

Figure 1. Arrhenius plot for the rearrangements $1 \rightarrow 2$ and $6\text{-Br-1} \rightarrow 6\text{-Br-2}$ in polyethylene. Rate constants were obtained from the disappearance of the UV (●), IR (■), or ESR (▼) signals of the reactant and from the appearance of the UV (○) or IR (□) peaks of the product.

Table I. Relative Rates of Hydrogen Tunneling^a

matrix	PE ^b	Ar	Kr	Xe
$1 \rightarrow 2$	1.0	2.3	6.3	23
$6\text{-Br-1} \rightarrow 6\text{-Br-2}$	6.2			23

^a At 10 K. ^b Polyethylene.

an external heavy-atom effect on the tunneling rate for a ground state process has not been observed before, but such effects are well known⁹ to enhance the rate of intersystem crossing from an excited triplet state T_1 to the singlet ground state S_0 . There is no fundamental difference between the present slow temperature-independent spin-forbidden chemical reaction from the electronic ground state of **1** to the electronic ground state of **2** and the much faster radiationless photophysical conversion of an electronically excited triplet molecule to its singlet ground state. Only the change in the equilibrium geometries between the initial and the final states is much larger in our case, leading to a highly unfavorable Franck-Condon factor.

An internal heavy-atom effect on the hydrogen-shift reaction was also observed (Figure 1). 6-Bromo-1,3-perinaphthadiyl (**6-Br-1**) rearranged to 6-bromophenylene (**6-Br-2**)¹⁰ with $E_a = 5.5 \pm 0.5$ kcal/mol and $A = 10^{6.2 \pm 0.5} \text{ s}^{-1}$ above ~ 120 K and with a temperature-independent rate of $k = 10^{-5.4 \pm 0.5} \text{ s}^{-1}$ below ~ 100 K. For **6-Br-1-2-*d*₂**, the temperature-independent rate constant was $k = 10^{-8.5 \pm 0.5} \text{ s}^{-1}$, again an isotopic effect of 1300. The bromine substituent thus has no effect on E_a and on the kinetic isotope effect within experimental error. Its chief effect clearly is to increase the spin-orbit coupling matrix element, whose square enters the theoretical expressions both for the tunneling and for the transmission coefficient in the Eyring equation. The comparable increase of the log A value for the temperature-independent and the thermally activated segments in the Arrhenius plot in Figure 1 is thus understandable.

We believe that the observation of external and internal heavy-atom effects on the temperature-independent rate of tunneling from **1** to **2** provides conclusive evidence for its spin-forbidden nature and an illustration of the absence of a fundamental

(8) The rate remained constant over the temperature ranges investigated (Ar, 10–30 K; Kr, 10–50 K; Xe, 10–60 K), chosen so as to assure adequate matrix rigidity.

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(10) The identification of the product as the 6-bromo as opposed to the 7-bromo derivative of **2** is based on the aliphatic and vinylic C–D stretching frequencies in the matrix IR spectra of the products obtained from **6-Br-1-*d*₁** and **6-Br-1-3-*d*₁**, respectively.

distinction between the temperature-independent “photophysical” process of intersystem crossing from an excited triplet to a ground singlet electronic state of a molecule and the “chemical” process of bond and atom rearrangement in a reaction of a ground state triplet molecule to the singlet ground state of its isomer. The distinction is merely an artifact of the Born-Oppenheimer approximation.

A minute fraction of the spontaneous $1 \rightarrow 2$ process undoubtedly occurs as a competing radiative decay (spin and Franck-Condon forbidden long-wavelength phosphorescence), but has not been detected.

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Reactivity of Nitroso Oxides. Oxygen Transfer As an Electrophilic Peroxy Radical

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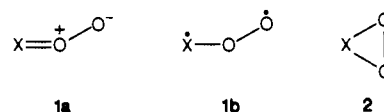
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Structure and reactivity of nitrenes formed by azide photolysis have been thoroughly studied by means of product analysis,¹ matrix techniques,² and laser flash spectroscopy.³ Arylnitrenes react with oxygen to yield nitroarenes⁴ and the chain decomposition of azides is inhibited by oxygen.⁵ Although an ESR study in low-temperature matrices revealed some structural features of intermediate nitroso oxides,⁶ little is known on their reactivity. In relation to the chemistry of carbonyl oxides (**1**, $X = R_2C$),⁷ we became interested in the reactivity of nitroso oxides (**1**, $X = RN$). In this paper we would like to report a trapping and tracer study showing that nitroso oxides behave as an electrophilic peroxy radical and isomerize unimolecularly to nitro compounds. This feature best described by structure **1b** is in sharp contrast with that of carbonyl oxides usually represented by dipolar structure **1a**.



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Table I. Substituent Effects on Oxygen Atom Transfers by Peroxy Species

peroxy species	substrate ^a	solvent	ρ -value ^b	Ph ₂ S/ Ph ₂ SO ^c	ref	peroxy species	substrate ^a	solvent	ρ -value ^b	Ph ₂ S/ Ph ₂ SO ^c	ref
PhCO ₃ ⁻	Ar ₂ SO	dioxane (aq)	+0.71	0	d	R ₂ S=O ⁺ -O ⁻	Ar ₂ SO	PhH	+0.25	0.13	10
PhCO ₃ H	Ar ₂ SO	PhH	-1.06	86	7a	perepoxide ^f	ArSOMe	PhH	+0.52	0.04	11
R ₂ C=O ⁺ -O ^{-e}	Ar ₂ SO	PhH	+0.26	0.06	7a	PhNOO	Ar ₂ SO	MeCN	-0.64	5.7	this work
						PhNOO	Ar ₂ S	MeCN	-0.98		this work

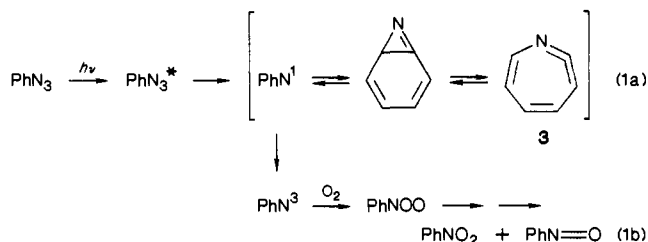
^aAr = X-C₆H₆. ^bHammett's ρ -value vs. σ . ^cRelative reactivity by competitive trapping. ^dCurci, R.; Modena, G. *Gazz. Chim. Ital.* **1964**, *94*, 1257. ^eFluorenone oxide. ^fA perepoxide from adamantylideneadamantane and ¹O₂.

Table II. ¹⁸O-Tracer Study on the Photooxidation of Phenyl Azide^a

run additive	products, %		mass data of PhNO ₂ ^b			formation of PhNO ₂	
	PhNO ₂	ArNO ₂	M	M + 2	M + 4	retention, %	scramble, % ^c
obsd							
1.	24		100	11.1	3.7	37	63
2. ArN=O ^d	<1	27	100	4.2	6.9	78	22
calcd							
retention			100	0.6	8.4	100	0
scramble			100	16.8	0.7	0	100

^aIrradiation (>350 nm) of 5 mM PhN₃ in MeCN under oxygen (³²O₂:³⁴O₂:³⁶O₂ = 100:0.6:8.4). ^bMass spectral data of PhNO₂, M = 123. ^cScramble means the two oxygen atoms in PhNO₂ are derived from two different oxygen molecules. ^d10 mM *p*-ClC₆H₄N=O.

While nitroso oxides are often written as an intermediate in the photooxidation of aryl azides,^{1,4} a recent laser flash study failed to detect their presence³ probably because of the predominant formation of dehydroazepine **3**. When 1–15 mM phenyl azide



in acetonitrile was irradiated at ≥ 350 nm⁸ under oxygen, nitrobenzene was obtained in 20–50% yields together with 3–5% of nitrosobenzene. Photooxidations using singlet oxygen sensitizers indicated that single oxygen is, as noted previously,^{4b} not involved in the reaction. Phenol was produced in 15% yield when 10% benzene was added as a cosolvent. Diphenyl sulfides and sulfoxides added were oxidized to diphenyl sulfoxides and sulfones, respectively; the yields were in the range 5–50% depending on concentrations and substituents. Control experiments showed that these oxidized products were not formed by the irradiation of nitro- or nitrosobenzene and nitrobenzene was not produced from nitrosobenzene alone. In the absence of oxygen, azobenzene, a dimeric product of triplet nitrene,⁹ was obtained. These facts suggest that phenyl nitrene and oxygen surely yield an oxygen-transfer agent, i.e., nitroso oxide as shown in eq 1b.

Relative reactivities of (X-C₆H₄)₂SO were 1.8, 1.3, 1.0, and 0.40 for *p*-MeO, *p*-Me, H, and *p*-Cl substituents, respectively. The relative rates for diphenyl sulfides were 1.4, 1.0, and 0.24 with *p*-Me, H, and *p*-Cl groups, respectively. The resulting Hammett's ρ -values vs. σ are -0.64 ($r = 0.984$) and ca. -0.98 for diphenyl sulfoxides and sulfides, respectively (Table I). The negative ρ -values and the reactivity order of Ph₂S > Ph₂SO indicate an electrophilic O-transfer from nitroso oxide intermediates. This is in sharp contrast to the nucleophilic O-transfers from carbonyl oxides,^{7,10} persulfoxides (1, X = R₂S),¹¹ and perepoxides (1, X = olefin).¹² The hydroxylation of benzene and cyclohexane in 15–20% yields indicates that nitroso oxides react as a free radical.

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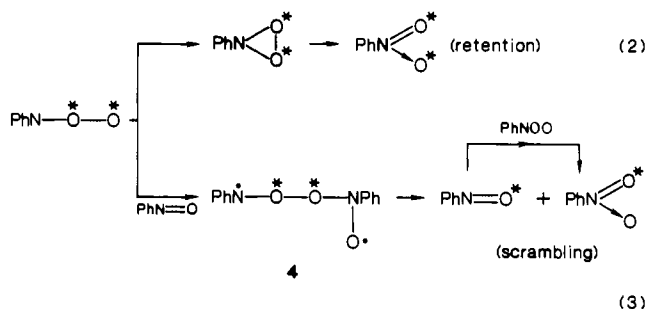
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The radical nature was corroborated by the facile oxygen transfer to nitrosobenzene, since nitroso compounds are well-known as a spin-trapping agent.¹³ Thus, the trapping of nitroso oxides with 20 mM *p*-ClC₆H₄N=O took place to give ca. 40% yield of *p*-ClC₆H₄NO₂ and only a trace amount of PhNO₂ in the photooxidation of 5 mM PhN₃. Competitive experiments afforded a relative reactivity order of PhN=O \gg Ph₂S > Ph₂SO > PhH, which together with the negative ρ -values suggest that nitroso oxides react as an electrophilic radical oxygen donor **1b**.

The isomerization of nitroso oxides to nitro compounds is worthy of scrutiny. If the conversion proceeds via an intramolecular process, e.g., **1** \rightarrow **2** \rightarrow nitro compound, two oxygen atoms in PhNO₂ should be retained (eq 2). A tracer study on the pho-



tooxidation of PhN₃ under oxygen containing ¹⁸O₂ in Table II revealed that nitrobenzene is derived from both the retention (eq 2) and scrambling pathways (e.g., eq 3). The percent retention decreased with the conversion of photooxidation, and the retention extrapolated at zero percent conversion was as high as 65%.

The scrambling pathway according to eq 3 was substantiated by trapping experiments. By increasing the concentration of *p*-ClC₆H₄N=O added, yields of PhNO₂ were decreased sharply but the percent retention in PhNO₂ increased significantly, approaching 100%. The sharp reduction in the yields of PhNO₂ and the almost sole formation of *p*-Cl- or *p*-MeC₆H₄NO₂ by the addition of *p*-Cl- or *p*-MeC₆H₄N=O supports the intermediacy of nonsymmetric acyclic adduct **4** in the oxygen transfer. These results clearly show that PhNOO isomerizes unimolecularly according to eq 2, which is competitive with eq 3 leading to the scrambled nitrobenzene. An alternative pathway for the electrophilic O-transfer by cyclic **2** is unlikely since the percent retention was not altered by the presence of sulfide or sulfoxide. Thus, the primary photoproduct in the photooxidation of phenyl azide is phenyl nitroso oxide which is ultimately converted to nitrobenzene either by unimolecular isomerization or by the

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pathway involving nitrosobenzene "chain carrier" (eq 3).

The nitroso oxide is thus shown to behave as an electrophilic peroxy radical **1b** and isomerize according to eq 2. These are in sharp contrast to the case of carbonyl oxides that are well pictured as dipolar **1a**. There is no evidence for the cyclization of carbonyl oxides (e.g., **1** → **2**);¹⁴ a high energy barrier for the cyclization is certainly due to the double-bond character of the C–O bond in **1a**.¹⁵ In contrast, the cyclization of nitroso oxides appears to be facile because of the diradical character of structure **1b**, reflecting diminished importance of double-bond nature in N–O. An extended ab initio MO calculation has suggested that most important is dipolar **1a** for carbonyl oxides but diradical **1b** for nitroso oxides.¹⁶ Our experimental results are consistent with the prediction. The structural weights (i.e., **1a**, **1b**, or **2**) and reactivities of XOO species are considered to be controlled by the difference in electronegativities between X and oxygen atom. This point is currently under investigation.

Registry No. (*p*-MeOC₆H₄)₂SO, 1774-36-3; (*p*-MeC₆H₄)₂SO, 1774-35-2; Ph₂SO, 945-51-7; (*p*-ClC₆H₄)₂SO, 3085-42-5; (*p*-MeC₆H₄)₂S, 620-94-0; Ph₂S, 139-66-2; (*p*-ClC₆H₄)₂S, 5181-10-2; PhNOO, 105785-77-1; PhN₃, 622-37-7.

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Femtosecond Photochemical Ring Opening Dynamics of 1,3-Cyclohexadiene from Resonance Raman Intensities¹

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Photoexcitation to the lowest allowed singlet state of 1,3-cyclohexadiene (CHD) gives rise to efficient ring opening to *all-cis*-hexatriene whose stereochemistry, as measured by product analysis² is overwhelmingly conrotatory, in accordance with the Woodward–Hoffmann rules.³ Due to the diffuseness of the electronic spectrum,⁴ the paucity of luminescence,⁵ and the exceedingly short excited-state lifetime,⁶ direct measurements of the excited-state structure and dynamics of CHD have not been performed. The existence of barriers to ring opening, the lifetime and extent of geometry change on the initially prepared excited-state surface, the degree of concertedness, and the participation of diradical or zwitterionic intermediates have remained unknown.⁷ The quantitative analysis of resonance Raman intensities provides

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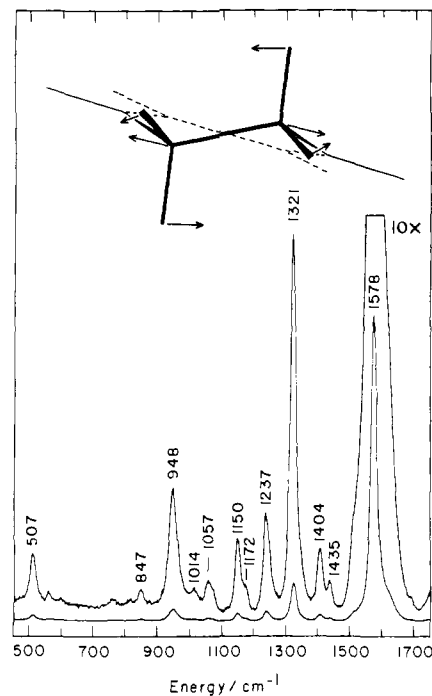


Figure 1. Resonance Raman spectrum of flowing neat cyclohexadiene excited with a D₂-shifted Nd:YAG laser at 292.6 nm (100 μJ/pulse, 20 Hz). The detection system consisted of an intensified reticon array coupled to a spectrograph having a slit width of 6 cm⁻¹. The inset depicts the ground-state geometry of cyclohexadiene, and the arrows give the geometry changes that occur along the 948 and 1321 cm⁻¹ normal modes 20 fs after excitation (multiplied by ~10). Motions of the diene moiety have been suppressed for clarity.

a powerful new method for examining excited-state structure and dynamics,^{8,9} which we apply here to cyclohexadiene. The resonance enhancement of the 1321-cm⁻¹ symmetric CH₂ wag and the 948-cm⁻¹ CH₂–CH₂ stretch reveals that the regio- and stereochemical preference predicted by the Woodward–Hoffmann rules is established within the first 20 fs following excitation via specific, rapid evolution along the conrotatory ring opening reaction coordinate.

The resonance Raman intensity of a vibration is determined primarily by the slope of the excited-state potential surface along that normal coordinate at the vertically excited geometry. Rapid photochemical dynamics are thus reflected by intense resonance Raman scattering by any normal modes having large projections onto the reactive coordinates.^{8,9} In our analysis, the excited state is treated as a harmonic potential characterized by a vertical excitation energy E_0 and a dimensionless origin shift Δ along each totally symmetric normal coordinate. The set of displacements is defined by the relative resonance Raman intensities and by the width of the electronic absorption envelope. The total absolute resonance Raman cross section permits an experimental partitioning of the total vibronic line width into homogeneous and

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