressure. The white solid was washed once with cold dichloromethane, dried *in vacuo*, weighed and transferred to the drybox. The IR spectrum in the region 4000–650 cm^{-1} was identical to that of an authentic sample of $NO^+BF_4^-$ with ν (NO^+) = 2341 cm^{-1} and ν (BF_4^-) = 1050 cm^{-1}:[48] Yield of $NO^+BF_4^-$ 39 mg (88%). The dichloromethane solutions were combined, washed with water, and dried. Removal of the solvent *in vacuo*, afforded crystalline thianthrene 5-oxide (120 mg, 98%). In a separate experiment, thianthrene cation radical tetrafluoroborate (133 mg, 0.44 mmol) and excess nitrogen dioxide (1.0 mmol) were mixed in dichloromethane at 25 °C under an argon atmosphere. The deep purple color of the solution bleached within a minute. It yielded a white suspension in a pale yellow solution together with a yellow/brown head gas. This mixture was stirred at 25 °C for an additional 2 h with no apparent change. After removal of the excess NO_2 *in vacuo*, nitrosonium tetrafluoroborate (36 mg, 71%) and thianthrene 5-oxide (97 mg, 95%) were isolated.

Nitrite. A dichloromethane solution of tetrabutylammonium nitrite (95 mg, 0.33 mmol) was added with the aid of a Teflon cannula to a deep purple solution of thianthrene cation radical tetrafluoroborate (92 mg, 0.31 mmol) in dichloromethane (50 mL). The color immediately bleached. UV–vis[43] and IR[12] spectral analysis (λ_{max} = 204, 214, 226 nm and ν_{NO} = 1876 cm^{-1}) of the head gases showed that nitric oxide was formed. The nitric oxide was removed *in vacuo*, and the dichloromethane solution washed with water (3 × 25 mL), dried, and evaporated *in vacuo*. The crude thianthrene 5-oxide was recrystallized from ethanol (70 mg, 97%).

Nitrate. A dichloromethane solution of PPN nitrate[19] (330 mg, 0.55 mmol, 10 mL) was added under an argon atmosphere to a deep purple solution of thianthrene cation radical tetrafluoroborate (166 mg, 0.55 mmol) in dichloromethane (90 mL) at 25 °C. The deep purple solution immediately bleached. The solution was stirred for a further 10 min, and the brown head gas was transferred to an evacuated gas phase IR cell (5-cm path length). The IR spectrum showed the characteristic stretching frequencies at 1629 and 1600 cm^{-1} of NO_2.[12] The NO_2 was removed *in vacuo*, and the dichloromethane solution was washed with water (3 × 25 mL) to yield thianthrene 5-oxide in quantitative yield. In a separate experiment, a dichloromethane solution of PPN nitrate (195 mg, 0.33 mmol, 10 mL) was added with the aid of a cannula into a vigorously stirred deep purple solution of thianthrene cation radical tetrafluoroborate (195 mg, 0.64 mmol) in dichloromethane (60 mL) under an argon atmosphere at 25 °C. The deep purple color immediately bleached, but the head gas remained colorless. The solution was stirred for a further 10 min, and the head gases transferred to an evacuated gas phase IR cell (5-cm path length). Neither NO nor NO_2 were observed in the IR spectrum. The solution was concentrated *in vacuo* to 25 mL and diluted with pentane (40 mL) to precipitate a white solid. The supernatant solution was removed with the aid of a cannula, and the solid was dried *in vacuo* and transferred to the drybox. IR analysis of the solid revealed the characteristic absorption band of nitrosonium[48] at ν = 2340 cm^{-1} in addition to the diagnostic IR bands of $PPN^+BF_4^-$. The solution was combined with the solid and diluted with dichloromethane (50 mL) washed with water (4 × 15 mL), and the solvent was evaporated *in vacuo*. Crystalline thianthrene 5-oxide was isolated in excellent yield (117 mg, 92%).

Acknowledgment. We thank S. M. Hubig for assistance with the time-resolved spectroscopic studies and the National Science Foundation, R. A. Welch Foundation, and the Texas Advanced Research Program for financial support.

Supplementary Material Available: The materials and instrumentation used, the stoichiometric oxidation of thioethers with nitrogen dioxide and the spectral characterization of the reaction profile are described in detail. The estimation of the degree of ionic disproportionation of nitrogen dioxide by thioethers, the relative intensities of the charge-transfer absorption bands of thioethers with NO_2, the isolation of thioether EDA complex with NO_2, and the quantum yields for the charge-transfer oxidations with NO_2 are described (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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