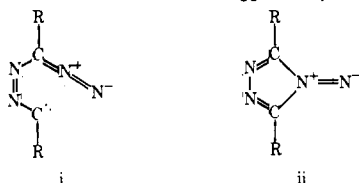


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- (10) D. S. King, C. T. Denny, R. M. Hochstrasser, and A. B. Smith, III, *J. Am. Chem. Soc.*, **99**, 271 (1977).
- (11) NOTE ADDED IN PROOF. A requirement for any proposed intermediate is that its transient absorption be in the red region of the optical spectrum. Possible examples are i and ii. Structure ii was suggested by the recent spectral



properties reported by Dervan for a 1,1-dialkyl-diazene; see W. D. Hinsberg, III, and P. B. Dervan, *J. Am. Chem. Soc.*, **100**, 1608 (1978). Interestingly, this diazene and its dimethyl and diphenyl derivatives (ii, R = H, CH₃, and C₆H₅) have been suggested to be the intermediate in the oxidative (Pb(OAc)₄) fragmentation of the corresponding 4-amino-1,2,4(4*H*)-triazole; see K. Sakai and J.-P. Anselme, *Tetrahedron Lett.*, 3851 (1970).

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Fluorescence and Photochemistry of the Charge-Transfer Band in Alcoholic Vanadium Trichloride Solution

Sir:

The primary photochemical and photophysical processes derived from the charge-transfer excited states of transition metal complexes have been the subject of extensive investigations in the past decade.¹ At present, however, our understanding of the photophysical properties of the charge-transfer excited state is still relatively limited because of the few luminescence data available.

We have found that vanadium(III) alcoholate complexes in the parent alcohol solution exhibit luminescence of relatively high quantum yield upon excitation at the charge-transfer band with competitive photoreduction² of vanadium(III) to vanadium(II). This appears to represent the first case of a transition metal complex displaying both photochemistry and luminescence from an upper excited state in fluid solution. Vanadium trichloride reacts with methanol, ethanol, and 1-propanol to form alcoholates, formulated in solution as $[V(RCH_2OH)_4Cl_2]Cl$.³ Absorption spectra of these complexes in solution show two distinct maxima at ~ 670 (ν_1 , ϵ_m 8) and 450 nm (ν_2 , ϵ_m 15–16) in the visible region.⁴ The ν_1 and ν_2 bands have been assigned as spin-allowed ligand-field transition attributable to ${}^3T_{2g} \leftarrow {}^3T_{1g}(F)$ and ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$ of vanadium(III) in octahedral symmetry, respectively. In contrast, a broad

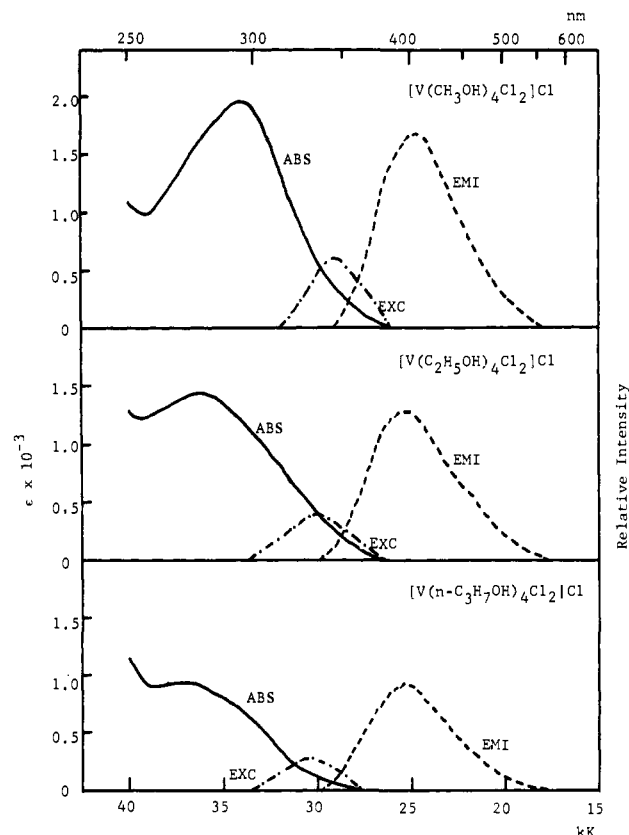


Figure 1. Absorption, emission, and excitation spectra of vanadium(III) alcoholates in room temperature solution.

Table I. Quantum Yields of Photoreduction and Fluorescence of Vanadium(III) Alcoholates in the Parent Alcohol at Room Temperature

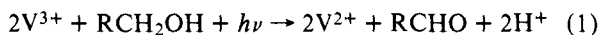
Complex	Φ_r^a	Φ_f^b		
		290	330	345
$[V(CH_3OH)_4Cl_2]Cl$	0.07 ± 0.01	0.000	0.002	0.004
$[V(C_2H_5OH)_4Cl_2]Cl$	0.22 ± 0.02	0.000	0.008	0.010
$[V(n-C_3H_7OH)_4Cl_2]Cl$	0.20 ± 0.02	0.000	0.020	0.021

^a Quantum yields of photoreduction of vanadium(III) to vanadium(II) upon irradiation with 313-nm light. ^b Fluorescence quantum yields for excitation at different wavelengths (nm).

absorption band of relatively high intensity (ϵ_m 900–1950) lies in the ultraviolet region of 250–400 nm (Figure 1). This band can be identified as a spin-allowed charge-transfer transition from ligand to metal (CTTM), based on the following photochemical results.

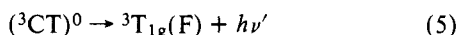
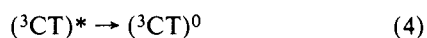
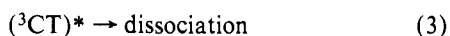
Irradiation of alcoholic vanadium trichloride solutions with 313-nm light resulted in the absorption spectral changes. As irradiation proceeded, the ν_1 and ν_2 bands characteristic of vanadium(III) decreased in intensity, while new absorption bands appeared at 570 (ν_1') and 380 nm (ν_2').⁵ The positions of the new absorption bands are in close agreement with the values⁶ of alcoholic vanadium dichloride solutions. ν_1' and ν_2' may be assigned as spin-allowed ligand-field transitions attributable to ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$ and ${}^4T_{1g}(P) \leftarrow {}^4A_{2g}$ of vanadium(II) in octahedral symmetry, respectively. In addition, the photoreduction of vanadium(III) to vanadium(II) was confirmed by the appearance of the characteristic vanadium(II) EPR signal. Quantum yields Φ_r of the photoreduction upon irradiation with 313-nm light (Table I) were determined from

the disappearance of the ν_2 band using ferrioxalate actinometry. The quantum yields were found to be zero order in a concentration range of 0.007 to 0.040 M vanadium(III). GC analysis demonstrated that, for every mole of vanadium(III) consumed in the course of irradiation of ethanolic vanadium trichloride solution, 0.5 mol of acetaldehyde is produced. The overall reaction may be represented by



The emission spectra (EMI) of vanadium(III) alcoholates in room temperature solution are shown in Figure 1 together with the excitation spectra (EXC) and the charge-transfer absorption spectra (ABS). The luminescence emission band⁷ is a mirror image of charge-transfer absorption band. We assign the observed luminescence as a fluorescence from the charge-transfer excited state, ${}^3CT \rightarrow {}^3T_{1g}(F)$, though the lifetime has not been measured. The differences in energy between the emission and absorption maxima (the Stokes shifts) are as much as 9–12 kK, as expected from the broad absorption bands. A large Stokes shift indicates a marked distortion of the excited-state potential energy surface with respect to the ground state along the configuration coordinate. The excitation spectra⁸ are not identical with the charge-transfer absorption spectra, as can be seen in Figure 1. The methanolic vanadium trichloride solution has an excitation spectrum beginning at 310 nm, while the ethanolic and 1-propanolic vanadium trichloride solutions begin at 295 nm. Table I shows fluorescence quantum yields Φ_f upon excitation at 290, 330, or 345 nm, as measured against quinine bisulfate in 0.1 N sulfuric acid as a standard.⁹ The significant reduction in fluorescence quantum yields with lower wavelength excitation may be accounted for in terms of a critical vibration approximation^{10,11} in a distorted charge-transfer excited-state surface with a shallow minimum along the reaction coordinate. The excitation at wavelengths shorter than 300 nm would cause dissociation of vanadium(III) alcoholates into fragments within the lifetime of a few vibrations in the excited state. At longer wavelengths, the dissociation process would compete with vibrational degradation process resulting in fluorescence.

In view of the experimental results, we assume the following mechanism upon irradiation with 313-nm light:



$({}^3CT)^*$ is a charge-transfer excited state of vanadium(III) alcoholate in an upper vibrational level (or continuous level) and $({}^3CT)^0$ is one in the lowest vibrational level. Nonradiative processes leading to the disappearance of the excited state must be involved, but the present data do not allow a precise description concerning the mechanism. This problem is the focus of further investigation.

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- (5) ν_1' 17.5 kK and ν_2' 26.5 kK for CH_3OH ; ν_1' 17.4 kK and ν_2' 26.3 kK for C_2H_5OH ; ν_1' 16.9 kK (ϵ 6) and ν_2' 25.6 kK (ϵ 4) for $n-C_3H_7OH$. Isobestic points appeared at 525 and 625 nm for the course of the photoreduction.
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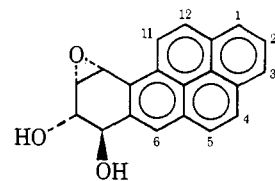
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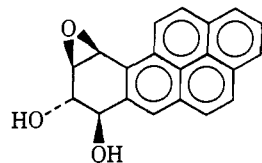
Structural Features Which Determine the Carcinogenesis, Mutagenesis, and Rates of Acid- and Water-Mediated Solvolysis of and Nucleophilic Attack upon Diol Epoxides, Bay-Region and Non-Bay-Region Tetrahydro Epoxides, and K-Region and Non-K-Region Arene Oxides

Sir:

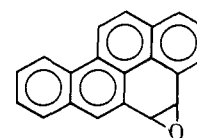
Microsomal mixed function oxidation of polycyclic aromatic hydrocarbons results in the formation of arene oxides. These are converted to phenols via the NIH shift¹ and to trans diols by epoxide hydase.² Dependent upon the structure of the trans diol, further epoxidation by microsomal mixed function oxidase may lead to the production of tetrahydrodiol epoxides which in turn are hydrolyzed to tetrahydrodiols. The mutagenic, cytotoxic, and carcinogenic properties of these products and intermediates have recently and are presently receiving considerable attention. The greatest effort has been expended upon compounds oxidatively derived from benzo[*a*]pyrene (BP), a ubiquitous environmental carcinogen. These studies have centered on the importance of the type of BP derivative and the various positional isomers in the causation of mutagenesis, necrosis, and carcinogenesis. Results to date indicate that there is no strict structural vs. activity relationship among the three activities and that the orders of activity may be changed in going from one test system to another.³⁻⁸ Nevertheless, the tetrahydrobenzo[*a*]pyrenediol epoxides (A and B) and the K-region 4,5-BP oxide (C) appear to be the most interesting of the various BP derivatives. The reaction of these compounds with both nuclear DNA and polydeoxy nucleotides have yielded identifiable covalent adducts.¹⁰ The modes of covalent bonding to DNA and polydeoxyribonucleic acids are dependent upon the nature of the BP derivative.⁹⁻¹⁰



anti-BPH₄ diol epoxide (A)



syn-BPH₄ diol epoxide (B)



K-region 4,5-BP oxide (C)