

immediate neighborhood of the complex ions with microscopic viscosity values lower than the macroscopic mean one and dependent on the distance from the complex. For this very reason, the observed results cannot be used to test the earlier proposal^{9,12} that the cage recombination is in this case a "secondary" rather than a "primary"¹⁶ one.

The results of this work show that cage recombination of the radical pair generated by excited-state bond homolysis is important in the photochemistry of $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$. Of course, the observed behavior is not meant to be a general rule for all $\text{Co}(\text{III})$ complexes. It might well be that in other complexes, especially in those where LMCT excited states are not dissociative with respect to one metal-ligand coordinate, radical recombination is unimportant. In any case, it seems likely that the study of the dependence of photoreaction quantum yields on solvent viscosity, if properly separated from other possible accompanying effects, could be of considerable diagnostic value.

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Additional Channel for Singlet-Triplet Intersystem Crossing in Unsaturated Aldehydes. 5-Hexenal¹

Sir:

Primary photochemical processes of unconjugated olefinic aldehydes have been little studied,² although those of conjugated aldehydes, such as acrolein³ and crotonaldehyde,⁴ have been much studied in detail. In the former classes of simple aldehydes, there are two seemingly isolated, potentially reactive sites as well as two low-lying triplet states, the $^3(n, \pi^*)$ state of the carbonyl group and $^3(\pi, \pi^*)$ state of the olefinic group. This interesting molecular electronic feature led us to study the primary photochemical transformation mechanism of 5-hexenal which would reflect the difference in the probabilities of populating the two triplet states and that in chemical reactivities of the two triplet states. The experiments were carried out in the gas phase at low pressures in order to minimize the collisional effects on the product formation yields.

5-Hexenal has an allylic γ hydrogen, and therefore it is expected to undergo an efficient Norrish type II process, as numerous carbonyl compounds do. At 312 nm, the type II photoelimination product quantum

yield of 1-butene from *n*-hexenal is 0.23 ± 0.03 , whereas that of 1,3-butadiene from 5-hexenal is 0.36 ± 0.03 of which 0.23 ± 0.03 is attributable to the singlet yield and 0.13 ± 0.02 to the triplet yield. At 254 nm, the yields of 1-butene and 1,3-butadiene are 0.26 ± 0.03 and 0.35 ± 0.03 , respectively, indicating little change if any. The yield of propylene (and acrolein) from 5-hexenal is 0.25 ± 0.05 at 312 nm and 0.22 at 254 nm. The triplet benzene ($^3B_{1u}$, 84.4 kcal/mol) sensitized decomposition of 5-hexenal gives the following quantum efficiency⁵ values: propylene = 0.09 ± 0.01 and 1,3-butadiene = 0.72 ± 0.07 .

Fluorescence quantum yields, Φ_F , and fluorescence decay times, τ_F , obtained for *n*-hexenal and 5-hexenal are shown in Table I. For 5-hexenal, values of τ_F at

Table I. Fluorescence Properties^a

Aldehyde	λ_{ex} , nm	$10^{-4}\Phi_F$	τ_F , nsec
<i>n</i> -Hexenal	330	(4 ± 1)	3.3 ± 0.3
	312	(1.8 ± 0.2)	2.2 ± 0.3
5-Hexenal	330	(3 ± 1)	2.4 ± 0.3
	312	(0.8 ± 0.1)	

^a 10 Torr aldehyde plus 2 Torr oxygen.

wavelengths less than 330 nm were too short (<1.5 nsec) to be measured directly. However, if it is assumed that the radiative rate constant, k_F , varies little throughout the $\pi^* \leftarrow n$ absorption band, then the value of τ_F at 312 nm may be estimated as 6×10^{-10} sec, where $\tau_F(312 \text{ nm}) = \Phi_F(312 \text{ nm})/k_F$ and $k_F = \Phi_F(330 \text{ nm})/\tau_F(330 \text{ nm})$.

Knowledge of τ_F and Φ_{II}^s , the singlet type II quantum yield, allows the calculation of the rate constants for the singlet type II process, $k_{II}^s(312 \text{ nm}) = \Phi_{II}^s(312 \text{ nm})/\tau_F(312 \text{ nm})$: $3.7 \times 10^8 \text{ sec}^{-1}$ for 5-hexenal, and $1.0 \times 10^8 \text{ sec}^{-1}$ for *n*-hexenal. The four times faster rate constant for 5-hexenal may be rationalized in terms of a more facile γ -hydrogen abstraction since the bond energy of an allylic C-H is ~ 6 kcal/mol less than that of a secondary C-H bond.⁶

Whether or not the enhanced type II reactivity of 5-hexenal is solely responsible for its factor of 2 smaller fluorescence quantum yield relative to *n*-hexenal over the wavelength interval studied may be examined in the following way. The fluorescence quantum yield may be defined as

$$\Phi_F = k_F / (k_F + k_{II}^s + k_\alpha^s + k_{ISC} + k_{IC}) \quad (1)$$

where the expected predominant reactive pathways are represented by the rate constants k_α^s , for α cleavage, and k_{II}^s . Rates of unimolecular nonradiative processes are given by k_{ISC} for intersystem crossing and k_{IC} for internal conversion. Substituting the known values of Φ_F , k_F , and k_{II}^s for 5-hexenal and *n*-hexenal at 312 nm into eq 1 yields the value of $(k_\alpha^s + k_{ISC} + k_{IC})$ to be $\sim 13 \times 10^8 \text{ sec}^{-1}$ for 5-hexenal and $\sim 4 \times 10^8 \text{ sec}^{-1}$ for *n*-hexenal.

Because the terminal olefinic group of 5-hexenal

(5) E. K. C. Lee in "Excited State Chemistry, A Symposium," J. N. Pitts, Jr., Ed., Gordon and Breach, New York, N. Y., 1970, p 59.

(6) (a) D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2136 (1969); (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1967, Table A-5.

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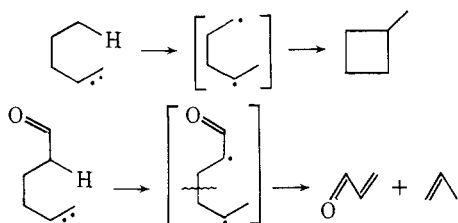
(2) (a) J. N. Butler, A. T. Drake, J. C. Mitchell, and P. Singh, *Can. J. Chem.*, **41**, 2704 (1963); (b) R. F. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, *ibid.*, **43**, 1934 (1965); (c) N. E. Lee and E. K. C. Lee, *J. Phys. Chem.*, **71**, 1167 (1967).

(3) (a) J. W. Coomber and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **91**, 547 (1969); (b) R. S. Becker, K. Inozuka, and J. King, *J. Chem. Phys.*, **52**, 5164 (1970).

(4) (a) E. R. Allen and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **91**, 3135 (1969); (b) J. W. Coomber and J. N. Pitts, Jr., **91**, 4955 (1969).

would not be expected to affect significantly the rates of α cleavage and internal conversion (if any) *vs.* the corresponding rates in *n*-hexanal, we feel that k_{ISC} is primarily responsible for the factor of 3 greater sum of $(k_{\alpha}^s + k_{ISC} + k_{IC})$ for 5-hexenal.

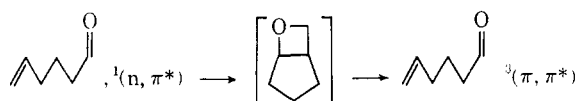
The Stern-Volmer half-quenching pressure, $P_{1/2}$, at λ_{ex} 254 nm of propylene production is equal to 0.14 ± 0.02 Torr of 5-hexenal where collisional relaxation of the S_1 state must be negligible. Hence, the immediate precursor of propylene cannot be the S_1 state. To accommodate this observation we propose that propylene production follows formation of the olefinic $^3(\pi, \pi^*)$ state. Support for this proposal is given by the analogous observation of the formation of methylcyclobutane and its decomposition products from the $Hg(6^3P)$ sensitized decomposition of 1-pentene.⁷ Abstraction of the hydrogen γ to the olefinic group by the terminal carbon will yield methylcyclobutane from 1-pentene and likewise propylene plus acrolein from 5-hexenal



The existence of the biradicals in brackets is purely speculative.

Additional support for the $^3(\pi, \pi^*)$ olefinic state precursor of propylene comes from the 8:1 ratio of 1,3-butadiene, type II product, to propylene in the triplet benzene sensitized decomposition of 5-hexenal. This ratio is nearly equal to the observed ratio (7:1) of the triplet benzene quenching efficiency of aldehydes to that of terminal olefins.⁸ This ratio of 1,3-butadiene to propylene production suggests that intramolecular energy transfer from the carbonyl $^3(n, \pi^*)$ state to the olefinic $^3(\pi, \pi^*)$ state is slow compared to type II elimination and α cleavage. Thus, in the direct photolysis of 5-hexenal the probability of populating the olefinic $^3(\pi, \pi^*)$ state is greater from the carbonyl $^3(n, \pi^*)$ state than from the $^3(n, \pi^*)$ state.

The intramolecular mechanism whereby energy is transferred from the carbonyl $^3(n, \pi^*)$ state may involve the formation of an oxetane intermediate in a manner analogous to that observed by Turro and his coworkers.⁹



They observe the formation of excited triplet products in the decomposition of dioxetanes. Alternatively, direct intramolecular energy transfer from carbonyl $^3(n, \pi^*)$ to olefinic $^3(\pi, \pi^*)$ may take place

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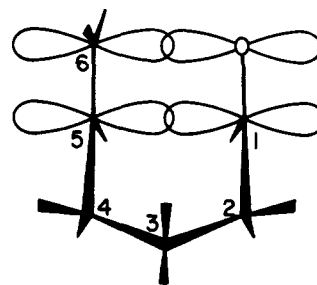


Figure 1.

through an oxetane-like exciplex as shown in Figure 1 in a scheme involving spin-orbit coupling.

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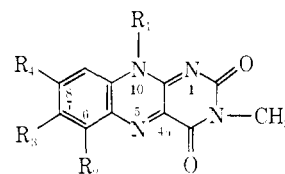
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Evidence for an Intermediate Adduct in the Ethylenediaminetetraacetic Acid Mediated Photoreduction of Flavines

Sir:

The photoreduction of flavines in the presence of EDTA serves as a desirable method for the production of 1,5-dihydroflavines and as such has received considerable attention.¹⁻⁵ The mechanism of the reaction has been suggested to involve disproportionation of flavine semiquinone^{1,2} without combination with EDTA² species. In a comprehensive investigation of the photolysis of flavines in the presence of various agents Walker, *et al.*,⁵ were unable to detect covalent adducts in the EDTA photocatalytic reduction of flavines.

We report herein evidence for the formation of an intermediate species in the photocatalytic reduction of isoalloxazines (I-IV)⁶ by EDTA; these species possess



- I, $R_1 = 2', 6'$ -dimethylphenyl; $R_2 = R_3 = R_4 = H$
 II, $R_1 = 2', 6'$ -dimethylphenyl; $R_2 = R_4 = SO_3^-$; $R_3 = H$
 III, $R_1 = CH_3$; $R_2 = R_4 = H$; $R_3 = CN$
 IV, $R_1 = CH_3$; $R_2 = R_3 = H$; $R_4 = CN$

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