Amine Oxidation. Part 15.[1] A Product and Stoicheiometric Study of the Oxidation of Aminoalcohols by Vanadium(V) Ions in Aqueous Perchloric Acid

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A study of the conditions under which aqueous diethanolamine (DEA) is oxidised by vanadium(V) ions reveals that in neutral or basic solution no reaction occurs at reflux or at lower temperatures. However, in acid solution with pH < 4 oxidation takes place. The products and stoicheiometry of the oxidation of DEA and of some related compounds in aqueous perchloric acid show that the aminoalcohols are extensively degraded. The oxidations resemble those of simple alcohols and involve an initial loss of hydrogen from the C–H bond α to the hydroxy-group. The mechanisms of this and subsequent oxidations in this multistep process are discussed.

A detailed knowledge of the mechanisms of oxidation by vanadium(V) compounds has important implications for their mode of action in industrial processes.[2] In this respect there have been numerous studies of the oxidation of organic compounds by aqueous solutions of pentavalent vanadium. The mechanisms of these processes have largely been deduced from kinetic evidence or from a combination of kinetic and product studies.[3]

One important application of vanadium(V) compounds is their use as corrosion inhibitors in aqueous-based acid gas separation systems used to remove carbon dioxide and/or hydrogen sulphide from other gases. A common arrangement uses large mild steel vessels with circulating strongly alkaline aqueous solutions of potassium carbonate, an aminoalcohol such as diethanolamine (DEA), and metavanadate ion.[4] The presence of the aminoalcohol improves interfacial transfer of the acid gas, and the vanadium(V) ions act as a corrosion inhibitor by maintaining a passive iron oxide layer on the surface of the reaction vessel. Reduction of the vanadium(V) could arise under the operating conditions, or by reaction with other components in the system. In order to prevent severe corrosion of the mild steel it is necessary to maintain the level of vanadium(V) through a regeneration procedure, and it has been noted that aminoalcohol is also lost through degradation.[5] The possible connection between the loss of these reagents has led us to investigate the oxidation of aminoalcohols by vanadium(V) ions and we report here the results from a product and stoicheiometric study of the oxidation of aminoalcohols and related compounds by vanadium(V) ions.

Aminoalcohols have been oxidised by inorganic[6] and organic oxidants[7] and by electrochemical methods[8] but the only previous study of vanadium(V) oxidation of aminoalcohols is the very recent report by Puutio and Virtanen on the oxidation of triethanolamine (TEA) and DEA.[9] The equivalent oxidation of other aliphatic amines is limited to the qualitative survey by Littler and Waters,[10] although the oxidation of alcohols by aqueous solutions of vanadium(V) ions has been extensively studied.[3]

Results and Discussion

Influence of Reaction Conditions on Oxidation of DEA by Vanadium(V) *Ions*.—U.v.–visible spectroscopy shows that no reaction occurs when aqueous solutions (pH 10.5—4.2, adjusted with perchloric acid) of sodium metavanadate (10^{-3}M) and DEA (10-fold excess) are maintained at 25 or 40 °C or at reflux in air or under nitrogen for 13—24 h. No reaction occurs when the concentrations of vanadium(V) ions and DEA are increased by 10-fold, showing that DEA is not susceptible to oxidation by polyvanadate species under these conditions.[11] However, at higher temperatures (130—180 °C) vanadium(V) is reduced to vanadium(IV), the extent of reaction decreasing with decreasing concentration of oxygen in the solution. The high-temperature reactions which are currently under investigation will be the subject of a future paper.

In an attempt to induce oxidation of DEA in an analogous manner to that reported by Murty *et al.*[12] for the oxidation of cyclohexanone and of lactic acid, the reactions at reflux were repeated with added copper(II) chloride, iron(III) chloride, or chromium(III) chloride. No reduction of vanadium(V) occurs at pH 10.3 or 7.5 although at the lower pH the reactions become cloudy from the precipitation of transition metal vanadates.

Since pentavalent vanadium is normally used as an oxidant in acidic solution (pH < 1)[3a] the reactions were studied at lower pH values. When an aqueous solution of DEA and vanadium(V) ions (pH 1.6) is heated to reflux for 3 h all the vanadium is precipitated as a green solid. Although magnetic susceptibility studies showed the solid to be paramagnetic, demonstrating the presence of vanadium(IV) ions, elemental analysis was inconclusive. Heating the solid in dilute perchloric acid (pH 1.5) gives blue-green solutions of tetravalent vanadium (u.v. spectroscopy). Some related aminoalcohols, namely TEA, *NN*-dimethylethanolamine, and 3-dimethylaminopropan-1-ol, give similar green solids.

When DEA and sodium metavanadate are heated at reflux in air in 2.0M-perchloric acid the solution remains homogeneous and u.v.–visible spectroscopy shows that the vanadium(V) is completely reduced to vanadium(IV). Unless otherwise stated all the product studies described below were carried out under these conditions.

Identification of Products from the Oxidation of Aminoalcohols by Vanadium(V) *Ions*.—The starting materials and products from most of the reactions are very soluble in water which precludes their extraction into an organic solvent. Direct analysis of the basic aqueous solutions, however, was achieved by ^{13}C n.m.r. spectroscopy combined in some instances with colorimetry.

A ^{13}C n.m.r. procedure was developed for characterising the products of the reaction of DEA with vanadium(V) ions and this was applied to the reactions of other substrates. At the end of the reaction the paramagnetic vanadium(IV) ions are reoxidised to vanadium(V) with sodium hypochlorite. Several oxidants were investigated for this reoxidation and of these

Stoicheiometric and product data for the oxidation of aminoalcohols and related compounds by vanadium(v) ions in 2.0M-perchloric acid

Substrate	Products detected by ^{13}C n.m.r.	Temperature (°C)	Time of reaction (h)	Moles of vanadium(v) consumed/moles of substrate
$HN(CH_2CH_2OH)_2$	$HCO_2H + H_3\overset{+}{N}CH_2CH_2OH$	100	165	12.3
$Me_2NCH_2CH_2OH$	$HCO_2H + Me_2\overset{+}{N}H_2$	100	70	6.0
$Me_2NCH_2CH_2CH_2OH$	$HCO_2H + Me_2\overset{+}{N}H_2$	100	65	8.9
$H_2NCH_2CHOHMe$	$HCO_2H + MeCO_2H$	100		
$H_2NCH_2CHOHPh$	$HCO_2H + PhCO_2H$	100	67	6.0
H_2NCH_2COPh	$HCO_2H + PhCO_2H$	100	47	4.8
$MeCH_2CHNH_2CH_2OH$	$HCO_2H + MeCH_2CO_2H$	100		
$H_2NCMe_2CH_2OH$	None detected	100	210	3.6
Me_3CCH_2OH	Me_3CCO_2H	60	480	4.1
$MeCH_2CH_2OH$	HCO_2H	100		
Me_3CCHO	Me_3CCHO	100	285	2.1
Me_2NCHO	$HCO_2H + Me_2\overset{+}{N}H_2$	100	21	0.0
Me_2NH	None detected	100	69	0.0
$PhCO_2H$	None detected	100	108	0.0

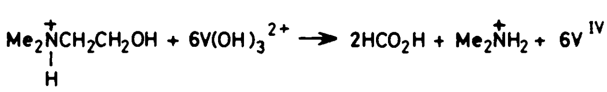
hypochlorite proved most suitable. Sodium hypochlorite cleanly and rapidly converts vanadium(IV) into vanadium(v) in aqueous perchloric acid and it does not react with perchloric acid solutions of DEA. Furthermore, warming reaction mixtures which have been treated with hypochlorite removes any excess of the reagent. This allows the recycling of vanadium(v) ions in reactions which helps to build up sufficient product for ^{13}C n.m.r. spectroscopy and avoid the use of high concentrations of vanadium(v). Three new absorptions [δ 167.2 (d in off-resonance), 59.1 (t), and 42.9 (t)] appear in the ^{13}C n.m.r. spectrum of the reaction mixture of DEA (0.5M) and sodium metavanadate (0.25M) which has been subjected to three oxidation cycles as described above. Comparison of the product absorptions with those from authentic materials shows them to correspond to the absorptions of formic acid and MEA. The products from other reactions were identified in a similar manner.

The Table records the products obtained from the vanadium(v) oxidation of some aminoalcohols and related compounds. These data reveal that the compounds are extensively degraded to carboxylic acids and ammonium ions. The absence of formaldehyde in any of the mixtures was confirmed with a negative chromatropic acid colour test.[13] However, since formaldehyde is known to be oxidised by vanadium(v),[14] the validity of the colour test was checked by reacting the two species in perchloric acid under the reaction conditions. Heating an equimolar solution of formaldehyde and sodium metavanadate at reflux for 16 h resulted in a 21% loss of substrate as assessed by the chromotropic acid test. This shows that sufficient formaldehyde would have been present in the aminoalcohol reactions for detection by this very sensitive test. The standard spot test to confirm the presence of formic acid by its reduction to formaldehyde[15] failed for these reactions since the vanadium(IV) ions are preferentially reduced to a brown solution that masks any other colour changes.

Stoicheiometry of the Oxidations of Aminoalcohols and Related Compounds by Vanadium(v) *Ions*.—The consumption of vanadium(v) in the oxidation of aminoalcohols was obtained by a modification of a procedure of West and Skoog[16] for the oxidation of polyhydric alcohols and hydroxycarboxylic acids with aqueous solutions of vanadium(v) (Table), and confirms the conclusions from the product analyses that the reactions of aminoalcohols with vanadium(v) ions are multistep oxidations involving C–C bond cleavage. Like polyhydric alcohols[16,17] and polyethylene glycol,[18] aminoalcohols are extensively degraded by vanadium(v) ions. Thus DEA consumes *ca.* 12 equiv. vanadium(v) which corresponds to its complete oxidation to formic acid and ammonium ion [equation (1)].

$$12V(OH)_3{}^{2+} + H_2\overset{+}{N}(CH_2CH_2OH)_2 \longrightarrow 4HCO_2H + NH_4{}^+ + 12V^{IV} \quad (1)$$

Influence of Substrate Structure on the Product Distribution.—The absence of detectable intermediates in the oxidation of DEA, other than MEA, suggests that each aminoalcohol group is oxidised independently and that for each group the initial oxidation is slow by comparison with subsequent steps. The influence of substrate structural modification on the product distribution gives further information on the fate of the carbon and nitrogen atoms of the aminoalcohol and on the mechanism of the oxidation. Thus the oxidation of *NN*-dimethylethanolamine requires six equiv. vanadium(v) and gives the dimethylammonium ion and formic acid [equation (2)]. This

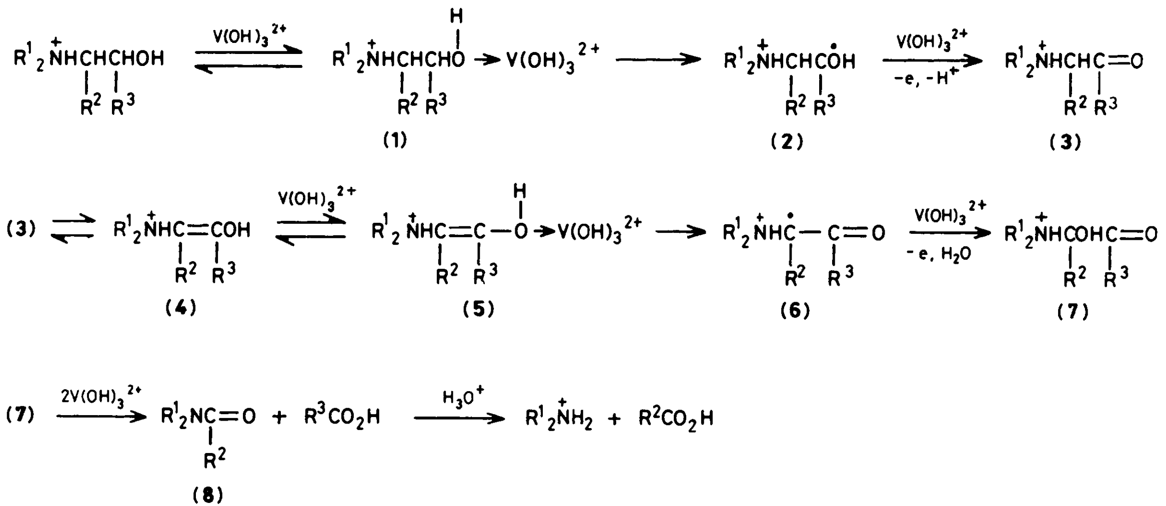


$$Me_2\underset{\substack{| \\ H}}{\overset{+}{N}}CH_2CH_2OH + 6V(OH)_3{}^{2+} \longrightarrow 2HCO_2H + Me_2\overset{+}{N}H_2 + 6V^{IV} \quad (2)$$

product distribution and the stability of the dimethylammonium ion to further oxidation confirm that the nitrogen ends up as an ammonium ion. A comparison of the reactions of *NN*-dimethylethanolamine and 3-dimethylaminopropan-1-ol shows that increasing the number of carbon atoms between the heteroatoms yields no new products, although the latter substrate requires more vanadium(v).

Alkylation of the carbons between the heteroatoms shows that both carbons in an ethanolamine group are oxidised to formic acid. Monoalkylation of either carbon results in the formation of formic acid with another carboxylic acid. For example, 1-aminopropan-2-ol and 2-aminobutan-1-ol give formic acid with acetic and propionic acid respectively, and 2-amino-1-phenylethanol is oxidised to formic and benzoic acids, the latter of which crystallises from the cooled reaction mixture. 2-Aminoacetophenone, a likely intermediate in the oxidation of 2-amino-1-phenylethanol, also gives benzoic and formic acids. Dialkylation of the alcoholic carbon makes the substrate much more resistant to oxidation indicating that, like the oxidation of simple alcohols,[19] the initial step of the reaction requires there to be a hydrogen on this carbon. Dialkylation of the amino carbon leads to a reduced degradation of the substrate with only four equiv. vanadium(v) being consumed. However, the expected product from this reaction, 2-amino-2-methylpropionic acid, could not be detected by ^{13}C n.m.r. spectroscopy [equation (3)] although this aminoacid is stable to

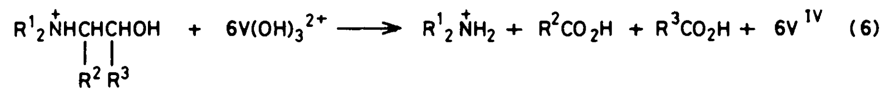
$$\overset{+}{N}H_3CMe_2CH_2OH + 4V(OH)_3{}^{2+} \longrightarrow \overset{+}{N}H_3CMe_2CO_2H + 4V^{(IV)} \quad (3)$$



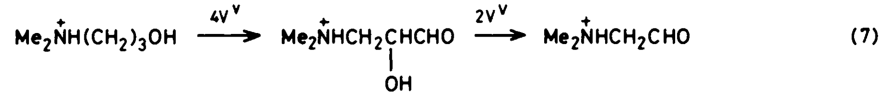
Scheme.

$$\overset{+}{N}H_3CH_2CHO \xrightarrow{V^V} \overset{+}{N}H_3CH_2CO_2H \qquad (4)$$

$$\overset{+}{N}H_3CMe_2CHO \overset{H_2O}{\rightleftharpoons} \overset{+}{N}H_3CMe_2CH(OH)_2 \xrightarrow{V^V} NH_3CMe_2CO_2H \qquad (5)$$



$$R^1{}_2\overset{+}{N}HCH(R^2)CH(R^3)OH + 6V(OH)_3{}^{2+} \longrightarrow R^1{}_2\overset{+}{N}H_2 + R^2CO_2H + R^3CO_2H + 6V^{IV} \qquad (6)$$



$$Me_2\overset{+}{N}H(CH_2)_3OH \xrightarrow{4V^V} Me_2\overset{+}{N}HCH_2CH(OH)CHO \xrightarrow{2V^V} Me_2\overset{+}{N}HCH_2CHO \qquad (7)$$

(9) (10)

oxidation by vanadium(V) ions under the reaction conditions. In agreement with the expected course of reaction the homomorphous compound, 2,2-dimethylpropanol, is oxidised by four equiv. vanadium(V) to 2,2-dimethylpropionic acid and 2,2-dimethylpropionaldehyde is oxidised to the same acid by two equiv. vanadium(V). The absence of the amino acid in the product mixture is attributable to its oxidation by hypochlorite in the recycling of the vanadium(V) ions. Thus, no organic material was detectable by ^{13}C n.m.r. spectroscopy when a perchloric acid solution of 2-amino-2-methylpropionic acid was heated with hypochlorite in the absence of vanadium(V) ions. (This surprising observation was not investigated further.)

When dimethylformamide is heated with sodium metavanadate in aqueous perchloric acid it is hydrolysed and no reduction of the vanadium(V) occurs.

Mechanism of Oxidation.—In 2.0M-perchloric acid the aminoalcohols exist as their ammonium ions and so not unexpectedly oxidation occurs at the alcoholic functional group as reported by Puutio and Virtanen[9] for the oxidation of TEA. In this respect these reactions can be treated as examples of alcohol oxidations. The mechanism illustrated in the Scheme for a monoethanolamine is consistent with the results above and with the mechanisms that have been proposed for the oxidation of alcohols[3a] and carbonyl and α-hydroxycarbonyl compounds.[3a]

The initial oxidation involves removal of the alcoholic α-hydrogen atom in an aminoalcohol–vanadium(V) complex (**1**) followed by a one-electron oxidation of the α-hydroxyalkyl radical (**2**) by a second vanadium(V) species to give the carbonyl compound (**3**). With aminoalcohols containing tertiary alcoholic groups which are unable to react in this manner oxidation must occur through C–C bond cleavage either directly or *via* the alkoxyl radical.[19] The second stage in the oxidation generates the resonance-stabilised α-keto-radical (**6**) by hydrogen-atom transfer either in a vanadium(V)–enol complex, the reported mode of oxidation of aldehydes by vanadium(V) ions,[20] or in a vanadium(V)–ketone complex as has been suggested for the oxidation of cyclohexanone.[21] Electron-transfer to a fourth vanadium(V) ion and reaction with water produces the α-hydroxycarbonyl species (**7**). The alternative pathway involving terminal oxidation of the aldehyde group to a carboxylic acid [equation (4)], which is not observed in the vanadium(V) oxidation of simple aliphatic aldehydes,[20] would not account for the products observed in this study. Amino carbonyl compounds such as 2-amino-2-methylpropionaldehyde from the oxidation of 2-amino-2-methylpropan-1-ol, which have no α-hydrogens and cannot react as described above, are probably oxidised *via* their hydrates to an aminoacid in an analogous manner to the oxidation of formaldehyde to formic acid [equation (5)].[14] The final two one-electron oxidations of (**7**) give the formamide (**8**) and a carboxylic acid in an analogous manner to the oxidative degradation of an aldose by vanadium(V) to formic acid and the next lower homologue.[22] Subsequent hydrolysis of the formamide gives an ammonium ion and a further molecule of carboxylic acid. Thus the overall oxidation of an ethanolamine group requires the six equiv. vanadium(V) observed in this study and can be represented by equation (6).

The first two oxidations of 3-dimethylaminopropan-1-ol, analogous to an ethanolamine, would give the α-hydroxyaldehyde (**9**) which as described above for aldoses would be degraded further to give the aminoaldehyde (**10**) [equation (7)].

Subsequent oxidation would give the dimethylammonium ion and formic acid and an overall consumption of eight equiv. vanadium(V).

Experimental

Materials.—All the inorganic and organic materials were commercial reagent grade unless otherwise stated and were obtained from Aldrich Chemical Co. Ltd., Fisons Scientific Apparatus Ltd., or Koch-Light Ltd. The organic compounds were purified by distillation before use. AnalaR perchloric acid (12.4M) was from Fisons Scientific Apparatus Ltd. The nitrogen was British Oxygen white spot grade.

Methods.—^{1}H N.m.r. spectra were recorded on Joel JNM-MH-100 (100 MHz) and Varian EM 360A (60 MHz) spectrometers. ^{13}C N.m.r. spectra were recorded on Joel JNM FX60 or FX90Q spectrometers with dioxane as an external standard. U.v.–visible spectra were obtained with a Pye-Unicam SP8000 spectrophotometer. Magnetic susceptibility measurements were carried out on a single-temperature Gouy balance (Newport Instruments).

Oxidation Procedures.—The attempted oxidations in the pH range 10.5—4.2 used aqueous solutions (20 cm^3) containing sodium metavanadate (2×10^{-6}—2×10^{-4} mol) and a 10-fold excess of DEA and the pH was adjusted with concentrated perchloric acid. These reaction mixtures were heated for the required reaction time at 25 or 40 °C or at reflux. For reactions under nitrogen the solutions were flushed with nitrogen for 2 h before being stoppered and heated. To some of the reaction mixtures the following compounds were added before heating: copper(II) chloride, iron(III) chloride, and chromium(III) chloride (2×10^{-5} mol). All the reactions were monitored by comparing the u.v.–visible spectra of aliquot portions before and after heating.

The oxidations at pH 1.6 were carried out at reflux as described above with sodium metavanadate (2×10^{-4} mol) and DEA (2×10^{-3} mol). After 3 h the mixture comprised a solution that contained no vanadium (u.v.–visible spectroscopy) and a green solid which was filtered off and dried *in vacuo*. Magnetic susceptibility measurements showed it to be paramagnetic.

The general procedure for oxidations for ^{13}C n.m.r. analysis used a 0.5M solution of the aminoalcohol in 2.0M-perchloric acid (20 cm^3) to which was added sodium metavanadate (0.61 g, 5×10^{-3} mol) and the mixture was heated at reflux until the solution became bright blue. Substrates which were not completely soluble in the reaction mixture were used as suspensions. After cooling the mixture, sodium hypochlorite (10—14% w/v, 1.5 cm^3) was added to regenerate the vanadium(V) and the solution was again heated at reflux until the solution became bright blue. The vanadium(V) was recycled in this way three to six times to build up sufficient concentration of oxidation products for ^{13}C n.m.r. spectroscopy. A final portion of sodium hypochlorite was added prior to analysis. The product from the reaction of 2,2-dimethylpropan-1-ol and of 2,2-dimethylpropionaldehyde was extracted into ether (2×20 cm^3) and after drying ($MgSO_4$) and removal of solvent was analysed by ^{13}C n.m.r. spectroscopy in $CDCl_3$ solution. The stability of DEA to oxidation by sodium hypochlorite was confirmed by repeating the above procedure in the absence of sodium metavanadate.

The oxidations of 1-phenylethanolamine and of 2-aminoacetophenone gave a white precipitate which was removed by filtration, recrystallised, and shown to be benzoic acid by comparison with authentic material (m.p. and ^{1}H n.m.r.).

Stoicheiometric Studies.—A 0.1M solution of ammonium metavanadate (30 cm^3) in 2.0M-perchloric acid was mixed with a 0.02M solution of the substrate (10 cm^3) in the same acid and heated to reflux until the colour of the solution remained constant. Substrates which were not completely soluble in the reaction solution were used as suspensions. The reaction mixture was cooled, diluted with 75% sulphuric acid (100 cm^3), and titrated with a 0.12M solution of iron(II) ammonium sulphate in 2.0M-perchloric acid using a 6.6×10^{-3}M solution of *N*-phenylanthranilic acid in aqueous sodium carbonate as indicator. The amount of vanadium(V) consumed in the oxidation was obtained by comparison of titres from solutions heated in the presence and absence of substrate.

Qualitative and Quantitative Estimations of Formaldehyde.—The chromotropic acid reagent was prepared by dissolving the sodium salt of chromotropic acid (2.5 g) in water (25 cm^3) and the solution was filtered before being diluted six-fold with 72% sulphuric acid. For qualitative tests a drop of the solution to be tested was heated with the reagent (5 cm^3) for 15 min at 60 °C. For quantitative estimations of formaldehyde a portion of the reaction mixture (0.5 cm^3) which had been diluted 10-fold with water was added to the reagent (5.0 cm^3) and heated at 60 °C for 15 min. The concentration of the formaldehyde was obtained by comparing of the absorption of the solution at 575 nm with values obtained from standard solutions of formaldehyde.

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References

1 Part 14, J. R. Lindsay Smith, J. M. Linford, L. C. McKeer, and P. M. Morris, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1099.

2 (*a*) G. W. Parshall, 'Homogeneous Catalysis, the Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes,' Wiley, New York, 1980; (*b*) R. A. Sheldon and J. A. Kochi, 'Metal-catalysed Oxidations of Organic Compounds,' Academic Press, New York, 1981.

3 (*a*) W. A. Waters and J. S. Littler, in 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York, 1965, vol. 5-A, ch. 3; (*b*) G. W. J. Fleet, in 'Organic Reaction Mechanisms,' eds. A. C. Knipe and W. E. Watts, Wiley, Chichester, 1981, ch. 4; see also earlier volumes.

4 (*a*) H. E. Benson, J. H. Field, and W. M. Epes, U.K.P., 1963, 925 679; (*b*) A. G. Eickmeyer, U.K.P., 1969, 1 142 317; (*c*) 'Ammonia,' Part II, eds. A. V. Slack and G. Russell James, Marcel Dekker, New York, 1974, pp. 115—287; (*d*) S. Strelzoff, 'Technology and Manufacture of Ammonia,' Wiley, New York, 1981, pp. 193—250.

5 M. L. Kennard and A. Meisen, *Hydrocarbon Process.*, 1980, 103.

6 (*a*) B. H. Nicolet and L. A. Shinn, *J. Am. Chem. Soc.*, 1939, **61**, 1615; (*b*) M. A. Smith and B. R. Willeford, *ibid.*, 1954, **76**, 2502; (*c*) K. S. Shukla, P. C. Mathur, and O. P. Bansal, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1301; (*d*) J. R. Lindsay Smith and L. A. V. Mead, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1172; (*e*) E. P. Burrows and D. H. Rosenblatt, *J. Org. Chem.*, 1983, **48**, 992.

7 (*a*) M. Meltsner, C. Wohlberg, and M. J. Kleiner, *J. Am. Chem. Soc.*, 1935, **57**, 2554; (*b*) M. Meltsner, L. Greenstein, G. Gross, and M. Cohen, *ibid.*, 1937, **59**, 2660; (*c*) C. B. Kremer and B. Kress, *ibid.*, 1938, **60**, 1301; (*d*) M. Meltsner, I. Kirshenbaum, and A. Stempel, *ibid.*, p. 1236; (*e*) M. Chandra, S. Lal, and O. P. Bansal, *J. Indian Chem. Soc.*, 1977, **54**, 1040.

8 (*a*) J. R. Lindsay Smith and D. Masheder, *J. Chem. Soc., Perkin Trans. 2*, 1976, 47; (*b*) J. R. Lindsay Smith and D. Masheder, *ibid.*, 1977, 1732.

9 M. Puutio and P. O. I. Virtanen, *Acta Chem. Scand.*, 1982, **A36**, 689.

10 J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 1959, 1299.

11 (*a*) N. Ingri and F. Brito, *Acta Chem. Scand.*, 1959, **13**, 1971; (*b*) W. P. Griffiths and T. D. Wickens, *J. Chem. Soc. A*, 1966, 1087; (*c*) M. T. Pope and B. W. Dale, *Q. Rev.*, 1968, **22**, 527; (*d*) O. Borgen, M. R. Mahmoud, and I. Shauvik, *Acta Chem. Scand.*, 1977, **A31**, 329.

12 G. S. S. Murty, B. Sethuram, and T. N. Rao, *Indian J. Chem.*, 1977, **15A**, 880.

13 C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 400.

14 T. J. Kemp and W. A. Waters, *Proc. R. Soc. London*, 1963, **A274**, 480.

15 F. Fiegl, in 'Spot Tests in Organic Chemistry,' Elsevier, Amsterdam, 1966, p. 434.

16 D. M. West and D. A. Skoog, *Anal. Chem.*, 1959, **31**, 583.

17 D. M. West and D. A. Skoog, *Anal. Chem.*, 1960, **32**, 280.

18 C. Dauphin, A. Dauphin, and M. Hamon, *Analysis*, 1979, **7**, 73.

19 Ref. 3*a*, p. 202.

20 J. R. Jones and W. A. Waters, *J. Chem. Soc.*, 1963, 352.

21 J. S. Littler, *J. Chem. Soc.*, 1962, 832.

22 (*a*) A. Kumar and R. N. Mehotra, *J. Org. Chem.*, 1975, **40**, 1248; (*b*) S. C. Pati and M. Panda, *Int. J. Chem. Kinet.*, 1979, **11**, 731.

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