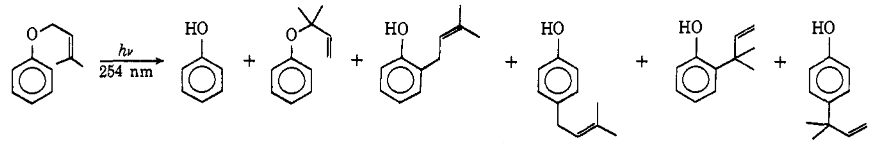
Table I.[a] Quantum Yields for Photoreactions of 3-Methyl-1-phenoxybut-2-ene



Solvent	1, ϕ_{dis}	ϕ_{app}					
		2	3	4	5	6	7
Cyclohexane	0.55	0.10	0.05	0.06	0.05	0.02	0.03
2-Propanol	0.75	0.11	0.03	0.18	0.15	0.05	0.07

[a] We suspect that the difference betweensthe quantum yield for the disappearance of **1** and the sum of product appearance quantum yields is largely due to polymerization of **1**.

by nitric oxide, suggest strongly that the reaction involves scission to phenoxy and dimethylallyl radicals—*i.e.*, the reaction is analogous to that of phenyl acetate.

The quantum yield for product formation from phenyl acetate in cyclohexane is 0.38,[5] which is not much greater than the quantum yield of product formation from **1** in cyclohexane. Since there is no evidence for the enhancement of intersystem crossing efficiencies by olefins, which themselves undergo intersystem crossing very inefficiently,[11] these results suggest that the photochemical reactivity of **1** is inconsistent with a general model in which enhancement of intersystem crossing is a prerequisite for photochemical dissociation.

The ^1L_b absorption of **1** is essentially identical with that of anisole in cyclohexane solution. The compounds should, therefore, have the same inherent fluorescent lifetime ($\tau_s{}^0$), 3.4×10^{-8} sec,[12] and rate constant for fluorescence (k_f), 2.9×10^7 sec^{-1}.[13] For anisole, the observed fluorescence lifetime (τ_s) is 8.3×10^{-9} sec.[9] Therefore, $1/\tau_s = k_f + k_{isc} + k_d = 1.2 \times 10^8$ sec^{-1}.

The fluorescence of **1** also is identical in band shape and position with that of anisole. However, the quantum yield of fluorescence is only 0.011.[14] From the ratio ϕ_f/k_f, we calculate that τ_s is about 3.7×10^{-10} sec. We can thus calculate a rate constant for the reaction, $k_r = \phi_r/\tau_s = 8.6 \times 10^8$ sec^{-1}.

The processes of back reaction and radiationless decay must account for the deactivation of the remainder of the S_1 states of **1**. Consideration of the data in Table I suggests that in cyclohexane the radicals recombine to give **3** roughly twice as often as to give **6** or **7**. If the same ratio holds for the rate of formation of **1** relative to **4** and **5**, we might expect the quantum yield for the back reaction in cyclohexane to be *ca.* 0.10. Thus we may estimate the rate constant for enhanced radiationless decay: $1/\tau_s - (k_{isc} + k_d) - k_r - k_{back} = k_x \cong 1.5 \times 10^9$ sec^{-1}. We conclude that nonchemical, nonradiative decay and chemical reaction are both markedly accelerated in **1**, relative to anisole.

Possibly the two accelerated nonradiative processes are closely related. Stretching of the weak C–O bond in the allyl ether should become highly anharmonic in the energy region close to or above the bond dissociation energy. Such anharmonicity may increase the Franck–Condon overlap between high and low vibrational states that is required to make a vibrational mode available as an energy sink in the internal conversion process. If so, the presence of "easily breakable" bonds may lead to acceleration of internal conversion even when the process does not lead ultimately to actual scission, either because the energy deposited initially is less than the dissociation energy or because internal vibrational relaxation removes energy from the dissociative mode before separation occurs.

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(14) This value was measured in cyclohexane relative to the fluorescence of a sample of anisole ($\phi_f = 0.24$)[12] of equal optical density.

(15) National Science Foundation Predoctoral Fellow, 1969–present.

Photochemical Behavior of *trans*-Chloroisothiocyanatobis(ethylenediamine)chromium(III)

Sir:

From recent investigations on the photochemistry of Cr(III) complexes containing two different types of ligands, the following features have emerged:[1] (i) generally, two distinct photoreactions take place;[2–6] (ii) the relative importance of the two photoreactions depends on the wavelength of irradiation;[3–6] (iii) the

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(1) For a critical review of the results obtained up to 1969, see V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970.

(2) L. Moggi, F. Bolletta, and V. Balzani, *Ric. Sci.*, **36**, 1228 (1966).

(3) H. F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)*, **57**, 282 (1968); **62**, 127 (1968).

(4) E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, **91**, 1076 (1969).

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(6) A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **49**, 1524 (1971).

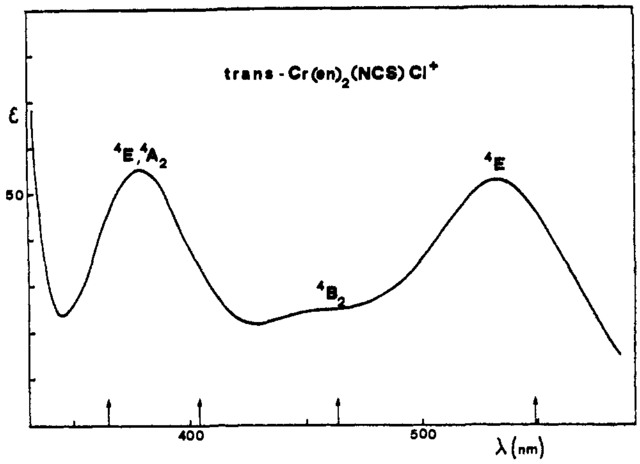

Figure 1. Visible absorption spectrum of *trans*-$Cr(en)_2(NCS)Cl^+$. The arrows indicate the wavelengths used for the excitation.

lowest quartet excited state is responsible for at least part of the predominant reaction mode;[7] (iv) the predominant reaction mode reflects the σ-antibonding orbital population of the lowest quartet excited state;[8] (v) the photoreactions can occur with stereochemical changes.[6,9,10] There is now a great need of data in order to confirm whether these features constitute the guidelines for arriving at a complete understanding of the photochemistry of the mixed-ligand Cr(III) complexes. We have begun a systematic investigation on the photochemical behavior of Cr(III) complexes containing *three* different types of ligands and we wish to report here some results concerning *trans*-$Cr(en)_2(NCS)Cl^+$.

The visible absorption spectrum of the complex is shown in Figure 1, where the wavelengths used for the irradiation are also indicated. The complex was reasonably stable in the dark under the experimental conditions used ($T \leq 15°$, pH ~3, time periods shorter than 120 min, complex concentration 2×10^{-2} *F*). Secondary thermal and photochemical reactions were also negligible. Regardless of the excitation wavelength, the irradiation of *trans*-$Cr(en)_2(NCS)Cl^+$ was found to cause the release of Cl^- and SCN^- ions and the consumption of H^+ ions. The corresponding quantum yields for these three processes have been gathered in Table I. No postphotochemical effect was observed.

Table I. Quantum Yields for H^+ Consumption and Cl^- and SCN^- Release[a]

	$^4T_{1g}(^4E, ^4A_2)$ 365 nm	$^4T_{1g}(^4E, ^4A_2)$ 404 nm	$^4T_{2g}(^4B_2)$ 464 nm	$^4T_{2g}(^4E)$ 549 nm
Φ_{H^+} [b]	0.04	0.06	0.06	0.009
Φ_{Cl^-} [c]	0.06	0.06	0.07	0.06[d]
Φ_{SCN^-} [c]	0.17	0.19	0.20	0.18[d]

[a] Precision ±15%. [b] Temperature 15°. [c] Temperature 1°. [d] ~0.2 at 15°.

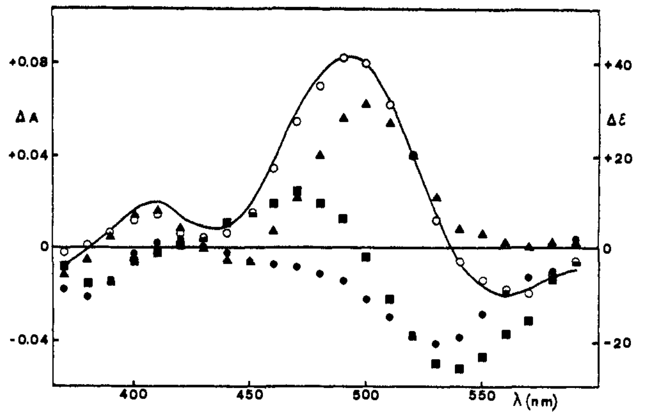

Figure 2. The curve represents the differential spectrum of an irradiated *vs.* a dark solution of *trans*-$Cr(en)_2(NCS)Cl^+$ ($\lambda_{exc} > 500$ nm). The patterns expected for the formation of the following couples of products (based on a 3:1 Φ_{SCN^-}/Φ_{Cl^-} ratio, see Table I) are also shown: (○) *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ and *cis*-$Cr(en)_2(NCS)H_2O^{2+}$; (▲) *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ and *trans*-$Cr(en)_2(NCS)H_2O^{2+}$; (■) *trans*-$Cr(en)_2(H_2O)Cl^{2+}$ and *cis*-$Cr(en)_2(NCS)H_2O^{2+}$; (●) *trans*-$Cr(en)_2(H_2O)Cl^{2+}$ and *trans*-$Cr(en)_2(NCS)H_2O^{2+}$. The patterns expected for each one of the couples involving $Cr(en)_2(H_2O)Cl^{2+}$ and $Cr(en)_2(H_2O)_2^{3+}$ as products are not shown for the sake of clarity. We have verified, however, that each of them is also in strong disagreement with the experimental spectrum.

$$\textit{trans}\text{-}Cr(en)_2(NCS)Cl^+ \xrightarrow[H_3O^+]{h\nu} Cr(en)(enH)(H_2O)(NCS)Cl^{2+} \quad (1)$$

$$\textit{trans}\text{-}Cr(en)_2(NCS)Cl^+ \xrightarrow[H_3O^+]{h\nu} Cr(en)_2(NCS)H_2O^{2+} + Cl^- \quad (2)$$

$$\textit{trans}\text{-}Cr(en)_2(NCS)Cl^+ \xrightarrow[H_3O^+]{h\nu} Cr(en)_2(H_2O)Cl^{2+} + SCN^- \quad (3)$$

The simplest hypothesis for a discussion of these results is to assume that light causes three distinct photoaquation reactions (eq 1–3). This hypothesis is also in line with previous experiences concerning other mixed-ligand Cr(III) complexes.[2–6,9] An alternative to reaction 1 could be the complete detachment of one ethylenediamine molecule from the complex; in this case, the quantum yield of the photoreaction leading to ethylenediamine aquation would simply be half that reported in Table I for H^+ consumption.

When the irradiation was carried out at λ > 500 nm, where the ethylenediamine photoaquation is negligible with respect to the Cl^- and SCN^- photoaquations, a differential spectrophotometric analysis of the irradiated *vs.* dark solutions yielded the spectrum shown in Figure 2. As one can see from the figure, *the experimental spectrum matches that expected for the formation of cis-$Cr(en)_2(NCS)H_2O^{2+}$ and cis-$Cr(en)_2(H_2O)Cl^{2+}$*, whereas it does not agree with the spectra that would have been obtained if any other couple of possible aquation products was formed.

The different wavelength dependence of Φ_{H^+} and Φ_{X^-} (X = Cl, SCN) suggests that the photoaquation of ethylenediamine is unrelated to the other photoreaction modes. Preliminary experiments have also shown that the quantum yields of Cl^- and SCN^- aquation exhibit a quite different temperature dependence, so that, for example, they have about the same value at 15°. If the quartet excited states are responsible for all or most of the reactivity, as seems to be a general feature in the photochemistry of Cr(III) complexes,[7,11–15] then

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(7) S. N. Chen and G. B. Porter, *Chem. Phys. Lett.*, **6**, 41 (1970).

(8) S. C. Pyke and R. G. Link, *J. Amer. Chem. Soc.*, **93**, 5281 (1971).

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(12) C. H. Langford and L. Tipping, *Can. J. Chem.*, **50**, 887 (1972).

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our results suggest that the state responsible for ethylenediamine aquation is $^4B_2$, whereas that responsible for Cl^- and SCN^- aquation is the lowest quartet, ^4E. This is in agreement with the expectations based on the MO approach,[16-18] according to which in our complex the $^4B_2$ excited state corresponds to the population of a σ-antibonding MO having predominant $d_{x^2-y^2}$ character, whereas the lowest ^4E state corresponds to the population of a σ-antibonding MO having predominant d_{z^2} character.

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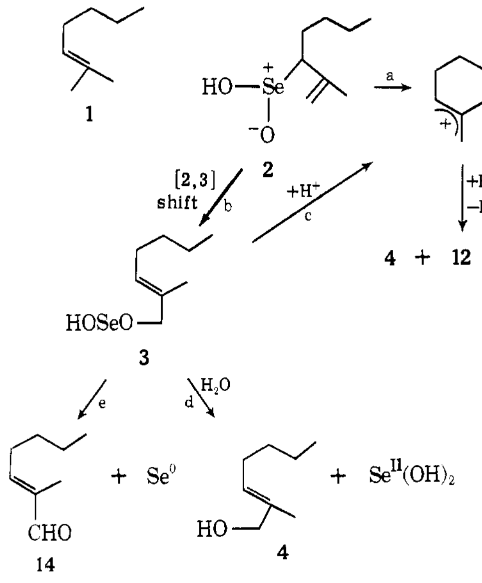
Selenium Dioxide Oxidation of Olefins. Evidence for the Intermediacy of Allylseleninic Acids

Sir:

In spite of considerable study[1] the mechanism of allylic oxidation of olefins by selenium dioxide remains controversial. Wiberg and Nielsen[2] favor initial formation of an allylseleninic acid (**2**) which then undergoes solvolysis to products (path a, Scheme I). Schaefer[3] and Trachtenberg,[4] both of whom have proposed different mechanisms not shown in Scheme I, argue against the involvement of allylseleninic acids (**2**) because of the known inertness of benzylseleninic acid to solvolysis. However, a [2,3] sigmatropic rearrangement (path b, Scheme I) of the allylseleninic acid (**2**) to a selenium(II) ester (**3**) occurred to us as a likely alternative to the solvolytic pathway a. We now report evidence which strongly suggests that the [2,3] sigmatropic shift indicated in path b is a facile process. The required rearrangement (path b) is well known for allylic sulfinates[5] and especially allylic sulfoxides,[6] but the equilibrium usually lies heavily in favor of the sulfur(IV) derivative. In the case of the selenium analogs (*e.g.*, **2** and **3**) it seemed likely that the selenium(II) derivative **3** would be more stable. Significantly, in contrast to the well known alkyl-, aryl-, and benzylseleninic acids and selenoxides[7] there are no reports of allyl analogs.

Scheme I[a]



[a] For convenience, the specific case for 2-methyl-2-heptene is illustrated, but the scheme is meant to apply to olefins in general.

A standard method for preparation of seleninic acids involves oxidation of a diselenide with hydrogen peroxide.[7] Attempts to prepare geranylseleninic acid (**6**) by oxidation of geranyl diselenide (**5**)[8] led to the results outlined in Table I (experiments 1–4). In experiments 1, 2, and 3 geranylseleninic acid (**6**) may[9] be formed but it rearranges rapidly to the selenium(II) ester of linalool (analog of **3**) which hydrolyzes (path d, Scheme I) to linalool (f) under the reaction conditions. Although the quantitative incorporation of solvent water (experiment 2) might suggest an S_N1 (path c), the fact that no methyl ethers are formed in tetrahydrofuran–methanol (experiment 3) using 98% H_2O_2 indicates that ^{18}O must enter by rapid exchange of the seleninic acid **6** prior to rearrangement. Geranylselenol (**8**),[8,10] geranyl monoselenide (**9**),[8] and geranyl linalyl selenide (**10**)[8] (experiments 5, 6, and 7, respectively) upon oxidation gave the alcohols expected from [2,3] rearrangement of the respective $C{=}CCSe^+O^-$ moieties followed by hydrolysis (paths b and d).

Büchi and Wüest established that selenium dioxide[11] selectivity attacks trisubstituted olefins such as **1** to give only the (*E*)-alcohol **4**. If our proposed mechanism is correct, then the sigmatropic rearrangement of the allylseleninic acid **2** must lead stereoselectively to the (*E*)-ester **3**. In order to test this hypothesis the allyl phenyl selenides **11** and **15** were prepared.[8,12]

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(1) For two recent reviews, see: E. N. Trachtenberg in "Oxidation," Vol. 1, R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 3; and R. A. Jerussi in "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 6, p 301.

(2) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, **29**, 3353 (1964).

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(8) All the organoselenium compounds described in this communication are new compounds and have been adequately characterized by analytical and spectral data. A brief outline of their preparations is as follows: **5** and **9** by the reaction of Na_2Se_2 and Na_2Se, respectively, with geranyl chloride; **11** by the action of C_6H_5SeNa on the corresponding chloride; **8** by LAH reduction of the corresponding selenocyanate, which in turn was obtained by treating KSeCN with geranyl chloride; **10** by treatment of **5** with $(C_6H_5)_3P$; and **15** by thermal rearrangement of **11**. A more complete discussion of these syntheses appears elsewhere: K. B. Sharpless and R. F. Lauer, submitted for publication.

(9) We cannot be sure the seleninic acid (6) actually forms since the [2,3] shift could occur before complete oxidation occurs (*e.g.*, at the selenoselinate stage). Baldwin and coworkers have reported such a rearrangement in the case of diallyl thiosulfinates [J. E. Baldwin, G. Hofle, and Se Chun Choi, *J. Amer. Chem. Soc.*, **93**, 2810 (1971)].

(10) Selenol 8 was added to excess H_2O_2 so as to favor direct (*i.e.*, not *via* 5) oxidation to 6 (experiment 5).

(11) G. Büchi and H. Wüest, *Helv. Chim. Acta*, **50**, 2440 (1967). The stereochemistry established by Büchi enabled Rapoport to use SeO_2 in the last step of a sirenin synthesis [J. J. Plattner, U. T. Bhalerao, and H. Rapoport, *J. Amer. Chem. Soc.*, **91**, 4933 (1969)].

(12) All attempts to prepare the selenol and diselenide analogs of **11** failed.[8] Thus, we had to be content with studying the rearrangement of the allyl phenyl selenoxide **16** rather than the desired allylseleninic acid **2**.