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Preliminary communication

PHOTOREACTIONS OF FERROCENE WITH VISIBLE LIGHT IN MICELLAR SOLUTION

DONNA M. PAPSUN, J. KERRY THOMAS* and JAY A. LABINGER*
Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 (U.S.A.)

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Summary

Photooxidation of ferrocene by CCl_4 and other organic oxidants is brought about by visible light in micellar solutions.

Photoinduced electron transfer reactions of organic molecules in micellar solutions have been the subject of extensive study [1]. We have been interested in the behavior of organo-transition metal compounds under these conditions, since the (generally) greater reducing power and (frequently) strong absorptions in the visible region of such species offer intriguing possibilities for enhanced or novel reactivity. We here report preliminary findings concerning the most familiar organo-transition metal compound: ferrocene.

It has long been known that ultraviolet light induces oxidation of ferrocene (Fc) to ferrocenium (Fc^+) by halocarbons such as CCl_4, apparently resulting from excitation of a charge transfer to solvent band around 300 nm; little or no effect of visible light has been observed [2]. We find that visible light is capable of effecting this reaction in micelles. Thus a solution containing Fc (1 m*M*) and CCl_4 (10—40 m*M*) in 0.1 *M* aqueous cetyltrimethylammonium chloride (CTAC), on irradiation (tungsten lamp, with 3—73 cutoff filter, giving zero transmittance below 400 nm) showed gradual formation of Fc^+. The latter was determined spectrophotometrically, using the characteristic peak at 620 nm. The rate of Fc^+ formation increases linearly with both $[CCl_4]$ and [Fc] (Fig. 1). The quantum yield is very low, approximately 4×10^{-5} for $[CCl_4]$ 40 m*M*. (Total light incident between 400—500 nm, 1.2 W; average light absorbed over this range, 16%; 10^{-7} mol Fc^+ produced in 1 h.) No significant formation of Fc^+ was detected on irradiation in neat CCl_4 or in CCl_4/EtOH under these conditions, nor in the micelle solution without irradiation.

Part of the micelle effect may be due to the micelle's ability to organize Fc and the electron acceptor in close proximity [3], although this alone cannot

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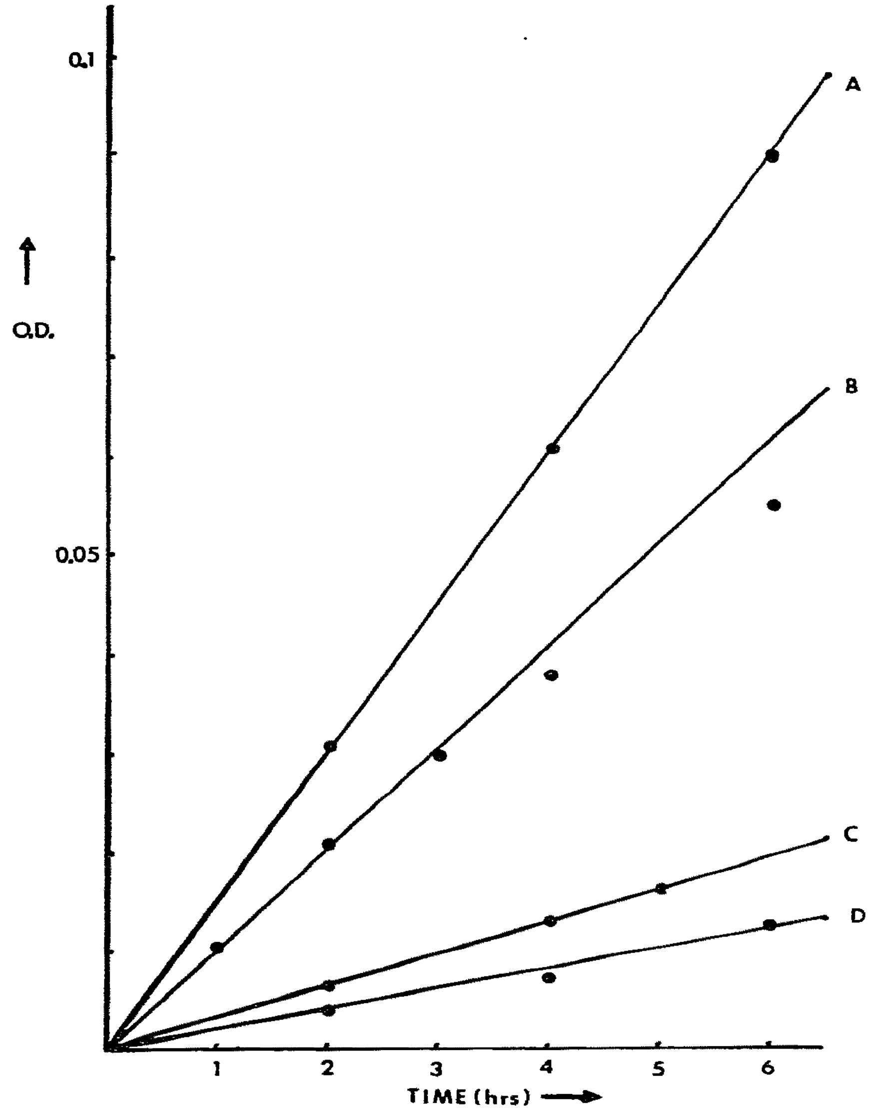

Fig. 1. Optical density at 620 nm vs. time of irradiation of Fc/CCl$_4$ in 0.1 *M* CTAC. [Fc] 1.5 m*M* (A), 1.0 m*M* (B—D); [CCl$_4$] 40 m*M* (A,B), 20 m*M* (C), 10 m*M* (D).

explain reactivity greater than in neat CCl$_4$. It appears likely that the major role of the micelle is to solubilize Fc in a highly polar medium, providing conditions favoring formation of ionic products. We measured the cyclic voltammetric $E_{1/2}$ of Fc at 0.205 V (vs. SCE) in CTAC, comparable to that observed for Fc$^+$ in aqueous solution and nearly 0.2 V more favorable for oxidation than in organic solvents [4]. Thus the Fc excited state, unreactive under normal conditions, might be sufficiently reducing here to give up an electron to CCl$_4$, albeit with low efficiency. Alternatively, reaction could be due to a CTTS transition of low intensity (because of the low [CCl$_4$]; we were unable to observe any change in the Fc absorption spectrum), explaining the low quantum yield, and strongly red-shifted in this highly polar medium. We attempted to detect the excited state by laser flash photolysis of an Fc-CTAC solution (excitation at 485 nm, Candela dye laser with LD-490 dye) but no transient absorption changes were detected, indicating an excited state lifetime of <100 ns.

Other micellar solutions such as cetyltrimethylammonium bromide and sodium dodecyl sulfate give similar results, although the presence of impurities leads to erratic behavior. (It should be noted that the commonly-used technique of sonication to speed dissolution can itself effect reaction even without irradiation.) Since Fc^+ is known to undergo photodecomposition under certain conditions [2], we examined it as well: no decrease in $[Fc^+]$ was observed after several hours visible irradiation of a CTAC solution. However, excitation of Fc^+ solutions at 347 nm (Q-switched, frequency doubled, Korad pulsed ruby laser) gives completely reversible formation of a new transient species with an absorption maximum at 390 nm. The intensity and lifetime (ca. 2—300 μs) depend strongly on Fc^+ concentration, pH (quenched by H^+) and medium (no signal in plain water); the signal appears to arise from excitation of an Fc^+-anion complex rather than of Fc^+ itself, as transient bleaching is observed around 350 nm but not at 620 nm.

Non-halocarbon electron acceptors also can oxidize Fc. Solutions of Fc and either sodium anthraquinone-1-sulfonate or 9,10-dicyanoanthracene (DCA) in CTAC give Fc^+ on visible irradiation; again, no reaction is found in EtOH. We also find that Fc quenches DCA fluorescence in CTAC solution. Fc is known to quench fluorescence of a wide range of organic excited state triplets; there has been some debate over whether energy or electron transfer is involved [5]. We see here that net electron transfer can be observed, at least under strongly polar conditions; since both Fc and DCA absorb in the visible, it is not clear whether the observed redox reaction and fluorescence quenching are due to the same photoprocess. Further work is needed to resolve this question.

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