The Oxidation of Hydrazine in Aqueous Solution by Complex Ions

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Stoicheiometries have been found for the oxidation of hydrazine in aqueous solution by tricarbonatocobaltate(III), barium permanganate, ethylenediaminetetra-acetatomanganate(III), trispyrophosphatomanganate(III), hexachloroiridate(IV), octacyanomolybdate(V), and of sulphite by the last three of these complexes. The results are discussed with reference to the lability of the complexes to ligand-substitution.

IN the oxidation of sulphite by metal complexes, a correlation has been suggested between the stoicheiometry of the reaction and the lability of the complex.[1] Substitution-inert complexes which behave as 1-equivalent oxidants were found to give quantitative oxidation to sulphate,

$$SO_3^{2-} + 2M(\mathrm{N}) \longrightarrow SO_4^{2-} + 2M(\mathrm{N}-\mathrm{I})$$

but substitution-labile complexes reacted with a lower, non-integral stoicheiometry, giving dithionate as an additional product,

$$SO_3^{2-} + (1+x)M(\mathrm{N}) \longrightarrow xSO_4^{2-} + \tfrac{1}{2}(1-x)S_2O_6^{2-} + (1+x)M(\mathrm{N}-\mathrm{I})$$

where x lies between zero and unity. With hydrazine, oxidation normally yields either molecular nitrogen alone, or molecular nitrogen and ammonia as the ultimate nitrogenous products.[2] The corresponding equations for 1-equivalent oxidants are similar to those with sulphite,

$$N_2H_4 + 4M(\mathrm{N}) \longrightarrow N_2 + 4M(\mathrm{N}-\mathrm{I})$$

$$N_2H_4 + (1+3x)M(\mathrm{N}) \longrightarrow xN_2 + \tfrac{1}{2}(1-x)(N_2 + 2NH_3) + (1+3x)M(\mathrm{N}-\mathrm{I})$$

However, there is insufficient evidence in the literature to show whether quantitative conversion into molecular nitrogen is a characteristic of the oxidation of hydrazine by substitution-inert complexes. The work now described was designed to elucidate this point and to extend previous studies with sulphite. Here and elsewhere in this paper the terms hydrazine (N_2H_4) sulphite (SO_3^{2-}) include the various protonated forms of the parent bases.

Oxidation of Hydrazine.—The stoicheiometry of the oxidation of hydrazine by a given reagent is expressed in terms of the consumption ratio, which is the change in oxidising agent concentration divided by the change in hydrazine concentration. Consumption ratios were usually obtained by determining the excess of one or other reagent at the end of the reaction. The reagent to be employed in excess was indicated by the feasibility of a suitable analytical method. For oxidations by the two manganese(III) complexes, consumption ratios were also obtained by determining the amount of ammonia formed. Agreement between the two methods was within experimental error, but for practical reasons ammonia determinations were restricted to systems in which a high proportion of ammonia was formed.

Results for oxidation by trispyrophosphatomanganate(III) are summarised in Table 1. In this very rapid reaction, the limiting consumption ratio as the pH is increased is seen to be dependent upon the method of mixing. These results show that the limit of *ca.* 3·3 previously obtained[3] by using method (*a*) (see Experimental section) is not of mechanistic significance. With ethylenediaminetetra-acetatomanganate(III) a fairly rapid reaction was observed. Initial concentrations of this complex and of hydrazine were *ca.* 21 and 6·7mM, respectively. In a set of 21 experiments, the consumption ratio changed gradually with pH from 1·11 at pH 2·4 to 1·68 at pH 7·5. Values of *ca.* 2·7 at pH 9·6 may be due to the oxidation of a part of the hydrazine by manganese(IV); the complex solution decomposes fairly rapidly to manganese dioxide at this pH.

TABLE 1

Consumption ratios for the system trispyrophosphatomanganate(III)–hydrazine

Temp. *ca.* 20 °C μ = *ca.* 1·0M

Mixing method *	pH	Initial concentrations (mM) $[Mn(P_2O_7)_3^{9-}]$	$[N_2H_4]$	Consumption ratio
a	2·06	7·08	11·6	1·12 ± 0·05
a	2·67	7·45	15·5	1·54 ± 0·06
a	3·92	7·62	11·6	2·80 ± 0·15
a	4·78	7·15	11·6	3·23 ± 0·20
a	5·97	7·31	11·6	3·52 ± 0·25
b	1·77	20·8	3·61	1·14 ± 0·08
b	2·84	22·2	3·61	1·63 ± 0·08
b	3·77	21·5	3·61	3·24 ± 0·07
b	4·95	21·1	3·61	3·74 ± 0·07
b	5·12	20·4	3·61	3·85 ± 0·08
c	1·96	7·21	11·6	1·06 ± 0·02
c	2·65	7·45	15·5	1·27 ± 0·06
c	3·85	7·23	11·6	2·05 ± 0·10
c	4·78	7·57	15·5	2·54 ± 0·16
c	4·82	7·58	15·5	2·62 ± 0·15
c	5·72	7·55	11·6	2·91 ± 0·15
d	4·82	12·3	1·89	3·93 ± 0·06
d	4·87	12·4	18·9	2·72 ± 0·13
d	6·33	12·4	1·89	3·91 ± 0·07
d	6·11	12·4	18·9	3·24 ± 0·14

* See text.

The oxidation by hexachloroiridate(IV) is rapid at pH 6·5 and requires several hours for completion at pH 1·6. Consumption ratios and their standard errors are shown in Table 2. Spectrophotometric examination[4] of the product solutions showed the iridium(III) was entirely in the form of hexachloroiridate(III) except

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[1] J. Vepřek-Šiška, D. M. Wagnerová, and K. Eckschlager, *Coll. Czech. Chem. Comm.*, 1966, **31**, 1248.

[2] L. F. Audrieth and B. A. Ogg, ' The Chemistry of Hydrazine,' Wiley, New York, 1951, ch. 6.

[3] W. C. E. Higginson, *Chem. Soc. Special Publ.*, No. 10, 1957, p. 95.

[4] J. C. Chang and C. S. Garner, *Inorg. Chem.*, 1965, **4**, 209.

for experiments at pH 1·6 in which *ca.* 20% was pentachloroaquoiridate(III), the remainder being hexachloroiridate(III). This monoaquo-complex appears to be formed by hydrolysis of hexachloroiridate(III) rather than as a direct product of the reduction of hexachloroiridate(IV). Similarly, Table 3 shows results obtained with octacyanomolybdate(V), present in excess. Consumption ratios exceeding 4·0 are virtually unknown in the oxidation of hydrazine. Hence, at pH 6·3 and 10·0 there appears to be a decomposition of part of the complex, induced by the oxidation reaction. Spontaneous decomposition was negligible during the 5 min allowed for the completion of the reaction at these pH values. The spectra of product solutions were consistent with those expected for mixtures of octacyanomolybdate-(V) and -(IV) in the proportions found. However, the presence of small amounts of species such as tetrahydroxotetracyanomolybdate(IV) [5] could not be excluded. The significance of such complexes is that oxidation of cyanide ligands could be the cause of the abnormally high consumption ratios.

TABLE 2

Consumption ratios for the system hexachloroiridate(IV)–hydrazine

Temp. *ca.* 20 °C $\mu = 0{\cdot}8$M

$[N_2H_4] = 9{\cdot}7$—$13{\cdot}6$mM

$[IrCl_6^{2-}] = 17$—24mM pH	Number of experiments	Consumption ratio
1·58	4	3·76 ± 0·04
4·25	5 *	3·73 ± 0·06
4·26	6	3·72 ± 0·02
6·45	4	3·53 ± 0·02

* Experiments in presence of air; all others under nitrogen.

TABLE 3

Consumption ratios for the system octacyanomolybdate(V)–hydrazine

Temp. *ca.* 20 °C $\mu =$ *ca.* 0·8M

$[Mo(CN)_8^{3-}] = 18$—22mM

pH	$[N_2H_4]$/mM	Number of experiments	Consumption ratio
2·37	4·80	2	4·09 ± 0·05
2·42	2·90	4	4·27 ± 0·04
4·28	4·78	3	3·93 ± 0·01
4·37	2·92	3	3·91 ± 0·03
6·31	3·87	2	5·05 ± 0·02
6·40	2·90	3	5·01 ± 0·01
10·02	2·89	3	4·91 ± 0·06

The reduction of the green complex tricarbonatocobaltate(III) by hydrazine is accompanied by a change of colour to a pale pink cobalt(II) solution. With hydrazine in approximately two-fold excess or more, an intermediate purple colour was formed. Consumption ratios obtained under various conditions are shown in Table 4. Spectrophotometric investigation showed that, at sufficiently high concentrations of hydrazine, the formation of the purple colour was complete within a few minutes, enabling its much slower disappearance to be studied separately. Measurements of the optical density at 520 nm, a maximum, of decomposing purple solutions were taken at appropriate intervals of time, and plots of log $(D_t - D_\infty)$ against t were linear, where D_t and D_∞ are optical densities at time t and at the end of the reaction, respectively. The first-order velocity constants k obtained from these plots are collected in Table 5. The rate of decomposition is independent of the excess of hydrazine, and the initial optical density of the reaction solution was similar at all three hydrazine concentrations. Stability constants for hydrazine as a unidentate ligand with various metal ions are similar to the corresponding constants for the ligand ammonia. If this is also true with cobalt(III), then we may conclude that the purple colour is due to a cobalt(III) complex containing several co-ordinated hydrazine molecules. Comparison of the spectra of tricarbonatocobaltate(III), the intermediate species, and various cobalt(III) ammines, also suggests that several nitrogen atoms are co-ordinated to cobalt(III) in the intermediate complex.

TABLE 4

Consumption ratios for the system tricarbonatocobaltate(III)–hydrazine

Temp. *ca.* 20 °C $\mu =$ *ca.* 1·2M

Initial concentrations (mM)

pH	$[Co(CO_3)_3^{3-}]$	$[N_2H_4]$	Number of experiments	Consumption ratio
6·81	5·11	49·51	4 *	1·86 ± 0·10
7·56	5·02	4·77	2	2·21 ± 0·05
7·61	5·06	0·958	3	3·12 ± 0·11
7·94	5·15	9·62	3 *	2·58 ± 0·02
9·43	7·95	9·53	4	2·13 ± 0·06
9·48	5·12	47·5	3 *	1·92 ± 0·17
9·48	10·20	1·99	3	3·02 ± 0·03

* Purple intermediate observed in experiments of this group.

TABLE 5

First-order rate constants for decomposition of intermediate in tricarbonatocobaltate(III)–hydrazine system

Temp. = 25·0 ± 0·1 °C $\mu = 0{\cdot}74$M

$[Co(CO_3)_3^{3-}] =$ *ca.* 5·0mM

pH	$[N_2H_4]$/mM	$10^4k/s^{-1}$
6·95	30·0	1·45
7·02	30·0	1·49
6·86	50·0	1·10
7·01	50·0	1·31
6·82	50·0	1·70
6·96	50·0	1·03
6·70	90·0	1·43
6·77	90·0	1·93

Tetra-amminecopper(II) has been reported [6] to oxidise hydrazine quantitatively to molecular nitrogen. We confirmed this by experiments at pH 10·0 and ionic strength 1·0M. Initial concentrations were 89·1mM-copper(II) and 19·1mM-hydrazine. The free ammonia concentration was *ca.* 1·5M, whence the proportions of copper(II) in various forms were calculated to be approximately $Cu(NH_3)_3^{2+}$ $\frac{1}{2}$%, $Cu(NH_3)_4^{2+}$ 70%, $Cu(NH_3)_5^{2+}$ 30%. The mean consumption ratio found

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[5] A. Bertoluzza, V. Carassiti, and A. M. Marinangeli, *Ann. Chim. (Italy)*, 1960, **50**, 806.

[6] E. Ebler, *Z. anorg. Chem.*, 1905, **47**, 371.

for this rapid reaction was 3·965 ± 0·025. The rapid oxidation of hydrazine by hexacyanoferrate(III) at pH 9·9 is known to be quantitative,[7] but was investigated as a check on our techniques for mixing oxidant and reductant in the absence of air, alkaline solutions of hydrazine being prone to aerial oxidation. With initial concentrations of 19·8mM-hexacyanoferrate and 1·99mM-hydrazine we found a mean consumption ratio of 4·025 ±0·035.

The use of permanganate as an oxidising agent in alkaline solution in the presence of barium ions leads to the formation of insoluble barium manganate(VI) and has been much investigated with organic reducing substrates.[8] The rapid reaction was studied at pH 12·6 with initial hydrazine, permanganate and barium ion concentrations of 5·81, 27·6, and 100mM, respectively. The mean consumption ratio was 4·02 ± 0·05. After separation from unchanged permanganate, the oxidation state of the manganese in the barium manganate precipitate was found to be 6·00 ± 0·17.

Oxidation of Sulphite.—The oxidation of sulphite by trispyrophosphatomanganate(III) is slower than the corresponding oxidation of hydrazine, and the consumption ratios were found to be independent of the method of mixing. The results are summarised in Table 6.

TABLE 6

Consumption ratios for the system trispyrophosphatomanganate(III)–sulphite

Temp. *ca.* 20 °C μ = *ca.* 1·1M

[$Mn(P_2O_7)_3{}^{9-}$] = 9·92mM

pH	[$SO_3{}^{2-}$]/mM	Number of experiments	Consumption ratio
2·40	3·77	5	1·52 ± 0·03
5·01	3·47	3	1·53 ± 0·01
6·35	3·72	3	1·49 ± 0·03
2·26	11·35	3	1·18 ± 0·02
5·16	10·07	2	1·27 ± 0·02
5·30	11·29	3	1·26 ± 0·03
6·49	11·20	3	1·30 ± 0·02

TABLE 7

Consumption ratios for the system octacyanomolybdate(V)–sulphite

Temp. *ca.* 20 °C μ = 0·94M

[$Mo(CN)_8{}^{3-}$] = 20—22mM

pH	[$SO_3{}^{2-}$]/mM	Consumption ratio
2·45	5·67	1·96 ± 0·04
2·46	6·72	1·94 ± 0·05
4·39	4·86	1·98 ± 0·02
6·46	6·73	1·99 ± 0·02
9·89	4·82	2·04 ± 0·02

Each consumption ratio is the mean from two identical experiments.

Oxidation by hexachloroiridate(IV) was carried out with both reactant concentrations *ca.* 20mM. At pH 4·40 *ca.* 15 min were allowed for completion of the reaction and the mean consumption ratio was 1·87 ± 0·03. The rapid reaction at pH 6·53 gave a mean consumption ratio of 1·81 ± 0·03. No evidence for any iridium product other than hexachloroiridate(III) was found on spectrophotometric examination of the reaction mixtures. Consumption ratios for the oxidation by octacyanomolybdate(V) are shown in Table 7. Reaction mixtures at pH 2·4 were allowed to stand *ca.* 30 min to ensure completion, but only a period of 5 min was necessary at higher pH values. Spectrophotometric examination of the product solutions gave no evidence of any molybdenum species other than the two octacyanomolybdate ions.

DISCUSSION

In Table 8 we summarise consumption ratios observed with various metal complexes as oxidants of hydrazine. In ease of ligand-substitution, the cobalt(III) complexes occupy a position between the first three, which are very labile, and the remaining complexes, which are highly inert. Considering these cobalt(III) complexes with the labile group, there is a division between the inert complexes, which give high consumption ratios, and the labile complexes, most of which give low consumption ratios. To this extent, there is a rough parallel with Vepřek-Šiška's findings in the oxidation of sulphite.[1] However, in the latter case, the chosen substitution-inert complexes gave quantitative oxidation to sulphate, whereas we do not invariably observe quantitative oxidation of hydrazine to molecular nitrogen by highly inert complexes. We now believe that a simple correlation between consumption ratios, in systems where these can vary, and lability is unlikely to be of general application. An explanation of the correlation observed with sulphite has been given,[1] and we have offered a more general interpretation.[9] Both interpretations are restricted to mechanisms in which the first step involves displacement by the reducing substrate of one or more ligands from the oxidising complex, but other types of mechanism may occur. For example, in the oxidation

TABLE 8

Consumption ratios for various oxidants with hydrazine

Oxidant	Lability *	pH	Rate or time for completion	Consumption ratio
$Cu(NH_3)_4{}^{2+}$	+	10·0	Rapid	4·0
$Mn(P_2O_7)_3{}^{9-}$	+	1·8—6·3	Very rapid	1·1—3·9
$Mn(EDTA)^-$	+	2·4—7·5	Rapid	1·1—1·7
$Co(CO_3)_3{}^{3-}$	±	6·8—9·5	1 min—h	1·8—3·1
$Co(NTA)(H_2O)_2$ †	±	3·5	Several h	1·1—1·2
$Fe(CN)_6{}^{3-}$	—	9·9	Rapid	4·0
$Mo(CN)_8{}^{3-}$	—	2·4—4·4	Min—h	3·9—4·3
$Mo(CN)_8{}^{3-}$	—	6·3—10·0	Rapid	*ca.* 5
$IrCl_6{}^{2-}$	—	1·6—6·5	Rapid—h	3·5—3·8
$MnO_4{}^-(+Ba^{2+})$	—	12·6	Rapid	4·0

* Lability: + labile, — inert, ± of intermediate character. † $Co^{III}(NTA)(H_2O)_2$ = (nitrilotriacetato)diaquocobalt(III); results with this complex obtained by Mr. M. A. Thacker (Ph.D. Thesis, Hull University, 1971).

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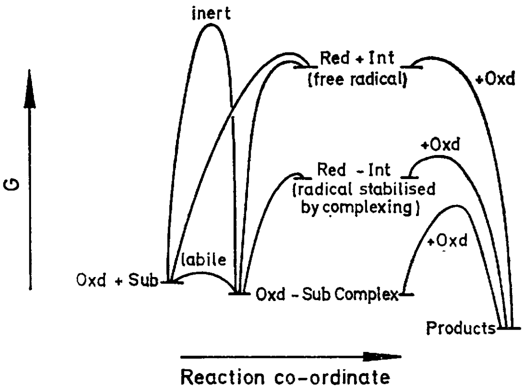
[7] C. J. Dernbach and J. Mehlig, *Ind. and Eng. Chem., Analyt.*, 1942, **14**, 58.

[8] A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 1953, 435.

[9] A. Brown and W. C. E. Higginson, *Chem. Comm.*, 1967, 725.

of sulphite by hexacyanoferrate(III), an addition compound is formed between the two reactants without the displacement of a cyanide ligand.[10] On the other hand, the rates of reaction of hydrazine and sulphite with hexachloroiridate(IV) indicate the likelihood of outer-sphere oxidation, and the nonstoicheiometric oxidation of these substrates is a consequence of alternative reaction paths for the free radicals so produced. Thus, several general types of mechanism are recognised for inert complexes, and these types do not all have the same stoicheiometric consequences. A similar situation presumably holds with substitution-labile oxidants.

Summarising, although the lability of the oxidant to substitution may be important, it is rarely the sole factor determining the mechanism and stoicheiometry of the oxidation of a given substrate. The strength of the oxidising agent, as measured by its standard redox potential has a complementary effect. For example, the direct formation of free radicals by an outer-sphere mechanism is likely to be the least favourable first step energetically for the weaker oxidising agents, but may be the preferred route for fairly strong oxidising agents of the substitution-inert type. Various possibilities are shown in the annexed Figure, which illustrates on a free-energy diagram the influence the lability of the oxidant can have on the mechanisms of such reactions. The effects of an increase in redox potential can be realised on the diagram by decreasing the activation free-energies of the various oxidation steps.



Paths in the oxidation of non-metallic substrates by metal complexes. Oxd = metal complex oxidising agent. Red = reduced form of metal complex. Sub = non-metallic reducing substrate. Int = intermediate, a free radical if Oxd is a 1-equivalent oxidant. Oxd-Sub complex = complex between oxidising agent and reducing substrate. Reaction by this route does not involve the formation of free radicals or other relatively high-energy intermediates.

Discussing individual oxidising agents, the large change in consumption ratio as pH is increased in the trispyrophosphatomanganate(III)–hydrazine reaction is specific to this particular system. Neither the oxidation of sulphite by trispyrophosphatomanganate(III), nor the oxidation of hydrazine by the manganese(III)–EDTA complex show such large changes.

Owing to the side reaction leading to consumption ratios in excess of 4·0, the nature of the reaction between octacyanomolybdate(V) and hydrazine cannot be inferred from our results. With sulphite this oxidant apparently gives quantitative conversion to sulphate which is not to be expected if the free radical $\cdot SO_3^-$ were formed by an outer-sphere oxidation. Since the rate of reaction is too great for ligand-displacement to occur, this may be another example of a mechanism involving the addition of sulphite to a cyanide ligand.[10]

With the permanganate, we expected an outer-sphere 1-equivalent oxidation of hydrazine yielding $\cdot N_2H_3$ free radicals. However, unless their further oxidation is greatly preferred to their dimerisation in solutions of high pH, the latter pathway should occur and should lead to a consumption ratio below 4·0,[3] in contrast to our findings. An alternative possibility is that the reaction involves the 2-equivalent oxidation of hydrazine.

$$MnO_4^- + N_2H_4 \longrightarrow MnO_4^{3-} + N_2H_2$$
$$MnO_4^- + N_2H_2 \longrightarrow MnO_4^{3-} + N_2$$
$$MnO_4^- + MnO_4^{3-} \longrightarrow 2MnO_4^{2-} \longrightarrow 2BaMnO_4$$

The consumption ratio of 4·0 obtained in the oxidation of hydrazine by tetra-amminecopper(II) is an exception to the pattern of lower consumption ratios for substitution-labile complexes. In spite of the low standard redox potentials of copper(II)–copper(I) couples, copper(II) is known to be particularly effective in the oxidation of free radicals, as has been demonstrated with aquocopper(II) in the oxidation of hydrazine.[11] Such complete oxidation of $\cdot N_2H_3$ to N_2H_2, with the consequent lack of formation of N_4H_6, the precursor of ammonia, could lead to a consumption ratio of 4·0. However, non-radical reactions leading to N_2H_2 formation are also possible, *e.g.*

$$Cu(NH_3)_4^{2+} + N_2H_4 \longrightarrow Cu(NH_3)_4(N_2H_4)^{2+}$$
$$Cu(NH_3)_4^{2+} + Cu(NH_3)_4(N_2H_4)^{2+} \longrightarrow 2Cu^I + N_2H_2$$
$$2N_2H_2 \longrightarrow N_2 + N_2H_4$$

Finally, the oxidation of hydrazine by tricarbonatocobaltate(III) occurs by an inner-sphere mechanism involving the intermediate formation of a cobalt(III) complex containing several hydrazine molecules. The first-order disappearance of this intermediate may be either its redox decomposition to the free radical $\cdot N_2H_3$ and a hydrazinocobalt(II) complex, or the slow loss of a hydrazine ligand to give a second hydrazinocobalt(III) complex which undergoes a relatively rapid redox decomposition. Although the latter type of mechanism for the decomposition of a complex intermediate is not common, other examples are known.[12]

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[10] R. S. Murray, *Chem. Comm.*, 1968, 824; J. M. Lancaster and R. S. Murray, *J. Chem. Soc.* (*A*), 1971, 2755.

[11] J. W. Cahn and R. E. Powell, *J. Amer. Chem. Soc.*, 1954, **76**, 2568.

[12] Lee Hin-Fat and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1970, 2836.

EXPERIMENTAL

With the exceptions noted, reagents were of AnalaR or similar pure grade. Sodium hexachloroiridate(IV) hexahydrate and sodium hexachloroiridate(III) dodecahydrate were obtained from Johnson–Matthey. Potassium ethylenediaminetetra-acetatomanganate(III) hydrate,[13] solutions of sodium trispyrophosphatomanganate(III),[14] potassium octacyanomolybdate(IV) dihydrate,[15] solutions of octacyanomolybdate(V),[16] and solutions of tricarbonatocobaltate(III) [17] were prepared as previously described. Tetra-amminecopper(II) solutions were obtained by dissolving copper(II) sulphate in *ca.* 2M-ammonia solution. Solutions of sodium sulphite contained 10^{-3} mol of disodium dihydrogen ethylenediaminetetra-acetate per mol of sulphite.

Oxidising and reducing agent solutions were standardised before use by appropriate methods. The iodometric method was usually employed for oxidising agents, except that octacyanomolybdate(V) solutions were standardised by potentiometric titration with potassium hexacyanoferrate(II) solution. Similar procedures were used for determining the excess of an oxidant after reaction with hydrazine or sulphate. If hydrazine was in excess it was usually determined by treatment with potassium iodate in acid solution, followed by the addition of potassium iodide and back-titration with thiosulphate. Other methods used for hydrazine were Andrews' titration and titration against iodine in alkaline solution.[18] Sulphite was determined by the addition of an excess of iodine solution followed by back-titration with thiosulphate. Ammonia was estimated by Kjeldahl distillation and titration with acid, after first removing any excess of hydrazine by quantitative oxidation to nitrogen with potassium iodate. In experiments with the permanganate–barium ion system, the barium manganate precipitate was removed from the excess of permanganate by filtration using a sinter covered with a compact layer of Kieselguhr. The washed precipitate and Kieselguhr were treated with 2N-perchloric acid and an excess of sodium oxalate was added. The remaining oxalate was then determined by titration with permanganate, enabling the number of oxidising equivalents in the barium manganate to be found.

Buffers were chloroacetate (pH 1·6—2·9), acetate (pH 3·3—5·4), phosphate (pH 5·5—7·0), borate (pH 7·5—9·1), and carbonate (pH 9·2—9·6). In all experiments involving a rapid redox reaction, the oxidising and reducing agent solutions were separately buffered to the required pH before mixing. The pH was measured by meter immediately after the completion of a reaction.

Solutions of reagents, and reaction mixtures were kept under nitrogen or argon, and were transferred by syringe or pipette with precautions to avoid contact with air. All solutions and reaction mixtures involving octacyanomolybdate(V) were kept in the dark and transferred in subdued light. Mixing was usually done by a rotating magnetic stirrer in a suitable glass vessel. The various methods of mixing employed in the trispyrophosphatomanganate(III)–hydrazine system were: *a* hydrazine was added, until present in excess, to a stirred manganese solution, *b* hydrazine was added to a stirred manganese(III) solution, the latter remaining in excess, *c* manganese(III) was added to a stirred hydrazine solution, the latter remaining in excess, *d* equal volumes of hydrazine and manganese(III) solutions were mixed rapidly by forcing each through a Perspex inlet channel of diameter 0·50 mm which formed a Y-junction with a single outlet channel of similar size.

Spectra in the tricarbonatocobaltate(III)–hydrazine system were taken on a Unicam SP 800 recording spectrophotometer. Kinetic measurements were made by using a Uvispek manual spectrophotometer. The reaction took place under nitrogen in a thermostat and a separate sample was taken for each reading of optical density.

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[13] Y. Yoshino, A. Ouchi, Y. Tsunoda, and M. Kojima, *Canad. J. Chem.*, 1962, **40**, 775.

[14] J. L. Lingane and R. Karplus, *Ind. and Eng. Chem., Analyt.*, 1946, **18**, 191.

[15] N. H. Furman and C. O. Miller, *Inorg. Synth.*, 1950, **3**, 160.

[16] O. Collenberg and B. Anderson, *Z. Elektrochem.*, 1925, **31**, 558.

[17] N. A. Laitinen and L. W. Burdett, *Analyt. Chem.*, 1951, **23**, 1268.

[18] Ref. 2, ch. 7.