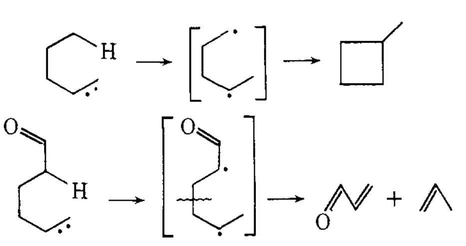
would not be expected to affect significantly the rates of α cleavage and internal conversion (if any) *vs.* the corresponding rates in *n*-hexanal, we feel that k_{ISC} *is primarily responsible for the factor of 3 greater sum of* $(k_\alpha{}^s + k_{ISC} + k_{IC})$ *for 5-hexenal.*

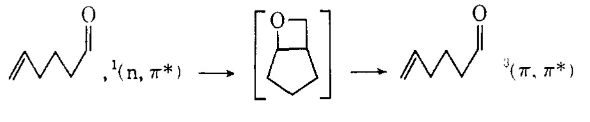
The Stern–Volmer half-quenching pressure, $P_{1/2}$, at λ_{ex} 254 nm of propylene production is equal to 0.14 ± 0.02 Torr of 5-hexenal where collisional relaxation of the S_1 state must be negligible. Hence, *the immediate precursor of propylene cannot be the* S_1 *state.* To accommodate this observation 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 spectulative.

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* $^1(n,\pi^*)$ *state than from the* $^3(n,\pi^*)$ *state.*

The intramolecular mechanism whereby energy is transferred from the carbonyl $^1(n,\pi^*)$ 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 $^1(n,\pi^*)$ to olefinic $^3(\pi,\pi^*)$ may take place through an oxetane-like exciplex as shown in Figure 1 in a scheme involving spin–orbit coupling.



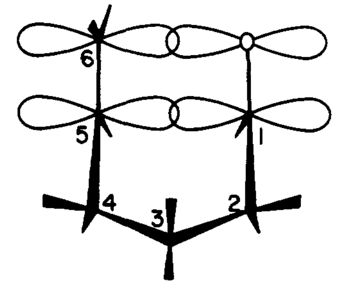


Figure 1.

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Received February 16, 1973

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[7] J. R. Majer, J. F. T. Pinkard, and J C. Robb, *Trans. Faraday Soc.*, **60**, 1247 (1964).

[8] (a) G. A. Haninger and E. K. C. Lee, *J. Phys. Chem.*, **73**, 1815 (1969); (b) E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968).

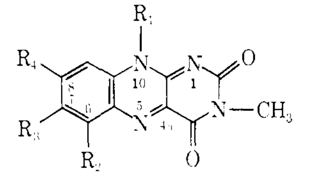
[9] N. J. Turro and P. Lechten, *J. Amer. Chem. Soc.*, **95**, 264 (1973).

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 EDTA[2] 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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[1] M. Green and G. Tollin, *Photochem. Photobiol.*, **7**, 129 (1968).

[2] O. Holmstron, *ibid.*, **3**, 97 (1964).

[3] W. R. Frisell, C. W. Chung, and C. G. Mackenzie, *J. Biol. Chem.*, **234**, 1297 (1959).

[4] K. Enn and W. H. Burgess, *J. Amer. Chem. Soc.*, **87**, 5766 (1965).

[5] W. H. Walker, P. Hemmerich, and V. Massey, *Eur. J. Biochem.*, **13**, 258 (1970).

[6] Synthesis of I, L. Main, G. J. Kasperek, and T. C. Bruice, *Biochemistry*, **11**, 3991 (1972). Synthesis of II, L. Hevesi and T. C. Bruice, *ibid.*, **12**, 290 (1973). III: mp 283–290° dec; ir 2210, 1720, and 1650 cm^{-1}; nmr (DMSO-d_6) δ 7.0–6.4 (m, 3 H), 3.66 (s, 3 H, N-10 CH_3), 3.37 (s, 3 H, N-3 CH_3). *Anal* Calcd for $C_{13}H_9N_5O_2$: C, 58.43; H, 3.37; N, 26.22. Found: C, 58.50; H, 3.49 N, 26.20. IV: mp 315–320° dec; ir 2210, 1710, 1670, 1625, and 1600 cm^{-1}. *Anal.* Calcd for $C_{13}H_9N_5O_2$: C, 58.43; H, 3.37; N, 26.22. Found: C, 58.59; H, 3.63; N, 26.14.

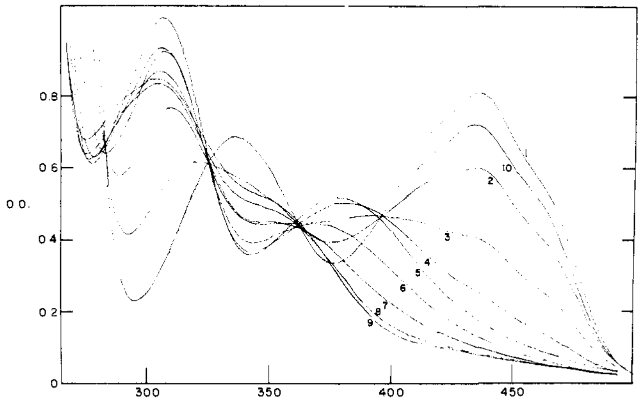

Figure 1. Photolysis of II (8×10^{-5} M) in the presence of EDTA (0.01 M) at pH 6.4. Traces 2 and 3 were recorded after 2 and 5 min of photolysis (total time); curves 4–9 were taken after an additional 0.1, 0.5, 1.5, 3.0, 5.0, and 8.0 hr of photolysis, respectively; curve 10 was traced after the admittance of air after prolonged photolysis. Initial sample contained in a 1-cm Thunberg cuvette was deoxygenated by alternatively evacuating and admitting V^{2+}-deoxygenated argon 20X. The photolysis was carried out with a No. 1 BBA floodlight at a distance of 6 in. The cuvette was kept at 25° in a water bath.

the characteristic spectra of a 4a adduct.[5,7] Photolysis of I and III in the presence of EDTA (0.01 M, pH 6.1, V^{2+}-scrubbed argon atmosphere) results in their direct conversion to the corresponding 1,5-dihydroisoalloxazines without the appearance of intermediates. In Figure 1 is presented the spectral time course for the photolysis of II in the presence of EDTA. Examination of the figure reveals that initial photolysis is associated with fairly tight isosbestic points (395, 362, 325, and 283 nm) which then break upon further irradiation. Spectra taken at intermediate times during the photolysis, *e.g.*, spectrum 5, show λ_{max} at 376 and 307 nm, which is in agreement with that for other 4a adducts.[5,6] Admittance of air at this point gave a 98% return of II_{ox} based on λ_{max} at 435 nm. This observation is noteworthy in that other 4a adducts have required illumination in the presence of O_2 to restore oxidized flavines.[5] Prolonged photolysis, shown in spectra 6–9, resulted in a decrease in absorbance at 376 and 307 nm and the appearance of a shoulder at 288 nm, characteristic of 1,5-dihydroflavine. Admittance of air at this point gave a 89% return of II_{ox} showing some irreversible photolysis of the isoalloxazine nucleus. These results are consistent with an A → B → C process. Much the same results were obtained when EDTA was replaced by phenylacetic acid which has previously been established to form 4a-addition products with flavines on photolysis.[6] In this case tight isosbestic points were obtained initially at 386, 361, and 321 nm which broke away on continued photolysis to yield a spectrum consistent with the production of reduced flavine. However, admittance of air provided only a 58% return of II_{ox}. The course of photolysis of IV in the presence of EDTA is shown in Figure 2. Examination of Figure 2 reveals that the spectrum of IV gives way to that anticipated of a 4a adduct with isosbestic points at 400, 345, 322, 288, and 266 nm. With prolonged illumination of the reaction mixture the 4a adduct failed to provide a species exhibiting the spectra of reduced flavine. Admittance of air regenerated IV_{ox} in ~99% yield.

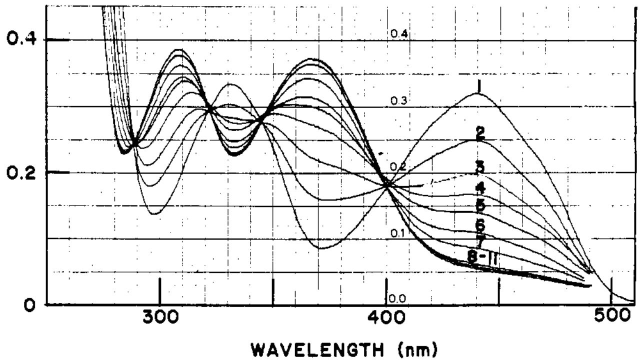

Figure 2. Photolysis of IV (3.5×10^{-5} M) in the presence of EDTA (0.01 M) at pH 6.4. Curve 1 was taken after deoxygenation (see caption, Figure 1); curves 2–10 were taken after 0.25, 0.5, 0.75, 1.0, 1.75, 2.75, and 7.75 min of photolysis (total time), respectively; curve 11 was taken after an additional 1 hr of photolysis and is identical with 8 below 400 nm. Photolysis was at 25° with a 100-W bulb at a distance of 6 in.

The present results establish that photoreduction of isoalloxazines with EDTA in aqueous solution may yield, depending on the isoalloxazine, an intermediate, the spectra of which suggest a 4a adduct. Further, the stability of the 4a adduct would appear to be a function of electronic and possibly steric factors. Thus, when H occupies the 6, 7, and 8 positions (I) or when there is a CN group at the 7 positon (III) no intermediate may be discerned on the path of photoreduction. Sulfonic acid substituents at the 6 and 8 positions (II) allow observation of the formation and photolysis of an intermediate while an 8-cyano group (IV) provides a stable 4a adduct which does not go on to 1,5-reduced isoalloxazine. Electron withdrawal by a substituent at the 8 position would thus appear to stabilize the adduct. These results do not differentiate between the two possibilities that: (1) EDTA photoreduction proceeds solely through a 4a adduct and (2) two mechanisms of EDTA photoreduction compete so that electron-deficient isoalloxazines are reduced *via* 4a-adduct intermediates while non-electron-deficient isoalloxazines are directly reduced to the 1,5 dihydro structure. In progress is an extensive study of the photocatalytic reaction of variously substituted isoalloxazines with EDTA. Our objective is the elucidation of the controlling structure–function relationships.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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Intramolecular Rearrangement of Pentacoordinate Nitrosyl Complexes

Sir:

Correlation of the MNO angle with coordination geometry for five-coordinate metal nitrosyl complexes is

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(7) (a) P. Hemmerich, S. Ghisla, U. Hartmann, and F. Müller, "Flavins and Flavoproteins," H. Kamin, Ed., University Park Press, Baltimore, Md., 1971, p 83; (b) W. H. Walker, P. Hemmerich, and V. Massey, *Helv. Chim. Acta*, **50**, 2269 (1967); (c) M. Brustlein, Ph.D. Thesis, University of Konstanz, Germany, 1971; (d) W. R. Knappe, Ph.D. Thesis, University of Konstanz, Germany, 1971.