Acta Chemica Scandinavica B 34 (1980) 409–412

Photochemistry of Radical Ions. II. Influence of Thermal Convection and Photoexcitation on Voltammetric Curves

HENRIK S. CARLSSON and HENNING LUND

Department of Organic Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

Cyclic voltammetric curves obtained during illumination of the microelectrode with a laser are influenced both by the excitation of the electrogenerated ion radicals and by the thermal convection induced by the local heating. The two types of influence have been separated in different ways.

Illumination with a laser of the working microelectrode during cyclic voltammetry influences the results obtained.[1] An enhancement of the current was observed and under certain conditions an emission of light. The current increase was assumed to be caused by electron transfer in connection with excitation of the ion radicals formed at the electrode together with some thermal convection induced by local heating of the solution by the lightbeam; the relative influence of the two factors, however, was not discussed.

The influence of photoexcitation of electrogenerated cation radicals was recently demonstrated;[2] previously a photobenzidine rearrangement of the tetraphenylhydrazine cation radical[3] was reported.

This paper describes attempts to separate the effect of thermal convection and photochemical excitation on voltammetric curves obtained on illumination of the electrode.

RESULTS AND DISCUSSION

Heat-induced convection. Irradiation of the working microelectrode during a cyclic voltammetric experiment in *N*,*N*-dimethylformamide (DMF) using the maximum power of the argon laser (approximately 7 W at a single wavelength) caused an increase in the temperature in the immediate neighbourhood of the electrode of about 10 K; the temperature was measured with a thermoelement as close as possible to the electrode. After about 10 s of irradiation the temperature remained constant; when the light was turned off, the temperature sank to the value of the surroundings within approximately 5 s.

If the solution contained a compound which produced an anion radical capable of absorbing light of the wavelength used, the temperature increased a little more in the potential region where the anion radical was formed; for a 5×10^{-3} M solution of pyrene (*1*) the extra increase in the temperature was 2–3 K.

The heating of the solvent caused some convection which influenced the voltammetric curves; the curves resembled those obtained at a rotating electrode. The enhancement of the reduction current of a compound, the anion radical of which did not have a strong absorption at the wavelength employed, was at most 1.5–2 times the original value.

Photoexcitation. A problem connected with photoexcitation of a species at an electrode is that the photoexcited species may be able to exchange an electron with the electrode. The result of such a back-donation would be that no influence of the light on the curve was observed. The difficulty can be circumvented if the excited system irreversibly can transfer at a high rate an electron to some electron acceptor whereby back-donation can be avoided.

Such an electron acceptor is chlorobenzene (*2*) (a "BX-compound"[4]), which after electron uptake rapidly dissociates into a chloride ion and a phenyl radical.[1,4] Another way of avoiding back-donation of electrons is to use a micellar solution.[5,6] Here

0302-4369/80/060409-04$02.50

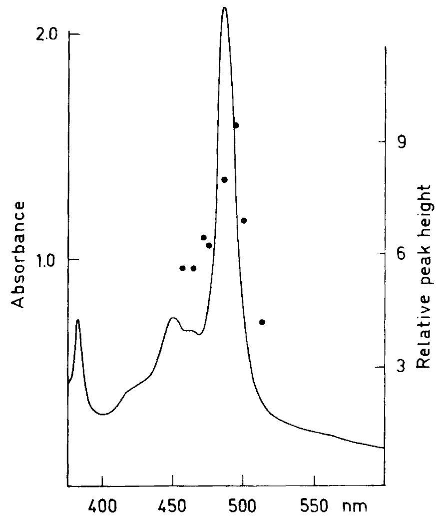

Fig. 1. Absorption spectrum of pyrene anion radical in DMF 0.1 M TBAI. The points are relative peak-heights in CV of pyrene (5×10^{-3} M) in DMF/TBAI containing 1.9×10^{-2} M chlorobenzene, scan rate 0.10 V s^{-1}, illuminated with light of different wave-length. The intensity of the light from the laser was adjusted to the same intensity. For the peak-height the unit is the peak-height without illumination.

BX-compounds have been employed in different ways.

The enhancement of the current due to illumination during cyclic voltammetry (CV) of *1* in the presence of *2* is much dependent on the wavelength of the light. Using the same light intensity (*I*), *i.e.* the same number of photons per second, the increase in peak current of pyrene is closely related to the absorption spectrum of pyrene anion radical ($1^{\cdot-}$) (Fig. 1).

Convection vs. *photoexcitation.* This problem has been attacked in different ways. One way is to employ a compound, which is reduced in two reversible or quasireversible waves, and where the dianion but not the anion radical reacts with a BX-compound under illumination. The increase in the first wave would reflect the influence of convection, whereas the enhancement of the second wave would be due to both factors.

Dimethyl terephthalate (*3*) is reduced in DMF in a reversible wave followed by a quasireversible one with a peak separation of 100 mV at $v=10$ V s^{-1}. The two waves are hardly affected by addition of *2*. The anion radical[7] of *3* ($3^{\cdot-}$) absorbs light at the wavelength of the laser, and the dianion (3^{2-}), of which it has not been possible to obtain a spectrum, is assumed also to absorb light in this region; pyrene dianion (1^{2-}) absorbs light in the same region as pyrene anion radical.[8]

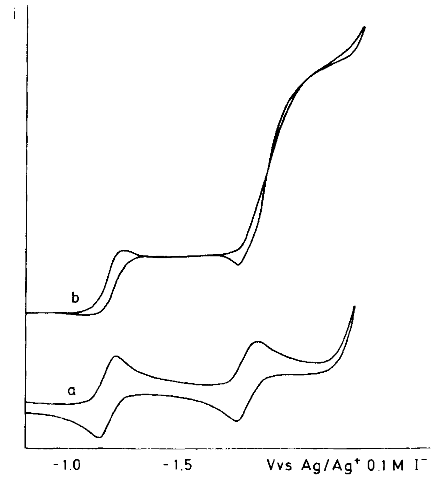

Fig. 2. Cyclic voltammograms of a solution of dimethyl terephthalate (5×10^{-3} M) and chlorobenzene (2×10^{-2} M) in DMF/TBAI without illumination (a) and with illumination (b). Scan rate 0.05 V s^{-1}.

Irradiation of a solution of *3* during CV causes a slight increase in the current, presumably due to convection. Addition of *2* to the irradiated solution brought about a considerable enhancement of the second wave, whereas the first wave was not noticeably influenced (Fig. 2).

The energy absorbed by $3^{\cdot-}$ is thus mainly transformed into heat, whereas the photoexcited dianion is able to transfer an electron to *2* and then again accept an electron from the electrode.

Another way is to mimick the heat-induced convection by a mechanically controlled one by stirring. Stirring a solution of *1* during CV without light increased the current of both the first and the second wave. The electrode was then illuminated and the light intensity adjusted so the increase of the first wave without stirring was similar to that with stirring, but without light. The two experiments were then repeated after addition of *2*, using the same stirring rate and light intensity. The CV in the stirred, unilluminated solution showed no extra increase in the current, whereas that in the unstirred,

Table 1. Limiting currents in μA of a 5×10^{-3} M solution of pyrene (*1*) in DMF/0.1 M TBAI alone and in the presence of chlorobenzene (*2*) under different conditions. *l* the electrode is illuminated with an argon laser; *s* the solution is stirred.

Compound	$-l-s$	$-l+s$	$+l-s$	$+l+s$
1	3.4	6.5	6.5	
1+*2*	3.4	6.5	19	21

illuminated solution showed a three-fold increase in the current. Stirring and illumination together produced only a small extra increase compared to illumination without stirring (Table 1).

A further difference between the effect on CV of *1* produced by stirring and illumination (without *2*) is that only one wave is observed during illumination with light of an intensity above a certain limit, which depends on the scan rate v, while the two normal waves are seen during the stirring experiment. However, at suitable values of the light intensity and v it is possible to observe a second reduction wave at potentials more negative than the first one, but less negative than the normal second wave of *1*. On increasing the intensity of the light the first wave grows only slightly, whereas the second wave grows more and moves toward less negative potentials, until it merges with the first wave (Fig. 3).

CV of *1* in DMF containing traces of proton donor shows generally an oxidation wave on the reverse sweep at $E_p=-0.75$ V (*vs.* Ag/AgI, 0.1 M I^-), when the sweep reversal occurs at potentials more cathodic than the second wave; this anodic wave has been proposed[9] to be caused by the oxidation of the anion of dihydropyrene (4^-).

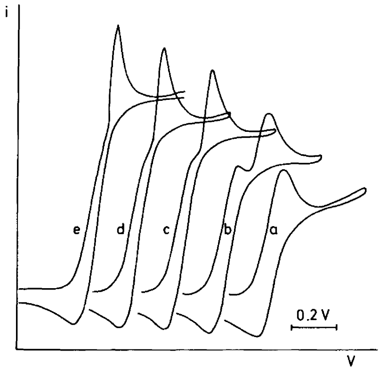

Fig. 3. Cyclic voltammograms of pyrene (5×10^{-3} M) in DMF/0.1 TEAI with different intensity of illumination of the electrode; argon laser (514.5 nm), scan rate 0.1 V s^{-1}. Relative intensity, a 0.0, b 0.25, c 0.60, d 1.02, e 1.36.

Using relatively fast sweep rates ($v>1$ V s^{-1}) an anodic wave is observed at $E_p=-0.75$ V during CV of *1* with illumination even when the reversal of the sweep occurs between E_1 and E_2 of *1*. At slow sweep rates this anodic wave is not observed, probably due to the heat-induced convection.

As mentioned above, the current increase due to heat-induced convection reaches a steady state after about 10 s of illumination, whereas the current reaches its maximum value in less than $\frac{1}{2}$ s when a solution of *1* and *2* is illuminated.

On illumination of pyrene during CV the current increases with the light intensity until it has reached a value approximately 2.8 times the original value.[1] In the presence of an excess of *2* no such limiting value is observed. However, if *t*-butyl chloride (*5*) is employed instead of *2*, the current reaches, after the initial rise, a plateau when the intensity of the light is augmented.

The dependence of the current on the concentration of the BX-compound is different for *2* and *5*; in a solution of *1* (5×10^{-3} M) a current plateau was not observed (at $2<5\times10^{-2}$ M), whereas a plateau was reached in the presence of 10^{-2} M *5* using the same light intensity as in the former experiment. A similar current-concentration dependence is observed, when an anion radical couples with *5*.[10]

The results indicate that although thermally induced convection plays a role it is not the only factor and a photoexcitation of an anion radical is involved.

The photostimulated electron transfer from *1* to *2* during CV could occur directly (eqn. (1)) from the excited anion radical to *2* or *via* 1^{2-} (eqn. 3)). The redox potential of $1^{\cdot-}/1^{2-}$ has not been measured, but as the peak potential is about -2.7 V (SCE),[11] and it reacts fast in a follow-up reaction, the standard potential is somewhat more negative than -2.7 V; the standard potential of *2* is -2.78 V (SCE),[12] so both reaction paths could be possible on energetic grounds. The reactions (1)–(7) might thus occur.

$$1^{\cdot-} \xrightarrow{h\nu} 1^{\cdot-*} \xrightarrow{2} 1+2^{\cdot-} \longrightarrow \mathrm{Ph}^{\cdot}+\mathrm{Cl}^- \qquad (1)$$

$$1^{\cdot-}+\mathrm{Ph}^{\cdot} \longrightarrow 1+\mathrm{Ph}^- \xrightarrow{\mathrm{H}^+} \mathrm{PhH} \qquad (2)$$

$$1^{\cdot -} + 1^{\cdot -*} \rightarrow 1 + 1^{2-} \qquad (3)$$

$$1^{2-} + 2 \rightarrow 1^{\cdot -} + 2^{\cdot -} \rightarrow \mathrm{Ph}^{\cdot} + \mathrm{Cl}^{-} \qquad (4)$$

$$1^{2-} + [\mathrm{H}^{+}] \rightarrow 4^{-} \qquad (5)$$

$$1^{2-} + 1 \rightleftharpoons 2\,1^{\cdot -} \qquad (6)$$

$$1^{2-} - \mathrm{e}^{-} \rightarrow 1^{\cdot -} \qquad (7)$$

In the presence of *2* there is no evidence for the formation of 1^{2-}, but no evidence against it either. In the absence of a BX-compound as electron acceptor reactions (5), (6) and (7) would compete. The formation of 4^{-} implies that 1^{2-} has been an intermediate, but it cannot be excluded that $1^{\cdot -*}$ has a sufficiently enhanced basicity to promote a hydrogen ion abstraction during its life-time.

In the presence of *5* the curves from CV of *1* suggest that a coupling occurs under illumination (8), where *6* represents the different isomers of

$$1^{2-} + 5 \rightarrow 1^{\cdot -} + t\text{-Bu}^{\cdot} + \mathrm{Cl}^{-} \rightarrow 6 + \mathrm{Cl}^{-} \qquad (8)$$

t-butyldihydropyrene.

The effect of light on voltammetric curves is thus, apart from the influence of convection, dependent on the rate of the follow-up reactions of the excited state or the dianion. Thus the anion radical of 1,4-dinitrobenzene absorbs light of the wavelength of the argon laser, but no effect of excitation on the curves is observable; this may be due to the relatively great stability of the dianion.

The conclusion is that irradiation of the microelectrode during CV produces a local heating; the resulting convection influences the shape of the observed curves moderately. In addition to that, a pronounced effect may be observed if an electron transfer from the photoexcited anion radical, possibly *via* the dianion or some other species, to an electron acceptor is fast enough to compete with the back-donation to the electrode.

EXPERIMENTAL

The apparatus and the lasers were the same as used previously.[1]

REFERENCES

1. Lund, H. and Carlsson, H. S. *Acta Chem. Scand. B 32* (1978) 505.
2. Moutet, J.-C. and Reverdy, G. *Tetrahedron Lett.* (1979) 2389.
3. Svanholm, U. and Parker, V. D. *J. Am. Chem. Soc. 94* (1972) 5507.
4. Lund, H., Michel, M.-A. and Simonet, J. *Acta Chem. Scand. B 28* (1974) 900.
5. Moroi, Y., Braun, A. M. and Grätzel, M. *J. Am. Chem. Soc. 101* (1979) 567.
6. Moroi, Y., Infelta, P. P. and Grätzel, M. *J. Am. Chem. Soc. 101* (1979) 573.
7. Yamamoto, M., Ohaka, M., Kitagawa, K., Nishimoto, S. and Nishijima, Y. *Chem. Lett.* (1973) 745.
8. Engdahl, K.-Å. and Rämme, G. *Chem. Phys. Lett. 41* (1976) 100.
9. Gruver, G. A. and Kuwana, T. *J. Electroanal. Chem. 36* (1972) 85.
10. Simonet, J., Michel, M.-A. and Lund, H. *Acta Chem. Scand. B 29* (1975) 489.
11. Aten, A. C., Büthker, C. and Hoijtink, G. J. *Trans. Faraday Soc. 55* (1959) 324.
12. Andrieux, C. P., Blocman, C., Dumas-Bouchiat, J.-M. and Savéant, J.-M. *J. Am. Chem. Soc. 101* (1979) 343.

Received January 18, 1980.