mation of the vast majority of Cr* states we observed does not proceed by this sequential mechanism, or indeed by *any* sequential mechanism involving an intermediate that reacts efficiently with CO.

We are not certain of the process by which Cr* is formed, but one pathway that readily accounts for the lack of CO quenching involves multiple-photon excitation of $Cr(CO)_6$ into a dissociative continuum, forming Cr* and CO directly. This pathway was proposed in a study of vacuum UV dissociation of $Fe(CO)_5$, in which CW argon and krypton resonance lamp irradiation was found to form Fe* in a one-photon process that clearly does not proceed via a sequential mechanism.[6] If the repulsive surfaces corresponding to each of the Cr* states are strongly intermixed, the branching ratios into the various Cr states could be expected to follow a statistical distribution,[26] as observed. Experiments are in progress to establish the mechanism more conclusively.

While most of the Cr states we detected are higher energy states, we were able to detect two lower lying Cr states indirectly. Formation of the emissive $t^5F^\circ_{1,2}$ and $v^5D^\circ_3$ states proceeds via 248-nm excitation of the low-lying a^5S_2 and a^5D_2 states,[27] from which emission was not observed. The laser-fluence dependence of the emission intensity indicates that the a^5S and a^5D states are formed in a two-photon process, as expected. The emission is exceptionally intense at low pressure, indicating that the a^5S and a^5D states are formed in very high yield relative to other Cr states. Most importantly, Cr($t^5F^\circ_{1,2}$) and Cr($v^5D^\circ_3$) emission is completely quenched at ~5 torr of CO, Ar, and He (Figure 1). This indicates that quenching occurs within a few collisions, since only about 2–5 collisions occur at 5 torr during our data collection cycle ($\leq$40 ns).

We can rule out quenching via collisional relaxation of the emitting Cr* states or of the a^5S and a^5D states, since collisional relaxation of electronically excited atoms by CO, Ar, and He occurs at a rate several orders of magnitude below the hard-sphere collision rate.[8,28,29] Quenching must therefore occur by inhibition of Cr(a^5S) and Cr(a^5D) formation. This strongly suggests that Cr(a^5S) and Cr(a^5D) are produced via reactions 1 and 2, with CO quenching occurring via reaction 3. The rate of reaction 3 is 0.1–0.5 times the hard-sphere collision rate, depending on CO pressure over the range 1–10 torr,[24] consistent with our observation that quenching requires only a few collisions. Reactions analogous to (3) do not occur with Ar and He,[24] but quenching by Ar and He, and in part by CO, can occur by collisional cooling of vibrationally hot $Cr(CO)_4$. ΔE_{298} for formation of Cr(a^5S_2) and Cr(a^5D_2) from $Cr(CO)_4$ is ~110 kcal/mol.[31] Thus, if only a small fraction of the 115 kcal/mol excitation energy in reaction 2 is partitioned into the CO products, Cr(a^5S) and Cr(a^5D) will not be accessible from thermalized $Cr(CO)_4$ by a one-photon process.

In conclusion, we have observed two pathways for KrF* laser multiple-photon dissociation of $Cr(CO)_6$ to Cr*. Higher energy Cr* states are apparently produced by a nonsequential process, involving direct excitation of $Cr(CO)_6$ into a dissociative continuum. Two lower energy Cr* states were found to be formed by a sequential mechanism, via a $Cr(CO)_4$ intermediate.

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[26] See the theoretical discussion by: Ohmichi, N.; Silberstein, J.; Levine, R. D. *Chem. Phys. Lett.* **1981**, *84*, 228.

[27] The a^5S_2 and a^5D_2 states lie 7593 and 7927 cm^{-1}, respectively, above the a^7S_3 ground state.

[28] Cundall, R. B. In *Transfer and Storage of Energy by Molecules. Electronic Energy*; Burnett, G. M.; North, A. M., Eds.; Wiley-Interscience: London, 1968; Vol. I, pp 1–63.

[29] Convincing evidence against quenching via Cr* collisional relaxation is obtained from identical experiments on $C_6H_6Cr(CO)_3$, where quenching of Cr($t^5F_{1,2}$) and Cr(v^5D_3) is *not* observed.[30]

[30] Tyndall, G. W.; Jackson, R. L., unpublished results.

[31] See ref 16 and 21. $Cr(CO)_4$–CO bond energy = 24 ± 6 kcal/mol.[32]

[32] Flectcher, T. R.; Rosenfeld, R. N., unpublished results.

External and Internal Heavy-Atom Effects on the Rate of Spin-Forbidden Proton Tunneling in the Triplet Ground State Biradical, 1,3-Perinaphthadiyl

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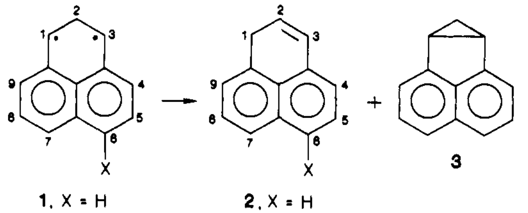
We wish to report that below ~100 K the rearrangement[2] of the 1,3-perinaphthadiyl biradical (**1**) by 2,1-hydrogen shift to yield phenalene (**2**) proceeds at a temperature-independent rate, which we attribute to quantum mechanical tunneling from the triplet ground state[3,4] of **1** to the singlet ground state of **2**. Support for the spin-forbidden nature of the rate-determining tunneling step was obtained from external and internal heavy-atom effects on the observed first-order rate constant.

Since **1** is readily accessible by UV irradiation of the cyclopropane **3** in rigid matrices, has been well characterized by several spectroscopic techniques,[2-5] is already known[2] to undergo a thermally activated 2,1-hydrogen shift to **2** at 119–133 K (1-pentanol glass, $E_a = 4.5 \pm 0.6$ kcal/mol, $A = 10^{4.5\pm1}$ s^{-1}), and belongs to the class of 1,3-biradicals whose properties and reactivity are of considerable current interest,[6] we have investigated the kinetics of the dark decay of **1** in solid polyethylene at 10–160 K. Depending on temperature and isotopic substitution,[4] the products are **2** and/or **3**. The observed rate of formation of **3** does not obey simple first-order kinetics and can be understood in terms of site effects.[7] On the other hand, the formation of **2**, which involves a much smaller geometrical change, follows the first-order law accurately over at least three half-lives and presently we consider only conditions under which **2** is the sole product.



1, X = H **2**, X = H
6-Br-**1**, X = Br 6-Br-**2**, X = Br

The Arrhenius plot for the reaction **1** → **2** (Figure 1) consists of a short linear segment above ~120 K ($E_a = 5.3 \pm 1.0$ kcal/mol, $A = 10^{5.1\pm1.0}$ s^{-1}) and a temperature-independent segment below ~100 K ($E_a = 0.0 \pm 0.1$ kcal/mol, $A = k = 10^{-6.1\pm0.5}$ s^{-1}). This suggests that tunneling from the ground triplet state of **1** into the ground singlet state of **2** dominates the reaction rate in the low-temperature limit. Indeed, at these temperatures the rate constant for the rearrangement of **1**-*2,2-d*$_2$ is $k = 10^{-9.2\pm0.5}$ s^{-1}, a deuterium kinetic isotope effect of 1300.

Direct evidence for the spin-forbidden nature of the rate-determining step was obtained by varying the atomic number of the surrounding solid solvent atoms (Table I).[8] To our knowledge,

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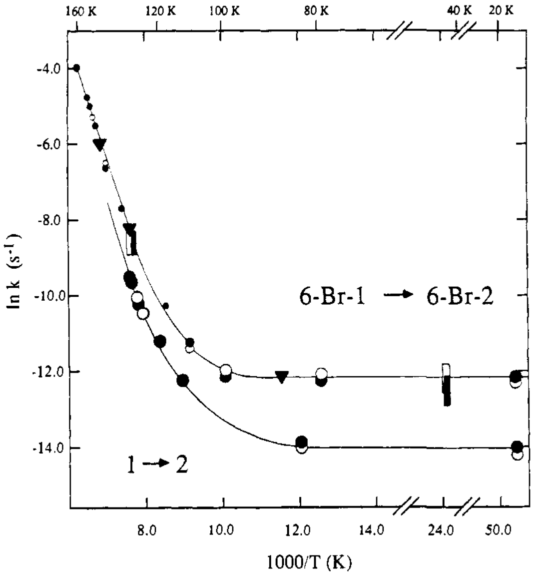

Figure 1. Arrhenius plot for the rearrangements **1** → **2** and 6-Br-**1** → 6-Br-**2** in polyethylene. Rate constants were obtained from the disappearance of the UV (●), IR (■), or ESR (▼) signals of the reactant and from the appearance of the UV (○) or IR (□) peaks of the product.

Table I. Relative Rates of Hydrogen Tunneling[a]

matrix	PE[b]	Ar	Kr	Xe
1 → **2**	1.0	2.3	6.3	23
6-Br-**i** → 6-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 known[9] 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-bromophenalene (6-Br-**2**)[10] with $E_a = 5.5 \pm 0.5$ kcal/mol and $A = 10^{6.2\pm0.5}\ \mathrm{s}^{-1}$ above ~120 K and with a temperature-independent rate of $k = 10^{-5.4\pm0.5}\ \mathrm{s}^{-1}$ below ~100 K. For 6-Br-**1**-*2,2*-d_2, the temperature-independent rate constant was $k = 10^{-8.5\pm0.5}\ \mathrm{s}^{-1}$, 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 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** → **2** process undoubtely occurs as a competing radiative decay (spin and Franck–Condon forbidden long-wavelength phosphorescence), but has not been detected.

Acknowledgment. This work was supported by a grant from the National Science Foundation, CHE 84-21117.

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(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**-*1*-d_1 and 6-Br-**1**-*3*-d_1, respectively.

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

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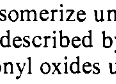
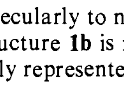
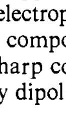
Structure and reactivity of nitrenes formed by azide photolysis have been thoroughly studied by means of product analysis,[1] matrix techniques,[2] and laser flash spectroscopy.[3] Arylnitrenes react with oxygen to yield nitroarenes[4] and the chain decomposition of azides is inhibited by oxygen.[5] 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**.


1a


1b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