Reactivity of nitroso oxides: effect of polar substituents and reaction mechanism

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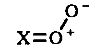
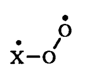
The structure and reactivity of nitroso oxide intermediates has been studied by trapping and tracer experiments in the photooxidation of substituted phenyl azides. *O*-Transfers with *p*-methoxyphenyl nitroso oxide were efficient and showed the reactivity order of PhN=O > Ph_2S > Ph_2SO > PhH. Sulfides and sulfoxides were oxidized electrophilically and the partial rate factor for the hydroxylation of benzenes afforded a negative *ρ*-value of −1.40 (σ^+). In the case of the *p*-nitrophenyl isomer, the radical reactivity was much more significant as exemplified in the hydrogen abstraction from toluene. Both isomers behave as electrophilic radicals as shown by the relative rates of hydrogen abstraction from aliphatic C–H bonds, *i.e.*, 1°:2°:3° = 1:7:50–60. An ^{18}O-tracer study revealed that the intramolecular cyclization of aryl nitroso oxides is competitive with intermolecular *O*-transfers.

The chemistry of XOO species is interesting because such structures are isoelectronic with ozone. One typical case is the structure and reactivity of carbonyl oxides (**1**; X = R_2C)[1] known as intermediates in the reaction of olefins with ozone. Carbonyl oxides behave as radicals and as electrophilic oxidants, but the most characteristic reaction is a nucleophilic *O*-transfer, which indicates the importance of the dipolar structure **1a**.[2] In the case of persulfoxides (**1**; X = R_2S)[3] and



1a



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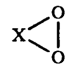

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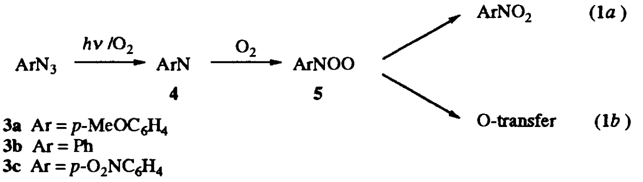
perepoxides (**1**; X = R_4C_2),[4] the dipolar structure **1a** is important, their characteristic reaction being nucleophilic *O*-transfer to sulfoxides. On the other hand, dioxiranes (**2**; X = R_2C) are produced from ketones and monoperoxysulfate and have been shown to react as an electrophilic *O*-transfer reagent.[5,6] Thus, contrasting reactivities have been noticed between carbonyl oxides and dioxiranes. Carbonyl oxides have been observed directly by laser flash photolysis[7] and low-temperature matrix techniques.[8] The conversion of **1** into **2** is known to proceed by photochemical activation[9] but not by thermal reaction.[10]

We became interested in the reactivity of nitroso oxides (**1**; X = RN) formed from nitrenes and oxygen. Involvement of nitroso oxide intermediates has been assumed, albeit with no evidence, in the photooxidation of aryl azides. An attempt to detect RNOO intermediates directly by laser flash technique was unsuccessful.[11] However, trapping experiments revealed that the nitroso oxide produced from phenyl nitrene and oxygen behaves as an electrophilic peroxyl radical.[12] Intermolecular *O*-transfers have been shown to occur competitively with intramolecular cyclization to yield nitrobenzene.[12b] However, the intervention of other active oxygen species could not be ruled out since arylnitrenes are known to undergo facile conversion into dehydroazepines, *etc.* This point could be clarified by examining the *p*-nitro substituted case since *p*-nitrophenylnitrene is known not to be converted into the seven-membered compound.[11] In this paper our study on the formation and reactivity of substituted nitroso oxides are summarized, and the significant effect of polar substituents demonstrated.

Results

Formation and trapping of substituted phenyl nitroso oxides

Irradiation of aryl azides (**3**) at > 350 nm in acetonitrile under oxygen afforded the corresponding nitrobenzenes in 20–30% yields. The results in Table 1 show that oxygen transfers occurred to the substrates added. Control experiments indicated these *O*-transfers were not observed on irradiation of ArN=O or $ArNO_2$ instead of ArN_3 under otherwise identical conditions. These results suggest that *O*-transfers proceed by way of active oxygen species produced from nitrenes and oxygen, *e.g.* aryl nitroso oxides **5**, according to eqn. (1).



3a Ar = *p*-$MeOC_6H_4$
3b Ar = Ph
3c Ar = *p*-$O_2NC_6H_4$

O-Transfers during the photooxidation of *p*-methoxyphenyl azide (**3a**) were effective; *e.g.*, *O*-transfer to Ph_2S and Ph_2SO occurred in 48 and 58% yields, respectively (runs 2 and 5 in Table 1). Trapping with benzene was ineffective (run 4) but *O*-transfer to nitrosobenzene was effective (run 3).

O-Transfers to sulfur compounds with phenyl (**3b**) and *p*-nitrophenyl azide (**3c**) were not as effective as the *p*-MeO case, as shown in runs 5–7. However, for **3c** *O*-transfer leading to the hydroxylation of benzene was quite effective (run 9). The 51% yield of nitrobenzene from **3c** and nitrosobenzene (run 8) indicates the predominant formation of an active *O*-transfer intermediate. The small amount of *p*-nitroazoxybenzene formed arises from the known reaction of arylnitrenes and nitrosobenzene.[11]

Relative reactivities

Trapping experiments show that the active oxygen species involved in the photooxidation of **3a–c** are of the same type but of somewhat different reactivity. Relative reactivities of various substrates were determined by competition experiments and are listed in Table 2. The reactivity order of substrates for the *p*-methoxy case (**3a**) are PhN=O > Ph_2S > Ph_2SO. The sulfides and sulfoxides must be oxidized electrophilically since the

Table 1 Products from the photooxidation of phenyl azides in the presence of additives, under oxygen[a]

Run No.	Ar in ArN_3	Additive	Product (%)[b] $ArNO_2$	Others
1	p-$MeOC_6H_4$	0.05 M Ph_2S	25	Ph_2SO (42)
2		0.05 M Ph_2SO	18	Ph_2SO_2 (58), Ph_2S (2)
3		0.01 M PhN=O	12	$PhNO_2$ (57)
4		50% PhH	22	PhOH (13)
5	Ph	0.05 M Ph_2SO	24	Ph_2SO_2 (10), Ph_2S (3)
6	p-$O_2NC_6H_4$	0.05 M Ph_2S	24	Ph_2SO (15)
7		0.05 M Ph_2SO	27	Ph_2SO (6), Ph_2S (6)
8		0.01 M PhN=O	8	$PhNO_2$ (51), azoxy (5)[c]
9		50% PhH	40	PhOH (34)

[a] Irradiation of 5 mmol dm^{-3} ArN_3 at > 350 nm in MeCN under oxygen for 4 h at *ca.* 20 °C. Conversions of $ArNO_2$ were > 80%. [b] Product yields are based on ArN_3 consumed. Minor products were the corresponding nitroso compounds, ArN=O, *ca.* 20% of the yields of $ArNO_2$. [c] Azoxybenzene, p-$O_2NC_6H_4N{=}N(O)C_6H_5$.

Table 2 Relative reactivity for *O*-transfer to sulfides, sulfoxides and nitrosobenzene[a]

Run No.	Ar in ArN_3	Substrates A/B	Product yields[b] (%/%)	Relative reactivity[c]
10	p-$MeOC_6H_4$	$(p\text{-}ClC_6H_4)_2S/Ph_2S$	10.6/42.5	0.25
11		$(p\text{-}ClC_6H_4)_2SO/Ph_2SO$	13.2/54.1	0.24
12		$(p\text{-}ClC_6H_4)_2S/Ph_2SO$	50.0/3.2	16
13		$PhN{=}O/Ph_2S$[b]	69.8/2.9[e]	24
14		p-Cl/p-$MeC_6H_4N{=}O$[f]	35.1/33.4[g]	1.1
15	p-$O_2NC_6H_4$	$(p\text{-}ClC_6H_4)_2S/Ph_2S$	4.2/17.1	0.25
16		$(p\text{-}ClC_6H_4)_2SO/Ph_2SO$	1.4/4.6	~0.30

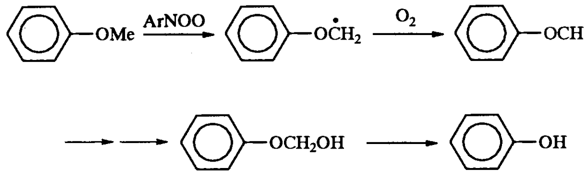
[a] Photooxidation of 5 mmol dm^{-3} ArN_3 at λ > 400 nm for 8 h in acetonitrile–dichloromethane (3:1) under oxygen; 50 mmol dm^{-3} of each substrate. [b] Product yields of sulfoxides and sulfones from the corresponding sulfides and sulfoxides, respectively. [c] Relative reactivities of A/B for the oxidation with substituted nitroso oxides. [d] Substrate concentration 10 mmol dm^{-3} each. [e] The yield of $PhNO_2/Ph_2SO$. [f] 5 mmol dm^{-3} Each of p-$ClC_6H_4N{=}O$ and p-$MeC_6H_4N{=}O$.

presence of an electron-attracting p-chloro substituent reduces the relative reactivity to 0.25 compared with unsubstituted substrate (runs 10–12). The substituent effect was the same for the case of **3c** (runs 15 and 16), that is, sulfides and sulfoxides are oxidized electrophilically by active oxygen species. Note also from Table 2 that no substituent effect for the oxidation of nitrosobenzenes was observed (*cf.* run 14).

Hydroxylation and hydrogen abstraction

Benzenes were oxidized to phenols. As listed in Table 3, the reactivity order of their hydroxylation with **3a** and oxygen was anisole > toluene > benzene > chlorobenzene. Anisole was oxidized most effectively and the hydroxylation occurred at the *o*- and p-positions (run 17). Partial rate factors were calculated, as listed in Table 3, from the relative rates and isomer distributions. A Hammett plot was obtained from the *m*- and p-factors to afford ρ-values of -1.81 (σ, $r = 0.878$) and -1.40 (σ^+, $r = 0.972$), r being the correlation coefficient. The correlation is much better with σ^+ constants, and the negative ρ value suggests the electrophilic hydroxylation of the aromatic nucleus. A similar result was obtained for the case of **3b** as reported previously.[12b] In contrast, hydroxylation with **3c** showed poor selectivity, *i.e.* the relative reactivities of the substituted benzenes were close to unity (runs 22–25). The low selectivity probably reflects the high reactivity of the p-nitrophenyl nitroso oxide.

Oxidation of side chains occurs competitively for the cases of anisole and toluene. For example, anisole also yielded phenol, arising from side-chain oxidation by the nitroso oxide intermediate according to eqn. (3). The ratios of side-chain oxidation to ring hydroxylation, phenol: methoxyphenols, were 0.25 and 1.0 for **3a** and **3c**, respectively (see the last column in Table 3). Side-chain oxidation increased for the nitro case. The same was true for the oxidation of toluene (*cf.* runs 18 and 23).



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In the intermolecular competition between ring hydroxylation and hydrogen abstraction, a similar trend was observed. The relative reactivities of cyclohexane and benzene of *ca.* 4 for **3a** and **3b** increased to 21 for the p-nitro case of **3c** (*cf.* runs 26–28). It is apparent that the electron-attracting group accelerates the hydrogen abstraction more effectively.

Hydroxylation of isopentane, which possesses primary, secondary and tertiary C–H bonds, is an interesting indicator of attacking radicals. The relative yields of alcohols were used to calculate the relative reactivity of the 1°:2°:3° hydrogens to be 1:8:50 and 1:8:60 for **3a** and **3c**, respectively (runs 29 and 30). The tertiary C–H is most reactive and the relative reactivities of 1°:2°:3° hydrogens are the same as those of the same hydrogens towards hydroxyl (*i.e.* 1:5:60)[†] and *tert*-butoxyl radicals (*i.e.* 1:12:44).[‡] Since the corresponding reactivity towards *tert*-butylperoxyl radical is 1:42:420, the reactivity of aryl nitroso oxides is rather close to the former oxyl radicals.

[†] The relative reactivity of $HO^\bullet$ radical was determined by irradiating hydrogen peroxide in acetonitrile containing 5% isopentane.[12b] Since the resulting value was practically constant with varying H_2O_2 concentrations from 0.01 to 0.15 mol dm^{-3}, the value was concluded to reflect the reactivity of $HO^\bullet$ rather than that of $HOO^\bullet$. The value is somewhat different from the earlier published results [*e.g.*, 1:5:10 (gas phase), W. A. Pryor, D. C. Fuller and J. P. Stanley, *J. Am. Chem. Soc.*, 1972, **94**, 1632]. A possible reason for the discrepancy may be the solvent effect of acetonitrile; *i.e.* its hydrogen bonding with hydroxyl radical makes the radical more selective.

[‡] For relative reactivities of C–H bonds towards radicals see, K. U. Ingold, *Free Radicals*, ed. J. K. Kochi, vol. 1, Wiley, New York, 1973, p. 74. Relative reactivities of 1°:2°:3° C–H bonds are 1:12:44, 1:40:420, and 1:50:2000 for $Bu^tO^\bullet$, $Bu^tOO^\bullet$ and $Br^\bullet$ radicals, respectively.

Table 3 Hydroxylation of substituted benzenes with nitroso oxide intermediates[a]

Run No.	Ar in ArN_3	Substrate[b]	Relative reactivity[c]	Phenol isomer[d] *o*/*m*/*p*	Partial rate factor[e] *o*/*m*/*p*	Side chain[f]/Ring
17	*p*-$MeOC_6H_4$	Anisole	4.5	64/ < 1/36	8.6/ < 0.2/9.7	0.25
18		Toluene	2.7	69/11/20	5.5/0.9/3.2	1.0
19		Benzene	1.0		1.0/1.0/1.0	
20		Chlorobenzene	0.63	58/22/20	1.1/0.4/0.8	
21	Ph	Anisole	6.0	66/ < 1/34	12/ < 0.2/12	0.25
22	*p*-$O_2NC_6H_4$	Anisole	1.2	72/12/16	1.4/0.23/0.61	1.0
23		Toluene	1.1	54/33/13	1.8/1.1/0.9	4.0
24		Benzene	1.0		1.0/1.0/1.0	
25		Chlorobenzene	0.43	57/22/21	0.7/0.3/0.5	

[a] For irradiation conditions see footnote *a* in Table 1. The corresponding nitrobenzenes, $ArNO_2$, were produced in 20–40% yields. [b] Substrates added as 25 vol% in MeCN. [c] Relative reactivity of substrate *vs.* benzene by competitive method. The values were obtained from the total yields (*i.e. ca.* 20% yield) as determined by GLC. [d] Isomer ratios of phenols obtained; means of two or three determinations (within ± 5%). Since the NIH shift was *ca.* 10%,[12b] its effect if any on the isomer distributions is within 5%. [e] Calculated from the relative reactivity and isomer distributions. [f] Relative rates of side chain attack and ring hydroxylation as determined from the corresponding product ratios. For the case of toluene the products from side-chain attack are benzyl alcohol and benzaldehyde (*ca.* 1 : 2), and ring products are cresols. For the case of anisole the side-chain product is phenol.

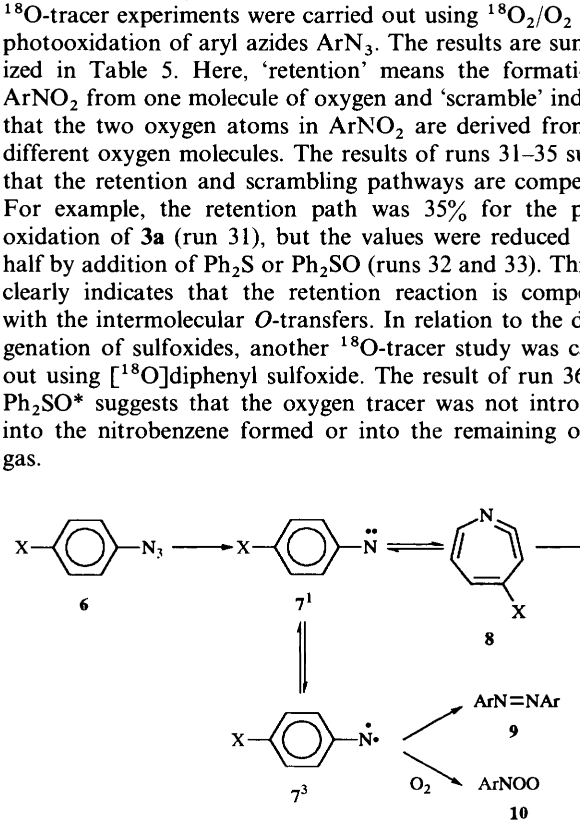
Table 4 Hydroxylation of cyclohexane and isopentane[a]

Run No.	Ar in ArN_3	Subtrate	Products (%)[b]	Relative reactivity
26	Ph	C_6H_{14}/C_6H_6[c]	Cyclohexanol (23),[d] PhOH (5.5)	4.1[e]
27	*p*-$MeOC_6H_4$	C_6H_{14}/C_6H_6	Cyclohexanol (11),[d] PhOH (3.0)	3.6[e]
28	*p*-$O_2NC_6H_4$	C_6H_{14}/C_6H_6	Cyclohexanol (30),[d] PhOH (1.4)	21[e]
29	*p*-$MeOC_6H_4$	5% Isopentane	Pentanols (1; 1°:2°:3° = 1:2:7)[f]	1:7.9:49[g]
30	*p*-$O_2NC_6H_4$	5% Isopentane	Pentanols (3.3; 1°:2°:3° = 1:1.5:5.8)[f]	1:7.7:59[g]

[a] Photooxidation of 5 mmol dm^{-3} ArN_3 at $\lambda > 400$ nm for 8 h in MeCN under oxygen. Conversion of ArN_3 was 80–95%, and yields of $ArNO_2$ were 20–40%. [b] Products were determined by GLC and are based on ArN_3 consumed. [c] Cyclohexane/benzene/acetonitrile (1 : 1 : 2). [d] Combined yields of cyclohexanol and cyclohexanone, the ratios being *ca.* 5 : 1. [e] Relative reactivity of cyclohexane and benzene for nitroso oxides. [f] Formation of the corresponding carbonyl compounds was negligible. [g] Relative reactivity of primary : secondary : tertiary C–H (per hydrogen) towards nitroso oxides. The values are the average of two determinations (differences to within ± 5%).

^{18}O-Tracer study

In order to clarify the formation of nitrobenzenes ($ArNO_2$), ^{18}O-tracer experiments were carried out using $^{18}O_2/O_2$ in the photooxidation of aryl azides ArN_3. The results are summarized in Table 5. Here, 'retention' means the formation of $ArNO_2$ from one molecule of oxygen and 'scramble' indicates that the two oxygen atoms in $ArNO_2$ are derived from two different oxygen molecules. The results of runs 31–35 suggest that the retention and scrambling pathways are competitive. For example, the retention path was 35% for the photooxidation of **3a** (run 31), but the values were reduced to *ca.* half by addition of Ph_2S or Ph_2SO (runs 32 and 33). This fact clearly indicates that the retention reaction is competitive with the intermolecular *O*-transfers. In relation to the deoxygenation of sulfoxides, another ^{18}O-tracer study was carried out using [^{18}O]diphenyl sulfoxide. The result of run 36 with Ph_2SO^* suggests that the oxygen tracer was not introduced into the nitrobenzene formed or into the remaining oxygen gas.



Scheme 1

Discussion

In the photolysis of phenyl azides (**6**) the facile conversion of phenyl nitrenes (**7**) is well known to yield dehydroazepine (**8**). Intermediates observable by laser-flash spectroscopy[13] or matrix isolation techniques[14] are only dehydroazepines for most phenyl azides. The interconversion between **7**^{3}, **7**^{1} and **8** as shown in Scheme 1 is known.[13] The conversion into **8** is slow for the case of *p*-nitrophenyl azide (**3c**) because of the strong electron-attracting group,[11] but the direct observation of reaction of the arylnitrene **7** with oxygen was unsuccessful.

The intervention of active oxygen species such as nitroso oxides (**10**) could be examined only by trapping experiments. Important features of the present trapping and tracer study are summarized below. (*i*) *O*-Transfers with **10c** (*p*-NO_2), which does not yield **8**, occurs similarly with **3a** and **3b**. The relative reactivity is in the order PhN=O > Ph_2S > Ph_2SO. (*ii*) Sulfides and sulfoxides are oxidized electrophilically by nitroso oxides. (*iii*) Benzene rings are hydroxylated electrophilically with the *p*-methoxyphenyl nitroso oxide **10a**; partial rate factors afford a negative ρ-value of -1.40 (σ^+). (*iv*) The reactivity order of aliphatic C–H bonds is 1°:2°:3° = 1:7:50–60, which is similar to their behaviour towards the hydroxyl radical. (*v*) An ^{18}O-tracer study revealed that the retention and scrambling pathways are competitive pathways for the formation of nitrobenzenes.

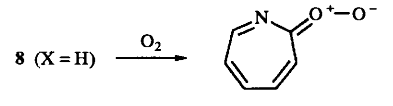
Electrophilic active oxygen species

Possible active oxygen species in the photooxidation of aryl azides are nitroso oxides (**10**) or oxygen adducts of dehydroazepine (**8**) such as **11** [eqn. (4)]. If carbonyl oxides such as **11** are intermediates, nucleophilic *O*-transfers to sulfoxides would, contrary to observation, be operative.

Table 5 ^{18}O-Tracer study on the formation of nitrobenzenes from the photooxidation of phenyl azides under oxygen[a]

Run No.	Ar in ArN_3	Additive (%)	Conversion (%)	Yield of $ArNO_2$[b]	Mass data of $ArNO_2$[c] M/(M + 2)/(M + 4)	Reten.: scram.[d]
Calc.						
	Retention				100/0.6/8.4	100:0
	Scrambling				100/16.8/0.7	0:100
Obs.						
31	p-$MeOC_6H_4$	0.05 M Ph_2S	85	14	100/10.8/3.3	35:65
32		0.05 M Ph_2SO	94	25[e]	> 100/55.7/7.5	16:84
33			>95	13[f]	> 100/66.9/7.9	13:87
34	Ph		41	28	100/10.7/4.0	41:59
35	p-$O_2NC_6H_4$	0.05 M Ph_2SO	90	30	100/14.0/2.1	19:81
36	Ph		>95	15	100/0.2/0.0[g]	[h]

[a] Irradiation of 5 mmol dm^{-3} ArN_3 at $\lambda > 350$ nm in MeCN under oxygen ($^{32}O_2$: $^{34}O_2$: $^{36}O_2$ = 100 : 0.6 : 8.4) for 4 h at *ca.* 20 °C. [b] Product yields are based on ArN_3 consumed. [c] Mass spectral data on $ArNO_2$; M = 153, 123 and 168 for A = p-$MeOC_6H_4$, Ph and p-$O_2NC_6H_4$ respectively. The data are means of three determinations (to within ± 0.7%). [d] Retention means the formation of $ArNO_2$ from one molecule of oxygen. Scrambling means that the two oxygen atoms in $ArNO_2$ are derived from two different oxygen molecules. [e] See run 1 for other products. [f] See run 2 for other products. [g] Reaction in the presence of $Ph_2S^{18}O$ (97.8% ^{18}O) under natural O_2 gas. ^{18}O did not occur in the $PhNO_2$ produced. [h] Scrambled oxygen ^{18}O–O was not detected in the remaining oxygen gas.



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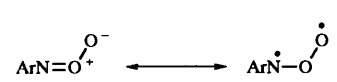
Moreover, similarly electrophilic active species resulted from the p-nitro case **3c** which does not yield **8**. The major product in the absence of oxygen is azobenzenes in 30–50% yields, indicating the presence of **7**.[3] These facts clearly suggest the intervention of nitoroso oxides **10** as shown in Scheme 1.

Nitroso oxides can be considered as electrophilic radicals since aliphatic C–H bonds are oxidized just as they are by hydroxyl radicals, which are known to be electrophilic. Sulfides and sulfoxides are likewise oxidized electrophilically. Thus, the diradical nature (**12b**) is more important than dipolar structure (**12a**).

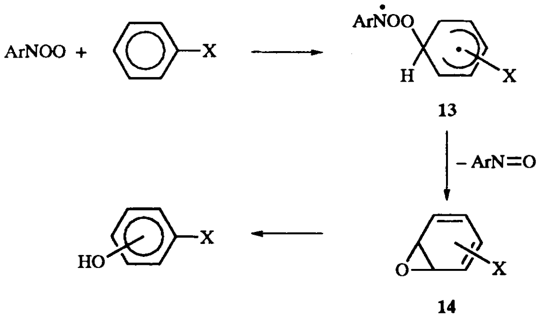


12b **12b**

The relative reactivity of the substrates was $Ph_2S \gg Ph_2SO$, in contrast with the case of carbonyl oxides,[2] even for the p-methoxy case (**3b**) where the dipolar structure **12a** would appear to be stabilized. The reactivity order PhN=O $\gg$ $Ph_2S > Ph_2SO$ with nitroso oxides is the same as with ozone, which lends further support to the electrophilic radical nature of the former. The order is different from that of peroxy acid oxidation, *i.e.*, $Ph_2S \gg$ PhN=O $> Ph_2SO$.[15] It is noteworthy that the reactivity of ArNOO is just like that of ozone.

Substituted benzenes were hydroxylated electrophilically by the p-methoxyphenyl nitroso oxide **10a** as exemplified by the negative ρ-value of -1.40 (σ^+). The correlation with σ^+ constants indicates the importance of electron-donating resonance in stabilizing the cyclohexadienyl radical intermediate **13**, the adduct of benzenes and nitroso oxides [eqn. (5)]. The conversion of **13** into arene oxides (**14**) is presumed to be quite facile because of the formation of stable non-radicals from diradicals. Intervention of arene oxides is demonstrated by the NIH shift accompanying hydroxylation with nitroso oxides.[12b] The reported shift values of 12–13% are significant since the NIH shifts are known to be reduced in the presence of oxygen.[16]

Note should be made here of the reactivity of the p-nitrophenyl nitoroso oxide **10c**. Although the selectivity of 1°:2°:3° = 50:7:1 for the oxidation of aliphatic C–H bonds was similar to that for the p-methoxy (**10a**) or unsubstituted nitroso oxide **10b**, yields for the oxidation of sulfur compounds were lower and no selectivity was observed for the hydroxylation of benzenes. These facts suggest lower selectivity for the p-nitro derivative, reflecting its high reactivity and hence shorter lifetime. A likely reaction of **10c** is the oxidation of solvent acetonitrile.



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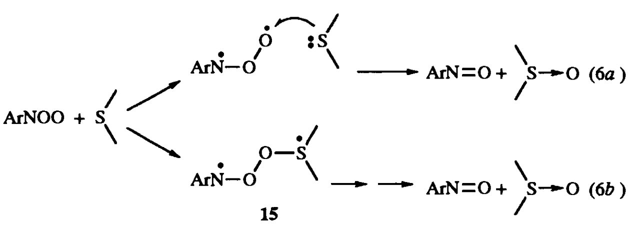
(5)

Reactions with sulfides and sulfoxides

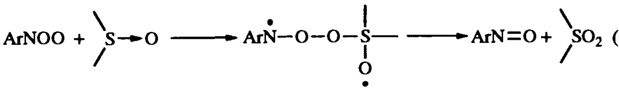
Electrophilic *O*-transfers to sulfur compounds occur with a relative rate $Ph_2S \gg Ph_2SO$ and the substituent effect is H > p-Cl. This selectivity suggests the importance of the diradical structure **12b**, rather than dipolar **12a**; the electrophilic nature is well represented theoretically by the 1,3-diradical structure.[17]

Oxidation of sulfides may take place by one-step [eqn. (6*a*)] and two-step mechanisms. The latter is likely since additions of radicals to sulfides to form sulfanyl radicals are known[18] and nitroso oxides are unstable intermediates of shorter lifetime. The O–O cleavage to yield sulfoxides [eqn. (6*b*)] is probably fast because of the formation of non-radicals from diradicals, *i.e.*, a double β-scission of the 1,4-diradical **15**. A similar adduct of sulfides with ozone have been assumed in the ozone oxidation.[19]



15

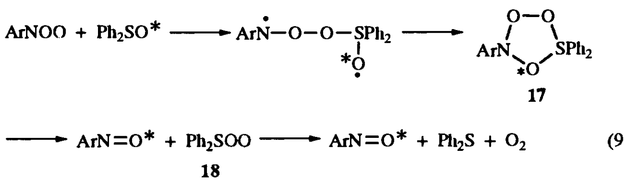
Sulfoxides was likewise oxidized electrophilically. This is in contrast with the nucleophilic oxidation with carbonyl oxides[2] and persulfoxides,[3] where the dipolar structure **1a** is important. The electrophilic oxidation with nitroso oxides indicates the importance of diradical structure and suggests *O*-transfers *via* the sulfanyl radical (**16**) as an adduct of ArNOO and trivalent sulfur [eqn. (7)]. As a related reaction, addition of hydroxyl radical to sulfoxides is known.[20] The O–O cleavage of **16** is facile, again because of the double β-scission of the diradical to yield non-radicals. The reactivity order $Ph_2S \gg Ph_2SO$ and the substituent effect H > *p*-Cl are due to the electrophilic nature of the ArNOO radical.



16 (7)

The deoxygenation of sulfoxides in the photooxidation of aryl azides (*cf.* runs 2, 5 and 7 in Table 1) is, although a minor reaction, interesting. Several modes of sulfoxide deoxygenation, exist [eqns. (8)–(10)].

$$ArN + Ph_2SO \longrightarrow ArN{-}O{-}SPh_2 \longrightarrow PhN{=}O + Ph_2S \qquad (8)$$



17

18

(9)

$$ArNOO + Ph_2SO^* \longrightarrow ArN{-}O{-}O{-}O^*{-}SPh_2$$

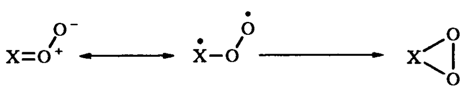
$$\longrightarrow ArN{=}O + Ph_2S{-}O^*{-}O \longrightarrow ArN{=}O + Ph_2S + {}^*O{-}O \qquad (10)$$

In order to determine the mechanism ^{18}O-tracer experiments were carried out using Ph_2SO^* (run 36 in Table 5). The deoxygenation by nitrenes [eqn. (8)] is likely in analogy to the reaction of carbenes.[21] However the major product was azobenzene and deoxygenation of sulfoxide was not observed in control experiments under argon, which eliminates pathway (8).

The pathway according to eqn. (9) is analogous to deoxygenation by carbonyl oxides containing strongly electron-attracting groups.[22] The deoxygenation of sulfoxides *via* the cyclic peroxide **17** depicted in eqn. (9) is not always unreasonable since the departure of oxygen from persulfoxides (*e.g.* **18**) is known.[23] However, an ^{18}O-tracer study revealed that the labelled oxygen atom was not introduced into nitrosobenzene and hence nitrobenzene,§ which rules out deoxygenation according to eqn. (9). The third possibility is eqn. (10), involving addition of the nitroso oxide to a sulfoxide oxygen. Scrambled oxygen gas, O–O*, could not be detected by GC–MS analysis of the remaining gas. Thus, no conclusion could be reached from the tracer study and the deoxygenation mechanism is deduced to be more complex.

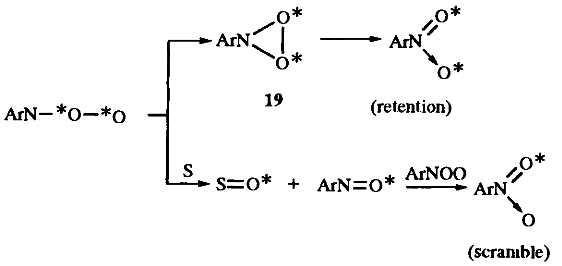
Diradical nature and cyclization

The conversion of carbonyl oxides (**1**; $X = R_2C$) into more stable dioxiranes is known not to occur thermally owing to the energy barrier of 20–30 kcal mol^{-1} for the cyclization.[1,6] On the other hand, the cyclic form of ozone (X = O) is calculated to be more unstable by 30–40 kcal mol^{-1} than the open bent structure.[24] Similar theoretical predictions have been reported for the case of nitroso oxides (X = HN).[25] An interesting point here is that the ratio of the diradical **1b** and the zwitterionic structure **1a** increases in the order H_2COO < HNOO < OOO.[26,27] When electron-attracting groups are introduced into the carbonyl oxide, its diradical nature increases.[27] Trapping experiments have characterized aryl nitroso oxides as electrophilic radicals, which is well explained by the theoretical prediction as mentioned above. That is, the diradical nature increases with the increase in electronegativity of X.



1a **1b** **2** (11)

The intramolecular cyclization of nitroso oxides was examined by using $^{18}O_2$–O_2. Since nitroso oxides oxidize nitrosobenzene to nitrobenzene efficiently, two pathways could be operative for the formation of nitrobenzenes. The doubly labelled oxygen atoms are introduced into one molecule of $ArNO_2$ according to the retention pathway [eqn. (12*a*)] or into two molecules by the scrambling pathway [eqn. (12*b*)]; S denotes substrate.



19

(retention)

(scramble)

(12*a*)

(12*b*)

As shown in Table 5, the retention of 37% (run 31) was reduced to less than half by addition of Ph_2S or Ph_2SO. This fact clearly indicates that cyclization to form the dioxaziridine **19** [eqn. (12*a*)] is competitive with intermolecular *O*-transfer [eqn. (12*b*)]. Thus, the cyclization of aryl nitroso oxides is shown to proceed competitively. Recent SCF and MRD-CI calculations on HNOO predicts that the cyclic structure **2** (X = HN) is only 4 kcal mol^{-1} less stable than the open radical form **1** and the activation energy for the conversion of **1** into **2** is as high as 45 kcal mol^{-1}.[28] However, ^{18}O-tracer experiments have proved the cyclization of nitroso oxides. The increased importance of diradical structure **1b** will lower the energy barrier for the cyclization of **1** to **2** because of the decreased double-bond nature of the X–O bond. Finally, we anticipate that dioxaziridines **19** are of short lifetime and will be readily converted into the corresponding nitrobenzenes. This conversion is calculated to be exothermic by 66 kcal mol^{-1}.

In conclusion, aryl nitroso oxides are produced efficiently from the photooxidation of aryl azides (**3a**,**c**) and transfer the oxygen atom as an electrophilic radical. The electrophilic nature is reflected in the oxidation of aliphatic C–H bonds and the hydroxylation of aromatic rings. *O*-Transfers to sulfides and sulfoxides are efficient with the *p*-methoxyphenyl nitroso oxide but inefficient with the *p*-nitrophenyl nitroso oxide because of its shorter lifetime.

Experimental

GC–MS spectra were recorded on JEOL D300 and Shimadzu QP-5000 mass spectrometers and NMR spectra were obtained with a Varian Gemini 200. GLC analyses were carried out with a Yanagimoto G180 gas chromatograph with 1 m or 2 m columns: PEG 20M, 20% on Chromosorb WAW; Carbowax,

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§ A control experiment for run 36 indicated that 70% of nitrobenzene was produced *via* the scrambling pathway. Thus, the major part of nitrobenzene was produced by further oxidation of the nitrosobenzene first formed.

2% on Chromosorb WAW; Gaskuropack 54; KG02 on Unipot HP. GPC purification was performed with a JAI LC908.

Materials

Phenyl azide was prepared and purified by distillation.[29] *p*-Methoxyphenyl azide was prepared[30] and recrystallized from ethanol, mp 34.1–34.8 °C (lit.,[30] 34–36 °C). *p*-Nitrophenyl azide was prepared[30] and crystallized from 50% methanol, mp 70.9–72.0 °C (lit.,[30] 71–72 °C). $^{18}O_2$ (99% pure) gas from CFA was diluted with natural O_2 gas. Other reagents were from commercial sources.

Typical procedure of the photooxidation

A 3 cm^3 acetonitrile solution of 5 mmol dm^{-3} aryl azide in a 20 cm^3 Pyrex test tube was purged with oxygen gas and irradiated with a 300 W medium-pressure Hg lamp through a 5% $NaNO_3$ filter solution (*i.e.*, > 350 nm) for 4 h at *ca.* 20 °C. Products were analysed by GLC and identified by GC–MS by comparison with authentic samples; PEG 20M and KG02 columns were used at 80–250 °C.

Relative reactivities of substrates during the photooxidation of aryl azides were determined competitively by adding excess amounts of two substrates. Relative reactivities were calculated from the relative yields and the results are listed in Tables 2, 3 and 4.

Hydroxylation of C–H bonds was carried out as noted previously.[12b]

^{18}O-Tracer study

A 1 cm^3 solution of 5 mmol dm^{-3} ArN_3 in MeCN was placed in a 2 cm^3 Pyrex test tube with a rubber septum cap. The solution was purged with argon, after which oxygen gas, $^{18}O_2:^{34}O_2:^{36}O_2 = 100.0:0.6:8.4$, was introduced through a syringe by exhausting the argon gas. Irradiation and product analyses were carried out as described above. The ^{18}O content in $ArNO_2$ was determined by GC–MS, and the results are listed in Table 5.

[^{18}O]Diphenyl sulfoxide was prepared by the 9,10-dicyanoanthracene-sensitized photooxidation of phenyl sulfides. In a 20 cm^3 tube were placed 10 cm^3 of 0.4 mmol dm^{-3} dicyanoanthracene in MeCN and 0.4 cm^3 Ph_2S. After cooling and evacuation of the reaction tube, $^{18}O_2$ gas (99% pure) was introduced and irradiated at λ > 350 nm for 65 h. The product sulfoxide was separated by passage through a silica gel column and purified by GPC (eluent, chloroform). The yield of purified [^{18}O]diphenyl sulfoxide was 74 mg and the ^{18}O-content was determined by GC–MS to be 97.8%.

The ^{18}O-tracer study using Ph_2SO^* was carried out as described above. The oxygen gas in solution after the irradiation was analysed conveniently by GC–MS by injecting the solution directly. The results are listed in run 36 in Table 5.

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References

1 (*a*) J. C. Mitchell, *Chem. Soc. Rev.*, 1985, **14**, 399; (*b*) R. L. Kuczkowski, *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, vol. 2, Wiley, New York, 1984, p. 197; (*c*) W. W. Sander, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 344; (*d*) W. H. Bunnelle, *Chem. Rev.*, 1991, **91**, 335.

2 Y. Sawaki, H. Kato and Y. Ogata, *J. Am. Chem. Soc.*, 1981, **103**, 3832.

3 Y. Sawaki and Y. Ogata, *J. Am. Chem. Soc.*, 1981, **103**, 5947.

4 A. P. Schaap, S. G. Rechter, G. R. Faler and S. R. Villasenor, *J. Am. Chem. Soc.*, 1983, **105**, 1691.

5 (*a*) J. O. Edwards, R. H. Pater, R. Curci and F. D. Furia, *Photochem. Photobiol.*, 1979, **30**, 63; (*b*) A. R. Gallopo and J. O. Edwards, *J. Org. Chem.*, 1981, **46**, 1684; (*c*) R. W. Murray and R. Jeyaraman, *J. Org. Chem.*, 1985, **50**, 2847; (*d*) F. Minisci, L. Zhao, F. Fontana and A. Bravo, *Tetrahedron Lett.*, 1995, **36**, 1697.

6 (*a*) W. Adam, R. Curci and J. O. Edwards, *Acc. Chem. Res.*, 1989, **22**, 205; (*b*) R. W. Murray, *Chem. Rev.*, 1989, **81**, 1187.

7 (*a*) T. Sugawara, H. Iwamura, H. Hayashi, A. Sekiguchi, W. Ando and M. T. H. Liu, *Chem. Lett.*, 1983, 1261; (*b*) H. L. Casal, S. E. Sugamori and J. C. Scaiano, *J. Am. Chem. Soc.*, 1984, **106**, 7623; (*c*) J. C. Scaiano, W. G. McGimpsey and H. L. Casal, *J. Org. Chem.*, 1989, **54**, 1612.

8 (*a*) G. A. Bell and I. R. Dunkin, *J. Chem. Soc., Chem. Commun.*, 1983, 1213; (*b*) I. R. Dunkin and G. A. Bell, *Tetrahedron*, 1985, **41**, 339; (*c*) W. W. Sander, *J. Org. Chem.*, 1989, **54**, 333.

9 (*a*) O. L. Chapman and T. C. Hess. *J. Am. Chem. Soc.*, 1984, **106**, 1842; (*b*) W. W. Sander, *Angew. Chem., Int. Ed. Engl.*, 1985, **25**, 988; (*c*) W. W. Sander, *J. Org. Chem.*, 1988, **53**, 121.

10 K. Ishiguro, Y. Hirano and Y. Sawaki, *J. Org. Chem.*, 1988, **53**, 5397.

11 T.-Y. Liang and G. B. Schuster, *J. Am. Chem. Soc.*, 1987, **109**, 7803.

12 (*a*) Y. Sawaki, S. Ishikawa and H. Iwamura, *J. Am. Chem. Soc.*, 1987, **109**, 584; (*b*) S. Ishikawa, S. Tsuji and Y. Sawaki, *J. Am. Chem. Soc.*, 1991, **113**, 4282.

13 (*a*) A. K. Schrock and G. B. Schuster, *J. Am. Chem. Soc.*, 1984, **106**, 5228; (*b*) E. Leyva, M. S. Platz, G. Persy and J. Wirz, *J. Am. Chem. Soc.*, 1986, **108**, 3783.

14 (*a*) O. L. Chapman and J.-P. LeRoux, *J. Am. Chem. Soc.*, 1978, **100**, 282; (*b*) I. R. Dunkin and P. C. P. Thompson, *J. Chem. Soc., Chem. Commun.*, 1982, 1192.

15 S. Ishikawa and Y. Sawaki, unpublished results.

16 T. Kurata, W. Watanabe, M. Kato and Y. Y. Sawaki, *J. Am. Chem. Soc.*, 1988, **110**, 7472.

17 K. Yamaguchi, K. Takada, Y. Otsuji and K. Mizuno, *Organic Peroxides*, ed. W. Ando, Wiley, Chichester, 1992, p. 21.

18 E. Block, *Reaction of Organosulfur Compounds*, Academic Press, New York, 1978, p. 214.

19 P. S. Bailey, *Ozonation in Organic Chemistry*, vol. 2, 1982, p. 207.

20 Ref. 18, p. 195.

21 W. Kirmse, *Carbene Chemistry*, 2nd edn., Academic Press, New York, 1971, p. 437.

22 K. Ishiguro, Y. Hirano and Y. Sawaki, *Tetrahedron Lett.*, 1984, **25**, 1487.

23 (*a*) C.-L. Gu and C. S. Foote, *J. Am. Chem. Soc.*, 1982, **104**, 6060; (*b*) Y. Watanabe, N. Kuriki, K. Ishiguro and Y. Sawaki, *J. Am. Chem. Soc.*, 1991, **113**, 2677.

24 D. Cremer, *The Chemistry of Peroxides*, ed. S. Patai, Interscience, New York, 1983, p. 24.

25 K. N. Houk and K. Yamaguchi, *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, vol. 2, Wiley, New York, 1984, p. 407.

26 P. C. Hiberty and C. Leforestier, *J. Am. Chem. Soc.*, 1978, **100**, 2012.

27 Ref. 17, p. 24.

28 T. Fueno, K. Yokoyama and S. Takane, *Theor. Chim. Acta*, 1992, **82**, 299.

29 R. O. Lindsay and G. F. Allen, *Org. Synth., Coll. Vol. III*, Wiley, New York, 1955, p. 710.

30 P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, 1951, **73**, 2438.

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