Tetrahedron Letters No.52, pp. 6457-6463, 1966. Pergamon Press Ltd.
Printed in Great Britain.

AN ELECTROCHEMICAL METHOD TO FOLLOW THE COURSE OF RAPID RADICAL ION REACTIONS

J. A. Harrison

Department of Physical Chemistry, The University
of Newcastle upon Tyne, Newcastle upon Tyne, 1

(Received 15 October 1966)

Introduction

The polarographic reduction of some aromatic hydrocarbons, carbonyl compounds, nitriles, nitro and other compounds to form radical anions is well known (1). Ionic species of this type are often postulated as intermediates in organic reactions (2). Only when the radical anions have a relatively long life time is it possible to prepare them chemically or electrochemically and study their reactions and, for example, their e.s.r. spectrum (3). Here a simple electrochemical method has been developed for following the course of organic reactions involving relatively short lived species or reactions which take place relatively rapidly. The method was first suggested by Koopmann and Gerischer (4), and used by them to measure the stationary concentration of radical anions in an e.s.r. experiment.

Experimental Method

The measurements have been carried out exclusively in D.M.F. solutions because of solubility requirements. The radical anion is formed at a stationary mercury drop for a definite length of time by applying a potential pulse to the electrode using a high speed potentiostat. The course of the general reduction process

$$R + e \rightleftharpoons R^{\cdot -} \qquad (I)$$

is observed as a current/time[*] curve, which is recorded oscillographically. Integration of the curve gives directly the number of radical anions moving out into the solution, by diffusion. When the potential pulse returns instantaneously to the base potential equation (I) is reversed and the radical anion is oxidised back to the parent. If the radical anion has not suffered any reaction during the time it has been in solution then very simply one would expect to regain by oxidation half the charge which has flowed in the reduction process. Qualitatively this can be seen as follows: the radical anion concentration during the oxidation step is zero at the electrode surface and in the bulk of solution, therefore an anion has equal chance to diffuse back to the electrode and appear as an oxidation current or diffuse into the solution and be lost. A similar constant current reversal method has also been used in electrochemistry to measure the rates of organic reactions. in aqueous solution in recent years (5,6,7) but suffers from the well known difficulty of separating effects due to double layer charging, and adsorption of substances prior to electron exchange from the reduction and oxidation currents. It was the purpose of the present work to test the above proposition at short times and investigate the course of some simple organic radical anion reactions.

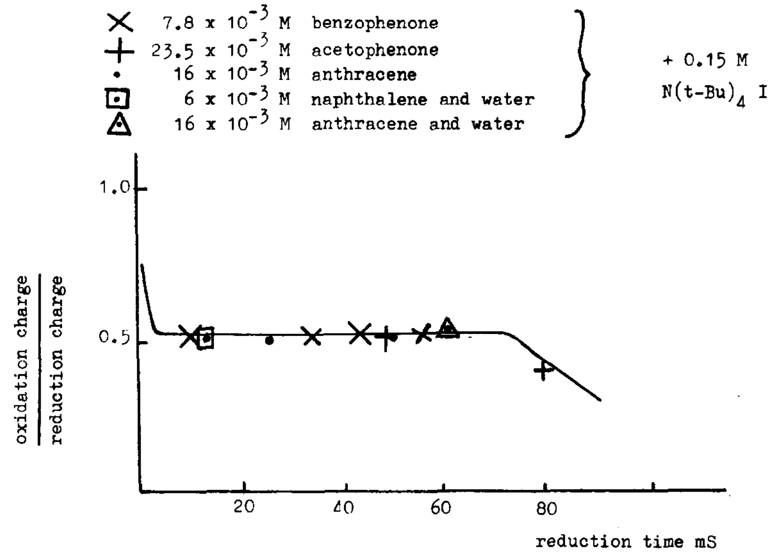
Experimental results

The compounds benzophenone, acetophenone, anthracene, naphthalene in D.M.F. solution are known from e.s.r. studies to reduce to long lived radical anions. The results of FIG. 1 confirm that all these radical anions is completely stable in solution and does not abstract hydrogen from D.M.F. or from water.

---

[*] Details of the apparatus and reduction kinetics will be published elsewhere.

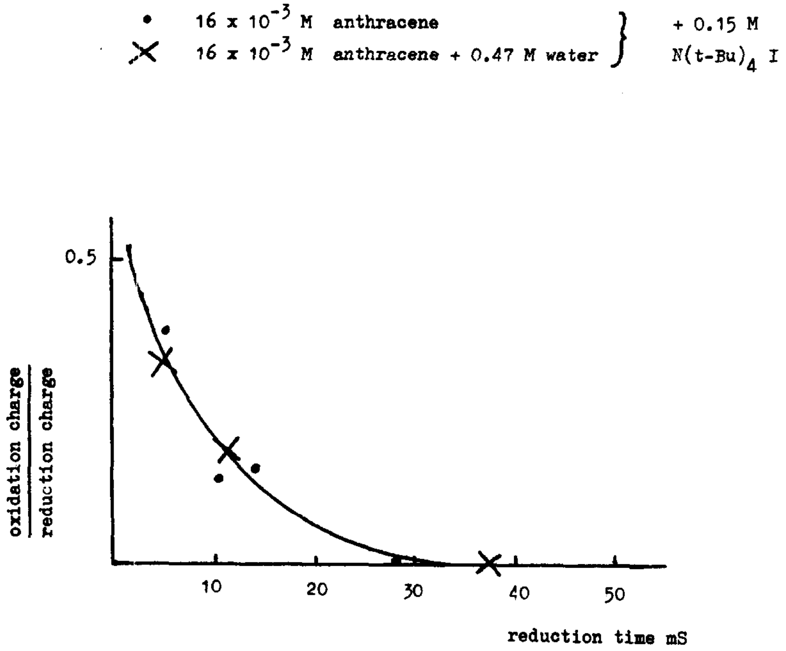
FIG. 1



Reduction times up to 70 ms only could be measured due to interference from convection which transports the radical anions away from the diffusion layer. This is a severe experimental condition which limits the technique to fairly rapid reactions. The radical anions react rapidly with the oxygen anion which is formed simultaneously when dissolved oxygen is present and this was reduced to a low level by bubbling purified nitrogen gas through the solution.

At higher reduction potentials as shown from the current time curves two electrons are transferred and a dianion is formed. An example for the reduction of anthracene is shown in FIG. 2. The anthracene dianion extracts hydrogen from D.M.F., not from water, with a first order rate constant 31.2 sec^{-1}. Disproportionation is not observed. This confirms that the second polarographic wave, which is usually ill-defined because of the eccentric behaviour of dropping capillaries in D.M.F., is in fact due to dianion formation.

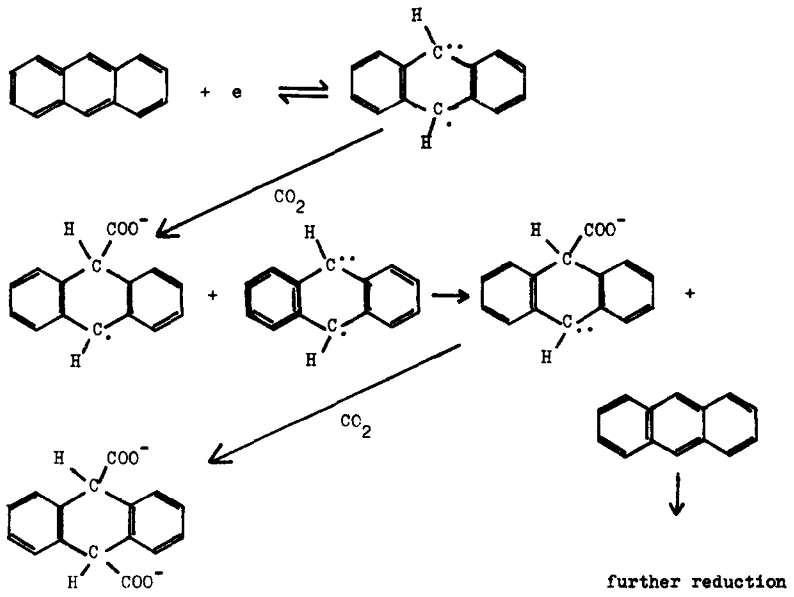
FIG. 2



It appears that two electrons are transferred in a single step. Benzaldehyde also forms a radical anion and a dianion but does not fit into the above scheme possibly due to a dimerization reaction. Measurements using a glassy carbon electrode show that metal organic intermediates are not formed.

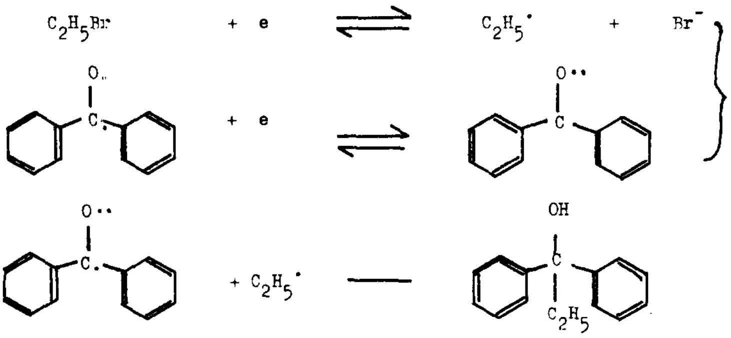
Two distinct types of experimental behaviour have been observed when the radical anions undergo subsequent reaction. These are typified by the radical anion reaction with carbon dioxide on one hand and ethyl bromide and oxygen on the other. The radical anions of anthracene and benzophenone react with CO_2.

In this case the concentration of the free radical anion (measured by the oxidation charge) is always zero. The one satisfactory way to explain this phenomenon is as follows.



The radical anion after the addition of one CO_2 molecule is in a potentially unstable situation and quickly takes an electron from a neighbouring unreacted radical ion. This leaves an anthracene molecule in the neighbourhood of the electrode surface which is further reduced, a fact which is clear from the experimental current time curve for the reduction. Benzophenone reacts with CO_2 in an exactly analogous manner. This mechanism explains the findings of Wawzonek and Gunderson (8). Carbon dioxide is probably reduced simultaneously with the hydrocarbons but the concentration of the carbon dioxide radical anion is only very low. The fact that two substances are reduced polarographically at the same potential is therefore not an infallible proof that the reduced forms react together.

The reactions of the anthracene anion in presence of dissolved oxygen and the benzophenone anion in ethyl bromide are experimentally quite different from the reactions with CO_2. In the case of benzophenone, for example, the amount of charge going into the simultaneous reduction of ethyl bromide leads to a corresponding decrease in the concentration of the free benzophenone radical anion concentration. Even when ethyl bromide is present in large excess there is no evidence that the benzophenone anion reacts with ethyl bromide itself. This leads to the scheme



the hydrogen ion in the last step being supplied from the D.M.F.

Except for the hydrogen extraction reaction of the anthracene dianion all these reactions are very fast, and it has not proved possible to measure rate constants. It is clear, however, that it is possible to recognize when two species react together and follow fairly complex reaction paths. In this way it should be possible, by making organic fragments at different potentials (using potential as an oxidising or reducing agent of exactly variable strength) and allowing these to react near to the electrode, to tailor make many organic molecules.

I wish to thank Professor Lord Wynne-Jones and Professor H. R. Thirsk for the generous provision of laboratory facilities, and Dr. M. Fleischmann for much discussion and encouragement.

REFERENCES

1. A Review of the Polarography of Organic Compounds in Aphrotic Solvents is given by S. Wawzonek, Talanta, 12, 1229 (1965).
2. P. Sykes, A Guidebook to Mechanism in Organic Chemistry, Longmans, 1962.
3. A Review is given by R. N. Adams, J. Electroanal. Chem., 8, 151 (1964).
4. R. Koopmann and H. Gerischer, Ber. d. Bunsen, 70, 121, (1966).
5. A. C. Testa and W. H. Reinmuth, Analyt. Chem. 32, 1518 (1960).
6. W. Jaenicke and H. Hoffmann, Zeit f. Elek., 66, 814 (1962).
7. H. B. Hermann and A. J. Bard, Analyt. Chem., 36, 510 (1964).
8. S. Wawzonek and A. Gunderson, J. Electrochem. Soc., 107, 537 (1960).