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# ELECTRONIC EFFECTS IN THE SEMICONDUCTOR - PHOTOCATALYZED OXIDATIVE CLEAVAGE OF OLEFINS

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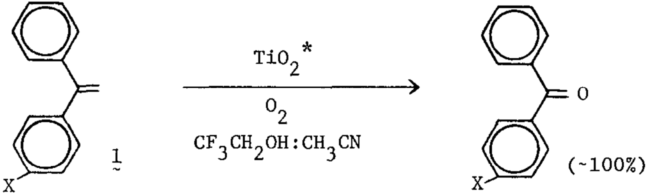
Abstract: A linear Hammett plot ($\rho^+ = -0.56$) is obtained from relative rates of $TiO_2$ powder sensitized oxidative cleavage of para-substituted 1,1-diphenylethylenes, better correlation having been observed with $\sigma^+$ parameters than with $\sigma$.

Despite intense interest in the application of semiconductors as photosensitizers for water cleavage and for solar energy conversion, the use of these photocatalysts in effecting organic transformations has been much less extensively scrutinized. Although irradiated semiconductor powders have been used to initiate cycloreversions, additions,[1] and oxidative decarboxylations,[2] photocatalyzed oxidations represent the main exceptions to this generalization.[3,4] While it has been established that primary formation of the hydroxy radical is mechanistically significant when these irradiations are conducted in aqueous suspension,[5] little mechanistic information is now available concerning the identity of intermediates formed from organic substrates at the surface of semiconductor powders irradiated as nonaqueous suspensions.

Our recent observation of photoinduced oxidative cleavage by this route, eq. 1,



a)X=H
b) =OMe
c) =Me
d) =Cl
e) $=NO_2$

(1)

has prompted us to investigate the effect of electronic perturbation of the olefinic substrate on the reaction efficiency. Olefins 1b - 1e, prepared by methylenation of the corresponding benzophenones with methylene triphenylphosphorane,[6] were found to cleave oxidatively under the previously described conditions,[4] giving rise, like the parent 1a, to near quantitative yields of benzophenones 2. Standard competition experiments[7] between pairs of the olefins (within the first 20% of conversion of starting materials) were conducted to establish the relative rates of oxidative cleavage within the series. Relative rates for the disappearance of reactant and for the formation of product gave identical results at low conversion. The relative rates for formation of 2, together with the oxidative peak potentials observed for the cyclic voltammetric waves of 1a - 1e, are listed in Table 1.

Table 1. Oxidative Peak Potentials and Relative Rates for $TiO_2$-Photocatalyzed Oxidative Cleavage of 1.

| Cmpd. | $E_{pa}$ (V vs. SCE) | k( 1 )/k( 1a ) |
|---|---|---|
| 1a | 1.75 | 1.00 |
| 1b | 1.30 | 2.99 |
| 1c | 1.61 | 1.45 |
| 1d | 1.72 | 0.98 |
| 1e | 1.96 | 0.49 |

A linear Hammett plot can be constructed from the kinetic data from Table 1 and $\sigma^+$ substituent parameters (Figure 1). Better linearity (correlation coefficient (r) = 0.97, $\rho^+$ = -0.56) is observed with $\sigma^+$ than with $\sigma$ (r = 0.83, $\rho$ = -0.64). Similar correlation (r = 1.00, $\rho^+$ = -0.37) is observed in analogous competition experiments with p-substituted styrenes.[8] This plot constitutes the first quantitative study of substituent effects on relative rates of organic photooxidations catalytically initiated on a heterogeneous surface.

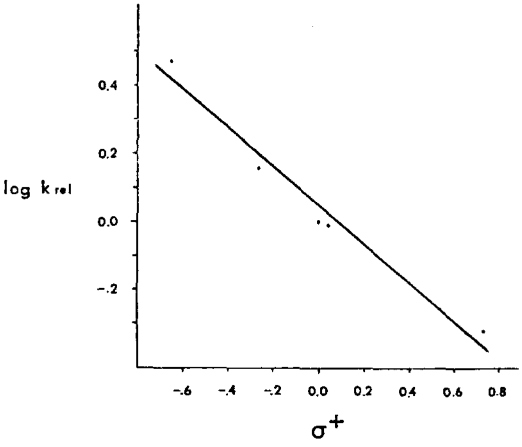


Figure 1. Hammett plot for $TiO_2$-photocatalyzed oxidative oxidative cleavage of 1.

The currently accepted mechanism for semiconductor powder photocatalysis involves the generation of an electron-hole pair in the primary photoprocess. Capture of the photogenerated hole by an adsorbed oxidizable substrate and/or the electron by a reducible substrate lead to net chemical reaction. For the reactant shown in equation 1, hole capture should give rise to an olefinic radical cation. That such an intermediate may be involved is consistent with our previously reported transient spectroscopic detection of the stilbene radical cation[9] as well as with the negative $\rho$ value and effective correlation with $\sigma^+$ shown in Figure 1.

The magnitude of the $\rho^+$ value, however, is more consistent with a radical than an ionic process in the rate determining step. Nearly no information regarding $\rho$ values for reactions involving the formation of cation radicals is available in the literature. One such claim, a kinetic study of the single electron oxidation of organic sulfides catalyzed by iron tetraphenylporphyrin,[10] reports a $\rho^+$ value of -0.26, while other reactions thought to proceed via rate determining single electron oxidation give poor correlation with electronic demands of the substituent.[11] Radical anion formation, i.e., rate determining single electron reduction, has a reported $\rho$ value of +1.50.[12] While we feel a priori that the development of substantial positive charge accompanying formation of a radical cation should lead to a larger negative slope than observed in Figure 1, we do observe that a nearly identical slope ($\rho^+ = -0.46$, $r = 0.92$) is observed if the oxidative peak potentials for <u>1a</u> - <u>1e</u> are similarly plotted. In both cases, the low $\rho$ value may reflect near diffusion-controlled electron transfer from an adsorbed olefin to the photogenerated hole formed at the surface of the irradiated powder, followed by slower electron transfer equilibration of the competing olefin with this photogenerated radical cation. Thus, either the slopes of Hammett plots for rate-determining radical ion processes are much lower than those observed for closed-shell cation or anion formation or the major fraction of positive charge development in our photocatalysis occurs at other than the rate determining step.

The low quantum efficiency observed in these reactions[9] surely indicates that pathways for the rapid deactivation of the excited semiconductor exist. Whether these pathways involve electron-hole pair recombination within the semiconductor or rapid back electron transfer from the adsorbed oxidized olefin is at present unknown. If the latter process were significant, one might reasonably expect to detect formation of transient radical ions and yet to characterize the reactive transition state as involving little further development of positive charge. Should such adsorbed radical cations persist on the surface of the irradiated semiconductor,[13] redox equilibration of the oxidized forms of the olefin, as suggested above, might obtain. In any case, it is interesting to note that the reported $\rho$ values for the decomposition of dioxetanes (-0.24),[14] permissible intermediates in our photocatalyzed oxidative cleavage,[4] or for the reaction of olefins with singlet oxygen (-0.82),[15] a species previously shown not to be involved in these photocatalyses,[4] are comparable to that found here.

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## References

1. K. Okada, K. Hisamitsu, and T. Mukai, Chem. Comm. 941 (1980); R.A. Barber, P. deMayo, and K. Okada, private communication.

2. B. Kraeutler and A.J. Bard, Nouv. J. Chem. **3**, 31, 1979.

3. See, inter alia, M. Fujihara, Y. Satoh, and T. Osa, Nature **293**, 206 (1981); M. Fujihara, Y. Satoh, and T. Osa, J. Electroanal. Chem. **126**, 277 (1981); H. Kasturirangan, V. Kamakrishnan, and J.C. Kuriacose, J. Catal. **69**, 216 (1981); J. Cunningham, D.J. Morrisseu, and E.L. Goold, J. Catal. **53**, 68 (1978); T. Kanno, T. Oguchi, H. sakuragi, and K. Tokumaru, Tetrahedron Lett. 467 (1980); J.W. Pavlik and S. Tantayanon, J. Am. Chem. Soc. **103**, 6755 (1981).

4. M.A. Fox and C.C. Chen, J. Am. Chem. Soc. **103**, 6757 (1981).

5. I. Izumi, W.W. Dunn, K.O. Wilbourn, F.R.F. Fan, and A.J. Bard, J. Phys. Chem. **84**, 3207 (1980).

6. G. Wittig and U. Schollkopf, Chem. Ber. **87**, 1318 (1954).

7. These competition experiments were conducted by irradiating ( $\lambda > 350$ nm) $TiO_2$ powder suspended in an aerated acetonitrile solution containing a mixture of two olefins of known, usually equal, concentration. The experimental conditions for the irradiation have been reported elsewhere.[4] Product appearance and substrate consumption were monitored by gas-liquid chromatography and kinetic analysis was conducted by standard procedures: H.Watanabe, N. Ohsawa, M. Sawai, Y. Fukasawa, H. Matsumoto, and Y. Nagai, J. Organomet. Chem. **93**, 173 (1975).

8. M.A. Fox and C.C. Chen, unpublished results. The lower chemical yield of the product of oxidative cleavage of the styrenes made quantation of the kinetics for these systems more difficult. The reported values were obtained by monitoring the consumption of olefin.

9. M.A. Fox, B.A. Lindig, and C.C. Chen, J. Am. Chem. Soc. **104**, 5828 (1982).

10. S. Oae, Y. Watanabe, and K. Fujimori, Tetrahedron Lett. 1189 (1982).

11. E. Pelizzetti and R. Giordano, J. Chem. Soc., Dalton Trans. 1516 (1979).

12. O. Ito, M. Matsuda,H. Tagaya, and T. Aruga, J. Am. Chem. Soc. **103**, 5484 (1981).

13. This redox equilibration is also consistent with the nearly complete kinetic domination of 1f (X = $NMe_2$, $E_{pa}$ = 0.61 V vs. SCE) in competition with 1a - 1e. Since different, more complex reactivity is observed with 1f than with 1a - 1e, its chemistry is not discussed here.

14. A. P. Schaap, Steven D. Gagnon, and K.A. Zaklika, Tetrahedron Lett. **23**, 2943 (1982).

15. K.A. Zaklika, B. Kaskar, and A. P. Schaap, J. Am. Chem. Soc. **102**, 386 (1980).

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