Electroörganic Preparations

XXV. Polarography and Reduction of Benzotriazole and Related Compounds

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Benzotriazole and its mono- and dimethylderivatives, 1-hydroxy-benzotriazole and its methyl derivatives, 1-acetylbenzotriazole and derivatives of the phenylbenzotriazoles have been investigated polarographically and by means of controlled potential reductions. The reduction of benzotriazole in acid solution is a four-electron reaction to *o*-aminophenylhydrazine.
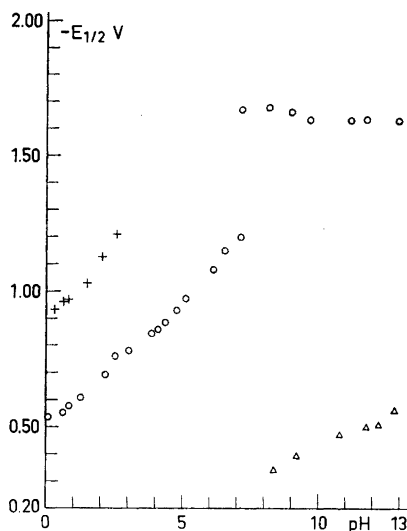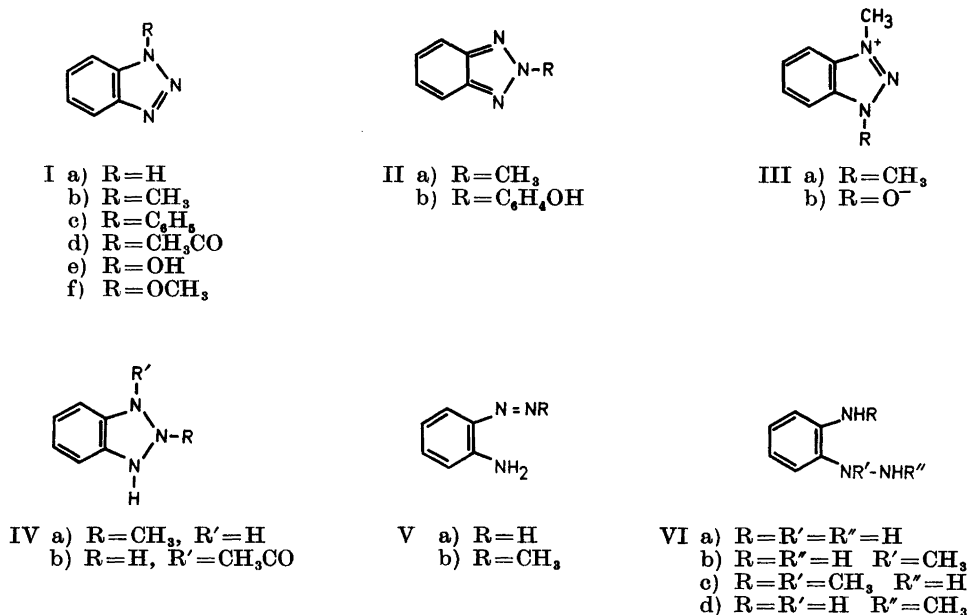
2-Methylbenzotriazole is in alkaline solution reduced to 1,3-dihydro-2-methylbenzotriazole, which in acid solution is rearranged to 1-(2'-aminophenyl)-2-methyldiimide. The reduction of 2-nitro-4'-hydroxyazobenzene to 2-(4'-hydroxyphenyl)benzotriazole-1-oxide and its further reduction have been investigated.

Benzotriazole is known to be polarographically reducible,[1] but the electrode reaction has not been investigated. This investigation is concerned with the polarographic behaviour of benzotriazole (Ia), 1-methylbenzotriazole (Ib), 2-methylbenzotriazole (IIa), 1,3-dimethylbenzotriazolium iodide (IIIa), 1-phenylbenzotriazole (Ic), 1-acetylbenzotriazole (Id), 1-hydroxybenzotriazole (Ie), 1-methoxybenzotriazole (If), 1-methylbenzotriazole-3-oxide (IIIb), 2-(4'-hydroxyphenyl)benzotriazole (IIb) and its 1-oxide, and 4,5,6,7-tetrachlorobenzotriazole. Further is the polarography of some of the reduction products, 2-methyldihydrobenzotriazole (IVa), 2-methyl-1-(2'-aminophenyl)-diimide (Vb), 2-aminophenylhydrazine (VIa) and derivatives thereof, reported.

Controlled potential reductions have been employed to elucidate the electrode reactions.

POLAROGRAPHIC INVESTIGATION

In Fig. 1 are plotted, as a function of pH, the cathodic half-wave potentials of 1-methoxybenzotriazole (If) and benzotriazole (Ia) and the anodic half-wave potentials of 2-aminophenylhydrazine (VIa). 1-Methoxybenzotriazole is in acid solutions reduced in two steps; the height of the first wave corresponds

I a) R=H
b) R=CH₃
c) R=C₆H₅
d) R=CH₃CO
e) R=OH
f) R=OCH₃

II a) R=CH₃
b) R=C₆H₄OH

III a) R=CH₃
b) R=O⁻

IV a) R=CH₃, R′=H
b) R=H, R′=CH₃CO

V a) R=H
b) R=CH₃

VI a) R=R′=R″=H
b) R=R″=H R′=CH₃
c) R=R′=CH₃ R″=H
d) R=R′=H R″=CH₃

Fig. 1. pH-Dependence of the half-wave potentials (SCE) of the cathodic waves of 1-methoxybenzotriazole (If) O and benzo-triazole (Ia) +, and the anodic wave of o-aminophenylhydrazine (VIa) △. The half-wave potentials of the second wave of If are close to those of Ia.
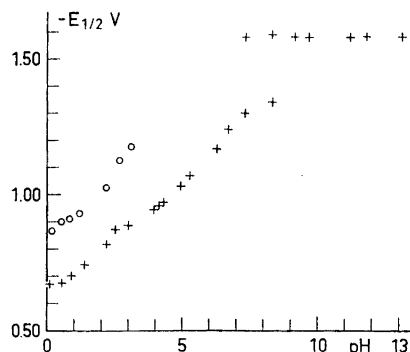
Fig. 2. pH-Dependence of the half-wave potentials (SCE) of the cathodic waves of 1-methylbenzotriazole-3-oxide (IIIb) + and 1-methylbenzotriazole (Ib) O. The half-wave potentials of the second wave of IIIb are close to those of Ib.

to a two-electron reduction, whereas the height of the second wave corresponds to a four-electron reaction. The half-wave potential of this second wave is nearly the same as that of benzotriazole, which suggests that benzotriazole is the primary reduction product from If; this second wave merges with that of the hydrogen ions about pH 3; benzotriazole is thus polarographically reducible only at pH < 3; the unprotonated benzotriazole and its anion are not reducible.

The height of the first wave of If diminishes between pH 5.5 and 8.5, where it disappears, and another wave appears at more negative potentials. Whereas the half-wave potentials of the first wave vary with pH with $\Delta E/\Delta \text{pH}$ about -0.10, this wave is independent of pH. The first wave represents the reduction of the protonated molecule and the latter that of the unprotonated species. In neutral solution the height of the first wave is partly determined by the rate of the recombination between hydrogen ions and the molecule.

The polarographic behaviour of 4,5,6,7-tetrachlorobenzotriazole is similar to that of benzotriazole; the half-wave potential is in strongly acid solution (pH 0) about 0.1 V less negative than that of Ia.

The anodic wave of o-aminophenylhydrazine resembles that of other phenylhydrazines[2] in that there is found a small adsorption prewave at more negative potentials than the main wave. As could be expected from the correlation between $E_{\frac{1}{2}}$ and the Hammett σ-values, the o-aminophenylhydrazine has a more negative half-wave potential [pH 13, $E_{\frac{1}{2}} = -0.49$ V (SCE)] than phenylhydrazine [pH 13, $E_{\frac{1}{2}} = 0.39$ V (SCE)]. The hydrazines obtained by reduction in acid solution of 1-methyl- (Ib) and 2-methylbenzotriazole (IIa), and 1,3-dimethylbenzotriazolium iodide (IIIa) give similar anodic waves with $E_{\frac{1}{2}} = -0.31$ V, -0.65 V, and -0.32 V (SCE), respectively, at pH 13.

The half-wave potentials of 1-methylbenzotriazole-3-oxide (IIIb) and of 1-methylbenzotriazole (Ib) are depicted in Fig. 2. IIIb is in acid solution reduced in two steps, a two-electron reduction followed by a four-electron reduction, and the half-wave potentials of the second wave are approximately the same as those of Ib, which suggests a reduction of IIIb to Ib. This is analogous to the electrochemical reduction of many heterocyclic N-oxides in acid solution. The reduction wave of Ib merges with that of the hydrogen ions about pH 3.

1,3-Dimethylbenzotriazolium iodide (IIIa) gives in acid solution a wave similar to that of Ib; at pH 1, $E_{\frac{1}{2}} = -0.80$ V (SCE). At pH >8 only a small, pH-independent wave is found at -1.3 V (SCE). The similarity in the polarographic reduction in acid solution of Ia, Ib, and IIIa lends support to the assumption that the wave is caused by the reduction of a species carrying a positive charge, i.e. the protonated form of Ia and Ib.

The first wave of IIIb disappears between pH 6 and 8 which is also found for many other N-oxides; in alkaline solution a pH-independent wave appears with a height corresponding to a one-electron reduction; a second wave which is pH-dependent is visible at more negative potentials between pH 9 and 12.

In Fig. 3 are given the half-wave potentials of 2-methylbenzotriazole (IIa), 2-methyl-1,3-dihydrobenzotriazole (IVa), and 1-methyl-2-(2′-aminophenyl)-diimide (Vb). IVa is the reduction product of IIa obtained in alkaline solution, and IVa is converted to Vb in acid solution.
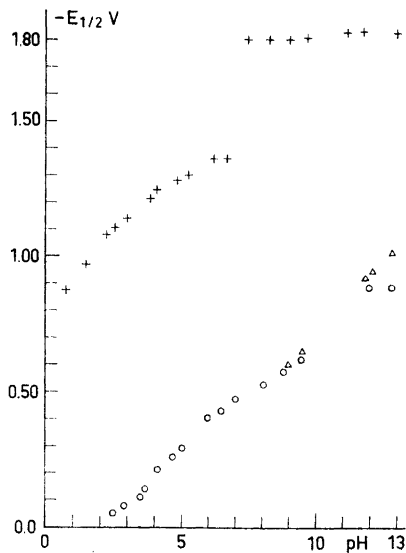
Fig. 3. pH-Dependence of the half-wave potentials (SCE) of the cathodic waves of 2-methylbenzotriazole (IIa) +, 1-methyl-2-(2'-aminophenyl)diimide (Vb) O, and the anodic wave of 2-methyl-1,3-dihydrobenzo-triazole (IVa) △.
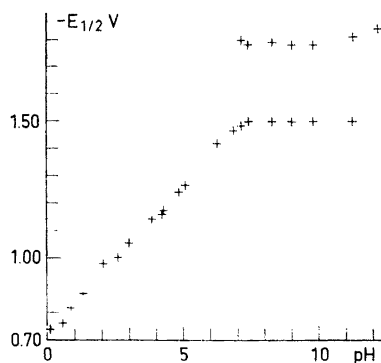
Fig. 4. pH-Dependence of the half-wave potentials (SCE) of the cathodic wave of 1-phenylbenzotriazole (Ic) +.

IIa gives a pH-dependent wave in acid solution with a height corresponding to a four-electron reduction. Between pH 4.5 and 7 this wave disappears and about pH 8 a pH-independent wave becomes visible. This wave is a two-electron wave.

Two features make the polarographic behaviour of IIa remarkable, the reducibility in alkaline solution of the unprotonated molecule and the formation of the protonated form prior to reduction in acid and slightly acid solution. The reducibility in alkaline solution may be connected with the special electronic distribution which is expressed in the formula with an *ortho*-quinoid benzene structure. This structure is also responsible for the low ability to add protons; whereas Ia and Ib form hydrochlorides and can be methylated easily, IIa does neither under ordinary conditions. One might thus expect a greater difference in polarographic behaviour between Ib and IIa than is found in acid solution.

IVa exhibits a pH-dependent anodic wave at rather positive potentials; the wave can, however, only be investigated at pH >8, as IVa is transformed rapidly into Vb at lower pH.

Below pH 3 the wave of Vb starts at the anodic dissolution wave of mercury; between pH 3 and pH 10 a pH-dependent two-electron wave is found; a small prewave is visible in most buffers. At pH >11 a pH-independent wave is found. The amino group is probably responsible for the somewhat irregular shape of the $E_{\frac{1}{2}}$-pH curve of Va between pH 3 and 10.

In Fig. 4 are plotted the half-wave potentials of 1-phenylbenzotriazole (Ic). This compound is in acid solution reduced in a four-electron reduction as Ia, but in alkaline solution Ic is, contrary to Ia, reducible; the reaction is here a two-electron reduction; a small adsorption prewave of nearly constant height is found at −1.50 V (SCE) at pH >8. The half-wave potential of the main wave in alkaline solution is only slightly dependent on pH.

The polarographic behaviour of 2-(4'-hydroxyphenyl)-benzotriazole (IIb) is similar to that of Ic, and their half-wave potentials are in acid solution not much different. In alkaline solution the $E_{\frac{1}{2}}$-pH curve forms an S-shaped curve probably due to the dissociation of the phenolic group. The N-oxide of IIb shows a wave due to the reduction of the N-oxide group at potentials about 0.6 V more positive than the wave of IIb. The wave is poorly defined at higher pH.

1-Acetylbenzotriazole (Id) gives a single pH-dependent wave with a height corresponding to a two-electron wave (Fig. 5). In alkaline and in strongly acid solution the compound is hydrolyzed, and in the latter solvent the wave of benzotriazole gradually appears with a height approximately twice that of Id. In Fig. 5 are also included the half-wave potentials of 1-hydroxybenzo-triazole (Ie). The second wave which has a height twice that of the first one is found at the same potentials as that of Ia. In solutions more alkaline than pH 7 no wave is visible, possibly due to dissociation of the compound.

CONTROLLED POTENTIAL REDUCTIONS

Benzotriazole was réduced in 4 N hydrochloric acid at −1.0 V (SCE) and the reaction consumed 4 electrons per molecule. On evaporation of the catholyte *in vacuo* under reduced pressure was isolated a hydrochloride which was considered to be *o*-aminophenylhydrazine (VIa) from the analysis and the
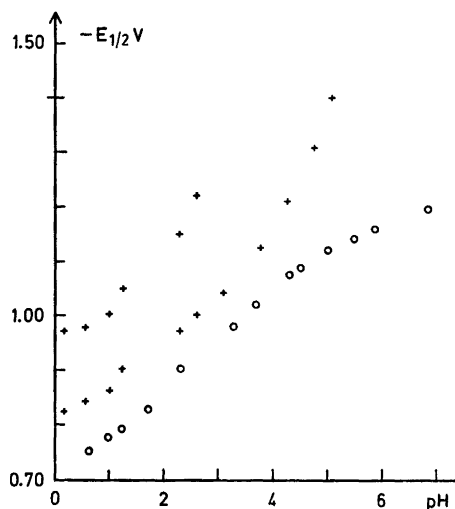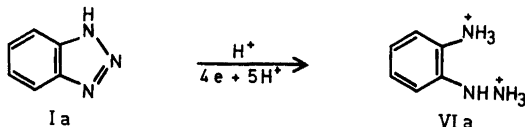
Fig. 5. pH-Dependence of the half-wave potentials (SCE) of the cathodic waves of 1-acetylbenzotriazole (Id) O and 1-hydroxybenzotriazole (Ie) +.

occurrence of an anodic wave at rather negative potentials (Fig. 1). The reaction is:


VIa has previously been prepared by reduction of o-nitrophenylhydrazine with tin and hydrochloric acid,[3] but is difficult to obtain pure by the chemical reduction. VIa is of potential value as an intermediate for the preparation of heterocyclic compounds, as it has three groups capable of condensing with suitable reagents to different ring systems.

1-Methylbenzotriazole (Ib) and 1,3-dimethylbenzotriazolium iodide are reduced similarly. The latter is believed to be reduced to 1-(2′-methylamino-phenyl)-1-methylhydrazine (VIc) from the available evidence (analysis, anodic wave, $E_{\frac{1}{2}} = -0.3$ V (SCE) at pH 13); as the reduction product of Ib gives an anodic wave at nearly the same potential as VIc, which is about 0.2 V more positive than the half-wave potential of VIa, the reduction product from Ib is assumed to be 1-(2′-aminophenyl)-1-methylhydrazine (VIb), but no conclusive proof is available.
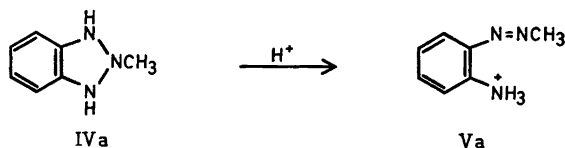
The preparation of 1,2-dimethylbenzotriazolium iodide by reaction between 2-methylbenzotriazole and methyl iodide in acetonitrile at 100° in a closed vessel was attempted. Besides unreacted 2-methylbenzotriazole only 1,3-dimethylbenzotriazolium iodide was isolated.

2-Methylbenzotriazole (IIa) is in acid solution reduced to 1-(2′-amino-phenyl)-2-methylhydrazine (VId) in a four-electron reduction. In alkaline solution the reaction consumes two electrons ($E = -1.8$ V (SCE)) and the reduction product shows an anodic wave at -1.0 V (SCE) at pH 13. The reduction product was difficult to isolate owing to its solubility in water and very easy reoxidation. When the product was oxidized anodically in alkaline solution, IIa was formed. From this it was concluded that the reduction did not result in cleavage of the ring and the reduction of IIb thus yielded 2-methyl-1,3-dihydrobenzotriazole IVa. The reactions are
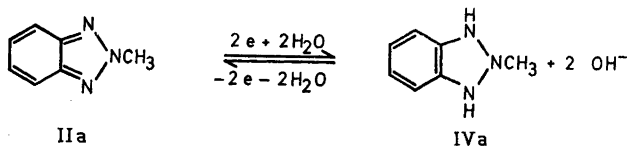
When the colourless alkaline solution of IVa was acidified with hydrochloric acid, a red solution resulted, which gave a cathodic wave at rather positive potentials (Fig. 3); when this solution was made alkaline, it turned yellow and gave still a cathodic polarographic wave and no anodic wave. The protonation of IVa thus produces an opening of the ring.

The compound thus obtained has been formulated as an azocompound (Va) which is in accordance with its polarographic (Fig. 3) and spectroscopic properties. The compound is reasonably stable at low temperature, but hydro-

IVa   Va

lyzes both in acid and base at higher temperatures. It does not yield IVa by ring closure in alkaline solution. A similar diimide was isolated by Krollpfeiffer et al.[4] by reduction of 1,2-dimethylbenzotriazolium methylsulphate with an alkaline solution of sodium dithionite.

1-Hydroxybenzotriazole yields on methylation two compounds, 1-methoxybenzotriazole (If) and 1-methylbenzotriazole-3-oxide (IIIb). Controlled potential reduction of If in acid solution at the potential of the first wave produced Ia in a two-electron reduction; this compound was also the product from a reduction of If $[E = -1.75$ V vs. (SCE)] in alkaline solution. IIIb produced Ib on reduction in acid solution at the plateau of the first polarographic wave $[E = -0.75$ V (SCE), pH $= 1]$. The results from the electrolysis thus support the assigned structures.

1-Acetylbenzotriazole (Id) hydrolyzes in aqueous solution, but by working in cold solutions it is possible to electrolyze the compound without serious complications due to hydrolysis. Id gives only a two-electron polarographic wave; no further waves due to the reduction product is found, so benzotriazole is not formed in the reduction. Controlled potential reduction consumed four electrons per molecule and the product gave in alkaline solution an anodic wave. The product was not isolated pure, but as the product showed an anodic wave at pH 13 at -0.65 V (SCE) and an absorption was found at 1650 cm^{-1} in the infrared spectrum, the compound is probably 2-acetaminophenylhydrazine.

The reduction of Id to 2-acetaminophenylhydrazine involves a slow step, as it gives a two-electron polarographic wave, but coulometrically a four-electron reduction. The primary reduction product could be either a phenyldiimide or a dihydrobenzotriazole.

IVb

Vc
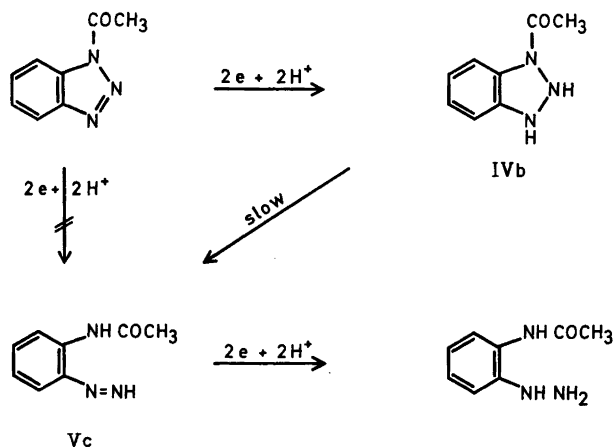
There seems no reason why the phenyldiimide Vc should be reduced through a slow step, whereas the dihydrocompound, IVb, may be transformed to Vc in a relatively slow reaction. If the ring opening of 1-acetyl-2,3-di-hydrobenzotriazole involves an attack of hydrogen ions as suggested above for the ring opening of IVa, it is reasonable that an acylation makes a reaction involving such a protonation slower than in the case of IVa, and that the reduction proceeds as suggested in the reaction scheme presented above.

Reduction in alkaline solution at −0.60 V (SCE) of 2-nitro-4'-hydroxy-azobenzene (VII) produces in a two-electron reaction 2-(4'-hydroxyphenyl)-benzotriazole-1-oxide, which at a more negative potential [−1.20 V (SCE)] could be reduced to 2-(4'-hydroxyphenyl)benzotriazole with the consumption of further two electrons per molecule. At −1.80 V (SCE) a reduction to the dihydroderivative takes place. These reactions can be formulated as
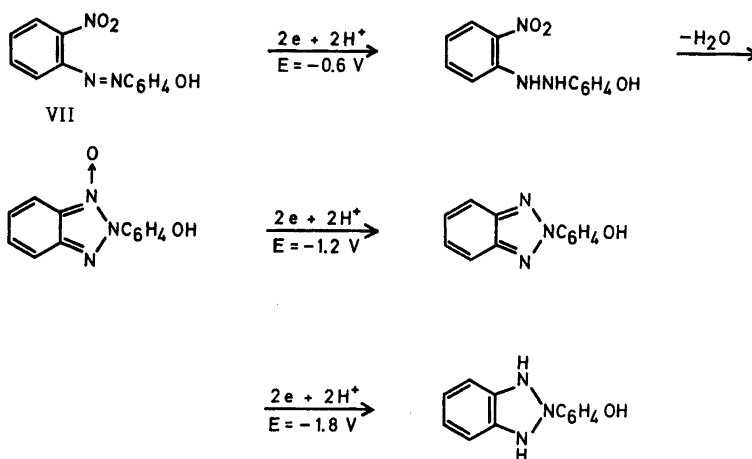
VII has previously been reduced to IIb at a nickel cathode,[5] but without control of the potential it was not possible to limit the reduction and isolate the N-oxide.

DISCUSSION

Benzotriazole can be reduced under Clemmensen conditions and with zinc and base to o-phenylenediamine,[6] and this is also formed by the reaction with sodium in ammonia in the presence of a proton donor;[7] without a proton donor a dihydroderivative is found. Lithium aluminium hydride or sodium borohydride do not attack the benzotriazole nucleus.[8] No chemical reductions of benzotriazoles have been reported to yield an o-aminophenylhydrazine.

The polarographic reduction which has been suggested to be a one-electron reduction[1] consumes, however, four electrons and produces o-aminophenyl-hydrazine.

The reduction is preceded by a protonation, and the product primarily formed by the uptake of two electrons might be either the dihydrobenzotriazole or the o-aminophenyldiimide. The results from the reduction of 2-methyl-

benzotriazole in alkaline solution show that the dihydrobenzotriazole (IVa) is not stable in acid solution but rearranges rapidly to Va. In the reduction of 1-acetylbenzotriazole it was suggested that the slow step in the reaction was the rearrangement of the dihydrocompound IVb to Va, but classical polarography is not capable of detecting any slow reactions in the reduction of benzotriazole; possibly oscillographic polarography could be able to do it. During a preparative reduction a small polarographic wave, starting at the dissolution wave of mercury, can be detected, which probably is caused by a small concentration of the diimide. There is thus yet no evidence of the presence of the dihydrobenzotriazole during the reduction, although it might be present as a short-lived intermediate, but some indication of the diimide as an intermediate, and the reaction can thus be formulated as
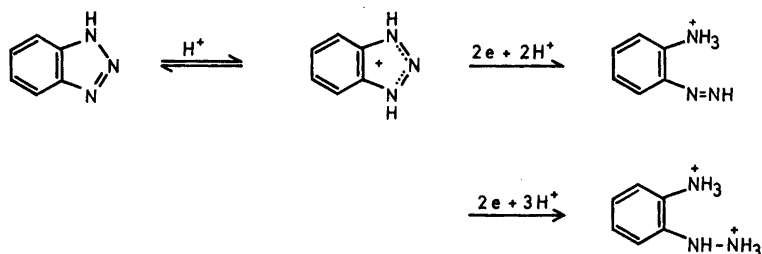
The reduction of benzotriazole is analogous to the reduction of aromatic triazenes in which are produced an aromatic amine and a hydrazine.[9] The wave height is, however, for the triazenes the same in both slightly acid and alkaline solution; in strongly acid solution the compounds rearrange too fast for a polarographic measurement. In the reduction of aromatic triazenes no conclusive evidence was found as to whether or not the reduction involved the primary formation of triazanes.

During the reduction of Ib and IIIa no cathodic wave comparable in size to that obtained during the reduction of Ia grew up; this is consistent with the proposed reaction route as the diimides which would give the assumed products VIb and VIc, respectively, would not be expected to be as stable as Va but would be either reduced or hydrolyzed rapidly.

o-Aminophenylhydrazine may react with reactive acid derivatives to produce a mixture of benzo-1,2,4-triazines and benzimidazoles and with α-dicarbonyl compounds to a mixture of benzo-1,2,5-triazepines and derivatives of quinoxaline; the proportion of the larger ring to the smaller ring in the reaction mixture depends on the choice of reagents and the reaction temperature.

The reduction of 2-nitro-4'-hydroxyazobenzene to 2-(4'-hydroxyphenyl)-benzotriazole-1-oxide has been formulated as a reduction of the azobenzene to a hydrazobenzene which then attacks the nitro group. The reaction is thus analogous to the ring closure of o-nitrophenylhydrazine in alkaline solution to benzotriazole-1-oxide.[10]

This is supported by polarographic evidence; the reduction is performed at a potential where the nitro group is not reducible, but where the azo group would be expected to be reducible.

EXPERIMENTAL

The polarograph was a recording polarograph Radiometer PO 4 d. The potentiostat was a Wadsworth Controlled Potential Electro-Depositor. For the anodic oxidations manual control of the anode potential was used.

Materials. 1- and 2-methylbenzotriazole was prepared according to Krollpfeiffer *et al.*[4] 1,3-Dimethylbenzotriazolium iodide[4] was obtained by reaction of Ib with methyl iodide in acetonitrile. 1-Hydroxybenzotriazole was made from *o*-nitrophenylhydrazine;[10] it was methylated according to Brady and Reynolds[11] to 1-methoxybenzotriazole and 1-methylbenzotriazole-3-oxide. 1-Acetylbenzotriazole was obtained by the method of Staab,[12] 1-phenylbenzotriazole according to Schöpff,[13] and 4,5,6,7-tetrachlorobenzotriazole according to Wiley *et al.*[14] 2-Nitro-4′-hydroxyazobenzene was prepared by the method of Elbs and Keiper.[5]

Reduction of benzotriazole (Ia). Benzotriazole (1 g) was reduced in 4 N hydrochloric acid at -1.0 V (SCE) at $0-5°C$. The solution turned reddish and a small polarographic wave starting at the anodic dissolution wave of the mercury appeared. The initial current was $2-3$ A and decreased gradually. The reaction consumed four electrons per molecule. The catholyte was evaporated *in vacuo* (1 mm) in a slow current of nitrogen at a bath temperature not exceeding 40°. The residue was recrystallised by dissolving it in methanol and precipitating it with dry ether. Yield 72.5 %. (Found: C 37.21; H 5.59. Calc. for $C_6H_5N_3,2$ HCl: C 36.75; H 5.62). The compound yielded an anodic wave (Fig. 1). Main bands in IR spectrum (KBr, cm⁻¹): 3470 (w), 3370 (w), $3350-2300$ (s), 1620 (w), 1580 (w), 1525 (ms), 1485 (ms), 1395 (s), 1300 (w), 1115 (w), 755 (s).

Similarly were reduced 1-methylbenzotriazole (Ib), 2-methylbenzotriazole (IIa), and 1,3-dimethylbenzotriazolium iodide (IIIa). Reduction product from Ib: Anodic wave (main wave) at pH 13, $E_{\frac{1}{2}} = -0.31$ V (SCE). (Found: C 38.5; H 6.25; N 19.9. Calc. for $C_7H_{11}N_3,2$ HCl; C 40.01; H 6.24; N 20.00). Principal bands in IR spectrum (KBr, cm⁻¹): $3400-2200$ (several broad bands), 1950 (w), 1580 (w), 1530 (m), 1475 (s), 1380 (m), 1280 (w), 1135 (m), 1055 (w), 1015 (w), 1005 (w), 900 (w), 775 (s). Reduction product from IIa: Anodic wave (main wave) at pH 13, $E_{\frac{1}{2}} = -0.65$ V (SCE). The product is unstable especially in neutral and alkaline solution. Reduction product from IIIa: Anodic wave (main wave) at pH 13, $E_{\frac{1}{2}} = -0.32$ V (SCE). (Found: C 40.2; H 6.5; N 18.4. Calc. for $C_8H_{13}N_3,2$ HCl: C 42.9; H 6.7; N 18.75). Principal bands in IR spectrum (KBr, cm⁻¹): $3400-2200$ (several broad bands), 2010 (w), 1600 (w), 1545 (m), 1515 (m), 1485 (m), 1430 (m), 1380 (s), 1110 (m), 1070 (w), 1015, 1010 (w), 965 (w), 908 (w), 780 (s).

Reduction of 2-methylbenzotriazole (IIa). 2-Methylbenzotriazole (0.5 g) was reduced in 0.2 N potassium hydroxide at -1.80 V (SCE) at $0-5°C$. The cathodic wave disappeared gradually and an anodic one grew. After the consumption of two electrons per molecule the cathodic wave had disappeared. The colourless solution was then oxidized anodically at -0.8 V (SCE). A cathodic wave appeared about -1.8 V (SCE) during the oxidation (1.9 electrons per molecule) and in the reoxidized solution 2-methylbenzotriazole was identified by polarography at different pH-values.

When a similar reduction was performed and the reduced solution made acid with hydrochloric acid a red solution resulted which both in acid and alkaline solution gave a cathodic, but no anodic wave (Fig. 3).

On raising pH the red solution turned yellow. Above 300 mμ the red solution had a broad maximum at 475 mμ and shoulders at 580 mμ and 335 mμ.

Reduction of 1-methoxybenzotriazole (If). 1-Methoxybenzotriazole (0.5 g) was reduced in N hydrochloric acid at -0.75 V (SCE). The first wave gradually disappeared and the second wave, which was at the same potential as that of benzotriazole, remained. The reduction consumed two electrons per molecule, and after completion the catholyte was made alkaline with solid sodium carbonate and extracted continuously with chloroform. The chloroform was dried and evaporated leaving a residue, m.p. 100°, which was identified as benzotriazole from the IR and NMR spectrum.

Reduction of 1-methylbenzotriazole-3-oxide (IIIb). 1-Methylbenzotriazole-3-oxide was reduced in an acetate buffer containing 35 % alcohol at -1.15 V (SCE). The reduction completed (two electrons per molecule), the catholyte was made alkaline with solid sodium carbonate and extracted continuously with chloroform, which was dried (potassium carbonate) and evaporated. The residue, m.p. $63-64°C$, was identified as 1-methylbenzotriazole from its IR and NMR spectrum.

Reduction of 1-acetylbenzotriazole (Id). 1-Acetylbenzotriazole (0.5 g) was reduced in 0.5 N hydrochloric acid containing 20 % ethanol at −0.95 V (SCE). The temperature was kept at 0°C. The reduction consumed four electrons per molecule, and the reduced solution gave at pH 13 an anodic wave at −0.65 V (SCE). An attempt to isolate the product was made, as described above for Ia, but no pure compounds were obtained; the IR spectrum of the crude product had an absorption at 1650 cm⁻¹.

Reduction of 2-nitro-4'-hydroxyazobenzene. 2-Nitro-4'-hydroxyazobenzene (1.0 g) was reduced in 0.1 N aqueous potassium hydroxide containing potassium chloride at −0.60 V (SCE) with the consumption of two electrons per molecule. The reduction completed, the catholyte was made slightly acid with glacial acetic acid; the precipitate was filtered and washed with hot water. It was recrystallised from ethanol-water, yield 82 %. The compound, m.p. 230−240° (decomp.) was identified as 2-(4'-hydroxyphenyl)benzotriazole-1-oxide from the analysis. (Found: C 63.3; H 3.9; N 18.6. Calc. for $C_{12}H_9N_3O_2$: C 63.5; H 3.96; N 18.5) and its ability to be reduced in a two-electron reduction to the parent triazole.

Reduction of 2-(4'-hydroxyphenyl)benzotriazole-1-oxide. 2-(4'-Hydroxyphenyl)benzo-triazole-1-oxide (1 g) was reduced at −1.2 V (SCE) in 0.1 N aqueous potassium hydroxide containing potassium chloride. The reduction consumed two electrons per molecule; the reduction completed, the catholyte was made slightly acid with glacial acetic acid and the precipitate filtered and washed with water. It was recrystallised from aqueous ethanol, m.p. 222−223°, and identified as 2-(4'-hydroxyphenyl)benzotriazole (IIb) from the m.p. 217−219°[5] and the analysis. (Found: C 68.6; H 4.3; N 20.2. Calc. for $C_{21}H_9N_3O$: C 68.3; H 4.26; N 19.9).

REFERENCES

1. Harrison, S. and Woodroffe, G. L. *Analyst* **90** (1965) 44.
2. Nagata, Y., Tachi, I. and Kitao, K. *Collection Czech. Chem. Commun.* **25** (1960) 3271.
3. Guha, P. C. and Ray, S. K. *J. Indian Chem. Soc.* **2** (1925) 83.
4. Krollpfeiffer, F., Rosenberg, A. and Mühlhausen, C. *Ann.* **515** (1935) 113.
5. Elbs, K. and Keiper, W. *J. prakt. Chem.* (2) **67** (1903) 580.
6. Wakae, M., Konishi, K., Furukawa, M. and Hamada, E. *Osaka Furitsu Kogyo-Shoreikan Hokoku* **27** (1962) 46; *Chem. Abstr.* **61** (1964) 3096.
7. Cappel, N. O. and Fernelius, W. C. *J. Org. Chem.* **5** (1940) 40.
8. Gaylord, N. G. and Kay, D. J. *J. Org. Chem.* **23** (1958) 1574.
9. Lund, H. *Studier over Electrodereaktioner i Organisk Polarografi og Voltammetri,* Aarhuus Stiftsbogtrykkerie A/S, Aarhus 1961.
10. Zincke, T. and Schwarz, P. *Ann.* **311** (1900) 329.
11. Brady, O. L. and Reynolds, C. V. *J. Chem. Soc.* **1928** 193.
12. Staab, H. A. *Chem. Ber.* **90** (1957) 1320.
13. Schöpff, M. *Ber.* **23** (1890) 1839.
14. Wiley, R. H., Hussung, K. H. and Moffat, J. *J. Am. Chem. Soc.* **77** (1955) 5105.