fluorescence.[23] There the effects of divalent cations have been attributed to their ability to "screen" negatively charged membrane surfaces. In our electrochemical studies the high positive charge density with solutions containing multivalent cations[24] that is likely to be concentrated in and near the outer Helmholtz plane is expected to stabilize the otherwise repulsive electrostatic interactions between electrode and protein. Additionally, intermolecular electrostatic repulsions between adjacent protein molecules near the electrode surface may be greatly diminished. Alternatively protein–cation association, which might result in a significant decrease in the effective negative charge of the protein may be important. Rates of reaction of such complexes, as, for example, reported for chloroplast and bacterial ferredoxins,[25] may differ considerably from those of the native protein. Consideration of the various interaction possibilities leads us to propose the simple model illustrated schematically in Figure 2.

The importance of protein–electrode binding as a prerequisite for electron transfer has been discussed previously.[2] For asymmetric protein molecules, binding in an orientation conducive to rapid heterogeneous electron transfer may depend upon *specific* interactions with the electrode surface. Though the 2[4Fe-4S] ferredoxin displays a remarkable 2-fold symmetry axis,[26] we note that rubredoxin,[27] flavodoxin,[28] and azurin[29] possess quite pronounced asymmetry both in terms of the location of redox centres and (to varying degrees) the distribution of charged and hydrophobic surface residues. The absence of cation sensitivity of azurin is consistent with the three-dimensional structure which shows[29] extensive *charge pairing* among side chains. In all these proteins the redox centers are contained within regions of invariant or semiconserved hydrophobic residues. Kinetic studies with flavodoxins have moreover implicated[30] the exposed dimethylbenzene ring of the flavin as "point of entry and exit of the electron". It is possible that the hydrophobic environment of the active-site regions of all four proteins may interact favorably[31] with extended aromatic arrays on the graphite basal plane[20] once the electrostatic repulsion is overcome.

In conclusion, we have demonstrated the direct electrochemistry of four different redox proteins and illustrated an interesting aspect of the influence of multivalent cations on heterogeneous electron transfer. Quantitative studies are currently in progress, which may allow comparison between the electrode reactions and those relevant to the biological functions of the proteins.

Acknowledgment. We are indebted to Prof. I. J. Higgins, Dr. A. P. F. Turner (Cranfield Institute of Technology), and N. A. Kitchen for assistance in the preparation of azurin. We acknowledge financial support from the Science and Engineering Research Council and the Atomic Energy Research Establishment, Harwell, under a program funded by the U.K. Department of Industry. This is a contribution from the Oxford Imperial Energy Group.

Registry No. Mg, 7439-95-4; $Cr(NH_3)_6^{3+}$, 14695-96-6; graphite, 7782-42-5.

---

(23) Barber, J. *Biochim. Biophys. Acta* **1980**, *594*, 253; *Ann. Rev. Plant Physiol.* **1982**, *33*, 261.

(24) See, for example: Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1982; Chapter 12.

(25) Armstrong, F. A. In "Advances in Inorganic and Bioinorganic Mechanisms"; Sykes, A. G., Ed., Academic Press: London, 1982; Vol. 1, pp 65–120.

(26) Adman, E. T.; Sieker, L. C.; Jensen, L. H. *J. Biol. Chem.* **1973**, *248*, 3987.

(27) Watenpaugh, K. D.; Sieker, L. C.; Jensen, L. H. *J. Mol. Biol.* **1979**, *131*, 509.

(28) Smith, W. W.; Burnett, R. M.; Darling, G. D.; Ludwig, M. L. *J. Mol. Biol.* **1977**, *117*, 195.

(29) Adman, E. T.; Jensen, L. H. *Isr. J. Chem.* **1981**, *21*, 8.

(30) Jung, J.; Tollin, G. *Biochemistry* **1981**, *20*, 5124.

(31) Tanford, C. *Science (Washington, D.C.)* **1978**, *200*, 1012; *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 4175.

State-Selective Photochemistry from the Higher Excited States of Methylbenzaldehydes: Intermolecular vs. Intramolecular Hydrogen Abstraction

Irwin C. Winkler[†] and David M. Hanson*

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11794. *Received August 15, 1983*

Abstract: We have found that the hydrogen abstraction reactions of 2,4,5-trimethylbenzaldehyde and 2,4-dimethylbenzaldehyde, each isolated in durene single crystals, do not occur via either of the lowest two triplet states but take place primarily through excited states above the singlet origins. The reactions can be directed to give different products by changing the wavelength of the photolyzing light.

Since Hammond and co-workers demonstrated the triplet nature of the photoreactive state responsible for the hydrogen abstraction reactions of aromatic carbonyl molecules,[1] much work has been done correlating the orbital nature (e.g., $n\pi^*$, $\pi\pi^*$) of the lowest triplet state of these molecules with their photoreactivity.[2] It is now generally believed that the reactions proceed via the lowest triplet state, T_1, and that $n\pi^*$ states are far more reactive than $\pi\pi^*$ states since the electron density at the carbonyl oxygen is decreased when an $\pi^* \leftarrow n$ transition occurs.[2a] The photoreactivity of aromatic carbonyls having a $T_1(\pi\pi^*)$ state has been attributed to configurational mixing[2b] with, or thermal population[3] of, a close lying second triplet state, T_2, which is predominantly $n\pi^*$ in character. In some systems, the extent of configurational mixing is not sufficient to explain the photoreactivity.[3] 2,4,5-Tri-

---

[†] Current address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

(1) (a) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789–2794 (1961); (b) G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795–2799 (1961); (c) G. S. Hammond and P. A. Leermakers, *ibid.*, **84**, 207–211 (1962).

(2) (a) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Am. Chem. Soc.*, **89**, 5466–5468 (1967); (b) N. C. Yang and R. L. Dusenbery, *ibid.*, **90**, 5899–5900 (1968); (c) P. J. Wagner, M. J. May, A. Hang, and D. R. Graber, *ibid.*, **92**, 5269–5270 (1970), and references therein.

(3) S. W. Mao and N. Hirota, *J. Mol. Phys.*, **27**, 327–336 (1974).

0002-7863/84/1506-0923$01.50/0

methylbenzaldehyde in a durene host crystal is known[4,5] to undergo hydrogen abstraction reactions characteristic of a triplet $n\pi^*$ state, and the activation energy for these reactions is about the same as the energy difference between T_2 and the $T_1(\pi\pi^*)$ state.

In a previous communication, however, we reported that the second triplet state of 2,4,5-trimethylbenzaldehyde isolated in a durene single crystal (TMB/D) has a charge distribution with a dipole moment characteristic of a $\pi\pi^*$ state, although the phosphorescence excitation spectrum has an intensity distribution characteristic of an $n\pi^*$ state.[6] These results were interpreted in terms of a second triplet state of extensively mixed orbital character, $T_2(n\pi^*)$ with $T_1(\pi\pi^*)$.

In order to determine whether hydrogen abstraction reactions occur from T_2 in spite of this mixing, or in fact proceed from other states, we measured the relative yields of the products obtained when exciting directly into the triplet and singlet manifolds. The same measurements also were made on 2,4-dimethylbenzaldehyde in a durene single crystal (DMB/D) since DMB has a second triplet state that is clearly $n\pi^*$ in character.[7] We found that *hydrogen abstraction does not occur from the lowest triplet states of either system.*

This result is not due to the effect of interstate coupling on the charge distribution and chemical reactivity since the outcome is the same for both TMB and DMB. Rather, the observations provide evidence that reaction mechanisms found for molecules in liquids cannot be generalized reliably to solid matrices. To our knowledge this is the first report of an attempt to cause a hydrogen transfer reaction by directly exciting a low-lying triplet state. The intramolecular reaction was detected after irradiation 3300 cm^{-1} above the $S_1(n\pi^*)$ origin, and the intermolecular reaction was observed after irradiation at a wavelength that excites the $S_2(\pi\pi^*)$ origin.

Experimental

Single crystal samples of TMB/D and DMB/D (7 and 1% by weight, respectively) were prepared by the Bridgman technique as previously described.[7,8] Crystals were cut to give a sample size of 2 mm × 2 mm × 1 mm and were then mounted on the cold finger of an Air Products cryorefrigerator. An O-ring was placed around the sample which was then covered with a thin quartz window to prevent sublimation. A thin copper plate with a 1.5-mm-diameter orifice was screwed onto the cold finger to secure the sample assembly and mask off a portion of the crystal for observation.

The optics were arranged such that the photolyzing and probe beams illuminated the same part of the sample. Excitation into the T_2 origin and S_1 origin of each system was accomplished with a Molectron UV 400/DL200 nitrogen pumped dye laser tuned to the absorption maxima of these bands: 406.1 and 379.4 nm, respectively, for TMB/D, and 407.2 and 380.5 nm, respectively, for DMB/D. The nitrogen laser (337.1nm) was used to excite approximately 3300 cm^{-1} above the S_1 origin, and a 75-W Xenon lamp filtered with a $NiSO_4$ solution filter and a Schott UG-11 glass filter giving a band pass from 290.3 nm to 359.7 nm with a maximum at 323.8 nm, was used to excite the second singlet states of these molecules (313.0 nm for TMB, 303.0 nm for DMB).[4,5] To ensure that essentially the same number of excited states were being produced per second at all the excitation wavelengths used for photolysis, the output from the different sources (the filtered Xenon lamp, the nitrogen laser, and the dye laser) was attenuated until the resulting phosphorescence intensity produced by each source with the sample at 15 K was the same as that produced with the dye laser tuned to the T_2 resonance. This normalization procedure is based on the assumption that the low-temperature quantum yields for intersystem crossing and phosphorescence are near unity and do not vary much with wavelength, as is the case for similar systems under these conditions.[9] Because of the large effect observed, vide infra, the use of this assumption to come to qualitative conclusions is reasonable. Phosphorescence was detected with a 1-m Spex 1704X spectrometer equipped with an EMI 6256 B photomultiplier tube in a refrigerated housing. During the experiment, the intensities of both the xenon lamp and the laser were monitored.

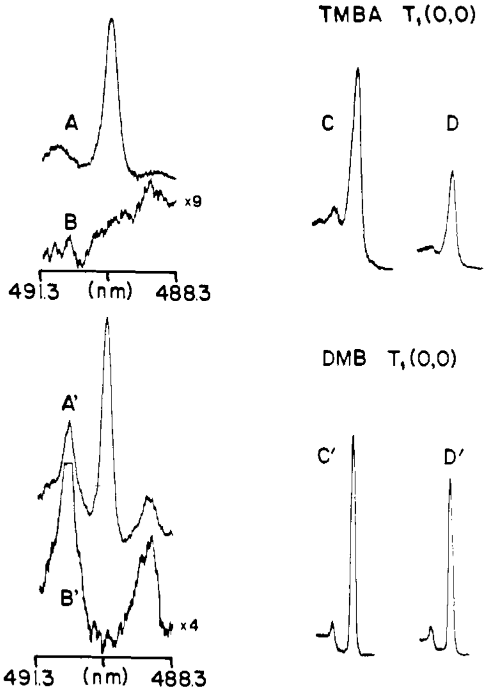

Figure 1. Spectra B and B′ are emission spectra in the region of the duryl radical fluorescence origin observed before photolysis and show only a part of the aldehyde phosphorescence of TMB and DMB, respectively. Spectra A and A′ are traces of the same wavelength region after photolysis at 313.0 and 303.0 [S_2 origins of TMB and DMB, respectively] and show the prominant duryl radical band at 489.8 nm. Spectra C and C′ show the $T_1(0,0)$ bands of TMB and DMB, respectively, before photolysis. Spectra D and D′ are the same bands after photolysis at 313.0 and 303.0 nm. No change in spectra B, C, B′, or C′ was observed when photolysis was attempted by exciting the T_2 or S_1 origins of these systems. Photolysis was done at 298 K, and spectra were recorded at 15 K.

The appearance of the characteristic green duryl radical fluorescence[10] at 489.8 nm and the disappearance or decrease in the TMB or DMB phosphorescence at 414.0 or 408.8 nm, respectively,[8] documented the occurrence of intermolecular hydrogen abstraction. The disappearance of the aldehyde phosphorescence accompanied by the appearance of a broad band in the absorption spectrum peaking at 405.0 nm indicated that another reaction had occurred, which has been attributed to intramolecular enol formation.[4] This absorption band was very prominent as the resulting yellow color could be observed visually.

The photolysis was done with the sample at 298 K because the reactions are known to be thermally activated.[4,5] Luminescence spectra were obtained with the sample at 15 K in order to resolve the features of interest. Absorption spectra were recorded at room temperature by using a Cary 14 spectrophotometer.

Results

Emission spectra in the region of the TMB, DMB, and duryl radical origins before and after room-temperature photolysis are shown in Figure 1. Before photolysis the only low-temperature emission observed in the region of the duryl radical fluorescence origin was the green tail of the aldehyde phosphorescence (spectra B and B′). After 1 h of laser irradiation at the wavelengths of the T_2 and S_1 origin bands with the samples at 298 K, no duryl radical fluorescence or change in aldehyde phosphorescence was observed. After 1 h of exposure to the UV light from the nitrogen laser, the TMB phosphorescence decreased by 40 ± 10% and the DMB phosphorescence decreased by 30 ± 10% but without the appearance of duryl radical emission. This decrease is similar to that seen in Figure 1 when comparing spectrum C with spectrum D and spectrum C′ with spectrum D′. The loss of aldehyde

---

[4] E. Migirdicyan, A. Despres, V. Lejeune, and S. Leach, *J. Photochem.*, **3**, 383–393 (1974/1975).

[5] E. Migirdicyan, *J. Chem. Phys.*, **55**, 1861–1870 (1971).

[6] I. C. Winkler and D. M. Hanson, *J. Am. Chem. Soc.*, **103**, 103–104 (1981).

[7] I. C. Winkler and D. M. Hanson, *J. Chem. Phys.*, **78**, 4836–4839 (1983).

[8] I. C. Winkler and D. M. Hanson, *J. Chem. Phys.*, **76**, 5739–5745 (1982).

[9] S. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Inc., Englewood Cliffs, New Jersey, p 244, 1969.

[10] S. Leach and E. Migirdicyan, *Chem. Phys. Lett.*, 1, 21–22 (1967).

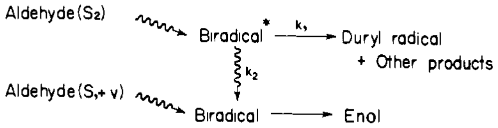

Figure 2. Pathways for the formation and relaxation of the biradical intermediate.

emission was accompanied by the development of yellow color in the crystal and a broad band in the absorption spectrum peaking at 405.0 nm. These effects were more pronounced in TMB than DMB, probably due to the greater TMB sample concentration. Duryl radical fluorescence was observed (spectra A and A′) along with a 50 ± 10% loss of TMBA phosphorescence and a 22 ± 10% loss of DMB phosphorescence (spectra D and D′) only after excitation into the second singlet states of these molecules with the filtered Xe lamp.

We traced the wavelength region of the duryl radical fluorescence origin in order to arrive at an estimate of the relative photochemical quantum yields. The noise level at maximum sensitivity was taken as the duryl radical emission intensity when the duryl radical band could not be seen (see spectra B and B′). We estimate the quantum yields of duryl radical production from TMB/D to be at least 125 ± 25 times greater when exciting S_2 than when exciting the $T_2(0,0)$, $S_1(0,0)$, $S_1(0,0 + 3300\ \text{cm}^{-1})$ states, and at least 58 ± 12 times greater in the case of DMB/D. These estimates take into account the intensity of the duryl radical band that grows in after photolysis (via S_2 excitation) and the difference in detection sensitivity used to trace the spectra in Figure 1C, but these are only *lower limits* since they are limited by our detection sensitivity for the duryl radical.

No yellow color was observed when duryl radicals were produced, and the samples showed no signs of cracking or sublimation at the end of the experiments. Other workers, using a more intense photolyzing light source, have observed enol formation when exciting the S_2 state of these systems.[4] A linear dependence, to within an uncertainty of 4%, of the phosphorescence intensity on the excitation intensity was found, thus, there is no evidence for multiphoton absorption during laser excitation at any of the photolysis wavelengths.

Discussion

These observations indicate that, contrary to previous assumptions,[4,5] the hydrogen abstraction reactions of TMB/D and DMB/D take place primarily through higher excited states with little or no photoreduction occurring through the lowest triplet states and that the intermolecular reaction requires a higher energy excitation than the intramolecular reaction. Other workers have observed hydrogen abstraction from states other than the lowest triplet state of benzaldehyde, acetophenone, and benzophenone in solid matrices.[11,12] For these cases, it has been suggested that the radical intermediates formed in the lowest triplet state of the reactant cannot separate in the matrix fast enough to prevent recombination. Thus, higher energy excitation involving the absorption of two photons is necessary to create the radicals in an excited state with enough energy to overcome the barriers to rotational and/or translational diffusion or to hydrogen abstraction. For the methyl-substituted benzaldehydes, the upper state photochemistry occurs following absorption of a single photon.[4,5]

A mechanism involving a biradical intermediate has been proposed by Migirdicyan et. al.[13] to account for both the inter- and intramolecular hydrogen abstraction reactions of the methylbenzaldehydes. According to this mechanism, absorption of a photon creates an excited state in which the aldehyde group rotates making possible a cyclic six-membered transition state. This rotation is necessary because in the durene host, the oxygen of the aldehyde lies in the plane of the benzene ring but is directed away from the *o*-methyl group.[14] A biradical is then formed by intramolecular hydrogen abstraction and can subsequently undergo electronic rearrangement to form the enol, or it can abstract a hydrogen from a neighboring durene molecule thus creating a duryl radical. The evidence cited to support this view is the absence of duryl radical production when the photolysis of 3,4-dimethylbenzaldehyde is attempted. However, for this compound, the absence of an *o*-methyl group also may cause the aldehyde to occupy a different position in the durene lattice such that the oxygen atom is no longer in a favorable position for hydrogen abstraction, or in other compounds the *o*-methyl group may serve to lock the aldehyde group into a reactive conformation.

Since we have observed that the intermolecular reaction occurs at a shorter photolysis wavelength than the intramolecular reaction, the biradical would have to be created in a higher state of excitation to be consistent with the idea of a common intermediate. Consideration of the possible relaxation routes, shown in Figure 2, open to the "excited biradical" argues against this mechanism. In order to produce a duryl radical, the "excited biradical" would have to abstract a hydrogen from a durene molecule before relaxing to a lower state via electronic or vibrational relaxation; i.e., the condition $k_1 > k_2$ would have to be satisfied. A more likely explanation is that the different reactions take place through different mechanisms, involving different electronic configurations, different intermediates, or possibly different conformations of similar intermediates in the crystal site. In the absence of further information we are unable to determine the nature of the photoreactive states of the aldehydes.

Considering the thermal activation required for these photoreactions,[5] the existence of intermediates formed by aldehyde group rotation seems reasonable. Previously this activation energy was thought to arise from the need to thermally populate the reactive $T_2(n\pi^*)$ state from the lower $T_1(\pi\pi^*)$ state.[15,16] Since we did not observe any photoreaction when populating the $T_2(n\pi^*)$ state directly, we conclude the activation barrier is not caused by the $T_1 - T_2$ energy spacing in this case.

In summary, we have found that the hydrogen abstraction reactions of TMB/D and DMB/D take place through excited states above the origin of the singlet manifold and that the reaction can be directed to give either the intermolecular product, the duryl radical, or a species believed to be an intermolecular product, an enol,[4] by changing the photolyzing wavelength.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. Hydrogen, 1333-74-0; 2,4,5-trimethylbenzaldehyde, 5779-72-6; 2,4-dimethylbenzaldehyde, 15764-16-6; durene, 95-93-2; duryl radical, 15220-27-6.

---

(11) H. Muria and K. Obi, *J. Phys. Chem.*, **79**, 2446–2450 (1975).

(12) C. Bräche, D. M. Burland, and G. C. Bjorklund, *J. Phys. Chem.*, **85**, 123–127 (1981).

(13) V. Lejeune, A. Despres, and E. Migirdicyan, preprint.

(14) M. Sharnoff, *Mol. Cryst.*, **5**, 297 (1969).

(15) P. J. Wagner in "Rearrangements in Ground and Excited States", Paul de Mayo, Ed., Academic Press, New York, p 405, 1980.

(16) M. V. Encina, E. A. Lissi, E. Lemp. A. Zanocco, and J. C. Scaiano, *J. Am. Chem. Soc.*, **105**, 1856–1860 (1983).