Carbon–Nitrogen Bond Cleavage in π-Radicals derived by Reduction of *N*-Benzyl- and *N*-Allyl-pyridinium Salts

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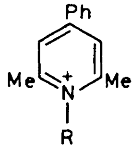
Certain 1-alkyl-2,4,6-trisubstituted pyridinium salts form π-radicals by electrochemical reduction which are stable in dimethylformamide on the time scale of cyclic voltammetry, whereas the corresponding 1-benzyl and 1-allyl compounds undergo carbon–nitrogen bond cleavage at measured rates which are dependent on the size of the 2,6-substituents.

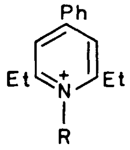
In the recent literature[1] it is proposed that the reaction between 1-benzyl-2,4,6-triphenylpyridinium salts, as well as other pyridinium salts, and the anion from nitromethane, as well as other nitroalkanes, proceeds by electron transfer to the pyridinium salt followed by cleavage of the carbon–nitrogen bond and finally radical pairing. For the reactants cited the product was 2-phenylnitroethane. A study[2] of the electrochemical reduction of alkylpyridinium salts should help in understanding such reactions and our results, using dimethylformamide (DMF) containing 0.2 M tetrapropylammonium fluoroborate as solvent, are briefly reported here.

1-Propylpyridinium salts[†] (**1a**)—(**4a**) show two one-electron reduction waves.[3] The first electron addition leads to a radical zwitterion, a π-radical, which is stable on the time scale of cyclic voltammetry. Under the same conditions the π-radicals from 1-propyl-, 1-propyl-4-phenyl-, and 1-propyl-2,4,6-trimethyl-pyridinium salts have much shorter lifetimes and probably undergo dimerization reactions.[4]

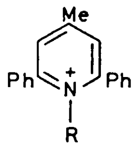
Cyclic voltammetry shows that 1-benzylpyridinium salts[†] (**2b**)—(**4b**) give radical-zwitterions which disappear by a first-order process whose rate constant depends on the 2,6-substituents, so that the radical-zwitterion from (**1b**) is stable on this time scale. Coulometry for reduction of (**4b**) at the potential of the first wave showed a one-electron process (observed 1.01 Faraday mol^{-1}) and 2,4,6-triphenylpyridine was isolated. Thus disappearance of the radical-zwitterion leads to triphenylpyridine and benzyl radicals. The corresponding 1-allylpyridinium salts[†] (**2d**)—(**4d**) show the same behaviour on cyclic voltammetry as the 1-benzyl compounds, indicating that resonance stabilization of the resulting allyl or benzyl radical is an important driving force for carbon–nitrogen bond cleavage.



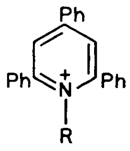
(**1**)



(**2**)



(**3**)



(**4**)

a; R = Pr
b; R = CH_2Ph
c; R = $CH_2C_6H_4X$
d; R = $CH_2CH{=}CH_2$

Anion is BF_4^-. E° *vs.* standard calomel electrode (**1a**) −1.27 V, (**2a**) −1.27 V, (**3a**) −1.19 V, (**4a**) −0.99 V.

The first sweep current–time trace at a spherical mercury electrode, after initiation of a triangular voltage sweep over the first electron transfer process, was stored using a transient recorder and microcomputer. Ratios of the anodic to the cathodic peak current and the corresponding times (= 2τ) to sweep from cathodic to anodic peak were noted. The theoretical data[5] relating $k\tau$ as a function of i_{pa}/i_{pc}, where k is the rate constant for decay of the reduced species,[5] was expressed as a Chebyshev polynomial and used to obtain k from our data. The results are collected in Tables 1 and 2.

The rate constant is increased and the activation energy decreased by bulky 2,6-disubstituents. An electronic effect is also likely to be present since the change of substituent from alkyl to phenyl must alter the π-radical electron density distribution. The Arrhenius pre-exponential factors determined are in the region of 10^{13} s^{-1} expected for a unimolecular reaction.

The series of benzylpyridinium radical-zwitterions derived from (**2c**) and (**3c**) show a scattered Hammett relationship between the rate constant of the bond cleavage reaction and the σ-value for the X-substituent. The series derived from (**2c**) has $\rho = +1.65 \pm 0.47$, correlation coeff. = 0.871. The ρ-value is in accord with a transition state where there is reduced inductive effect of the positive nitrogen centre at the

Table 1. Kinetics of the carbon–nitrogen bond cleavage of π-radicals derived from 1-benzylpyridinium salts in DMF containing 0.2 M Pr_4NBF_4 at 25.00 °C.

π-Radical derived from	Rate constant k/s^{-1}	Arrhenius parameters[a] $E_A/kJ\ mol^{-1}$	log *A*
(**1b**)	<0.02		
(**2b**)	0.481 ± 0.087	79.0 ± 11	13.65
(**3b**)	8.48 ± 0.59	73.1 ± 3.1	13.71
(**4b**)	240 ± 50		
(**2d**)	0.605 ± 0.064		

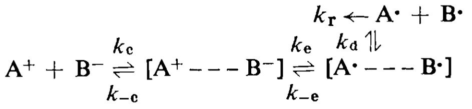
[a] For equation $k = A \exp(-E_A/RT)$ over the temperature range of 15 to 40 °C for (**2b**) and −18 to 35 °C for (**3b**).

Table 2. Rate constants for carbon–nitrogen bond cleavage in π-radicals derived from 1-benzylpyridinium salts in DMF containing 0.2 M Pr_4NBF_4 at 25.00 °C.

X-group	σ-value[a]	(**2c**) k/s^{-1}	(**3c**) k/s^{-1}
4-NMe_2	−0.6	0.027 ± 0.004	
4-OMe	−0.268	0.855 ± 0.096	9.77 ± 0.13
4-Me	−0.170	0.679 ± 0.067	8.65 ± 0.75
H	0.0	0.481 ± 0.087	8.48 ± 0.59
4-Cl	+0.227	1.408 ± 0.118	26.8 ± 2.2
3-CF_3	+0.415	2.591 ± 0.208	43.2 ± 2.7

[a] Taken from H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.

[†] Prepared from the appropriate primary amine and oxonium fluoroborate.



$$\begin{tikzcd} & & k_r & A^\cdot + B^\cdot \arrow[l] \arrow[d, shift left, "k_d"] \\ A^+ + B^- \arrow[r, shift left, "k_c"] & {[A^+ --- B^-]} \arrow[l, shift left, "k_{-c}"] \arrow[rr, shift left, "k_e"] & & {[A^\cdot --- B^\cdot]} \arrow[ll, shift left, "k_{-e}"] \arrow[u, shift left] \end{tikzcd}$$

$$A^+ = (\mathbf{4b}),\ B^- = \bar{C}H_2NO_2$$

$$\Delta E = E^\circ_A - E^\circ_B$$

Scheme 1

benzyl carbon and where there is more radical character on this carbon, thus resulting in the poor Hammett correlation.

Steps in the reaction between (**4b**) and anions from nitroalkanes may be formulated as in Scheme 1 where the reacting, pairs are shown as forming some type of encounter complex before electron transfer. Precise data are not available, but the redox potential of the nitroalkane carbanion is more positive than that of the pyridinium salt so that ΔE in Scheme 1 is negative. Thus the thermodynamics of electron transfer are unfavourable for driving the reaction from left to right ($k_{-e} > k_e$) and the reaction will only be so driven if decomposition of A· competes successfully with back electron transfer from A· to B·. We find $k_r = ca.\ 2 \times 10^2\ s^{-1}$ and before considering the reaction further an estimate of k_{-e} is needed, using the theory of Marcus[6] for outer-sphere electron-transfer processes.

The electron-transfer rate constant can be related to the self-exchange rate constants for the A⁺/A· couple (k_a) and for the B·/B⁻ couple (k_b), as shown in equation (1). Self-exchange rates for delocalised species are usually high and in the region of $10^8\ l\ mol^{-1}\ s^{-1}$ for aromatic π-radicals[7] so that k_{-e} is expected to be greater than this value.

$$k_e = ca.\ (k_a k_b)^{\frac{1}{2}} \exp(F\Delta E/2RT);$$
$$k_{-e} = ca.\ (k_a k_b)^{\frac{1}{2}} \exp(-F\Delta E/2RT) \qquad (1)$$

Since $k_{-e} \gg k_r$, decomposition of A· within the encounter complex [A· - - - B·] is insignificant compared to back electron transfer. The encounter complex dissociates at a diffusion-controlled rate and the forward reaction can still proceed for A· molecules, which so escape the complex because the bimolecular rate for complex reformation will be negligible compared to k_r.

The forward reaction rate is governed by the slow forward electron transfer which will be favoured by ion-pair or charge-transfer complex formation [A⁺ - - - B⁻]. However decomposition of A· takes place outside the encounter complex with its radical partner B·.

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