A Kinetic Study of the Electrochemical Reduction of Azibenzil [PhCOC(N_2)Ph] in Acetonitrile Solution: Evidence for the Transient Formation of a Carbene Anion Radical

Donald Bethell,[a] Linda J. McDowall,[a] and Vernon D. Parker[b]

[a] *The Robert Robinson Laboratories, The University of Liverpool, P.O. Box 147, Liverpool, L69 3BX, U.K.*
[b] *Laboratory of Organic Chemistry, Norwegian Institute of Technology, N-7034, Trondheim-NTH, Norway*

Electrode kinetic studies on the reduction of azibenzil PhCOC(N_2)Ph in MeCN solution indicate that the reaction follows an ECE_h mechanism, the chemical step most probably involving unimolecular loss of N_2 from the diazoalkane anion radical with formation of the related carbene anion radical.

Considerable interest has in recent years surrounded the behaviour of diazoalkane ion radicals, in particular the question of whether in solution they lose nitrogen in a unimolecular process with consequent generation of carbene ion radicals. Anion radicals of the carbenes diphenylmethylene[1] and fluorenylidene[2] have previously been suggested to be intermediates in the electrochemical reduction of the related diazoalkanes, but detailed kinetic studies have in both cases provided powerful evidence to the contrary.[3] We now report a kinetic study of the reduction of azibenzil [PhCOC(N_2)Ph, ABN_2] and provide evidence that in this case the diazoalkane anion radical does decompose in a unimolecular process which, it is argued, leads to the benzoylphenylmethylene anion radical.

ABN_2 shows irreversible cyclic voltammetric (c.v.) behaviour on reduction at a mercury electrode in MeCN–Et_4NBF_4 (0.1 M) at 281.7 K, with $E^{p}_{red.} = -1.51$ V (*vs.* Ag/Ag^+) at a scan rate (v) of 100 mV s^{-1}. Linear sweep voltammetry (l.s.v.) gave the results in Table 1; the average value of $\Delta E^p/\Delta \log v$ is 27.2 mV over an eight-fold range of substrate concentrations in close agreement with the value of 28.0 mV required for a chemical reaction following heterogeneous electron transfer first order in $ABN_2^{\cdot-}$.[4] Likewise, derivative cyclic voltammetry (d.c.v.) under similar conditions gave a response (the scan rate $v_{\frac{1}{2}}$ necessary to yield a derivative current ratio of 0.5) which was invariant with azibenzil concentration confirming the first order kinetic law. Use of CD_3CN as solvent revealed a small kinetic isotope effect varying with temperature in the following way: 273.1 K 1.35, 281.3 K 1.19, 286.6 K 1.02, 293.1 K 1.03. These results point to the absence of solvent involvement in the main follow-up reaction, although there may be competition by hydrogen transfer from MeCN, as found in the reduction of Ph_2CN_2,[3b] to a small extent. The indications then are that the chemical reaction of $ABN_2^{\cdot-}$ is unimolecular decomposition. Overall, the reduction cannot, however, follow a simple *EC* mechanism. A plot of $I_p v^{-\frac{1}{2}}$ *vs.* $v^{\frac{1}{2}}$ is curved with a slope that indicates that the number of electrons involved is one when $v = 200$ V s^{-1} (no reaction of $ABN_2^{\cdot-}$) and two when $v = 1$ V s^{-1} (reaction of $ABN_2^{\cdot-}$ complete). An ECE_h mechanism (rapid homogeneous electron transfer to the product of the first order chemical reaction) is indicated, and the rate coefficients in Table 1 were calculated from theoretical data on this basis.

Table 1. Linear sweep voltammetry and derivative cyclic voltammetry on azibenzil in acetonitrile solution at 281.7 K

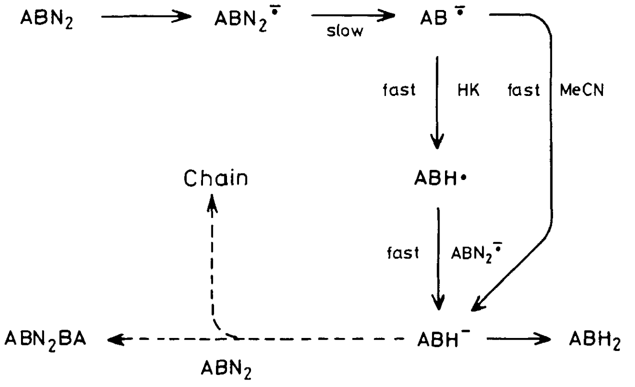
	L.s.v.	D.c.v.	
$[ABN_2]$/mM	$\Delta E^p/\Delta \log v$/mV[a]	$v_{\frac{1}{2}}$/V s^{-1}	k/s^{-1} [b]
0.50	27.5 ± 0.2	79.1	361
1.00	26.0 ± 0.2	85.0	387
2.00	27.5 ± 0.2	78.5	358
4.00	27.9 ± 0.1	—	—
		Mean	368 ± 17

[a] Values are the mean of five replicates for measurements at 0.100 and 1.00 V s^{-1}. [b] Calculated for theoretical data for an ECE_h mechanism.

The c.v. of ABN_2 shows only one electroactive product at concentrations up to 5 mM with $E^{p}_{ox.}$ at −0.25 V, corresponding to oxidation of the carbanion PhCO$\bar{C}$HPh (ABH^-). The dimeric azine PhCOC(Ph)=N–N=(Ph)CCOPh (ABN_2BA), the major product in the case of 9-diazofluorene reduction, is not detectable. On the other hand, constant current electrolysis of ABN_2 at 303.2 K at a platinum cathode with concentration 50 mM affords the corresponding azine in yields of about 40% together with deoxybenzoin $PhCOCH_2Ph$ (ABH_2, 28%).† The concentration–time curve for ABN_2 shows the

---

† Two other, as yet unidentified, products were present, the relative proportions of which appear to depend upon the current density. Both are also products of the electrochemical reduction of ABN_2BA.



Scheme 1

sigmoid shape associated with a chain reaction producing azine.[5] We have also observed that ABH^- (5 mM) generated from ABH_2 in dimethyl sulphoxide solution reacts with ABN_2 (0.05 M) converting it in high yield to the azine within a few minutes.

We conclude that these observations are best interpreted in terms of the reaction sequence shown in Scheme 1. The key step is the transient generation of the carbene anion radical [$AB^{\cdot-}$; $\mathrm{PhCO\dot{\bar{C}}Ph} \leftrightarrow \mathrm{PhC(O^-){=}\dot{C}Ph}$], hydrogen transfer to which (by protonation or atom abstraction) occurs rapidly, with subsequent transfer of the second electron. Other unimolecular reactions of $ABN_2^{\cdot-}$ such as cyclisation or C–C bond cleavage for which precedents exist under quite different reaction conditions[6] appear to be excluded by the c.v. evidence, although in the absence of a full product analysis they cannot be completely ruled out.

Received, 28th November 1983; Com. 1562

References

1 R. N. McDonald, F. M. Triebe, J. R. January, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, 1980, **102**, 7867 and references therein.
2 R. N. McDonald, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, 1978, **100**, 995.
3 (a) V. D. Parker and D. Bethell, *Acta Chem. Scand., Ser. B*, 1981, **35**, 691; (b) D. Bethell and V. D. Parker, *J. Chem. Soc., Perkin Trans. 2*, 1982, 841.
4 V. D. Parker, *Acta Chem. Scand., Ser. B*, 1981, **35**, 259.
5 D. Bethell, L. J. McDowall, and V. D. Parker, *J. Chem. Soc., Perkin Trans.* 2, submitted for publication.
6 P. Yates and B. Shapiro, *J. Am. Chem. Soc.*, 1959, **81**, 212.