282. *The Oxidation of Hydrazine in Aqueous Solution. Part I. The Nature of 1- and 2-Electron-transfer Reactions, with Particular Reference to the Oxidation of Hydrazine.*

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The classification of oxidising agents as 1- or 2-electron-transfer reagents, depending on the products of their reaction with hydrazine, is discussed and further evidence is presented. A new empirical criterion is suggested and its implications in terms of the reaction mechanism are considered. The more detailed nature of 1- and 2-electron transfer reactions is discussed.

IN one of the earliest papers in which 1- and 2-electron-transfer reactions were distinguished, Kirk and Browne (*J. Amer. Chem. Soc.*, 1928, **50**, 337, *q.v.* for references) discussed the implications of previous work on the oxidation of hydrazine, and common features of the reaction of a large number of oxidising agents with hydrazine were pointed out (for a review see also Audrieth and Ogg, " The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, 1951, Chap. VI). They conclude: " The hitherto unaccountable similarity in the behaviour of various oxidants of widely divergent potentials towards hydrazine is now explained on the ground that they are *mono-delectronators* yielding ammonia as the only by-product of the reaction, or *di-delectronators* yielding both ammonia and hydronitric acid." (The main product of the reaction is nitrogen gas.) Hydrazoic acid formation in boiling, strongly acid solution containing excess of hydrazine thus becomes a criterion for the presence of a 2-electron-transfer oxidising agent. Departure from the rather critical reaction conditions can lead to a great diminution in the yield of hydrazoic acid or even to its disappearance.

Although Kirk and Browne stated that positive and negative ions are included in each class, we noticed that, of the reagents to which they referred specifically, all the simple metal ions fell into the one class while oxy-acids and their salts, and uncharged oxidising agents such as hydrogen peroxide, belonged to the other, giving hydrazoic acid as a reaction product. Thus an alternative distinction could be between reagents able or unable to form a co-ordinate complex of the type $Ox \leftarrow NH_2 \cdot NH_2(H^+)$. In an attempt to decide the true basis for the classification we have determined the products of oxidation by the hydroxyl radical and by the thallic ion. Each of these falls into a different class depending on whether it is considered as a 1- or 2-electron-transfer reagent, or as a non-complex-forming or a complex-forming oxidising agent respectively.

Experimentally, oxidation by the hydroxyl ion is much easier to carry out in cold solutions than in the boiling solutions necessary for the formation of hydrazoic acid. Also, solutions containing thallic ion are often unstable when hot. However, as the annexed Table shows, a grouping similar to Kirk and Browne's is obtained if distinction is made between (*a*) reagents which oxidise hydrazine at room temperature in acid solution to nitrogen and water only, irrespective of the order of addition, and (*b*) other reagents which under similar conditions yield nitrogen and ammonia in variable quantities. The number of equivalents of the latter class of reagents consumed per molecule of hydrazine is always lower than 4 and varies to some extent with the manner of mixing. For the former reagents, which correspond to those which form hydrazoic acid in boiling acid solution, 4 equivalents of oxidising agent are consumed. Except where stated, the results quoted are from the previous work to which reference is made above, though we have checked most of the stoicheiometries. The behaviour of the hydroxyl radical and thallic ion, neither of which has previously been examined as an oxidising agent for hydrazine, leads us to believe that Kirk and Browne's classification into 1- and 2-electron-transfer reagents is correct.

Our criterion cannot be applied in as many cases as Kirk and Browne's since several reagents, notably salts of oxy-acids, which react at higher temperatures, do not react at all at room temperature. We consider Kirk and Browne's conclusions to be unsatisfactory for several oxidising agents; hydrogen peroxide and potassium peroxydisulphate are important examples since these reagents give rise to the highest reported yields of hydrazoic acid (Browne and Shetterly, *J. Amer. Chem. Soc.*, **1909**, **31**, 783). However, Davis (Thesis, Manchester Univ., 1951), using small amounts of ethylenediaminetetra-acetic acid (disodium salt) to sequester heavy-metal ions, has shown that reaction between hydrazine and hydrogen peroxide in aqueous solution at 25° is catalysed by traces of metal ions even if " pure " reactants are used, and that there is no good evidence for a direct reaction. Under conditions similar to those used in hydrazoic acid formation he concluded that the catalysed reaction predominates. Since it is possible that the formation of hydrazoic acid is due to the oxidation of hydrazine by a metal-ion intermediate and not by hydrogen peroxide itself, Kirk and Browne's classification of hydrogen peroxide as a 2-electron-transfer oxidising agent in this reaction is of doubtful value. In the case of potassium peroxydisulphate there is some evidence for trace-metal catalysis unless the reagents are reasonably pure. Kolthoff and Miller's work at higher temperatures (*J. Amer. Chem. Soc.*, 1951, **73**, 3055) makes it probable that reaction occurs in the absence of heavy-metal ions, but whether peroxydisulphate or one of its decomposition products reacts with the hydrazine would be difficult to decide.

Reagent	Stoicheiometry (cold)	HN_3 (cold)	HN_3 (hot)	Remarks
Ce(IV)	1·05—1·4	+	—	
Fe(III)	1·1—1·35	+	—	Very slow reaction at 25°; higher stoicheiometries in hot soln.
Mn(III)	1·09—1·47	+	—	Complex acetate
OH	1·07—1·96	+	N.I.	See Exptal. section
I_2	4	—	—	Very slow reaction at 25°; HIO?
Br_2	4	—	+	
Cl_2	N.I.		+	
KIO_3	4	—	—	
$KBrO_3$	4	—	+	Needs high HCl concn. for quant. reaction in cold
$KClO_3$	No reaction		+	
$K_2S_2O_8$ ...	No reaction		+	Reactive species in hot solution doubtful
H_2O_2	No reaction		+	,, ,, ,,
Tl(III)	4	—	+	See Exptal. section
$K_2Cr_2O_7$ ...	3—4	+	+	1- and 2-Electron-transfer possible
V(V)	3·5—4	+	+	,, ,, ,,
$KMnO_4$ ...	1·45—2·2	+	+	,, ,, ,,

N.I. = Not investigated.

Kirk and Browne suggested that the halogens may act either as 1- or 2-electron-transfer reagents and actually referred to iodine as a " mono-delectronator." 1-Electron-transfer oxidation by any of these reagents seems unlikely for reactions with a non-metallic substrate, and in dilute acid conditions bromine and iodine lead to quantitative formation of nitrogen. The form in which iodine reacts is uncertain, for Berthoud and Porret's interpretation of the kinetics of the oxidation in acid solution is that hypoiodous acid is the reactive species (*Helv. Chim. Acta*, 1934, **17**, 32).

Previous workers attempted to explain the different products obtained with 1- and 2-electron-transfer reagents in terms of the reactions of the various radicals which it was assumed could be formed in the initial processes. The reaction schemes below which we consider explain the different behaviour of 1- and 2-electron-transfer reagents in cold, acid solution are simpler than those developed previously (see Audieth and Ogg, *op. cit.*, p. 128). In agreement with the earlier mechanisms we depict hydrazine and the derived radicals as possessing zero charge. Almost certainly this is not always the case, but there is no evidence necessitating that the radicals should react in a particular form, and there is little evidence about hydrazine itself. The formulæ used therefore merely represent the oxidation state of the nitrogen atoms concerned and not the detailed structure of the radical. We suggest that the quantitative oxidation of hydrazine to nitrogen by 2-electron-transfer reagents is in accord with the scheme

$$N_2H_4 \xrightarrow[-(2e)]{} N_2H_2 \dashrightarrow N_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

in which N_2H_2, once formed, can lead to nitrogen but not to ammonia. Whether the N_2H_2 becomes nitrogen through further oxidation or by a disproportionation reaction between two such radicals giving nitrogen and hydrazine is immaterial for our present purpose. The variable stoicheiometry obtained with the 1-electron-transfer reagents results from two competing reactions which can follow the initial formation of N_2H_3 :

$$\begin{tikzcd}
 & & \tfrac{1}{2}N_4H_6 \arrow[r, dashed] & \tfrac{1}{2}N_2 + NH_3 \quad . \quad . \quad . \quad . \qquad (2a) \\
N_2H_4 \arrow[r, "-(e)"] & N_2H_3 \arrow[ur, "\text{Dimerisation}"] \arrow[dr, "-(e)"'] & & \\
 & & N_2H_2 \arrow[r, dashed] & N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2b)
\end{tikzcd}$$

Reaction (2*a*) leads to a stoicheiometry of 1, and (2*b*) to stoicheiometry of 4; so the stoicheiometry for 1-electron-transfer reagents may lie between 1 and 4 depending on the proportion of these two reactions. In alkaline solution even 1-electron-transfer reagents produce nitrogen quantitatively. The effect of the large change in hydrogen-ion concentration must therefore be to increase greatly the rate of oxidation of N_2H_3 relatively to the dimerisation. (For similar mechanisms, otherwise interpreted, see Cuy and his collaborators, *J. Amer. Chem. Soc.*, 1924, **46**, 1796, 1810.)

For reaction with 1-electron-transfer reagents, equations (2*a*) and (2*b*) predict that the consumption of oxidising agent per mole of hydrazine will be lower if the hydrazine is kept in excess than if the oxidising agent is kept in excess. This we have observed, especially with ceric sulphate, ferric sulphate, and potassium permanganate. The last is not, strictly, a 1-electron-transfer reagent but a complex oxidising agent in that the change in acid solution of the valency state of the manganese from (VII) to (II) probably involves both 1- and 2-electron-transfer reactions. This and similar oxidising agents therefore have some of the properties of both the simple types of oxidising agent. Thus in acid solution less than 4 equivalents of potassium permanganate are consumed and the stoicheiometry can be varied by altering the conditions of mixing. On the other hand, small quantities of hydrazoic acid are produced if reaction is carried out with hot solutions. The products of the oxidation of hydrazine by complex electron-transfer reagents, like those of 1-electron-transfer reagents, can be expressed in terms of two limiting overall reactions which take place simultaneously: $N_2H_4 - (e) \longrightarrow \tfrac{1}{2}N_2 + NH_3$, and $N_2H_4 - 4(e) \longrightarrow N_2$. The proportion in which these occur determines the stoicheiometry. In practice the 1-electron-transfer reagents generally have stoicheiometries fairly near to 1, and the complex reagents, probably because of the occurrence of 2-electron-transfer steps, nearer to 4.

Detailed Nature of Electron-transfer Reactions.—1- and 2-Electron-transfer reactions may be defined as processes in which two species change their oxidation number by one or two units respectively in one kinetic step. An electron-transfer reaction, even between two metal ions, can almost always be represented as an atom- or radical-transfer reaction as well as a process involving the actual transfer of electrons. For example, compare the alternative schemes by which three different types of reaction may be represented:

(i) $HO + N_2H_4 \longrightarrow HOH + N_2H_3$

or $HO + N_2H_4 \longrightarrow HO^- + N_2H_4^+ \longrightarrow HOH + N_2H_3$

(ii) $Fe^{++} + HO{\cdot}OH \longrightarrow (Fe \cdots \overset{H}{O} \cdots OH)^{++} \longrightarrow FeOH^{++} + OH$

or $Fe^{++} + HO{\cdot}OH \longrightarrow Fe^{+++} + (HO{\cdot}OH)^- \longrightarrow Fe^{+++} + HO^- + OH$

(iii) $Fe^{+++} + Cl^- + Ti^{+++} \longrightarrow FeCl^{++} + Ti^{+++} \longrightarrow (Fe \cdots Cl \cdots Ti)^{5+} \longrightarrow$
$Fe^{++} + TiCl^{+++} \longrightarrow Fe^{++} + Cl^- + Ti^{4+}$

or $Fe^{+++} + Ti^{+++} \longrightarrow Fe^{++} + Ti^{4+}$

For these and other 1-electron-transfer reactions in solution there seems to be no certainty as to the actual mechanism, and the term " electron-transfer reaction " as usually employed should merely be taken to mean an oxidation–reduction reaction. In the few cases where evidence is available, the reaction does not involve the transfer of electrons; thus Halperin and Taube have shown that oxygen-atom transfer occurs in the oxidation of sulphite to sulphate by chlorate (*J. Amer. Chem. Soc.*, 1950, **72**, 3319). Such a reaction is a clear example of a 2-electron-transfer reaction (in its usual sense) occurring in a simple process. In the same way, oxidation of hydrazine by iodate may occur by oxygen-atom transfer from IO_3^- or IO_2^+ (see Morgan, Peard, and Cullis, *J.*, 1951, 1865) and this may also be true of the reaction with other oxy-acids.

The oxidation by Tl(III) may involve a similar process, but may on the other hand involve the series

$$\mathrm{Tl(III)} + N_2H_4 \longrightarrow \mathrm{Tl(II)}\cdot N_2H_3 \longrightarrow \mathrm{Tl(I)}\cdot N_2H_2 \longrightarrow \mathrm{Tl(I)} + N_2H_2$$

in which a single 1-electron-transfer oxidation forms Tl(II) in the vicinity of N_2H_3. Before these two can separate, Tl(II), which must be a stronger oxidising agent than Tl(III), is able to oxidise N_2H_3, a stronger reducing agent than N_2H_4, to N_2H_2. The reaction of V(V) with hydrazine emphasises this distinction. V(V) is reduced by hydrazine in acid solution to V(IV), and between 3·5 and 4 V(V) ions are reduced per hydrazine molecule oxidised. This compares with the stoicheiometries between 1 and 1·5 observed with Ce(IV), Fe(III), and Mn(III). We therefore suggest that the predominant reaction with V(V) is $\mathrm{V(V)} + N_2H_4 \longrightarrow \mathrm{V(III)} + N_2H_2$. The reaction $\mathrm{V(V)} + \mathrm{V(III)} \longrightarrow 2\mathrm{V(IV)}$ then occurs rapidly; the appropriate redox potentials are; V(V)/V(IV) = 1·00, V(IV)/V(III) = 0·36. (Redox potentials quoted have generally been taken from Latimer, " The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall Inc., New York, 2nd Edn., 1952.) The overall reaction thus approximates to $4\mathrm{V(V)} + N_2H_4 \longrightarrow 4\mathrm{V(IV)} + N_2$. Kirk and Browne (*loc. cit.*) have shown that V(III) is formed in the reaction mixture when hot, and also that hydrazoic acid can be formed. The comparatively small quantity of ammonia produced at room temperature, implying the formation of small quantities of N_2H_3, can be interpreted in two ways : either there can be two distinct reactions between V(V) and N_2H_4, *viz.*, $\mathrm{V(V)} + N_2H_4 \longrightarrow \mathrm{V(III)} + N_2H_2$ and $\mathrm{V(V)} + N_2H_4 \longrightarrow \mathrm{V(IV)} + N_2H_3$, of which the former predominates; or the reaction can be written :

$$\begin{tikzcd}[row sep=small] & & \mathrm{V(III)} + N_2H_2 \\ \mathrm{V(V)} + N_2H_4 \arrow[r] & \mathrm{V(IV)}\cdot N_2H_3 \arrow[ur] \arrow[dr] & \\ & & \mathrm{V(IV)} + N_2H_3 \end{tikzcd}$$

The second possibility corresponds to the two-stage mechanism suggested for oxidation by Tl(III), but here the intermediate form, V(IV), is a much less powerful oxidising agent than Tl(II) (redox potential Tl(II)/Tl(I) > 1·25) and hence a small proportion of the $\mathrm{V(IV)}\cdot N_2H_3$ complexes may dissociate before the subsequent oxidation to N_2H_2 takes place.

We consider that in the oxidation of hydrazine by 2-electron-transfer reagents the single-stage type of mechanism is the more probable. It is very likely to occur when oxy-acids bring about oxygen-atom transfer, and the following considerations make it probable with metal-ion 2-electron-transfer oxidising agents. If the two-stage mechanism is correct we should expect the rate of reaction to be determined by the first stage only, since the second stage is virtually an independent reaction : one would then expect a parallel between the rates of reaction of the similar ions of Fe(III) and Tl(III) with hydrazine, and the corresponding redox potentials of Fe(III)/Fe(II) and Tl(III)/Tl(II). The latter potential cannot be measured, but from the slow reaction between Tl(III) and Fe(II) in perchloric acid solution (Johnson, *J. Amer. Chem. Soc.*, 1952, **74**, 959) which has been shown to involve a rate-determining 1-electron-transfer reaction between these two species (Ashurst and Higginson, unpublished work) we estimate that it is not greater than the potential of Fe(III)/Fe(II). Though the redox potentials are similar, the rate of reaction of hydrazine with Tl(III) in acid solution is about 10^4 times faster than the rate of reaction with Fe(III), which suggests that in oxidation by Tl(III) part of the energy liberated in the second stage, $N_2H_3 \xrightarrow{-(e)} N_2H_2$ (almost certainly more exothermic than $N_2H_4 \xrightarrow{-(e)} N_2H_3$ since a π-bond is probably formed in N_2H_2), is able to lower the activation energy of reaction below that of the corresponding 1-electron-transfer process. This is only a way of saying that the successive 1-electron-transfer oxidations cannot be differentiated and that only one process can be distinguished in this and possibly other 2-electron-transfer oxidations of hydrazine. Because the stability expected for N_2H_2 is greater than that expected for N_2H_3, the oxidation of hydrazine appears to be a particularly favourable case for occurrence of a 2-electron-transfer reaction in a single step. That oxidation to N_2H_2 by V(V) is more rapid than that to N_2H_3 can now be understood even though the redox potential of V(V)/V(III) (= 0·68) is appreciably smaller than that for V(V)/V(IV) (= 1·00).

Though the suggestion that a 2-electron-transfer reaction may involve two successive 1-electron-transfer processes occurring before the reactants separate does not seem to be applicable to the oxidation of hydrazine, its application in other reactions is possible. For instance, Cahill and Taube (*ibid.*, p. 2312) concluded, on the basis of oxygen isotope fractionation in the reduction of hydrogen peroxide, that whereas Ti(III) is a 1-electron-transfer reagent, Fe(II), Cr(II), and Cu(I) behave as 2-electron-transfer reagents and are oxidised to Fe(IV), Cr(IV), and Cu(III) respectively. The annexed Table summarises measurements of the rates of reaction of several reducing agents with hydrogen peroxide, together with pertinent redox potentials. The temperature was 25°, and the hydrogen peroxide concentration was 0·040M. Although the validity of direct comparison between redox potentials and rates of reaction of electron-transfer reagents of different charge type with a common substrate is doubtful, a rough correlation is to be expected. It can be seen that the correlation between the half-life of reaction (measured on the concentration of metal ion) and the redox potential of the first 1-electron step is better than that between the half-life and the overall potential for the 2-electron step: compare for instance Cu(I) with Hg(I), and Fe(II) with Tl(I) or Mn(II). We suggest that, in this reaction, though Fe(IV), Cr(IV), and Cu(III) may be formed, reaction occurs in two stages, and it is only because a very strong oxidising agent, the hydroxyl radical, of redox potential ≏2·0, is produced adjacent to the Fe(III), Cr(III), or Cu(II) formed in the first, rate-determining stage of reaction that further oxidation giving the appearance of a 2-electron-transfer process can occur.

M(I)		Cr(II)	Sn(II)	Cu(I)	U(IV)	Fe(II)
M(II)		Cr(III)	Sn(III)	Cu(II)	U(V)	Fe(III)
M(III)		Cr(IV)	Sn(IV)	Cu(III)	U(VI)	Fe(IV)
Redox potentials	M(II)/M(I)	−0·41	>0·15 (<0·85)	0·15	0·62	0·77
	M(III)/M(II)	>1·5	<0·15	>1·8	0·05	>1·7
	M(III)/M(I)	>0·55	0·15	>0·97	0·33	>1·23
Acid, and concn.			HCl 2N	HCl 2·5N	H_2SO_4 0·67N	H_2SO_4 0·67N
Initial concn. of M(I)			0·020M	0·020M	0·020M	0·0328M
Half-life (sec.) (measured on [M(I)])		Short	<15	<15	≏15	<15

M(I)		$PtCl_4^{=}$	Hg_2^{++}	Mn(II)	Tl(I)	Ag(I)
M(II)		Pt(III)	Hg(I) + Hg(II)	Mn(III)	Tl(II)	Ag(II)
M(III)		$PtCl_6^{=}$	2Hg(II)	Mn(IV)	Tl(III)	Ag(III)
Redox potentials	M(II)/M(I)	>0·68	>0·92	1·51	>1·25 (≏1·73)	1·98
	M(III)/M(II)	<0·68	<0·92	0·95	<1·25 (≏0·77)	≏2·0
	M(III)/M(I)	0·68	0·92	1·23	1·25	≏2·0
Acid, and concn.		HCl 0·67N	$HClO_4$ 0·67N	H_2SO_4 0·67N	H_2SO_4 0·67N	$HClO_4$ 0·67N
Initial concn. of M(I)		0·008M	0·067M	0·0772M	0·067M	0·067M
Half-life (measured on [M(I)])		≏3 hr.	N.R.	>150 hr.	N.R.	N.R.

N.R. = No reaction.

EXPERIMENTAL

Materials.—Commercial hydrogen peroxide (Laporte, stabiliser-free) was used. Fe(II) in usual sources of Ti(III) caused considerable decomposition of the peroxide, and our titanium trichloride solutions were prepared by electrolytic reduction of a pure specimen of tetrachloride in hydrochloric acid. Other reagents were of "AnalaR" grade or were purified by appropriate methods.

Oxidation of Hydrazine by the Hydroxyl Radical.—If hydrogen peroxide is titrated in acid solution with Ti(III) in the presence of hydrazine, the amount of Ti(III) consumed drops below the theoretical value [$2\mathrm{Ti(III)} \equiv \mathrm{H_2O_2}$]. However large the excess of hydrazine, the Ti(III) consumed never becomes less than half this theoretical amount. Neither Ti(III) nor hydrogen peroxide reacts with hydrazine under these conditions, nor does hydrogen peroxide in the presence of Ti(IV). These observations can be most simply explained if hydroxyl radicals, formed in the 1-electron-transfer reaction $\mathrm{Ti(III)} + \mathrm{H_2O_2} \longrightarrow \mathrm{Ti(IV)} + \mathrm{HO^-} + \mathrm{OH}$, may then react with more Ti(III) [Ti(III) + OH ⟶ Ti(IV) + OH^-], or with $N_2H_5^+$, the proportion of these two reactions depending on the concentrations and the specific rate constants. We have used Ti(III), rather than other reducing agents, in this work since the oxidised form, Ti(IV), is unlikely to cause complications by acting as an oxidising agent.

The products of reaction were determined as follows. Hydrogen peroxide (0·1M) was dropped slowly from a burette into a closed vessel containing a stirred solution of titanous chloride (0·1M) and 0·014—0·182M-hydrazine hydrochloride. The acid strength (HCl) was *ca.* 0·5M and the total volume of solution 100 ml. When all the Ti(III) had been oxidised, the yellow colour of the Ti(IV)–H_2O_2 complex appeared and addition was stopped. Before the hydrogen peroxide titration the solution was degassed by freezing and pumping, and titration was performed at a pressure of *ca.* 50 mm. of pure nitrogen, a known volume being used so that the nitrogen evolved in the reaction could be found by a measurement of the total gas at the end of the reaction. When the end-point was reached, the contents of the titration vessel were frozen (liquid air), the gas in the vessel was pumped off (Töpler), and its pressure in a calibrated bulb measured. A small amount of oxygen ($1 - 3 \times 10^{-5}$ mole) in the evolved gas, formed by decomposition of the hydrogen peroxide, was estimated colorimetrically with alkaline pyrogallol and the amount of hydrogen peroxide consumed was corrected appropriately. Excess of hydrazine in the reaction mixture was estimated by iodine in alkaline solution, and then ammonia formed was found by the Kjeldahl method. Trial experiments showed that this procedure was suitable.

From the amounts of Ti(III) and hydrogen peroxide consumed, the number of hydroxyl radicals reacting with hydrazine was calculated. In the presence of small amounts of hydrazine, most of the hydroxyl radicals react with Ti(III) and the error in the hydroxyl stoicheiometry, OH/N_2H_4, became large. The values obtained agreed, within the limits of this error, with the hydroxyl stoicheiometry calculated from the amount of ammonia formed, on the assumption that the two limiting reactions for the oxidation of hydrazine in acid solution hold in this case. The nitrogen balance achieved was fairly good, as appears in the following Table of typical results.

Initial $[N_2H_4]$ (M)	$\frac{\Delta Ti(III)}{\Delta H_2O_2}$	OH/N_2H_4 stoicheiometry		N_2H_4 decompd. (millimole)	N_2 formed (millimole)	NH_3 formed (millimcle)	$\frac{2N_2 + XH_3}{2\Delta N_2H_4}$
		from titration	from NH_3 formed				
0·182	1·50 ± 0·04	1·06 ± 0·1	1·07	2·995	1·52	2·93	1·00
0·047	1·66 ± 0·04	1·40 ± 0·2	1·39	1·415	0·79	1·23	0·99
0·024	1·75 ± 0·04	1·80 ± 0·3	1·66	0·769	0·50	0·60	1·04
0·014	1·84 ± 0·04	2·30 ± 0·6	1·96	0·368	0·25	0·25	1·02

We conclude from these experiments that the hydroxyl radical behaves in the same manner as the simple metal ions, in that both nitrogen and ammonia are products of its reaction. The stoicheiometry can be varied within wide limits; values in the region of 3 were obtained in other experiments.

Oxidation of Hydrazine in Acid Solution by Thallic Sulphate.—A stock thallic sulphate solution was prepared by Sherrill and Haas' method (*J. Amer. Chem. Soc.*, 1936, **58**, 953) except that dithallium trioxide was precipitated by sodium hydroxide instead of by ammonia. The solution was standardised gravimetrically as thallous chromate, after reduction by sulphur dioxide, and also volumetrically by the Andrews' procedure (after similar reduction). Tl(I) in the solution was determined volumetrically in the same way. The volumetric method for Tl(III) described by Partington and Stonehill (*Trans. Faraday Soc.*, 1935, **31**, 1357) gave values 1—2% low. The rate of reaction between Tl(III) and hydrazine in N-sulphuric acid was determined by removing samples of a mixture of equal amounts of 0·045M-Tl(III) and 0·1M-hydrazine, adding an excess of standard Ce(IV), and back-titrating the mixture with standard Fe(II) (ferroin indicator). Under these conditions Tl(I) is not oxidised by Ce(IV). Reaction between the latter and hydrazine is not stoicheiometric, but consistent results can be obtained if a standard procedure is used; we found that 1·06Ce(IV) ≡ N_2H_4. The reaction was complete within 2 min., and, approximately, 2Tl(III) ≡ N_2H_4. The stoicheiometry was determined accurately by estimating Tl(I), and, if present, excess of hydrazine, in similar mixtures by Andrews' method, 5 min. after mixing. It was necessary to know the time for complete reaction, since if 2Tl(III) ≏ N_2H_4, the titration would remain almost the same whether reaction was complete or not. The results were the same whichever reagent was in excess, and irrespective of the order of addition: (2·004 ± 0·005)Tl(III) ≡ N_2H_4. The residues were analysed for ammonia by Kjeldahl's method; within the limits of error (≡ ±0·2% of N_2H_4) no ammonia was formed. At 80° traces (*ca.* 1%) of hydrazine were formed, as shown by distillation into a Fe(III) solution.

With the exception of Mn(III) the stoicheiometries of reaction of the substances listed in the first Table (p. 1381) were checked at room temperature, except where the method is already established as quantitative (iodate, bromate, and bromine). The methods used in previous work have been followed (for references see Audrieth and Ogg, *op. cit.*, p. 138).

Reactions with Hydrogen Peroxide.—The rates of reaction of 0·040M-hydrogen peroxide at 25° with various reagents under the conditions indicated in the second Table (p. 1384) were measured by quenching samples, at suitable times, in excess of standard Ce(IV) solution. The excess was determined by titration with a standard Fe(II) solution (ferroin as indicator). In most cases, as shown by trial experiments, this procedure caused oxidation of the unchanged reducing agent. Ag(I), Hg(I), and Tl(I) were unaffected; of the others, all except Mn were not reduced from their higher oxidation state in the subsequent back-titration against Fe(II). The hydrogen peroxide was oxidised by the Ce(IV) in all cases.

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