Electron Transfer Reaction between 1,3-Dinitrobenzene and Methyl 1-Ethylpyridine-4-carboxylate Radical

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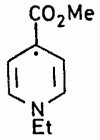
The rate constant (k_2) for the reaction of 1,3-dinitrobenzene (DNB) with the title radical (Py·) in acetonitrile is 0·29 l mol^{-1} s^{-1} and in isopropyl alcohol is 10·5 l mol^{-1} s^{-1}. Solvent sensitivity criteria confirm that the reaction involves electron transfer but the magnitude of k_2 is much lower than that for the reaction of Py· with 4-nitrobenzyl chloride (k_2 24,000 l mol^{-1} s^{-1} in acetonitrile). The polarographic reduction potential of DNB and the life-time of the radical anion were also determined in order to elucidate the mechanism of the reaction. The proposed mechanism is (a) $Py\cdot + DNB \rightleftharpoons Py^+,DNB^-$ (fast, reversible electron transfer); (b) $Py^+,DNB^- \rightleftharpoons Py^+ + DNB^-$ (fairly fast, reversible ion-pair dissociation); (c) $Py^+ + DNB^- \longrightarrow$ Py–DNB (rate-limiting nucleophilic addition to the ring); (d) Py–DNB + Py· $\longrightarrow$ Py–DNB–Py (fast radical combination). Absorption maxima are reported for K^+DNB^- and Na^+DNB^-.

THE reaction of methyl 1-ethylpyridine-4-carboxylate radical (Py·) (1) with benzyl halides follows two general mechanisms, atom transfer and electron transfer.[1] Only benzyl halides substituted with strong electron-withdrawing groups [*e.g.*, 4-nitrobenzyl chloride (NBCl)] react with Py· by the electron-transfer route in the solvents we have used. In order to find out whether or not the electron-transfer step was rate limiting, we selected a nitro-compound with a reduction potential similar to that of 4-nitrobenzyl chloride, but one which lacked the capacity for undergoing rapid unimolecular decomposition subsequent to the electron-transfer step. The compound selected was 1,3-dinitrobenzene (DNB),[2]



(1)

and the features of concern are illustrated in equations (1) and (2). [Full details on the mechanisms and solvent

$$Py\cdot + DNB \longrightarrow Py^+ + DNB^- \qquad (1)$$

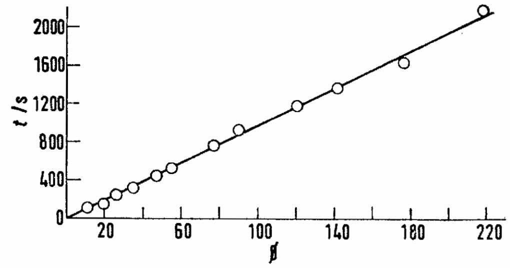
$$Py\cdot + NBCl \longrightarrow Py^+ + NBCl^- \longrightarrow NB\cdot + Cl^- \qquad (2)$$

sensitivity criteria, *etc.*, for equation (2) are given in refs. 1 and 3.] We have therefore measured the rate constant for the reaction of Py· with DBN in two solvents of different Z value, examined the reduction potential of DNB in acetonitrile, carried out cyclic voltammetric studies on DNB to check for anion stability, explored several methods for generating the radical anion at concentrations high enough for spectroscopic measurements, and observed the radical anion in the visible region of the spectrum.

RESULTS

1,3-Dinitrobenzene in acetonitrile exhibits two one-electron reduction potentials at −1·22 and −1·56 V *versus* Ag–AgClO$_4$, using a three-electrode system. Both reduction steps were completely reversible by cyclic voltammetry up to sweep rates of 33 mV s^{-1} at a hanging mercury drop electrode.

Rate constants for the reaction of 1,3-dinitrobenzene and Py· were calculated from equation (3) (see Figure) according to the mechanistic steps (4) and (5) and were constant for >75% reaction.



Plot of ϕ [from equation (3)] against time for the reaction of DNB and Py· in propan-2-ol: $[Py\cdot]_0 = 1{\cdot}27 \times 10^{-4}$M, $[DNB]_0 = 1{\cdot}12 \times 10^{-4}$M

$$k = (1/t)\,.\,[1/(2A_0 - B_0)]\{\ln B_0[(2A_0 - B_0) + B]/2A_0B\} = \phi/t \qquad (3)$$

$$A + B \xrightarrow{\text{slow}} C + D \qquad (4)$$

$$C + B \xrightarrow{\text{fast}} \text{products} \qquad (5)$$

$$B = [Py\cdot],\ A = [DNB]$$

The products do not have strong absorptions in the visible region, thus excluding any species with an anionic σ-complex structure.[4] They are not stable and are sensitive to air, as are the products previously obtained from the reaction of pyridinyl radicals and halogenocarbons.

The electrochemical and kinetic results for the reaction of Py· with 1,3-dinitrobenzene and 4-nitrobenzyl chloride are compared in the Table. Since the reaction of pyridinyl radical (1) with nitroaromatic compounds involved electron transfer, and since the products of such an electron transfer should produce the pyridinium ion and the radical anion of the nitroaromatic compound, the radical anion was generated in other ways. 1,3-Dinitrobenzene with sodium in 1,2-dimethoxyethane yielded a radical anion (orange solution) which exhibited absorption at 490 nm (ε *ca.*

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[1] (*a*) M. Mohammad and E. M. Kosower, *J. Amer. Chem. Soc.*, 1971, **93**, 2713; (*b*) see also M. Mohammad, *Austral. J. Chem.*, 1973, **26**, 229.

[2] A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, 1961, **83**, 1852.

[3] M. Mohammad and E. M. Kosower, *J. Amer. Chem. Soc.*, 1971, **93**, 2709.

[4] M. J. Strauss, *Chem. Rev.*, 1970, **70**, 667.

100). A similar species was produced using potassium in the same solvent at low temperature (−70°), but the reaction was much slower and the radical anion was produced to a lesser extent, $\lambda_{max.}$ 495 nm ($\varepsilon_{apparent}$ *ca.* 100). Spectroscopic data for nitroaromatic radical anions has, in general, not been reported because the low absorption intensities make it rather hard to relate the e.s.r. to the optical spectra. Ward,[5] among others, has analysed the e.s.r. spectra of 1,3-dinitrobenzene radical anion in combination with several cations.

Comparison of 1,3-dinitrobenzene and 4-nitrobenzyl chloride

Process	1,3-Dinitrobenzene	4-Nitrobenzyl chloride [g]
Reduction potential [a]	−1·22 V (−1·10) [f]	−1·16 V
Radical anion stability [g] $t_{\frac{1}{2}}$ (s) [b]	1000	*ca.* 0·03
Rate constants for reaction with radical (1) [b] (l mol^{-1} s^{-1})		
in CH_3CN (*Z* 71·3) [c]	0·29	24,0000
in $(CH_3)_2CHOH$ (*Z* 76·1) [c]	10·5	*d*
in $CH_3OCH_2CH_2OCH_3$ (*Z* 59·1) [c]		8·3
Solvent sensitivity of rate constants [e] as $\Delta\Delta F^*/\frac{1}{2}\,\Delta Z$	0·84	0·78

[a] *versus* Ag–$AgClO_4$ in CH_3CN containing 0·1M-$AgClO_4$ and 0·1M-tetra-n-butylammonium perchlorate. [b] At 25°. [c] Solvent polarity parameters, *Z*, are those used in refs. 1 and 3. [d] Too fast to measure by available techniques. [e] *Cf.* refs. 1 and 3; difference in transition state free energies in two solvents divided by half the difference in *Z* value for the same solvents. [f] *versus* Ag–$AgNO_3$ (0·01M) in CH_3CN containing 0·1M-tetra-n-butyl ammonium perchlorate. M. Mohammad and Riaz Ahmad, unpublished results. [g] See refs. 1 and 6.

DISCUSSION

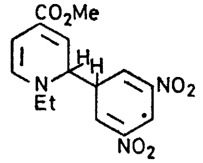
The most important result of this work is the fact that the rate constant for the reaction of pyridinyl radical (1) with 1,3-dinitrobenzene is so much less than that for the reaction of the radical with 4-nitrobenzyl chloride (and 4-nitrobenzoyl chloride, see ref. 1*b*). The mechanism of the reactions must be similar in that both exhibit solvent sensitivity[1] ($\Delta\Delta F^*/\frac{1}{2}\Delta Z$) of *ca.* 0·8, which is consistent only with an electron-transfer step in the reaction.[2] Careful analysis of the reaction of radical (1) with 4-nitrobenzyl chloride[1,3] suggested that the electron-transfer step was fairly rapid and reversible, and that the rate-limiting step was probably the dissociation of the initially formed ion-pair. This unusual behaviour is in large part due to the instability of the radical anion of 4-nitrobenzyl chloride.[6] The 1,3-dinitrobenzene radical anion is relatively stable. The kinetics for the reaction of DNB with radical (1) are apparently bimolecular, yet two radicals disappear for each DNB reacting. The linearity of the fit to the kinetic equation (3) is such (see Figure) that we believe that the second radical is consumed after the rate-limiting step. We are reasonably certain that the dinitrobenzene radical anion does not react readily with the pyridinyl radical since electrochemical experiments in which radical (1) and the radical anion of 4-nitrotoluene are generated in the same solution reveal complete reversibility for both reduction waves in cyclic voltammetry. A mechanism which accommodates these facts involves nucleophilic addition of the radical species produced to the pyridinyl radical [equations (6)—(9)]. The adduct (2) and final product (3) are proposed.

$$\mathrm{Py}\cdot + \mathrm{DNB} \rightleftharpoons \mathrm{Py}^+,\mathrm{DNB}\cdot^- \qquad (6)$$

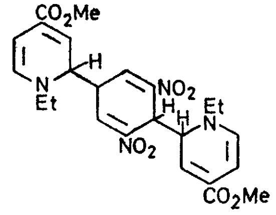
$$\mathrm{Py}^+,\mathrm{DNB}\cdot^- \rightleftharpoons \mathrm{Py}^+ + \mathrm{DNB}\cdot^- \qquad (7)$$

$$\mathrm{Py} + \mathrm{DNB}\cdot^- \xrightarrow{\text{slow}} \mathrm{PyDNB}^- \qquad (8)$$

$$\mathrm{PyDNB}\cdot + \mathrm{Py}\cdot \longrightarrow \mathrm{PyDNBPy} \qquad (9)$$



(2)



(3)

The low intensity observed for the visible absorption bands of 1,3-dinitrobenzene radical anion ion-pair is not unexpected, and is found for a number of other simple stable radicals (*e.g.* pyridinyl radical[7]).

EXPERIMENTAL

1,3-Dinitrobenzene was recrystallized three times (from CCl_4) and vacuum sublimed, m.p. 90·5—91°. Experimental techniques for the rate measurements, the preparation of the pyridinyl radical, the electrochemical techniques (both polarographic and cyclic voltammetry), and the solvent purifications have been described.[1,3] Formation of the sodium and potassium salts of dinitrobenzene radical anion was carried out in the standard way.

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[5] R. L. Ward, *J. Amer. Chem. Soc.*, 1961, **83**, 1296; *J. Chem. Phys.*, 1967, **36**, 1405.

[6] M. Mohammad, J. Hajdu, and E. M. Kosower, *J. Amer. Chem. Soc.*, 1971, **93**, 1792.

[7] E. M. Kosower and E. J. Poziomek, *J. Amer. Chem. Soc.*, 1964, **86**, 5515.