Desulfurization appears to be a general process whose chemistry parallels that of deoxygenation although the energetic difference between the reactions is manifest in the examples presented above.

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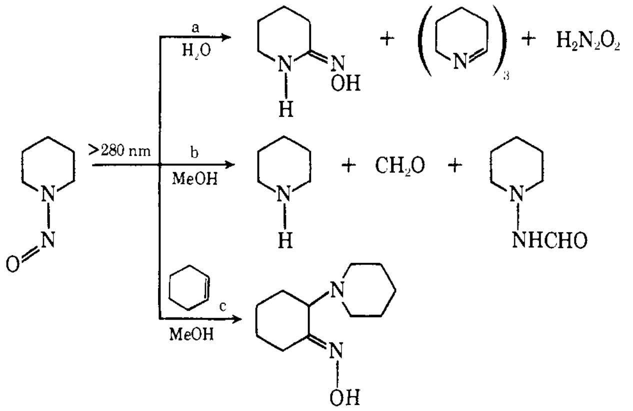
Flash Photolysis of *N*-Nitrosopiperidine. The Reactive Transient

Sir:

The photoreactions of *N*-nitrosopiperidine in the presence of a mineral acid are outlined in the following scheme. Pathway a has been postulated, from certain evidence, to occur by eliminating HNO in the primary photoprocess,[1-3] and is termed as photoelimination. Photoaddition pathway c has been shown to give 1-nitroso-2-piperidinocyclohexane as the primary adduct.[4-7] In addition it is now found that *N*-nitrosopiperidine also photolytically reacts with methanol to give piperidine hydrochloride, formaldehyde, and *N*-piperidinoformamide[8] shown as pathway b. The latter is therefore referred to as photoreduction. We have carried out flash photolysis experiments which indicate that a common reactive transient derived from a singlet excited state of the *N*-nitrosopiperidine–acid complex is responsible for the observed photoreactions.



The 1- and 0.4-μsec flash photolysis apparatus[9] used in this investigation was an improved version of that reported previously.[10,11] Flash photolysis, through a Vycor filter, of degassed or oxygen-saturated aqueous solutions containing 1×10^{-4} *M* *N*-nitrosopiperidine and 0.01 *M* HCl, produced a transient[12] whose absorbance changes indicated first-order kinetic decay with a lifetime ($\tau_{obsd} = 1/k_{obsd}$) of 54 ± 2 μsec. The similar photolysis of degassed or undegassed methanol solutions containing 6×10^{-5} *M* *N*-nitrosopiperidine and 0.01 *M* HCl produced a transient which, while having the same absorbance characteristics as the transient generated in an aqueous solution, exhibited a first-order kinetic decay with a lifetime of 8 ± 2 μsec. No transient was observed in the absence of either an acid or *N*-nitrosopiperidine. Flash excitation of the $n \rightarrow \pi^*$ transition band in the 340-nm region (5×10^{-3} *M* *N*-nitrosopiperidine, 0.01 *M* HCl, and soft glass filter)[13] produced a weaker transient with the same lifetimes indicating that the transients generated from either the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition band are the same species.

When the concentration of methanol in water was varied, the initial absorbancy $(OD)_0$ of the transient remained virtually constant but the lifetime (τ_{obsd}) was reduced proportionally to the methanol concentration. The second-order rate constant of the reaction of the transient with methanol ($k_r = (4.8 \pm 0.3) \times 10^3$ M^{-1} sec^{-1}) was obtained from the slope of the plot of the pseudo-first-order rate constants (k_{obsd}) *vs.* the concentration of methanol. In a similar manner, the transient was found to react with cyclohexene in a solvent mixture[14] of methanol and water (2:1, v/v) with a quenching rate constant $k_r = (2.4 \pm 0.1) \times 10^7$ M^{-1} sec^{-1}. The rate of the addition of the transient to cyclohexene is, therefore, about 5000 times faster than that of the reduction of the transient by methanol. This rate ratio explains why photoaddition takes place exclusively without a complication from the photoreduction in methanol as observed previously.[4]

The lowest triplet energy (E_T) of *N*-nitrosopiperidine is now determined to be about 59 kcal/mol by quenching experiments of the triplet transients[15,18] that are generated by flash photolysis of naphthalene and 2,2′-binaphthyl in aqueous acidic solutions. While the xanthenone (E_T = 74 kcal/mol) triplet transient was quenched by *N*-nitrosopiperidine at nearly the diffusion-controlled rate ($k_q = 1.4 \times 10^9$ M^{-1} sec^{-1}), the photoreactions of *N*-nitrosopiperidine do not occur with

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(9) Both flash photolysis apparatus used two independent, synchronously triggered, capacitor–spark gap lamp circuits. The 1-μsec apparatus used two 0.3-μ F 25-kV capacitors (one in each circuit). In the 0.4-μsec apparatus, two 0.05-μF 35-kV capacitors were used. The lamp configuration and the procedure were the same as that used previously (ref 10).

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(11) R. W. Yip, *Rev. Sci. Instrum.*, 40, 1035 (1969).

(12) The concentration of *N*-nitrosopiperidine was generally in the vicinity of or lower than 10^{-4} *M* in order to provide the >300-nm region transparent so that the decay curve of the transient can be recorded at any wavelength in the region of 300–400 nm. *N*-Nitrosopiperidine exhibits absorptions at 235 nm (ϵ 8300) for π–π^* and 349 (ϵ 88.5) for n–π^* transition bands in methanol.

(13) In this case it was not possible to observe the transient at a wavelength shorter than ~375 nm because of the high concentration of *N*-nitrosopiperidine required for absorption at 349 nm. The decay kinetics of the transient were monitored at 400 nm.

(14) The mixture solvent allows a wider variation of the lifetimes that can be determined accurately.

(15) The triplet transients of naphthalene and 2,2′-binaphthyl were quenched by *N*-nitrosopiperidine ($<10^{-4}$ *M*) with k_q of 1.4×10^9 and 7.5×10^7 M^{-1} sec^{-1}, respectively. The diffusion-controlled rate constant in methanol at 20° was approximately calculated by the modified Debye equation to be 1.04×10^{10} M^{-1} sec^{-1}. The triplet energies quoted in ref 17 and 18 are adopted.

(16) G. Porter and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **264**, 1 (1961).

(17) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, 88, 4769 (1966).

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xanthenone sensitization. Furthermore, in a methanol solution containing 0.01 N HCl, nitrosopiperidine quenches naphthalene fluorescence[19] with $k_q \cong 10^{10}$ M^{-1} sec^{-1}. The fact that naphthalene also sensitizes the photoreactions of N-nitrosopiperidine indicates that the transient is derived from a singlet state but not from a triplet state of N-nitrosopiperidine. This conclusion is also supported by the observation that conjugated dienes do not quench the nitrosamine photoreactions.[7]

The absorption spectrum of the above transient is very similar to that of the transient generated from flash photolysis of N-chloropiperidine in 0.01 N aqueous H_2SO_4 solution;[20] both exhibit increasing absorbance from the 450-nm region toward shorter wavelength and an apparent maximum at about 295 nm. The latter transient reacts with methanol with a second-order rate constant of 4.9×10^3 M^{-1} sec^{-1} in agreement with the rate constant of hydrogen abstraction by piperidinium radical (10^3–10^4 M^{-1} sec^{-1}) determined by the rotating sector method.[21] It is concluded that, in the photolysis of N-nitrosopiperidine, piperidinium radical derived from the lowest singlet excited state is the reactive transient which initiates elimination, reduction, and addition reactions. The absence of quenching in an oxygen-saturated solution (1.43×10^{-3} M of O_2)[22] places an upper limit of the rate constant for oxygen quenching at $\sim 1 \times 10^6$ M^{-1} sec^{-1}. This rate constant seems to be too low for triplet quenching in an aqueous solution[23] since the observed value is closer to those found for oxygen quenching of reactive radicals.[24]

The involvement of an aminium radical in the photoaddition of a nitrosamine to an olefin demands that the addition mechanism must be a stepwise radical process. It is indeed found that the photoaddition of N-nitrosopiperidine to both *trans*- and *cis*-2-butenes gives the same mixture of erythro and threo adducts.[25]

[19] For emission studies, a high-pressure Hanovia xenon compact arc lamp (150 W) and a Farrand grating monochrometer were used for excitation and a Jarrell-Ash 82-810 monochromater with an EMI6256A photomultiplier tube was used as the detecting system.

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[22] Calculated from Henry's law using $K = 2.9 \times 10^7$ for the solubility of oxygen in water. The K is taken from "Handbook of Chemistry and Physics," 47th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967.

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[26] Photoreactions of Nitroso Compounds in Solution. XVIII. For part XVII see: Y. L. Chow, R. A. Perry, and B. C. Menon, *Tetrahedron Lett.*, 1549 (1971).

[27] The author thanks the National Research Council of Canada and the President's Research Fund of Simon Fraser University for their generous support of this research.

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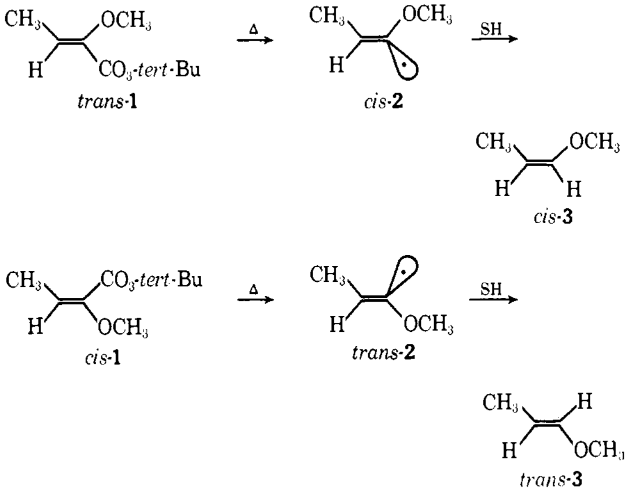
Vinyl Radicals. VI. The Configurational Stability of *cis*- and *trans*-1-Methoxy-1-propenyl Radicals

Sir:

We describe experiments which demonstrate the configurational stability of *cis*- and *trans*-1-methoxy-1-propenyl radicals. These radicals (*cis*- and *trans*-**2**) are prepared by the thermal decomposition of the corresponding *tert*-butyl *trans*- and *cis*-1-methoxy percrotonates (**1**) and are quenched by hydrogen transfer from cumene to give *cis*- and *trans*-methyl 1-propenyl ethers (**3**) with retention of stereochemistry.



trans-1-Methoxycrotonic acid is readily available as a crystalline solid (mp 60-61°) by the reaction of 2,3-dibromobutyric acid with NaOMe–MeOH.[1] The trans stereochemistry is assigned on the basis of the chemical shifts of the vinyl protons[2] (δ 6.35; calcd, 5.9) in the free acid and the corresponding methyl ester (δ 6.13; calcd, 5.67). A cis–trans mixture of the isomeric 1-methoxycrotonic acids (*ca.* c/t = 0.3) is obtained by the benzophenone-sensitized photoisomerization[3,4] (Pyrex filter) of the trans acid in acetonitrile. Further enrichment in cis acid is achieved by preferential removal of the trans isomer by crystallization from hexane, or by partial gas-chromatographic (gc) separation of the methyl esters followed by mild hydrolysis to the free acids. The cis stereochemical assignment is in accord with the chemical shifts of the vinyl protons[2] of the free acid (δ 5.35; calcd, 5.38) and the methyl ester (δ 5.12; calcd, 5.18).

The composition of any particular mixture of acids is determined by integration of the vinyl region of the nmr spectrum or by esterification with Ag_2O–MeI and gc assay of the cis–trans composition of the mixture of methyl esters. The corresponding *tert*-butyl peresters (**1**) are prepared by the sequential reaction of the free acids with N,N'-carbonyl diimidazole and *tert*-butyl hydroperoxide in THF at room temperature.[5] The peresters are purified by chromatography on Al_2O_3 and give satisfactory analyses, peroxide titers, and spectral data. The isomeric perester composition (*cis*-**1**/*trans*-**1**) of gross mixtures is established by in-

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