

Photochemistry of Radical Ions

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Irradiation with light of a suitable wave-length in the visible region of ion radicals, produced during a cyclic voltammetric experiment, leads to an enhancement of the peak current. The species produced is a more reactive electron transferring reagent than the parent ion radical. The preliminary results suggest that a divalent ion is produced.

Different combinations of photochemistry and electrochemistry have been reported.¹⁻¹⁰ Electrochemical monitoring of intermediates generated by photolysis has been used in several investigations,¹⁻⁵ and a rotating photo-electrode, akin to the ring-disk electrode, has been applied to photochemical studies.^{6,7}

Of preparative interest is the photobenzidine rearrangement of electrochemically generated tetraphenylhydrazine cation radicals⁸ and the electrochemical regeneration of the oxidizing agent, a quinone, in the photochemical oxidation of several substrates.⁹ Furthermore, the photoassisted synthesis at a semiconductor electrode has been applied to the oxidation of carboxylates at an n-type TiO_2 -electrode.¹⁰

Anion radicals have been investigated by flash photolysis,¹⁰⁻¹⁵ but the photochemical reactions of ion radicals have in general not received much attention. Some results from an investigation of the photochemical behaviour of electrolytically generated ion radicals are reported below.

An argon laser was used as light source, and pyrene anion radical ($I^{\cdot-}$) was chosen as a model substance, because it has a strong absorption band¹⁶ at the wave length of the argon laser (about 500 nm) and pyrene (I) has a negligible absorption in that region. A further advantage of $I^{\cdot-}$ is that it has been investigated by flash photolysis.¹¹⁻¹³

Besides $I^{\cdot-}$ perylene anion radical ($2^{\cdot-}$) and thianthrene cation radical ($3^{\cdot+}$) have also been included in the investigation.

RESULTS

Irradiation of the microelectrode (a planar, mercury-covered, circular platinum electrode, diameter 0.5 mm) with an argon laser during a cyclic voltammetric experiment of I in dimethylformamide (DMF) containing tetrabutylammonium iodide (TBAI) or fluoroborate (TBAF) produced an enhancement of the cathodic current on the forward scan and a diminishing of the anodic current on the reverse scan; at sufficient light intensities (I) the anodic peak of $I^{\cdot-}$ disappeared (Fig. 1).

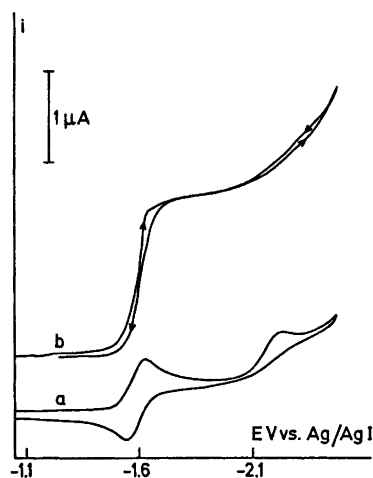


Fig. 1. Cyclic voltammetric curves ($v = 40 \text{ mV s}^{-1}$) of pyrene ($5 \times 10^{-3} \text{ M}$) in DMF/0.1 M TBAI.

a, Without light; b, with light ($\lambda = 5145 \text{ \AA}$).

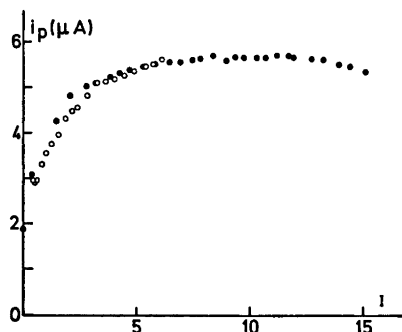


Fig. 2. i_p vs I (light intensity at $\lambda = 4880 \text{ \AA}$) of pyrene (10^{-2} M) in DMF/0.1 M TBAI, $v = 40 \text{ mV s}^{-1}$, intensity relative measurement (see experimental). ●, ○, experiments on different days.

The dependence of the peak height (i_p) on I at sweep rates (v) equal to 40 mVs^{-1} is shown in Fig. 2. i_p grows initially with I , but di_p/dI diminishes with I and approximates 0 at $i_p \approx 2.8 i_{p_0}$, where i_{p_0} is the peak height in the absence of light. At very low v (10 mVs^{-1}) the limiting value of i_p is larger than $3 i_{p_0}$.

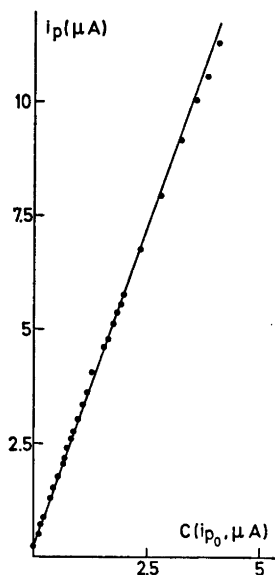


Fig. 3. Dependence of peak height (i_p) under influence of light ($\lambda = 4880 \text{ \AA}$) on concentration of pyrene in the range 0 to $5 \times 10^{-2} \text{ M}$ of pyrene in DMF/0.1 M TBAI. As a measure for the concentration is taken i_{p_0} , the peak height in the absence of light ($v = 40 \text{ mV s}^{-1}$).

A measurement of the dependence of i_p on λ at constant I was not possible using an argon laser, as the absorption band of I^- covers the wave-length region of the laser. It was found, however, that I^{2-} , which has an absorption minimum close to 500 nm , gave a much smaller increase in i_p for a given I than I^- did.

The relative increase of i_p at a constant I depended on v , the increase being largest at low v . The resulting i_p was thus only slightly dependent of v .

At constant I and v the ratio i_p/i_{p_0} was found to be independent of the concentration of I (Fig. 3); this argues against the observed effect being due to light induced thermal convection.

Visual examination of the electrode was made during a CV-experiment at relatively low I . At potentials anodic to the reduction of I the green light was reflected from the electrode; at E close to E_p the reflection disappeared due to the absorption of the light by I^- . At the potential where I^- was reduced to I^{2-} a red corona was observed around the electrode. The light emission might be a fluorescence of pyrene dianion, but the phenomenon has not yet been investigated in detail. It might be mentioned that pyrene dianion has an absorption maximum close to 600 nm .¹³

It has previously been found¹⁷ that catalytic currents involving electron transfer in solution can be observed in voltammetry of compounds (A, e.g. aromatic hydrocarbons) giving relatively stable anion radicals in the presence of other compounds (BX, e.g. aromatic halides) producing unstable anion radicals. It was also found that a large difference in the reduction potential between that of A and that of BX resulted in a slow electron transfer from A^- to BX.

Addition of chlorobenzene (Cl) to a solution of I in DMF/0.1 M TBAF caused very little change in the voltammetric curves. Irradiation produced an enormous increase (Fig. 4) in the rate of electron transfer to Cl ; an increase in i_p can be observed not only with a laser, but even with an ordinary halogen car light.

If the BX compound is aliphatic, the electron transfer from A^- to B \cdot competes with the coupling to AB^- ; the coupling reaction removes the catalyst A from the catalytic circle and causes the increase in the peak height to reach a limiting value. The lower this value is, the more efficient the coupling reaction

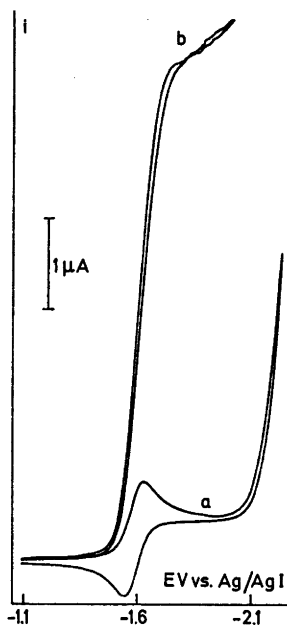


Fig. 4. Cyclic voltammetric curves of pyrene (2×10^{-3} M) in DMF/0.1 M TBAI and *m*-chlorotoluene (8×10^{-2} M). a, Without light and b, with light ($\lambda = 4880 \text{ \AA}$) ($v = 40 \text{ mV s}^{-1}$).

competes with the catalytic reduction.

The voltammetric curve of *I* is only slightly affected by addition of *t*-butylchloride (5); irradiation of *I* in the presence of 5 resulted in an increase in i_p close to two times i_{p_0} . *I* is thus very efficiently removed from the catalytic circle.

Perylene anion radical ($2^{\cdot-}$) has an absorption minimum close to 500 nm.¹⁶ Irradiation during a CV-experiment of 2 produced an increase both in the first and second peakheight and the relative increase was similar in both cases.

Thianthrene (3) cation radical has $\lambda_{\text{max}} = 546 \text{ nm}$.¹⁹ A CV-experiment of 3 showed that irradiation produced an increase in the anodic peak-height and a diminishing of the cathodic peak on the reverse scan in a way analogous to that of *I*.

An experiment was designed to test whether the influence of the light was dependent on illumination of the electrode or if it was confined to the absorption of light by the ion radicals. The light beam was aimed parallel to the plane of the electrode and very close to it.

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It was found that i_p increased on irradiation although the increase for a given *I* was smaller than when the light beam was at a right angle to the electrode.

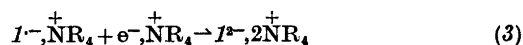
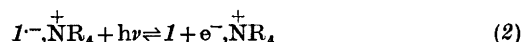
DISCUSSION

The difference in response between *I* and 2 at λ about 500 nm suggests that the anion radical rather than the parent compound is involved in the observed phenomenon, as $I^{\cdot-}$ absorbs light at $\lambda \sim 500 \text{ nm}$, whereas $2^{\cdot-}$ does so only to a much smaller degree.

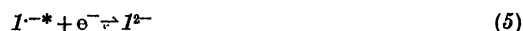
From the flash photolysis experiments of the ion pair $I^{\cdot-}, \text{Cs}^+$ Engdahl and Rämme¹³ concluded that irradiation of $I^{\cdot-}, \text{Cs}^+$ with visible light (λ about 500 nm) caused ejection of an electron from $I^{\cdot-}, \text{Cs}^+$ with the formation of *I* and e^-, Cs^+ , which reacted with $I^{\cdot-}$ to $I^{2-}, 2\text{Cs}^+$. $I^{\cdot-}$ was then formed rapidly from this reactive intermediate and *I*.

A formation of a dianionic on species irradiation with light of $\lambda \sim 500 \text{ nm}$ of *I* during CV at a potential close to the first peak potential of *I* is in accordance with the experimental data presented in Fig. 2, but other interpretations may be possible.

If, however, in a working hypothesis, the current increase described above for *I* is assumed to be due to a transient formation of a dianionic species, different mechanisms may operate; here two will tentatively be considered. One mechanism could be analogous to that suggested¹³ to explain the flash photolysis experiment [(*I*), (2), (3)].



where e^- is an electron delivered from the electrode. In the present context it is not essential whether the electron trap is the electron ion pair shown or another electron trap, as long as it functions reversibly and is an efficient electron donor. Alternatively (*I*) may be followed by (4) and (5).



The rationale for (5) is that the HOMO of $I^{\cdot-}$ which was the LUMO in I again is empty in $I^{\cdot-*$ as the electron occupies a level of higher energy. If the level in question is not significantly perturbed by the occupancy of the higher lying orbital, $I^{\cdot-*$ should be able to accept an electron from the electrode at a potential only slightly more negative than the reduction potential of I .

Irradiation of $I^{\cdot-}, Cs^+$ in tetrahydrofuran (THF) with light of wavelength 460 nm to 580 nm causes¹³ the ejection of an electron from $I^{\cdot-}$, and a similar ejection should be possible from $I^{\cdot-}, Bu_4N^+$ in DMF. The larger size of Bu_4N^+ compared to Cs^+ and the better solvation by DMF compared to THF suggest¹⁵ an easier ejection in the former case than in the latter one.

If, however, the electron is not ejected,¹⁶ then the second possibility [(1), (4), (5)] may come into play; it would require a fast electron transfer from the electrode to $I^{\cdot-*$ and an intense light, if a second electron should be transferred from the electrode during the very short lifetime of $I^{\cdot-*$.

The large increase in the current of I in the presence of an aromatic BX-compound could be explained by either mechanism; BX would function as an irreversible electron sink both for the solvated electron (or other electron trap) or for the dianionic species by electron transfer in solution.

Although the light absorption may induce some convection, which may modify the shape of the voltammetric curve, the large increase

in catalytic current even at low light intensities cannot be explained in that way.

This communication is intended only to demonstrate an influence of light on electrochemistry of ion radicals; many questions with regard to mechanism are at the present stage highly speculative, and the preparative use of a possibly extended and more efficient coupling reaction is largely unexplored. Much work remains to be done before the theoretical and practical aspects of the phenomenon have been elucidated.

EXPERIMENTAL

The cell and the electrode are shown in Fig. 5. The cell consisted of pyrex with a planar pyrex window, the electrode of a platinum wire ($\phi = 0.5$ mm) ground in plane with the glass and covered electrolytically with a thin layer of mercury.

The equipment for cyclic voltammetry has been described previously.¹⁷ Spectra of $I^{\cdot-}$ and $2^{\cdot-}$ in DMF/TBAI were obtained on electrochemical reduction of a suitable concentration of I resp. 2 in the usual manner. The cells for spectroscopy were present in the electrolytic cell during the reduction and filled by dipping the 1 mm cell into the catholyte after completion of the reduction.

Two lasers were used, an Ar^+ (ion) laser (max 700 mW at 4880 Å) with cavity etc. homemade and an Ar^+ (ion) laser (total max 15 W) Spectra-Physics Model 170 ion laser with model 270 Power Supply.

Photoelectrochemical experiment. DMF, dried over molecular sieves A4, was purged with nitrogen and passed 3 times through a small column of active, neutral alumina; before the last treatment on the column the supporting electrolyte was dissolved in the DMF. The cell was purged with nitrogen for about half an hour before the DMF-solution was added.

The beam was sent through a glass plate held at an angle of about 45° to the beam, and the beam was centered at the electrode using a low intensity. The intensity of the reflection from the glass plate was measured by a Radiometer powermeter, Model 550-1; if the intensity of the reflection was too high for the meter, another glass plate was put into the reflected beam, and the intensity of the reflection from this beam was measured. Only relative measurements of intensity were made.

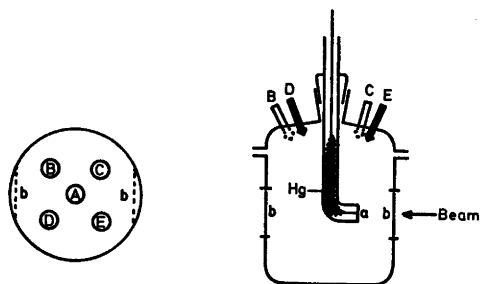


Fig. 5. Cell for CV under illumination, seen from above (left) and side-view (right). A, inlet for the working electrode a; B, inlet and outlet for nitrogen; C, inlet for counter electrode; D, inlet for addition of material; E, inlet for reference electrode; b, plane pyrex window.

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