Amine Oxidation. Part 13.[1] Electrochemical Oxidation of Some Substituted Tertiary Alkylamines

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The anodic oxidation of some polyamines and amino-alcohols has been studied by linear sweep voltammetry at a glassy-carbon electrode in basic aqueous methanol. Although most of the substrates show one oxidation wave, a few show two. It is concluded that the second, less anodic wave comes from the oxidation of substrate diffusing to the anode, whereas substrate adsorbed to the anode gives rise to the more anodic wave. In general the introduction of an electron-withdrawing heteroatom substituent into a tertiary amine destabilises the aminium radical forming in the potential-determining step and raises the oxidation peak potential, the magnitude of this effect being related to the separation between the substituent and the oxidation centre. In some of the substrates through-bond or through-space interactions occur. These effects, which stabilise the forming aminium radical and lower the E_p value, are superimposed on the inductive or field effects.

RECENTLY we reported the influence of electronic effects on the ease of oxidation of some heteroatom-substituted tertiary alkylamines by the one-electron oxidant potassium hexacyanoferrate(III).[2] Apart from this study and the extensive investigations of Rosenblatt and his co-workers [3] into the oxidation of 1,4-diazabicyclo-[2.2.2]octane, the oxidation of diamines, amino-alcohols, and related compounds has received limited attention.[4]

The close similarity between the processes that occur during the chemical one-electron oxidation of tertiary alkyl- and aralkyl-amines [5] and those brought about by electrochemical oxidation [6] has led us to examine the electrochemical oxidation of some polyamines and amino-alcohols. The results, which are compared with those from the chemical studies, reveal further information about the influence of structural and electronic effects, and in particular the role of through-bond and through-space interactions, in amine oxidation.

RESULTS

Linear Sweep Voltammetry.—The linear sweep voltammograms for the heteroatom-substituted tertiary alkylamines were recorded at 298 K using the same solvent system as previously [6b] (30% v/v methanol in water containing sodium perchlorate and hydroxide). The peak potentials ($E_p \pm 0.01$ V) of a selection of polyamines and amino-alcohols together with some reference monoamines are recorded in Tables 1 and 2. Some of the polyamines and one amino-alcohol gave two oxidation waves, and the peak potentials of the second wave are also recorded (Tables 1 and 2).

The Tables include values for βn_a, $i_p/ACV^{\frac{1}{2}}$, and $i_p/\beta^{\frac{1}{2}}$ for the first oxidation wave as defined by equation (1) for an

$$i_p = 3.01 \times 10^5 n\, (\beta n_a)^{\frac{1}{2}} D^{\frac{1}{2}} A C V^{\frac{1}{2}} \qquad (1)$$

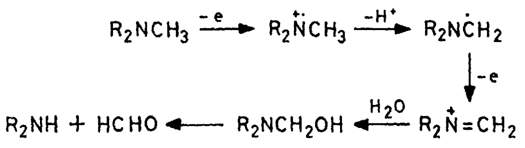
irreversible electron transfer [7] where i_p is the peak current (A), n is the total number of electrons transferred per molecule of reactant, β is the charge-transfer coefficient, n_a is the number of electrons transferred in the rate-determining step, D is the diffusion coefficient (cm^2 s^{-1}), A is the area of the anode (cm^2), C is the concentration of reactant (mol cm^{-3}), and V is the sweep rate (V s^{-1}).

The vertical ionisation potentials (I_p/eV) of many of the amines as measured by photoelectron spectroscopy are reported in Tables 1 and 2.[8]

Product Studies.—The reaction mixture after the controlled potential electrolysis (0.80 V *versus* s.c.e.) of *NNN′N′*-tetraethylethane-1,2-diamine (22) in aqueous solution was shown to contain formaldehyde and *NNN′*-triethylethane-1,2-diamine.

DISCUSSION

From studies on the electrochemical oxidation of tertiary monoamines it was concluded that the transition state for the potential-determining step occurs late on the reaction co-ordinate and resembles the aminium radical rather than the substrate amine [6b] (Scheme). The



SCHEME

introduction of an oxygen or a second nitrogen atom into the tertiary amine should influence the stability of the aminium radical and hence the oxidation potential of the amine. From simple inductive or field effect arguments the greater the separation between the substituent and the oxidation centre the smaller should be its influence. Thus for the acyclic αω-ditertiary diamines and amino-alcohols increasing the chain length should decrease the influence of the substituent $-I$ effect and increase the $+I$ effect of the alkyl side chain,

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[2] L. A. V. Mead and J. R. Lindsay Smith, *J.C.S. Perkin II*, 1976, 1172.

[3] (*a*) W. H. Dennis, L. A. Hull, and D. H. Rosenblatt, *J. Org. Chem.*, 1967, **32**, 3783; (*b*) L. A. Hull, W. P. Giordano, D. H. Rosenblatt, G. T. Davis, C. K. Mann, and S. B. Millikan, *J. Phys. Chem.*, 1969, **73**, 2147; (*c*) G. T. Davis, M. M. Demek, and D. H. Rosenblatt, *J. Amer. Chem. Soc.*, 1972, **94**, 3321; (*d*) D. H. Rosenblatt, M. M. Demek, and G. T. Davis, *J. Org. Chem.*, 1972, **37**, 4148.

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[5] C. A. Audeh and J. R. Lindsay Smith, *J. Chem. Soc.* (*B*), (*a*) 1970, 1280; (*b*) 1971, 1741.

[6] (*a*) L. A. Hull, G. T. Davis, and D. H. Rosenblatt, *J. Phys. Chem.*, 1969, **73**, 2142; (*b*) J. R. Lindsay Smith and D. Masheder, *J.C.S. Perkin II*, 1976, 47.

[7] H. Matsuda and Y. Ayabe, *Z. Electrochem.*, 1955, **59**, 494.

[8] E. E. Ernstbrunner and J. M. Mellor, unpublished observations.

TABLE 1

Voltammogram parameters for the oxidation of some diaminoalkanes and amino-alcohols at 298 K with a potential sweep rate of 33 mV s^{-1}; *ca.* 10^{-2}M-amine, 10^{-3}M-NaOH, and 10^{-1}M-$NaClO_4$ in 30% v/v methanol in deionised water

		Substrate $R^1[CH_2]_mR^2$		First wave					
	m	R^1	R^2	E_p/V *versus* s.c.e.	βn_a	$i_p/ACV^{\frac{1}{2}}$ / μA $s^{\frac{1}{2}}$ mM^{-1} cm^{-2} $V^{-\frac{1}{2}}$	$i_p/\beta^{\frac{1}{2}}$*	Second wave E_p/V *versus* s.c.e.	I_p/eV
(1)	5	NMe_2	H	0.70	0.53	597	107		
(2)	1	NMe_2	NMe_2	*ca.* 0.95	0.28 †	1 008 †	244 †	*ca.* 0.98	8.28 [a]
(3)	2	NMe_2	$\overset{+}{N}Me_3ClO_4^-$	1.01	0.30	597	141		
(4)		NMe_2	NMe_2	0.72	0.37	589	125	0.91	8.30 [‡,a]
(5)		NMe_2	NHMe	0.83	0.31	814	189	*ca.* 0.90	8.53 [‡,a]
(6)		NMe_2	NH_2	0.87	0.30	783	184	*ca.* 0.95	
(7)	3	NMe_2	NMe_2	0.76	0.48	884	165	1.35	8.31 [a]
(8)		NMe_2	NHMe	0.76	0.69	1 016	158	1.35	8.5 [‡,a]
(9)		NMe_2	NH_2	0.85	0.40	868	177		8.38
(10)		NHMe	NHMe	0.95	0.42	799	159		
(11)	4	NMe_2	NMe_2	0.74	0.53	1 023	181		
(12)	5	NMe_2	NMe_2	0.72	0.60	1 078	179		
(13)	6	NMe_2	NMe_2	0.73	0.44	938	182		
(14)	7	NMe_2	NMe_2	0.72	0.50	954	174		
(15)	8	NMe_2	NMe_2	0.74	0.44	946	184		
(16)	9	NMe_2	NMe_2	0.73	0.37	1 031	219		8.42 [a]
(17)	2	NMe_2	OH	0.77	0.53	636	113		8.79 [a]
(18)	3	NMe_2	OH	0.76	0.53	605	107		8.83 [a]
(19)	4	NMe_2	OH	0.75	0.53	597	106		
(20)	5	NMe_2	OH	0.73	0.48	837	156		8.53 [a]
(21)	2	NEt_2	H	0.73	0.48	791	147		8.06 [b]
(22)	2	NEt_2	NEt_2	0.57	0.44	814	151	0.88	7.93 [‡,a]

[*] Where *A* and *V* are constant, *C* is corrected to 10^{-5} mol cm^{-3}, and n, n_a, and *D* are assumed to be constant. [†] Assuming complex wave to be a simple wave. [‡] Photoelectron spectrum gives evidence for a small splitting <0.3 eV.

[a] Ref. 8. [b] A. M. Halpern and T. Gartman, *J. Amer. Chem. Soc.*, 1974, **96**, 1393.

TABLE 2

Voltammogram parameters for the oxidation of some heteroatom-substituted cyclic, bicyclic, and tricyclic amines at 298 K with a potential sweep rate of 33 mV s^{-1}; *ca.* 10^{-2}M-amine, 10^{-3}M-NaOH, and 10^{-1}M-$NaClO_4$ in 30% v/v methanol in deionised water

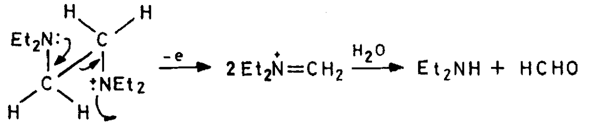
		First wave				
	Substrate	E_p/V *versus* s.c.e.	βn_a	$i_p/ACV^{\frac{1}{2}}$ / μA $s^{\frac{1}{2}}$ mM^{-1} cm^{-2} $V^{-\frac{1}{2}}$	Second wave E_p/V *versus* s.c.e.	I_p/eV
(23)	3-Hydroxy-*N*-methylpiperidine	0.85	0.48	551		8.60 [a]
(24)	*N*-Methylpiperidine	0.80	0.48	512		8.29 [b]
(25)	2-Hydroxymethyl-*N*-methylpiperidine	0.78	0.48	613		8.64 [a]
(26)	1,2-Dimethylpiperidine	0.78	0.48	620		8.28 [a]
(27)	*N*-(2-Hydroxyethyl)piperidine	0.75	0.53	582	0.93	8.59 [a]
(28)	*N*-(2-Aminoethyl)piperidine	0.89	0.28	807		8.24 [a]
(29)	*N*-Ethylpiperidine	0.79	0.44	713		8.26 [a]
(30)	*NN'*-Dimethylhexahydropyrimidine	0.95	0.40	636		8.34 [*,a]
(31)	*N*-Methylpiperazine	0.91	0.21	551		8.64 [*,a]
(32)	*NN'*-Dimethylpiperazine	0.89	0.40	667		8.77,[c] 8.41 [d]
(33)	*N*-Methylmorpholine	0.93	0.44	512		8.62 [d]
(34)	*trans*-1,5-Dimethyldecahydronaphthyridine	0.84	0.32	923	1.06	8.60 [*,a]
(35)	*NN'N''*-Trimethylhexahydro-*s*-triazine	0.98	0.53	931	1.33	8.25 [a]
(36)	*NN'*-Dimethyl-1,4-diazacycloheptane	0.65	0.53	729	0.89	
(37)	*N*-Methylazacycloheptane	0.60	0.64	752		8.29 [b]
(38)	*NN'*-Dimethyl-1,5-diazacyclo-octane	0.48	0.32	791	0.84	8.00 [a]
(39)	*N*-Methylazacyclo-octane	0.51	0.60	705		8.06 [a]
(40)	1,4-Diazabicyclo[2.2.2]octane	0.74	0.96	574		7.61 [†,c,e]
(41)	1,4-Diazabicyclo[2.2.2]-octane mono(methoperchlorate)	>1.5				
(42)	1-Aza-4-thioniabicyclo[2.2.2]octane perchlorate	>1.5				
(43)	1,5-Diazabicyclo[3.2.1]octane	1.17	0.74	900		8.89 [†,c], 8.24 [†,e]
(44)	1-Azabicyclo[2.2.2]octan-3-ol	1.00	0.60	582		8.16 [a]
(45)	1-Azabicyclo[2.2.2]octan-3-one	1.15	0.80	760		8.24 [†,f]
(46)	3-Hydroxyimino-1-azabicyclo[2.2.2]octane	1.07	0.27	512		8.17 [a]
(47)	1-Azabicyclo[2.2.2]octane	0.96	0.69	1 023		8.02 [f,g]
(48)	Hexamethylenetetramine	*ca.* 1.36				8.26 [h]
(49)	1,3,6,8-Tetra-azatricyclo[4.4.1.$1^{3,8}$]dodecane	0.69	0.80	938	1.04	7.39 [‡,i]

[*] Photoelectron spectrum gives evidence of a small splitting <0.3 eV. [†] Splitting between non-bonded orbitals >0.7 eV.

[a] Ref. 8. [b] K. Yoshikawa, I. Morishima, and M. Hashimoto, *J. Amer. Chem. Soc.*, 1974, **96**, 288. [c] Ref. 15. [d] Ref. *b* in Table 1. [e] Ref. 16. [f] Ref. 18. [g] P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Letters*, 1969, 4025. [h] M. J. S. Dewar and S. D. Worley, *J. Phys. Chem.*, 1969, **50**, 654. [i] Ref. 17.

resulting in an overall lowering of the E_p value. The observed oxidation peak potentials (for the first oxidation waves) for these amines agree quite well with this prediction, with the values for the longer chain substrates approaching that of the monoamine 1-dimethylaminopentane (1) (Table 1). Similarly heteroatom substitution in a mono- or bi-cyclic amine in general raises its oxidation peak potential (Table 2). The reduction of the E_p values of diamino-ethane and -propane on *N*-methylation or *N*-ethylation can also be rationalised in terms of the $+I$ effects of the alkyl groups aiding the oxidation.[5a] Similar conclusions were drawn from the second-order rate constants for the oxidation of these amines by aqueous alkaline potassium hexacyanoferrate(III).[2] When the E_p values of the acyclic and monocyclic amines and their homomorphs are plotted against the logarithms of their second-order rate constants there is a fair linear relationship (correlation coefficient $r = 0.88$), although not as good as that obtained for monoamines.[6b]

The low values of the first oxidation peak potentials of *NNN'N'*-tetramethyl- and *NNN'N'*-tetraethyl-ethane-1,2-diamine [(4) and (22)] relative to their homologues implicate a through-bond interaction between the nitrogens which stabilises the incipient radical cation.[9] This conclusion is reinforced by the formation of formaldehyde by oxidative fragmentation of the latter diamine [Grob fragmentation, equation (2)], for the stereochemical requirements for a Grob fragmentation have been shown to be the same as those for a through-bond interaction.[10] Acetaldehyde and not formaldehyde is the expected product from oxidative dealkylation of *NNN'N'*-tetraethylethane-1,2-diamine (22). By analogy with the above, Grob has shown that both synchronous and stepwise fragmentation can occur in the reactions of acyclic γ-chloro-amines despite the unfavourable loss of entropy in the fragmentation process.[10a]



(2)

Two oxidation waves were obtained in the linear sweep voltammograms of several polyamines and of one amino-alcohol. In no substrate with >3 carbon atoms between the heteroatoms was there more than one oxidation wave; however, not all those with <4 carbons between the heteroatoms showed two oxidation waves. Interestingly the second oxidation waves of the diaminoethanes all occur at approximately the same potential and at a lower value than those of the diaminopropanes. Masui *et al.*[11] reported two oxidation waves from the oxidation of tertiary monoamines at glassy-carbon electrodes in aqueous basic solution and attributed the second, more anodic, wave to oxidation of product, secondary amine. However, in our study of the oxidation of tertiary monoamines in basic aqueous methanol we found no evidence of a second oxidation wave.[6b]

Considering the possibility that the second oxidation waves observed in this study arise from oxidation products, then for *NNN'N'*-tetramethyl-ethane-1,2-diamine (4) and -propane-1,3-diamine (7) any product common to both amines cannot account for both the second oxidation waves. This eliminates the expected products dimethylamine and formaldehyde. Further, these products can also be eliminated as the cause of the second oxidation waves, for two oxidation waves would be expected from the electrochemical oxidation of all amines of general structure RCH_2NMe_2. The two possible amino-aldehyde products, dimethylamino-acetaldehyde and -propionaldehyde, arising from oxidative deamination, can also be ruled out, for the former would be expected to have a higher oxidation potential than the latter, which is contrary to the values obtained. Nor do the second oxidation waves arise from the demethylated ditertiary diamines for the *NNN'*-trimethyl-, *NN*-dimethyl-, and *NN'*-dimethyl-alkanediamines [(5), (6), (8), (9), and (10)] are all oxidised at potentials well below that of the corresponding second wave of the parent ditertiary diamine. Further *NNN'*-trimethyl- and *NN*-dimethyl-ethane-1,2-diamine [(5) and (6)] and *NNN'*-trimethylpropane-1,3-diamine (8) also show two oxidation waves with the second E_p value close to that of *NNN'N'*-tetramethyl-ethane-1,2-diamine (4) and -propane-1,3-diamine (7), respectively.

The fact that *NNN'N'*-tetramethylethane-1,2-diamine monomethoperchlorate (3) gives only one oxidation wave with a peak potential of 1.01 V suggested that the second oxidation waves of the polyamines might arise from the oxidation of intermediates of the type $Me_2N[CH_2]_m\overset{+}{N}Me_2$ or $Me_2N[CH_2]_m\overset{+}{N}{=}CH_2Me$ formed in the first oxidation step. This explanation can be rejected for it does not account for the two oxidation waves of *N*-(2-hydroxyethyl)piperidine (27), the similarity of the second E_p values of the diaminoethanes, and the second E_p value of *NNN'N'*-tetramethylpropane-1,3-diamine (7) being greater than that of *NNN'N'*-tetramethylethane-1,2-diamine (4).

We conclude that the second oxidation waves in these electrochemical oxidations cannot be due to further oxidation of products from the first oxidation. An alternative explanation comes from the work of Wopschall and Shain[12] on adsorption at electrode surfaces. They conclude that adsorption of the reactant on the anode in an oxidation process can lead to an extra oxidation wave at a more anodic potential than that required for a diffusion process, and that the greater the free energy of adsorption the greater the separation

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[9] (*a*) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499; (*b*) R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1.

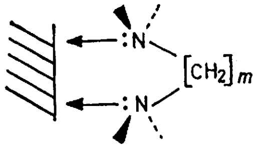
[10] (*a*) C. A. Grob, *Angew. Chem. Internat. Edn.*, 1969, **8**, 535; (*b*) R. Gleiter, W.-D. Stohrer, and R. Hoffmann, *Helv. Chim. Acta*, 1972, **55**, 893.

[11] M. Masui, H. Sayo, and Y. Tsuda, *J. Chem. Soc.* (*B*), 1968, 973.

[12] P. Wopschall and I. Shain, *Analyt. Chem.*, 1967, **39**, 1514.

between the diffusion and adsorption peaks. We suggest that for those substrates that show two oxidation waves the more anodic wave arises from oxidation of diamine adsorbed on the anode.

The adsorption process for an αω-diamine can be pictured as shown (Figure) with both nitrogens attached to the anode surface. The free energy of adsorption will thus, like the free energy of activation for the cyclisation of an ω-aminoalkyl bromide[13] or anchimeric assistance in the solvolysis of ω-substituted alkyl halides,[14] depend on the relative magnitudes of the enthalpy and entropy changes which in turn will depend on the size of *m*. As the value of *m* increases so will the loss of entropy as the diamine is adsorbed become greater and the value of the enthalpy of adsorption become more negative. Consequently when $m = 1$ there is a weak adsorption of substrate, when $m = 2$ or 3 stronger adsorption, and when $m > 3$ there is little or no adsorption.



FIGURE

Confirmation for this conclusion comes from equation (1) which predicts, assuming C, D, A, and V are constant and the E_p value arises from the oxidation of only one nitrogen, that $i_p/\beta^{\frac{1}{2}} =$ constant. The values of $i_p/\beta^{\frac{1}{2}}$ for the ditertiary diamines where $m > 3$ are about 90% greater than that of 1-dimethylaminopentane (1) (Table 1), whereas for $m = 2$ or 3 this ratio is intermediate between that of the monoamine and those of the longer chain diamines. Thus when $m > 3$ the two tertiary amino-groups appear to be acting independently and there is effectively double the concentration of amine present in the solution, whereas this is not the case for *NNN'N'*-tetramethylethane-1,2-diamine (4) and to a lesser extent *NNN'N'*-tetramethylpropane-1,3-diamine (7) where part of the diamine is adsorbed on the anode. *NNN'N'*-Tetramethylmethanediamine (2) has a complex oxidation wave and the peak current is a combination of those from free and adsorbed substrate.

Through-bond interactions are known to occur between the nitrogen lone pairs in 1,4-diazabicyclo[2.2.2]octane (40),[15,16] 1,5-diazabicyclo[3.2.1]octane (43),[16] and 1,3,6,8-tetra-azatricyclo[4.4.1.1^{3,8}]dodecane (49),[17] and between the nitrogen lone pairs and carbonyl group in 1-azabicyclo[2.2.2]octan-3-one (45).[18] In some instances, namely 1,4-diazabicyclo[2.2.2]octane (40) and 1,3,6,8-tetra-azatricyclo[4.4.1.1^{3,8}]dodecane (49), this through-bond effect stabilises the aminium radicals from these amines sufficiently to overcome the electron-withdrawing inductive or field effect of the substituent on the oxidation centre and the substrate is more easily oxidised than its homomorph. This can be revealed by the first ionisation potentials (I_p) and the splittings of the non-bonded orbitals as measured by photo-electron spectroscopy,[15-17] E_p values from cyclic voltammetry,[19] and the second-order rate constants for oxidations by potassium hexacyanoferrate(III).[2] The E_p values obtained in this study for seven bi- and tri-cyclic amines [excluding hexamethylenetetramine (48) for which the E_p value is only approximate] show a good linear correlation with the corresponding I_p values suggesting that similar interactions take place in both systems (correlation coefficient $r = 0.97$). Interestingly the strong electron-withdrawing influence of a positively charged substituent increases the E_p value of 1-azabicyclo[2.2.2]octane to a potential above that of the solvent background wave (>1.5 V) [compare (40) with (41) and (42)].

Through-bond or through-space effects causing small splittings of the non-bonded orbitals can be detected in the photoelectron spectra of the conformationally flexible hexahydropyrimidine,[8,15] piperazine,[8,15] and 1,5-decahydronaphthyridine systems; however, the E_p values from this study show that the dominant influence on the ease of electrochemical oxidation of these amines is the inductive or field effect of the heteroatom substituent on the oxidation centre. Thus the oxidation peak potential of *N*-methylpiperidine (24) is increased by the effective inductive or field effect of the substituent to give the following orders of E_p values: *N*-methylpiperidine (24) < *NN'*-dimethylpiperazine (32) < *N*-methylpiperazine (31) < *N*-methylmorpholine (33), and *N*-methylpiperidine (24) < *NN'*-dimethylpiperazine (32) < *NN'*-dimethylhexahydropyrimidine (30) < *NN'N''*-trimethylhexahydro-*s*-triazine (35). It is noteworthy that the difference between the oxidation potentials of *N*-methylpiperidine (24) and *NN'*-dimethylhexahydropyrimidine (30) (0.15 V) is greater than the difference between those of *NN'*-dimethylhexahydropyrimidine (30) and *NN'N''*-trimethylhexahydro-*s*-triazine (35) (0.03 V). It is possible that in the hexahydrotriazine there is more effective through-space stabilisation of the forming aminium radical than in the hexahydropyrimidine by overlap with a neighbouring nitrogen lone pair. A similar explanation was used to rationalise the faster one-electron chemical oxidation of the hexahydrotriazine than the hexahydropyrimidine.[2] Current views on the conformational preferences of these ring systems are consistent with this interpretation.[20] Interestingly the hexahydrotriazine gives two oxidation

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[13] G. H. Whitham, 'Alicyclic Chemistry,' Oldbourne, London, 1963, p. 10.

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[15] S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, 1974, **96**, 7930.

[16] Y. Yamada, A. Y. Hirakawa, T. Tsuboi, and H. Ogata, *Bull. Chem. Soc. Japan*, 1973, **46**, 2244.

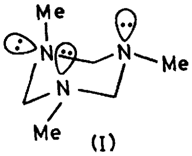
[17] S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, 1974, 96, 6424.

[18] C. C. Levin, R. Hoffmann, W. J. Hehre, and J. Hudec, *J.C.S. Perkin II*, 1973, 210.

[19] S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, 1972, **94**, 7114.

[20] (*a*) R. A. Y. Jones, A. R. Katritzky, and M. Snarey, *J. Chem. Soc.* (*B*), 1970, 135; (*b*) C. H. Bushweller, M. Z. Lourandos, and J. A. Brunelle, *J. Amer. Chem. Soc.*, 1974, **96**, 1591; (*c*) I. D. Blackburne, A. R. Katritzky, and Y. Takeuchi, *Accounts Chem. Res.*, 1975, **8**, 300.

waves and the more anodic adsorption wave which requires that two of the nitrogens are adsorbed onto the anode could be achieved through conformation (I), which would also allow the through-space interaction described above.



(I)

In the larger ring system of 1,5-diazacyclo-octane, linear sweep voltammetry shows further evidence for an interaction between the nitrogens for the E_p value of *NN'*-dimethyl-1,5-diazacyclo-octane (38) is less than that for *N*-methylazacyclo-octane (39). The lower E_p value of the diazacyclo-octane, which can be attributed to a transannular 1,5-interaction between a nitrogen lone pair and the incipient radical cation, is consistent with the observation of the stabilised radical cation in the oxidation of the diamine by potassium hexacyanoferrate(III),[2] the low ionisation potential of 2,3,4,5-tetrahydro-1,5-propano-1*H*-naphtho[1,8-*bc*]-1,5-diazocine [21] and the long-lived nature of the radical cations of 2,3,4,5-tetrahydro-1,5-propano-1*H*-naphtho[1,8-*bc*]-1,5-diazocine [22] and 1,5-dithiacyclo-octane.[23] It is probable that in all these radical cations there is a two-centre three-electron bond between the two heteroatoms.[22]

An explanation of the differences between the E_p values of the three β-hydroxypiperidines and those of their homomorphs is not possible at present. Further information is needed about the preferred conformations of these systems and the effective inductive or field effect of the hydroxy-group on the piperidine nitrogen.

EXPERIMENTAL

The spectroscopic, analytical, and electrochemical methods were as reported previously.[6b,24]

Materials.—Sodium hydroxide, sodium perchlorate, and methanol were AnalaR reagents. Some of the amine substrates were commercially available and were purified before use, and the preparations of the others have been reported [2] or are described below. *NNN'N'*-Tetramethylethane-1,2-diamine monomethoperchlorate (3) was prepared by adding a methanolic solution of *NNN'N'*-tetramethylethane-1,2-diamine monomethiodide [25] to an equimolar amount of silver perchlorate in methanol. The silver iodide was removed by filtration and the methanol by evaporation to give the *monomethoperchlorate*, m.p. 149—152° (from ether–methanol) (Found: C, 36.2; H, 8.0; N, 11.9. $C_7H_{19}ClN_2O_4$ requires C, 36.4; H, 8.3; N, 12.1%). 1-*Aza*-4-*thioniabicyclo*[2.2.2]*octane perchlorate* (42) was obtained from the corresponding bromide [26] by the method described above and was recrystallised from methanol. It decomposed without melting above 160° (Found: C, 31.2; H, 5.1; N, 6.0. $C_6H_{12}ClN_2O_4S$ requires C, 31.4; H, 5.3; N, 6.1%). 3-Hydroxyimino-1-azabicyclo[2.2.2]octane (46) was prepared from 1-azabicyclo[2.2.2]octan-3-one (45) following the method of Sternbach and Kaiser [27] and was purified by sublimation (120 °C and 15 mmHg). The oxime had m.p. 210—215° (lit.,[27] 213—217°) (Found: C, 59.9; H, 8.6; N, 20.1. Calc. for $C_7H_{12}N_2O$: C, 60.0; H, 8.6; N, 20.0%).

Product Study.—*NNN'N'*-Tetraethylethane-1,2-diamine (22) was oxidised by controlled potential electrolysis [6b] (0.80 V) and a portion of the solution from the anode compartment was shown to contain formaldehyde by the chromotropic acid test.[28] Blank tests with the solvent and acetaldehyde were negative. The remaining cell contents were first acidified and extracted with ether and then made strongly basic and re-extracted with ether. The latter extract was dried ($MgSO_4$), concentrated, and analysed by g.l.c. [20% (w/w) Apiezon L on Celite (100—120 mesh) coated with 5% (w/w) KOH, at 130 °C; flow rate (nitrogen) 20 cm^3 min^{-1}]. This analysis combined with g.l.c.–mass spectrometry showed the presence of unchanged substrate and *NNN'*-triethylethane-1,2-diamine.

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