

Compilation of Rate Constants for the Reactions of Metal Ions in Unusual Valency States

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Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

NSRDS receives advice and planning assistance from a Review Committee of the National Research Council of the National Academy of Sciences-National Academy of Engineering. A number of Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

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The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.



ERNEST AMBLER, *Director*

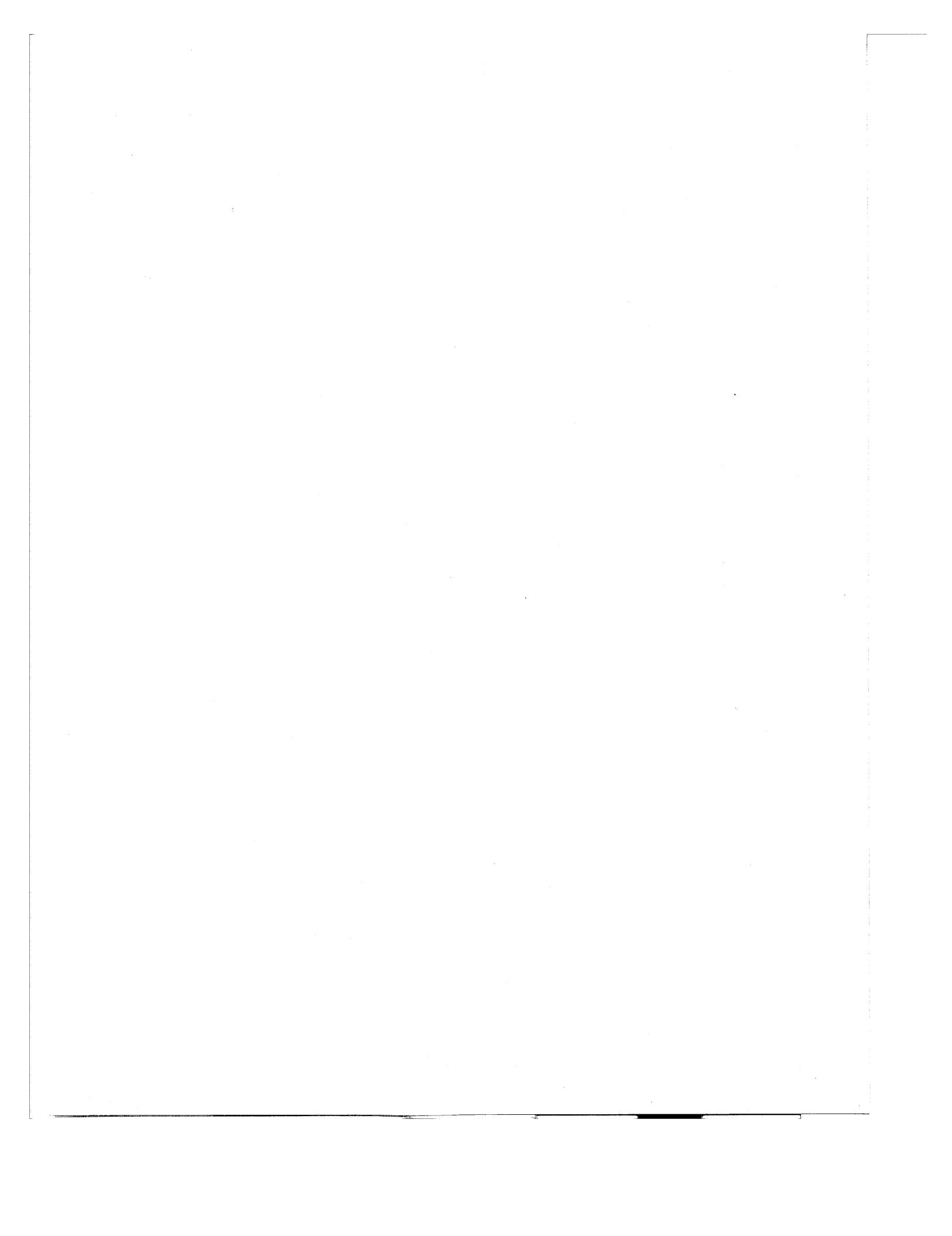
Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or G values (molecules formed or destroyed per 100 eV). Various indirect methods based on G values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, *e.g.* rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

Contents

	Page
Introduction.....	1
Arrangement of the tables	2
List of abbreviations	4
Table 1. Silver(0) and (II) reactions	5
Table 2. Gold(0) and (II) reactions.....	6
Table 3. Cadmium(I) reactions.....	7
Table 4. Cobalt(I) reactions.....	13
Table 5. Chromium(I), (II) and (V) reactions	20
Table 6. Copper(I) and (III) reactions	24
Table 7. Europium(II) reactions.....	29
Table 8. Iron(II) reactions	30
Table 9. Mercury(0) and (I) reactions.....	31
Table 10. Indium(II) reactions.....	35
Table 11. Iridium(II) reactions	35
Table 12. Manganese(I) reactions	35
Table 13. Molybdenum(II) reactions	36
Table 14. Nickel(I) reactions	37
Table 15. Lead(I) reactions	44
Table 16. Praesodymium(IV) reactions	45
Table 17. Platinum(I) and (III) reactions	46
Table 18. Rhodium(II) reactions.....	50
Table 19. Ruthenium(I), (II), (III) and (IV) reactions	51
Table 20. Samarium(II) reactions	53
Table 21. Thallium(0) and (II) reactions	55
Table 22. Thulium(II) reactions.....	59
Table 23. Ytterbium(II) reactions	60
Table 24. Zinc(I) reactions.....	62
Table 25. Intramolecular electron transfer reactions for some metal complexes	65
References.....	66



Compilation of Rate Constants for the Reactions of Metal Ions in Unusual Valency States*

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Kinetic data have been compiled for reactions of uncommon oxidation states of metals which are produced by radiolysis of aqueous solutions of metal ions. Most of the reaction rates are for transient species, and the rates were determined by pulse radiolysis; some data were obtained by flash photolysis and gamma radiolysis. Metal ions from Groups IB, IIB, IIIA, IVA, VIB, VIIIB, and the lanthanides are included in the compilation.

Key words: Aqueous solution; chemical kinetics; complex ions; electron transfer; metal ions; radiation chemistry; rates; transients..

Introduction

The discovery of the hydrated electron as a major product of the radiolysis of water and the development of pulse radiolysis have together resulted in the accumulation, during the last ten years, of a considerable amount of information on the chemistry of unusual valency states of metal ions in aqueous solution, which has been reviewed recently (G. V. Buxton and R. M. Sellers, 77-0121).¹ For the most part attention has been focussed on hyper-reduced states produced in reaction (1), which affords a simple, and often unique, method of their formation. Reactions of hydroxyl radicals and hydrogen atoms, and of simple radicals derived from them, with metal ions have been less commonly studied.



This compilation lists the rate constants for reactions of these metal ions in unusual valency states. In the majority of cases the species are unstable, generally decaying by dismutation (2), or reaction with the solvent or a solute (3). This instability has been the principal criterion on which the decision to include data in this tabulation has been based. However, because the bulk of information on these metal ions has been obtained by pulse radiolysis methods, we have also included some rate constants for the reactions of stable metal ions such as Cu^+ , Cr^{2+} and Eu^{2+} measured by these methods. In these examples, indicated in the tables, much other data not recorded here has been obtained by other techniques.

*This is a data review prepared for, and in cooperation with, the Radiation Chemistry Data Center of the Radiation Laboratory, University of Notre Dame, Indiana 46556. The Laboratory is operated under contract with the Department of Energy. The work of the Center is supported in part by the National Bureau of Standards, Office of Standard Reference Data.

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¹Literature references are given at the end of this paper.

Arrangement of the Tables

The tables are listed in alphabetical order of the chemical symbols of the metals involved. Within each table the arrangement is by oxidation state, starting with the lowest, and is further subdivided according to the complexing ligands in the order aquo ions (and hydrolysed forms), inorganic ligands in alphabetical order of the first letter of the chemical symbol of the principal element of that ligand (e.g. N for ammonia), and organic ligands in alphabetical order of their written names. For each individual transient species the reactants are in the order: inorganic species, organic radicals, both in alphabetical order of their chemical symbols, followed by organic compounds in alphabetical order of their written names.

Table 25 is somewhat different, and lists the rate constants for some intramolecular electron transfer reactions. The reactions are subdivided according to the method of production of the transient species. Note that all the rate constants in this table are first order, and have therefore units of s^{-1} . Reactions of metallo-proteins and related compounds are not dealt with in this compilation.

The data given for each reaction are the measured rate constant, and a brief description of the experimental conditions etc. as outlined below. Literature data published to approximately mid-1976 are covered.

Reaction: Three main methods have been used to measure the rate constants reported here:

- (i) by monitoring the rate of removal of the absorption of the metal species at some convenient wavelength
- (ii) by monitoring the rate of formation of some product
- (iii) by competition kinetics.

Methods (i) and (iii) have the disadvantage that they do not involve characterisation of the products of the reaction, and in many instances in the literature no additional experiments have been performed to overcome this. Often the reaction type has been assumed. Particular attention has been given to this problem in this compilation. Where there is no experimental information on the products given in the original work or elsewhere, only the left hand side of the equation is given, followed in brackets by the possible type of reaction as originally suggested, or as seems appropriate. If experimental evidence is given, the products are quoted, and the nature of the evidence indicated in the column headed 'Comments'.

In some cases the reactive intermediates themselves have not been fully characterised, and in such instances brief details of the method and conditions of formation are given.

Rate Constants: Most of the rate constants listed were measured under conditions where the reaction obeyed first order kinetics and no knowledge of absolute concentrations of the *transient* species is required. Error limits on the rate constants are those quoted in the original work. In the great majority of cases their magnitude is $\pm 10 - 15\%$ of the rate constant value, which is typical of the precision of the mean of pseudo first order rate constants measured by pulse methods. If the data source gives no errors none are shown here, but they should be assumed to be at least $\pm 25\%$ to allow for the possibility that the rate constant is derived from a single measurement.

Second order rate constants are prefaced by " $2k =$ " or " $2k/\epsilon_\lambda =$ " as appropriate. In cases where it is not clear whether the value refers to $2k$ or k this is noted in the 'Comments' column. The measured quantity is $2k/\epsilon_\lambda$ and is subject to the same limitations given above for pseudo first order rate constants. Calculation of $2k$ requires a knowledge of ϵ_λ , and where this quantity is quoted in the original work it is given under 'Comments'. In many instances, however, the values of ϵ_λ used to calculate $2k$ have not been clearly stated.

Evaluation of ϵ_λ requires a knowledge of the concentration of transient species present which, in radiation chemical systems, means that the dose per pulse and the G value² of the species must be known. In our experience these quantities are each likely to be uncertain by $\pm 10\%$, so that the error in $2k$ may be as much as three times as large as the error in $2k/\epsilon_\lambda$. Therefore, in the absence of any quoted errors, the error in $2k$ should be assumed to be $\pm 50\%$.

² G is the number of molecules of a species produced per 100 eV of absorbed energy.

Equilibrium constants are quoted under the 'Rate Constants' heading, and are prefixed by "K—" followed by the appropriate units. If the individual rate constants for the forward and reverse processes are known these are shown as " k_f " and " k_r " respectively. Activation energies are prefaced by " $E_a =$ " and are given in units of kJ mol⁻¹.

Ionic Strength (η): Ionic strengths have either been taken directly from the original work, or calculated from the conditions given. In the few instances where the formation of ion pairs has been taken into account the values are followed by an asterisk. If insufficient information is given to enable the ionic strength to be calculated the column has been left blank. The ionic strength of rate constants extrapolated to zero ionic strength is given as " $\rightarrow 0$ ". Unfortunately in a number of studies little or no attempt has been made to maintain the ionic strength constant. The practice of many reaction kineticists of adding a high concentration of inert electrolyte, such as NaClO₄, has not been widely adopted by radiation chemists, no doubt because of possible complications due to direct radiolysis of the electrolyte (cf. J. Konstantatos and D. Katakis, 67-0019). There is no reason however why an ionic strength of say 0.1 or 0.5 mol dm⁻³ should not become standard for pulse radiolytic measurements. It is to be hoped that more consideration will be given to this problem in future studies.

Temperature: Where temperatures are quoted in the original work these have been given. In the absence of any information temperatures are given as room temperature (RT). The temperature ranges over which activation parameters have been measured are given as appropriate. Since many of the rate constants quoted in these tables are near the diffusion controlled limit and have therefore small activation energies, little uncertainty is engendered by an imprecise knowledge of the temperature. For example a change in temperature of 5° from 25° changes k by 11% for an activation energy of 16 kJ mol⁻¹.

Comments: Information and comments relevant to the reactions and rate constants are given in this column as outlined above. No attempt has been made to give a complete description of the conditions employed in the measurement of the rate constants quoted, but where the concentration of one or more of the solutes exceeds 0.1 mol dm⁻³ this has been noted.

References: The references are listed following the tables in order of the serial number of the paper in the files of the Radiation Chemistry Data Centre at the University of Notre Dame. The first two digits of this number represent the year in which the work was published. The references in the tables also give the first four letters of the first author's name and a dot for each additional author up to a maximum of four dots.

List of Abbreviations

Reaction:	af	adduct formation
	dis	dismutation (disproportionation)
	et	electron transfer
	int et	intramolecular electron transfer
	O at	oxygen atom transfer
	pt	proton transfer
	et - is	inner sphere electron transfer
	?	uncertain
Rate Constant:	$2k$	rate constant for second order reaction
	ϵ_λ	extinction coefficient at wavelength λ
	E_a	activation energy (units kJ mol^{-1})
	K	equilibrium constant
	$\text{p}K$	acid dissociation constant ($= -\log_{10}K$)
	k_f	rate constant for forward reaction of equilibrium
	k_r	rate constant for reverse reaction of equilibrium
	?	value uncertain
Ionic Strength: (I)	$\rightarrow 0$	extrapolated to zero ionic strength
	*	calculated taking into account the formation of ion pairs
Temperature:	var	various
pH:	RT	room temperature
Method:	nat	natural pH of the solution
	comp.	competition kinetics
	f.ph.	flash photolysis
	γ	γ -radiolysis
	pr	pulse radiolysis
Chemical Symbols:	bpy	bipyridyl
	en	ethylenediamine
	gly	glycine
	EDTA ⁴⁻	ethylenediamine tetraacetate
	NAD ⁺	nicotinamide adenine dinucleotide
	NTA ³⁻	nitrilotriacetate
	PNDA	<i>p</i> -nitroso- <i>N,N</i> -dimethylaniline
	L	ligand (specified in table).

TABLE 1. Silver(0) and Silver(II) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
<i>Ag(0) - aquo ions and complexes</i>								
1.1	$\text{Ag}^0 + \text{Ag}^+ \rightarrow \text{Ag}_2^+$	5.9×10^9	-	RT	-	pr	Product characterised by absorption spectrum and charge.	Puki..68-0431
		$(6.5 \pm 0.3) \times 10^9$	-	29	1.0	pr	-	Farh...73-1053
		$(5.2 \pm 0.3) \times 10^9$	-	29	1.0	pr	Measured at pressure of 6.72 kbar.	Farh...73-1053
1.2	$\text{Ag}_2^+ + \text{Ag}^+ \rightarrow \text{Ag}_3^+ + \text{Ag}_2^0$	3.8×10^9	→ 0	RT	-	pr	Products characterised by absorption spectrum.	Puki..68-0431
1.3	$\text{Ag}_2^0 + \text{Ag}^+ \rightarrow \text{Ag}_3^+$	ca. 10^9	-	RT	-	pr	Product characterised by absorption spectrum.	Puki..68-0431
1.4	$\text{Ag}_2^0/\text{Ag}_3^+ + \text{MnO}_4^- (\text{et})$	1.2×10^{10}	0.003	RT	-	pr	Measured by the rate of depletion of the MnO_4^- absorption.	Baxe..65-0385
1.5	$\text{Ag}_2^+ + \text{O}_2 (\text{ct or af})$	3.8×10^8	-	RT	-	pr	Product uncertain, but transfers an electron to 1,4-benzoquinone (see Sell.76-1134).	Baxe..65-0393
1.6	$\text{Ag}_2^+ + 1,4\text{-benzo-quinone} \rightarrow \text{Ag}_3^{2+}(?) + (1,4\text{-benzoquinone})^-$	$(1.5 \pm 0.3) \times 10^8$	-	25±2	5.8	pr	Measured by the rate of formation of the semiquinone in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Sell.76-1134
1.7	$\text{Ag}_2^+ + \text{menaquinone} \rightarrow \text{Ag}_3^{2+}(?) + (\text{menaquinone})^-$	slow	-	-	7.0	pr	Only 24% electron transfer, which may be due to side reactions. Solutions contained 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73-1047
<i>Ag(0) - ammine complexes</i>								
1.8	$\text{Ag}^0 + \text{Ag}(\text{NH}_3)_2^+ \rightarrow \text{Ag}_2(\text{NH}_3)_n^+$	5.2×10^9	-	RT	-	pr	Ag^0 generated from $e_{\text{aq}}^- + \text{Ag}(\text{NH}_3)_2^+$ - might be same as product of $e_{\text{aq}}^- + \text{Ag}^+$. Product contains unknown number of ammine ligands.	Puki.68-0435
1.9	$\text{Ag}_2(\text{NH}_3)_n^+ + \text{Ag}_2(\text{NH}_3)_n^+ \rightarrow \text{Ag}_3(\text{NH}_3)_n^{2+} ?$	$2k = 2.6 \times 10^{10}$	-	RT	-	pr	Product uncertain; gives ultimately Ag_2^0 .	Puki.68-0435
1.10	$\text{Ag}_2(\text{NH}_3)_n^+ + \text{Ag}(\text{NH}_3)_2^+ \rightarrow \text{Ag}_3(\text{NH}_3)_n^{2+} ?$	10^8	-	RT	-	pr	Measured from rate of formation of product, nature of which is uncertain.	Puki.68-0435
<i>Ag(II) - aquo complex</i>								
1.11	$\text{Ag}^{2+} + \text{Ag}^{2+} \rightarrow \text{Ag}^+ + \text{Ag}^{2+}$	1.5×10^8	-	RT	-	pr		Puki..68-0431
1.12	$\text{Ag}^{2+} + \text{anisole} \rightarrow \text{Ag}^+ + \text{anisole}^+$	$(3.8 \pm 0.4) \times 10^7$	-	20±2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75-1171

TABLE 1. Silver(0) and Silver(II) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
1.13	$\text{Ag}^{2+} + 1,2\text{-dimethoxybenzene} \rightarrow \text{Ag}^+ + (1,2\text{-dimethoxybenzene})^+$	$(6.0 \pm 0.6) \times 10^7$	—	20±2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75-1171
1.14	$\text{Ag}^{2+} + 1,3\text{-dimethoxybenzene} \rightarrow \text{Ag}^+ + (1,3\text{-dimethoxybenzene})^+$	$(6.3 \pm 0.6) \times 10^7$	—	20±2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75-1171
1.15	$\text{Ag}^{2+} + 1,4\text{-dimethoxybenzene} \rightarrow \text{Ag}^+ + (1,4\text{-dimethoxybenzene})^+$	$(4.6 \pm 0.5) \times 10^7$	—	20±2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75-1171
1.16	$\text{Ag}^{2+} + 1,2,3\text{-trimethoxybenzene} \rightarrow \text{Ag}^+ + (1,2,3\text{-trimethoxybenzene})^+$	$(2.5 \pm 0.3) \times 10^7$	—	20±2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75-1171
1.17	$\text{Ag}^{2+} + 1,2,4\text{-trimethoxybenzene} \rightarrow \text{Ag}^+ + (1,2,4\text{-trimethoxybenzene})^+$	$(7.0 \pm 0.7) \times 10^7$	—	20±2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75-1171
1.18	$\text{Ag}^{2+} + 1,3,5\text{-trimethoxybenzene} \rightarrow \text{Ag}^+ + (1,3,5\text{-trimethoxybenzene})^+$	$(5.6 \pm 0.6) \times 10^7$	—	20±2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75-1171

*If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for 2k).

TABLE 2. Gold(0) and Gold(II) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
<i>Au(0) from $\text{Au}(\text{CN})_2^- + e_{\text{aq}}^-$</i>								
2.1	$\text{Au}^0 + \text{Au}^0 \rightarrow \text{Au}_2^0$	$(3.2 \pm 0.9) \times 10^9$ $(2.9 \pm 0.7) \times 10^9$	0.001 0.1	RT RT	11 13	pr pr	Product assumed. Solutions contained $9.8 \times 10^{-3} \text{ mol dm}^{-3} \text{ H}_2$.	Ghos.68-0302 Ghos.68-0302
<i>Au(0) from $\text{Au}(\text{CN})_2^- + H$</i>								
2.2	$\text{Au}^0 + \text{Fe}(\text{CN})_6^{4-} (\text{et?})$	5.5×10^8	—	RT	—	pr	—	Ghos.68-0302
2.3	$\text{Au}^0 + \text{N}_2\text{O}$ (et or O at)	5.5×10^8	—	RT	—	pr	—	Ghos.68-0302
2.4	$\text{Au}^0 + \text{O}_2$ (et or af)	3.6×10^9	—	RT	—	pr	—	Ghos.68-0302
<i>Au(II) from $\text{Au}(\text{CN})_2^- + OH^-$</i>								
2.5	$\text{Au}^0 + \text{Au}^0 \rightarrow \text{Au}_2^0$	$(5.0 \pm 1.0) \times 10^9$	0.015	RT	2	pr	—	Ghos.68-0302
2.6	$\text{Au}^{\text{II}} + \text{Au}^{\text{II}}$ (dis or af)	$(2.4 \pm 0.6) \times 10^8$ $(4.8 \pm 1.2) \times 10^8$	0.01	RT	2 4,7	pr pr	Solutions contained $0.1 \text{ mol dm}^{-3} \text{ HCl}$. Solutions contained $0.01 \text{ mol dm}^{-3} \text{ KCl}$.	Ghos.68-0302 Ghos.68-0302
<i>Au(II) from $\text{AuCl}_4^- + H$</i>								
2.7	$\text{Au}^{\text{II}} + \text{Au}^{\text{II}} \rightarrow \text{Au}^{\text{I}} + \text{Au}^{\text{III}}$	$(1.4 \pm 0.3) \times 10^9$ $(8.6 \pm 0.7) \times 10^8$ $(1.2 \pm 0.1) \times 10^9$ $(2.7 \pm 0.6) \times 10^7$ $(2.5 \pm 0.2) \times 10^7$	0.01 0.011 0.131 0.02 0.11	20 20 20 20 20	2 2 2 2 2	pr pr pr pr pr	Nature of products — see ref. 70-0580. Solutions contained $10^{-3} \text{ mol dm}^{-3} \text{ Cl}^-$. Solutions contained $10^{-3} \text{ mol dm}^{-3} \text{ Cl}^- + 0.12 \text{ mol dm}^{-3} \text{ NaClO}_4$. Solutions contained $10^{-2} \text{ mol dm}^{-3} \text{ Cl}^-$. Solutions contained $10^{-1} \text{ mol dm}^{-3} \text{ Cl}^-$.	Baxe.70-0580 Baxe.70-0580 Baxe.70-0580 Baxe.70-0580 Baxe.70-0580

*If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for 2k).

TABLE 3. Cd(I) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
<i>Cd²⁺</i>								
3.1	$\text{Cd}^{2+} + \text{BrO}_3^- (\text{et})$	$(1.25 \pm 0.2) \times 10^8$ $E_a = 13.4 \pm 1.7 \text{ kJ}$ mol^{-1}	0.08 0.08	RT 3 - 90	nat nat	pr pr	- -	Meye.68-0855 Meye.70-1228
3.2	$\text{Cd}^{2+} + \text{Cd}^{2+} \rightarrow \text{Cd}_{2\text{d}}^{2+}$	$2k = ca. 1.2 \times 10^9$	0.4	25 ± 2	nat	pr	Measured at 300 nm taking $\epsilon_{300} = 8080 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Rate constant estimated from studies of Cd^{2+} decay in presence of several different OH scavengers.	Buxt.75-1027
		$2k = 3.0 \times 10^9$	0.002	RT	nat	pr	Measured at 300 nm taking $\epsilon_{300} = 16500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Rate constant estimated from computer analysis of Cd^{2+} decay. Competing reactions taken to be $\text{Cd}^{2+} + \text{H}_2\text{O}_2$ and $\text{Cd}^{2+} + \text{R} \cdot (\text{R} = \text{CH}_3\text{COHCH}_3, \text{CH}_3\text{CHOH}, \text{CH}_3\text{OH})$. Product identified from effect of ionic strength on its decay.	Kelm.75-1064
		$2k = 5.0 \times 10^9$	0.004	RT	nat	pr	Measured at 313 nm taking $\epsilon_{313} = 14000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Rate constant independent of OH scavenger used.	Bark.75-1153
3.3	$\text{Cd}^{2+} + \text{Co}(\text{en})_3^{3+} (\text{et})$	$(1.6 \pm 0.2) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
3.4	$\text{Cd}^{2+} + cis\text{-Co}(\text{en})_2\text{Cl}_2^{2+}$ (et)	$(2.3 \pm 0.3) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
3.5	$\text{Cd}^{2+} + trans\text{-Co}(\text{en})_2\text{Cl}_2^{2+}$ (et)	$(2.6 \pm 0.4) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
3.6	$\text{Cd}^{2+} + \text{Co}(\text{en})_3\text{CO}_3^{2+} (\text{et})$	$(6.7 \pm 1.0) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
3.7	$\text{Cd}^{2+} + cis\text{-Co}(\text{en})_2\text{F}_2^{2+}$ (et)	$(6.0 \pm 0.9) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
3.8	$\text{Cd}^{2+} + \text{Co}(\text{en})_2\text{FH}_2\text{O}^{2+} (\text{et})$	$(4.1 \pm 0.6) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
3.9	$\text{Cd}^{2+} + cis\text{-Co}(\text{en})_2\text{NH}_3\text{Cl}^{2+}$ (et)	$(1.75 \pm 0.26) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
3.10	$\text{Cd}^{2+} + cis\text{-Co}(\text{en})_2\text{NH}_3\text{NO}_2^{2+}$ (et)	$(2.8 \pm 0.7) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
3.11	$\text{Cd}^{2+} + \text{Co}(\text{NH}_3)_6^{3+} (\text{et})$	$(1.72 \pm 0.3) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
3.12	$\text{Cd}^{2+} + \text{Co}(\text{NH}_3)_6\text{Br}^{2+} (\text{et})$	$(25 \pm 0.4) \times 10^8$	0.08	RT	4.0	pr	-	Meye.69-0428
3.13	$\text{Cd}^{2+} + \text{Co}(\text{NH}_3)_6\text{Cl}^{2+} (\text{et})$	$(2.2 \pm 0.3) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
3.14	$\text{Cd}^{2+} + \text{Co}(\text{NH}_3)_6\text{CN}^{2+} (\text{et})$	$(9.1 \pm 1.4) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
3.15	$\text{Cd}^{2+} + \text{Co}(\text{NH}_3)_6\text{F}^{2+} (\text{et})$	$(5.4 \pm 0.8) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
3.16	$\text{Cd}^{2+} + \text{Co}(\text{NH}_3)_6\text{fumarate}^{2+}$ (et or af?)	$(8.3 \pm 2.1) \times 10^8$	0.08	RT	5-6	pr	Products of the reaction have relatively large absorption.	Meye.69-0428
3.17	$\text{Cd}^{2+} + \text{Co}(\text{NH}_3)_6\text{H}_2\text{O}^{2+}$ (et)	$(6.2 \pm 0.9) \times 10^8$	0.08	RT	4.0	pr	-	Meye.69-0428

TABLE 3. Cd(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^a	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
3.18	$\text{Cd}^+ + \text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ (et)	$(9.0 \pm 1.3) \times 10^8$	0.08	RT	7.1	pr	-	Meye.69-0428
3.19	$\text{Cd}^+ + \text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ (et)	$(1.41 \pm 0.2) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
3.20	$\text{Cd}^+ + \text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ (et)	$(1.32 \pm 0.2) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
3.21	$\text{Cd}^+ + \text{Co}(\text{NH}_3)_5\text{OOCCH}_3^{2+}$ (et)	$(9.0 \pm 1.3) \times 10^7$	0.08	RT	5-6	pr	-	Meye.69-0428
3.22	$\text{Cd}^+ + \text{Cr}^{3+}$	$< 10^7$	-	RT	nat	pr	-	Baxe..66-0848
3.23	$\text{Cd}^+ + \text{CrO}_4^{2-}$ (et)	$(9.8 \pm 1.0) \times 10^8$	0.02*	25±2	nat	pr	-	Buxt..76-1072
3.24	$\text{Cd}^+ + \text{Cr}_2\text{O}_7^{2-}$ (et)	$(1.6 \pm 0.2) \times 10^{10}$	0.02*	25±2	nat	pr	-	Buxt..76-1072
3.25	$\text{Cd}^+ + \text{Cu}^{2+}$ (et)	$(1.2 \pm 0.2) \times 10^8$	0.08	RT	nat	pr	-	Meye.68-0855
		$(1.1 \pm 0.2) \times 10^9$	0.04	RT	5-8	γ	Measured by competition kinetics using NO_3^- as competitor and taking $k(\text{Cd}^+ + \text{NO}_3^-) = 3.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.	Fiti70-0117
3.26	$\text{Cd}^+ + \text{H}_2\text{O}_2 \rightarrow$ $\text{Cd}^{2+} + \text{OH} + \text{OH}^-$	$(1.55 \pm 0.2) \times 10^9$ $(2.2 \pm 0.2) \times 10^9$ 2.8×10^9 $E_a = 9.2 \pm 0.8 \text{ kJ mol}^{-1}$	-	RT 25 RT	nat nat nat	pr pr pr	- - -	Meye.68-0855 Buxt..76-1072 Buxt..67-0062 Buxt..76-1072
3.27	$\text{Cd}^+ + \text{H}_3\text{O}^+$	$< 10^6$	0.08	RT	-	pr	-	Meye.68-0855
3.28	$\text{Cd}^+ + \text{IO}_3^-$ (et)	$(2.3 \pm 0.3) \times 10^8$ $(2.1 \pm 0.2) \times 10^9$	0.08 0.04	RT	nat 5-8	pr γ	- Measured by competition kinetics using NO_3^- as competitor and taking $k(\text{Cd}^+ + \text{NO}_3^-) = 3.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.	Meye.68-0855 Fiti70-0117
3.29	$\text{Cd}^+ + \text{MnO}_4^-$ (et)	$(7.8 \pm 0.8) \times 10^8$	-	ca.22	7.0	pr	Measured by the rate of depletion of the MnO_4^- absorption in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73-1104
		1.3×10^{10}	ca. 0.004	20	nat	pr	Measured by the rate of depletion of the MnO_4^- absorption.	Baxe..65-0305
3.30	$\text{Cd}^+ + \text{Ni}^{2+}$	$< 10^7$	-	RT	nat	pr	-	Baxe..66-0848
3.31	$\text{Cd}^+ + \text{NO}_3^-$ (et)	$(2.0 \pm 0.3) \times 10^9$ $E_a = 12.5 \pm 1.7 \text{ kJ mol}^{-1}$	0.08 0.08	RT 3 - 90	nat nat	pr pr	- -	Meye.68-0855 Meye.70-1228
3.32	$\text{Cd}^+ + \text{NO}_3^-$ (et)	$(3.5 \pm 0.5) \times 10^8$	0.08	RT	nat	pr	-	Meye.68-0855

TABLE 3. Cd(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
3.33	$\text{Cd}^+ + \text{N}_2\text{O} \rightarrow \text{CdO}^+ + \text{N}_2$	$< 2 \times 10^6$ 1×10^6 $(3.5 \pm 0.4) \times 10^6$ $E_a = 45.6 \pm 1.3 \text{ kJ mol}^{-1}$	- - -	RT RT 25	nat nat nat	pr pr pr pr	- - Solutions contained 0.1 mol dm ⁻³ methanol. Products inferred from γ -ray induced chain reaction in the system $\text{Cd}^{2+} + \text{HCO}_3^- + \text{N}_2\text{O}$. $G(\text{N}_2)$ measured in the system $\text{Cd}^{2+} + \text{N}_2\text{O}$, (see ref. 73-0039).	Meye.68-0855 Buxt..67-0062 Buxt..76-1072
3.34	$\text{Cd}^+ + \text{O}_2$ (et or af)	$(2.4 \pm 0.4) \times 10^6$ 3.3×10^6 $(3.6 \pm 0.4) \times 10^6$	- - -	RT RT 25 ± 2	nat nat nat	pr pr pr	Absorption spectrum of products similar to that of O_2^- ; but decay slower (see ref. 76-1072). Product transfers an electron to <i>p</i> -benzoquinone (see ref. 76-1134). Evidence possibly indicates product to be CdO_2^+ .	Meye.68-0855 Baxe..66-0848 Buxt..76-1072
3.35	$\text{Cd}^+ + \text{OH} \rightarrow \text{Cd}^{2+} + \text{OH}^-$	$ca. 8 \times 10^6$ 1.8×10^{10} 2×10^{10}	- - -	25 RT RT	nat nat nat	pr pr pr	Estimated from decay of Cd^+ in absence of OH scavengers taking into account the major competing reaction $\text{Cd}^+ + \text{Cd}^+$. Experimentally determined rate constant for the decay of Cd^+ in the absence of OH scavengers. Not corrected for $\text{Cd}^+ + \text{Cd}^+$ or other competing reactions. Estimated from computer analysis of the decay of the optical absorption and conductivity of Cd^+ in the absence of OH scavengers, taking $\text{Cd}^+ + \text{Cd}^+$ and $\text{Cd}^+ + \text{H}_2\text{O}_2$ as the competing reactions. Products identified from conductivity changes.	Buxt.75-1027 Baxe..66-0848 Kelm..75-1064

TABLE 3. Cd(I) reactions — Continued

No.	Reaction.	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹ *	<i>I</i>	<i>t</i> /°C	pH	Method	Comments	Ref.
3.36	Cd ⁺ + Pb ²⁺ (et)	7.5 x 10 ⁷	—	RT	nat	pr	—	Baxe..66-0848
3.37	Cd ⁺ + Ru(NH ₃) ₆ ³⁺ (et)	(2.2 ± 0.3) x 10 ⁹	0.08	RT	nat	pr	—	Nav..70-1229
3.38	Cd ⁺ + S ₂ O ₈ ²⁻ → Cd ²⁺ + SO ₄ ²⁻ + SO ₄ ²⁻	(2.4 ± 0.2) x 10 ⁹	0.02*	25±2	nat	pr	Product identification: SO ₄ ²⁻ observed to form at same rate as Cd ⁺ decayed.	Buxt..76-1072
3.39	Cd ⁺ + Zn ²⁺	< 10 ⁷	—	RT	nat	pr	—	Baxe..66-0848
3.40	Cd ⁺ + ·CH ₃ OH → CdCH ₃ OH ⁺	2 x 10 ⁸	—	RT	nat	pr	Product inferred from conductivity measurements.	Kelm..75-1064
3.41	Cd ⁺ + CH ₃ CHOH → CdCH ₃ CHOH ⁺	< 2 x 10 ⁸ (1.3 ± 0.7) x 10 ⁹	—	RT	nat	pr	—	Bark..75-1153 Kelm..75-1064
3.42	Cd ⁺ + ·CHOHCH ₂ OH	< 2 x 10 ⁸	—	RT	nat	pr	—	Bark..75-1153
3.43	Cd ⁺ + CH ₃ COHCH ₃ → CdCH ₃ COHCH ₃ ⁺	< 2 x 10 ⁸ (2.4 ± 1.2) x 10 ⁹	—	RT	nat	pr	Product inferred from conductivity measurements.	Bark..75-1153 Kelm..75-1064
3.44	Cd ⁺ + ·CHOHCHOHCH ₂ OH	< 2 x 10 ⁸	—	RT	nat	pr	—	Bark..75-1153
3.45	Cd ⁺ + ·CH ₃ (CH ₂) ₂ COH → Cd ²⁺ + (CH ₃) ₂ C=CH ₂ + OH ⁻	ca. 1 x 10 ⁹	—	RT	nat	pr	Isobutene detected as product.	Kelm..75-1064
3.46	Cd ⁺ + -(CH ₂ CH ₂ O) _n (CHCH ₂ O)-	< 2 x 10 ⁸ < 2 x 10 ⁸	—	RT	nat	pr	Radical from polyethylene glycol (mw 10 ⁴) + OH.	Bark..75-1153 Bark..75-1153
3.47	Cd ⁺ + allyl alcohol	< 5 x 10 ⁷	—	25±2	nat	pr	—	Buxt..76-1072
3.48	Cd ⁺ + 9,10-anthra-quinone → Cd ²⁺ + (9,10-anthraquinone) ⁻	(1.03 ± 0.1) x 10 ⁹	—	ca.22	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao..73-1104
3.49	Cd ⁺ + benzophenone → Cd ²⁺ + (benzophenone) ⁻	1.0 x 10 ⁹	—	RT	7.0	pr	Measured by the rate of formation of the ketyl radical in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao..75-1032
3.50	Cd ⁺ + 1,4-benzoquinone → Cd ²⁺ + (1,4-benzoquinone) ⁻	(4.1 ± 0.8) x 10 ⁹	—	25±2	5.4	pr	Measured by the rate of formation of the semiquinone in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Sell..76-1134
		4.4 x 10 ⁹	—	RT	7.0	pr	Measured in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao..75-1032
		(7.7 ± 0.8) x 10 ⁹	—	ca.22	7.0	pr	Measured in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao..73-1104

TABLE 3. Cd(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
3.51	$\text{Cd}^+ + 2\text{-hydroxy-1,4-naphthoquinone} \rightarrow \text{Cd}^{2+} + (\text{2-hydroxy-1,4-naphthoquinone})^-$	$(3.57 \pm 0.4) \times 10^9$	-	ca.22	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao.73-1104
3.52	$\text{Cd}^+ + \text{menaquinone} \rightarrow \text{Cd}^{2+} + (\text{menaquinone})^-$	$(4.6 \pm 0.5) \times 10^9$	-	RT	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao.73-1047, Rao.75-1032
		$(4.68 \pm 0.5) \times 10^9$	-	ca. 22	7.0	pr	Measured in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao.73-1104
3.53	$\text{Cd}^+ + \text{NAD}^+ \rightarrow \text{Cd}^{2+} + \text{NAD}\cdot$	$(2.9 \pm 0.3) \times 10^9$	-	ca. 22	7.0	pr	Measured by the rate of formation of NAD· in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao.73-1104
3.54	$\text{Cd}^+ + 1,4\text{-naphthoquinone-2-sulphonate} \rightarrow \text{Cd}^{2+} + (1,4\text{-naphthoquinone-2-sulphonate})^-$	$(7.35 \pm 0.7) \times 10^9$	-	ca. 22	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao.73-1104
3.55	$\text{Cd}^+ + \text{PNDA (et)}$	1.4×10^{10}	-	RT	nat	pr	-	Dain.68-0066
3.56	$\text{Cd}^+ + \text{riboflavin} \rightarrow \text{Cd}^{2+} + (\text{riboflavin})^-$	$(5.10 \pm 0.5) \times 10^9$	-	ca. 22	7.0	pr	Measured by the rate of formation of the reduced riboflavin in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao.73-1104
<i>Cd(I) complexes</i>								
<i>CdEDTA³⁻</i>								
3.57	$\text{CdEDTA}^{3-} + \text{BrO}_3^- \text{ (et)}$	$(8.9 \pm 1.8) \times 10^6$ $E_a = 4.6 \pm 1.2$ kJ mol^{-1}	0.16 0.16	RT 3-90	11.3 11.3	pr pr	- -	Meye.70-1228 Meye.70-1228
3.58	$\text{CdEDTA}^{3-} + \text{CdEDTA}^{3-} \text{ (et or af)}$	$'k'/\epsilon_{330} = (5.8 \pm 1.5) \times 10^8$ cm s^{-1} $'k' = (4 \pm 2) \times 10^7$	0.16	RT	11.3	pr	Unclear whether k or $2k$.	Meye.70-1228
3.59	$\text{CdEDTA}^{3-} + \text{IO}_3^- \text{ (et)}$	$(2.7 \pm 0.6) \times 10^8$	0.16	RT	11.3	pr	-	Meye.70-1228
3.60	$\text{CdEDTA}^{3-} + \text{NO}_2^- \text{ (et)}$	$(3.2 \pm 0.6) \times 10^6$ $E_a = 8.4 \pm 1.2$ kJ mol^{-1}	0.16 0.16	RT 3 - 90	11.3 11.3	pr pr	- -	Meye.70-1228 Meye.70-1228
3.61	$\text{CdEDTA}^{3-} + \text{NO}_3^- \text{ (et)}$ $\text{Cd(en)}_n^+ \text{ (n unknown)}$	$(1.66 \pm 0.3) \times 10^7$	0.16	RT	11.3	pr	-	Meye.70-1228
3.62	$\text{Cd(en)}_n^+ + \text{BrO}_3^- \text{ (et)}$	$(1.28 \pm 0.3) \times 10^6$	0.64	RT	11.4	pr	-	Meye.70-1228
3.63	$\text{Cd(en)}_n^+ + \text{IO}_3^- \text{ (et)}$	$(2.5 \pm 0.5) \times 10^6$	0.64	RT	11.4	pr	-	Meye.70-1228
3.64	$\text{Cd(en)}_n^+ + \text{NO}_2^- \text{ (et)}$	$(1.12 \pm 0.2) \times 10^6$	0.64	RT	11.4	pr	-	Meye.70-1228
3.65	$\text{Cd(en)}_n^+ + \text{NO}_3^- \text{ (et)}$	$(4.5 \pm 0.9) \times 10^6$	0.64	RT	11.4	pr	-	Meye.70-1228

TABLE 3. Cd(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
<i>Cd(gly)</i>								
3.66	$\text{Cd}(\text{gly}) + \text{BrO}_3^- (\text{et})$	$(6.1 \pm 1.2) \times 10^7$	0.21	RT	10.5	pr	-	Meye..70-1228
3.67	$\text{Cd}(\text{gly}) + \text{IO}_3^- (\text{et})$	$(1.8 \pm 0.4) \times 10^8$	0.21	RT	10.5	pr	-	Meye..70-1228
3.68	$\text{Cd}(\text{gly}) + \text{NO}_2^- (\text{et})$	$(8.5 \pm 1.7) \times 10^8$	0.21	RT	10.5	pr	-	Meye..70-1228
3.69	$\text{Cd}(\text{gly}) + \text{NO}_3^- (\text{et})$	$(2.4 \pm 0.5) \times 10^8$	0.21	RT	10.5	pr	-	Meye..70-1228
<i>CdNTA²⁻</i>								
3.70	$\text{CdNTA}^{2-} + \text{BrO}_3^- (\text{et})$	$(1.02 \pm 0.2) \times 10^7$	0.10	RT	10.7	pr	-	Meye..70-1228
3.71	$\text{CdNTA}^{2-} + \text{CdNTA}^{2-}$ (et or af)	$'k'/\epsilon_{\text{SSO}} = (1.2 \pm 0.4) \times 10^5$ cm s^{-1}	0.10	RT	10.7	pr	Unclear whether k or $2k$.	Meye..70-1228
		$'k' = (8 \pm 4) \times 10^8$	0.10	RT	10.7	pr	Unclear whether k or $2k$.	Meye..70-1228
3.72	$\text{CdNTA}^{2-} + \text{IO}_3^- (\text{et})$	$(6.1 \pm 1.2) \times 10^8$	0.10	RT	10.7	pr	-	Meye..70-1228
3.73	$\text{CdNTA}^{2-} + \text{NO}_2^- (\text{et})$	$(4.2 \pm 0.8) \times 10^7$	0.10	RT	10.7	pr	-	Meye..70-1228
3.74	$\text{CdNTA}^{2-} + \text{NO}_3^- (\text{et})$	$(4.5 \pm 0.9) \times 10^7$	0.10	RT	10.7	pr	-	Meye..70-1228
<i>Cd(I)-radical complexes</i>								
3.75	$\text{CdCH}_3\text{CHOH}^+ + \text{H}_2\text{O} \rightarrow$ $\text{Cd}^{2+} + \text{CH}_3\text{CH}_2\text{OH} + \text{OH}^-$	257 s^{-1}	-	RT	nat	pr	Products inferred from conductivity measurements.	Kelm..75-1064
3.76	$\text{CdCH}_3\text{COHCH}_3^+ + \text{H}_2\text{O} \rightarrow$ $\text{Cd}^{2+} + \text{CH}_3\text{CHOHCH}_3 + \text{OH}^-$	161 s^{-1}	-	RT	nat	pr	Products inferred from conductivity measurements.	Kelm..75-1064
3.77	$\text{Cd}_2^{2+} + \cdot\text{CH}_2(\text{CH}_3)_2\text{COH} \rightarrow$ $\text{Cd}^{2+} + \text{Cd}^{2+} + (\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{OH}^-$	$ca. 1 \times 10^9$	-	RT	nat	pr	Isobutene detected as product.	Kelm..75-1064

*If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 4. Cobalt(I) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
4.1	$\text{Co}^{+}_{\text{aq}}$ $\text{Co}^{+} + \text{Br}_2^- (\text{et})$	$(1.0 \pm 0.3) \times 10^{10}$	-	RT	nat	f.ph.	Competing reactions $\text{Br}_2^- + \text{Br}_2^-$ and $\text{Co}^{+} + \text{Co}^{+}$ not considered.	Thor..70-7726
4.2	$\text{Co}^{+} + \text{BrO}_3^- (\text{et})$	$(4.8 \pm 0.5) \times 10^9$ $(7.1 \pm 1.1) \times 10^9$	0.019^* $\rightarrow 0$	25 ± 2 RT	nat nat	pr pr	- -	Buxt..76-1072 Buxt..76-1072
4.3	$\text{Co}^{+} + \text{Cd}^{2+}$	$< 10^7$	-	RT	nat	pr	-	Baxe..66-0848
4.4	$\text{Co}^{+} + \text{Co}^{+} (\text{et or af})$	$2k < 4 \times 10^9$	0.019^*	25 ± 2	nat	pr	Estimated at 370 nm taking $\epsilon_{370} = 2080 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Buxt..75-1027
4.5	$\text{Co}^{+} + \text{Cu}^{2+} (\text{et})$	$(4.1 \pm 0.4) \times 10^8$ $(1.06 \pm 0.36) \times 10^{10}$	0.019^* 0.04	25 ± 2 RT	nat 5-8	pr γ	- Measured by competition kinetics using NO_3^- as competitor and taking $k(\text{Co}^{+} + \text{NO}_3^-) = 1.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.	Buxt..76-1072 Fit..70-0117
4.6	$\text{Co}^{+} + \text{H}_2\text{O}_2 \rightarrow$ $\text{Co}^{2+} + \text{OH} + \text{OH}^-$	$(1.6 \pm 0.2) \times 10^8$ 1.9×10^9 $E_a = 13.0 \pm 1.0 \text{ kJ mol}^{-1}$	- - -	25 RT 1 - 30	nat nat nat	pr pr pr	- - - Products identified in γ -radiolysis studies (see ref. 73-0039).	Buxt..76-1072 Buxt..67-0062 Buxt..76-1072
4.7	$\text{Co}^{+} + \text{IO}_3^- (\text{et})$	$(4.3 \pm 0.4) \times 10^9$ $(4.9 \pm 0.8) \times 10^9$	0.019^* 0.04	25 ± 2 RT	nat 5-8	pr γ	- Measured by competition kinetics using NO_3^- as competitor and taking $k(\text{Co}^{+} + \text{NO}_3^-) = 1.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.	Buxt..76-1072 Fit..70-0117
4.8	$\text{Co}^{+} + \text{MnO}_4^- (\text{et})$	1.06×10^{10}	ca. 0.004	20	nat	pr	Measured by the rate of depletion of the MnO_4^- absorption.	Baxe..65-0385
4.9	$\text{Co}^{+} + \text{N}_2\text{O} \rightarrow \text{CoO}^{+} + \text{N}_2$	7×10^8 $(1.0 \pm 0.1) \times 10^9$	-	RT	nat	γ	Estimated from N_2 yields in the γ -radiolysis of $\text{Co}^{2+} + \text{N}_2\text{O}$ solutions.	Buxt..67-0062
4.10	$\text{Co}^{+} + \text{NO}_3^- (\text{et})$	$(1.8 \pm 0.2) \times 10^9$	0.019	25 ± 2	nat	pr	-	Buxt..76-1072
4.11	$\text{Co}^{+} + \text{Ni}^{2+}$	$< 10^7$	-	RT	nat	pr	-	Baxe..66-0848

TABLE 4. Cobalt(I) reactions — Continued

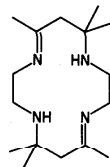
No.	Reaction	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹ a	<i>I</i>	<i>t</i> /°C	pH	Method	Comments	Ref.
4.12	Co^+ + O_2 (et or af)	$(6.0 \pm 0.6) \times 10^9$	—	25±2	nat	pr	Absorption of products similar to that of O_2^- but decay slower (see ref. 76–1072). Product transfers an electron to 1,4-benzoquinone (see ref. 76–1134). Evidence possibly indicates product to be CoO_2^+ .	Buxt..76–1072
4.13	Co^+ + OH (et)	<i>ca.</i> 8 x 10 ⁹	—	25±2	nat	pr	Estimated from decay of Co^+ in absence of OH scavengers, taking into account the major competing reaction $\text{Co}^+ + \text{Co}^+$.	Buxt..75–1027
4.14	$\text{Co}^+ + \text{Ph}^{2+}$	< 10 ⁷	—	RT	nat	pr	—	Baxe..66–0848
4.15	$\text{Co}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Co}^{2+} + \text{SO}_4^- + \text{SO}_4^{2-}$	$(2.8 \pm 0.5) \times 10^9$	0.019	25±2	nat	pr	Formation of SO_4^- inferred from the absorption produced on pulse radiolysis of solutions of $\text{Co}^{2+} + \text{S}_2\text{O}_8^{2-}$.	Buxt..76–1072
4.16	$\text{Co}^+ + \text{Zn}^{2+}$	< 10 ⁷	—	RT	nat	pr	—	Baxe..66–0848
4.17	$\text{Co}^+ + \text{allyl alcohol} \rightarrow (\text{Co-allyl alcohol})^+$	<i>ca.</i> 10 ⁹	—	25±2	nat	pr	Product characterised by its absorption spectrum.	Buxt..76–1072
4.18	$\text{Co}^+ + 9,10\text{-anthra-quinone} \rightarrow \text{Co}^{2+} + (9,10\text{-anthraquinone})^-$	$(1.05 \pm 0.1) \times 10^9$	—	<i>ca.</i> 22	nat	pr	Measured by the rate of formation of the semiquinone in the presence of <i>ca.</i> 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao..73–1104
4.19	$\text{Co}^+ + \text{benzophenone} \rightarrow \text{Co}^{2+} + (\text{benzophenone})^-$	2.5×10^9	—	RT	7.0	pr	Measured by the rate of formation of the ketyl radical in the presence of <i>ca.</i> 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao..75–1032
4.20	$\text{Co}^+ + 1,4\text{-benzoquinone} \rightarrow \text{Co}^{2+} + (1,4\text{-benzoquinone})^-$	4.0×10^9	—	RT	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of <i>ca.</i> 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao..75–1032
		$(5.1 \pm 0.5) \times 10^9$	—	25±2	4.7	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Sell..76–1134
		$(7.35 \pm 0.7) \times 10^9$	—	<i>ca.</i> 22	7.0	pr	Measured in the presence of <i>ca.</i> 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao..73–1104

TABLE 4. Cobalt(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
4.21	$\text{Co}^+ + \text{menaquinone} \rightarrow \text{Co}^{2+} + (\text{menaquinone})^-$	$(4.0 \pm 0.4) \times 10^9$	-	RT	7.3	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73-1047 Rao.75-1032
		$(4.1 \pm 0.1) \times 10^9$	-	ca. 22	7.0	pr	Measured in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73-1104
4.22	$\text{Co}^+ + 1,4-\text{naphthoquinone-2-sulphonate} \rightarrow \text{Co}^{2+} + (1,4-\text{naphthoquinone-2-sulphonate})^-$	$(6.83 \pm 0.7) \times 10^9$	-	ca. 22	7.3	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73-1104
4.23	$\text{Co}^+ + \text{riboflavin} \rightarrow \text{Co}^{2+} + (\text{riboflavin})^-$	$(2.55 \pm 0.3) \times 10^9$	-	ca. 22	7.0	pr	Measured by the rate of formation of the reduced riboflavin in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73-1104
<i>Co(I) complexes</i>								
<i>Co(CN)₆⁴⁻ (from Co(CN)₆³⁻ + e_{eq})</i>								
4.24	$\text{Co(CN)}_6^{4-} + \text{H}_2\text{O} \rightarrow \text{Co(CN)}_6^{3-} + \text{OH}^-$	$(1.1 \pm 0.1) \times 10^5 \text{ s}^{-1}$	-	20	ca. 13	pr	Measured in the presence of ca. 0.1 mol dm^{-3} H_2 . Proton transfer mechanism implied from isotope effect (compare entry 4.25).	Vene.71-0097
4.25	$\text{Co(CN)}_6^{4-} + \text{D}_2\text{O} \rightarrow \text{Co(CN)}_6^{3-} + \text{OD}^-$	$(1.9 \pm 0.2) \times 10^4 \text{ s}^{-1}$	-	20	ca. 13	pr	Measured in D_2O in the presence of ca. 0.1 mol dm^{-3} H_2 .	Vene.71-0097
<i>CoL⁺ (L = 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)</i>								
4.26	$\text{CoL}^+ + \text{H}_2\text{O} \rightarrow \text{CoLH}^{2+} + \text{OH}^-$	20	0.001	RT	9-10	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76-1001
4.27	$\text{CoL}^+ + \text{H}_3\text{O}^+ \rightarrow \text{CoLH}^{2+} + \text{H}_2\text{O}$	1.2×10^9	0.015	RT	3.5-4.2	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76-1001

TABLE 4. Cobalt(I) reactions — Continued

No.	Reaction	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹ ^a	<i>I</i>	<i>t</i> /°C	pH	Method	Comments	Ref.
4.28	$\text{CoL}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{CoLH}^+ + \text{HPO}_4^{2-}$	3.0×10^7	0.005 -0.01	RT	5.5	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76-1001
4.29	$\text{CoL}^+ + \text{N}_2\text{O}$ (et)	9.0×10^6	0.01	RT	9.2	pr	Reaction possibly involves two electron oxidation to Co(III) complex.	Tait..76-1001
4.30	$\text{CoL}^+ + \text{O}_2 \rightarrow \text{CoLO}_2^+$	9.0×10^6	0.02	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Reaction does not involve the formation of CoL^{2+} , assumed therefore to involve the coordination of the O_2 .	Tait..76-1001
4.31	$\text{CoL}^+ + \text{Co(bpy)}_3^{3+}$ (et)	1.2×10^6	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1001
4.32	$\text{CoL}^+ + \text{Co(en)}_3^{3+}$ (et)	7.9×10^6	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1001
4.33	$\text{CoL}^+ + \text{Co(NH}_3)_6^{3+}$ (et)	7.5×10^6	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1001
4.34	$\text{CoL}^+ + \text{CoL}^{2+}$ (et)	4.0×10^6	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1001
4.35	$\text{CoL}^+ + \text{CoL}'^{2+}$ (et)	6.7×10^6	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1001
4.36	$(\text{L}' = 2,3,9,10\text{-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,2,8,10-tetraene})$ $\text{CoL}^+ + \text{Cr(bpy)}_3^{3+}$ (et)	1.2×10^6	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1001



CoL^+ ($L = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene}$).

TABLE 4. Cobalt(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^a	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
4.37	$\text{CoL}^+ + \text{Fe}(\text{bpy})_3^{3+} (\text{et})$	2.3×10^7	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1001
4.38	$\text{CoL}^+ + \text{H}_2\text{O} \rightarrow \text{CoLH}^{2+} + \text{OH}^-$	48	0.001	RT	9-10	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76-1001
4.39	$\text{CoL}^+ + \text{H}_3\text{O}^+ \rightarrow \text{CoLH}^+ + \text{H}_2\text{O}$	3.1×10^9	0.015	RT	3.5-4.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76-1001
4.40	$\text{CoL}^+ + \text{HPO}_4^{2-} \rightarrow \text{CoLH}^{2+} + \text{PO}_4^{3-}$	1.0×10^5	0.06- 0.3	RT	10.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76-1001
4.41	$\text{CoL}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{CoLH}^+ + \text{HPO}_4^{2-}$	9.8×10^7	0.005- 0.01	RT	5.5	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76-1001
4.42	$\text{CoL}^+ + \text{NH}_4^+ \rightarrow \text{CoLH}^+ + \text{NH}_3$	6.8×10^5	0.015- 0.1	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76-1001
4.43	$\text{CoL}^+ + \text{N}_2\text{O} (\text{et})$	3.9×10^7	0.01	RT	9.2	pr	Reaction possibly involves two electron oxidation to Co(III) complex.	Tait..76-1001
4.44	$\text{CoL}^+ + \text{O}_2 \rightarrow \text{CoLO}_2^+$	1.7×10^9	0.02	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Reaction does not involve formation of CoL^{2+} , assumed therefore to involve the coordination of the O_2 .	Tait..76-1001
4.45	$\text{CoL}^+ + \text{Ru}(\text{NH}_3)_6^{2+} (\text{et})$	4.0×10^8	0.016- 0.028	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1001

TABLE 4. Cobalt(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
4.46	$\text{CoL}^+ + \text{Ru}(\text{NH}_3)_6\text{NO}^{3+}$ (et)	3.9×10^7	0.016–0.028	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1001
4.47	$\text{CoL}^+ + \text{acetic acid} \rightarrow \text{CoLH}^+ + \text{CH}_3\text{COO}^-$	7.5×10^7	0.01–0.05	RT	4.8	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.48	$\text{CoL}^+ + 9,10\text{-anthraquinone}-2\text{-sulphonate} \rightarrow \text{CoL}^{2+} + (\text{9},\text{10-anthraquinone}-2\text{-sulphonate})^-$	4.4×10^8	0.004	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption.	Tait..76–1001
4.49	$\text{CoL}^+ + 3\text{-benzoylpyridine}$ (et + ?)	4.6×10^8	0.004	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Only 50% electron transfer to the 3-benzoylpyridine. Other reaction pathway(s) not characterised.	Tait..76–1001
4.50	$\text{CoL}^+ + \text{fluorenone} \rightarrow \text{CoL}^{2+} + (\text{fluorenone})^-$	4.3×10^8	0.004	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Ketyl radical product characterised by its absorption.	Tait..76–1001
4.51	$\text{CoL}^+ + \text{menaquinone} \rightarrow \text{CoL}^{2+} + (\text{menaquinone})^-$	4.6×10^8	0.004	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption.	Tait..76–1001
4.52	$\text{CoL}^+ + \text{methyl iodide}$ (et)	4.7×10^8	0.015	RT	9.2	pr	No evidence for substitution (S_N2) reaction pathway.	Tait..76–1001
4.53	$\text{CoL}^+ + \text{Co(bpy)}_3^{2+}$ (et)	8.5×10^7	0.016–0.028	RT	6.5	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1001

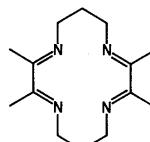
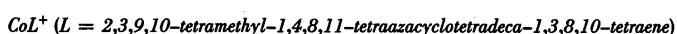


TABLE 4. Cobalt(I) reactions — Continued

No.	Reaction	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹ *	<i>I</i>	<i>t</i> /°C	pH	Method	Comments	Ref.
4.54	CoL^+ + $\text{Cr}(\text{bpy})_3^{3+}$ (et)	1.6×10^8	0.016–0.028	RT	6.5	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1001
4.55	$\text{CoL}^+ + \text{H}_2\text{O}^+ \rightarrow \text{CoLH}^{2+} + \text{H}_2\text{O}$	1.6×10^8	0.06–0.6	RT	0.25–1.25	pr	Measured in the presence of 2 mol dm ⁻³ 2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.56	$\text{CoL}^+ + \text{O}_2 \rightarrow \text{CoLO}_2^+$	1.1×10^8	0.02	RT	6.5	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Reaction does not involve formation of CoL^{2+} , assumed therefore to involve the coordination of O_2 .	Tait..76–1001
4.57	$\text{CoL}^+ + \text{acetic acid} \rightarrow \text{CoLH}^{2+} + \text{CH}_3\text{COO}^-$	6.2×10^4	0.01–0.05	RT	4.8	pr	Measured in the presence of 2 mol dm ⁻³ 2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.58	$\text{CoL}^+ + 9,10\text{-anthraquinone-2,6-sulphonate} \rightarrow \text{CoL}^{2+} + (9,10\text{-anthraquinone-2,6-sulphonate})^-$	3.8×10^8	0.004	RT	6.5	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption.	Tait..76–1001
4.59	$\text{CoL}^+ + \text{indigosulphonate} \rightarrow \text{CoL}^{2+} + (\text{indigosulphonate})^-$	4.9×10^8	0.004	RT	6.5	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Radical anion product characterised by its absorption.	Tait..76–1001
4.60	$\text{CoL}^+ + \text{riboflavin} \rightarrow \text{CoL}^{2+} + (\text{riboflavin})^-$	1.0×10^8	0.004	RT	6.5	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Radical anion product characterised by its absorption.	Tait..76–1001

*If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for 2*k*).

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
<i>Cr(I) Reactions</i>								
<i>Cr⁺_{aq}</i>								
5.1	$\text{Cr}^+ + \text{H}_2\text{O}$	$< 5 \times 10^3 \text{ s}^{-1}$	-	22 ± 2	3.0-4.3	pr	Estimated from first order, dose dependent decay of Cr^+ . Major competing reactions thought to be $\text{Cr}^+ + \text{H}_2\text{O}_2$. H_2 detected as product ($G = 2.9$ at pH 3.4).	Cohe.74-1142
<i>CrH²⁺ (from H + Cr²⁺)</i>								
5.2	$\text{CrH}^{2+} + \text{H}_2\text{O}$	$< 1 \text{ s}^{-1}$	-	22 ± 2	0-2	pr	-	Cohe.74-1142
5.3	$\text{CrH}^{2+} + \text{H}_2\text{O}^+ \rightarrow \text{Cr}^{3+} + \text{H}_2 + \text{H}_2\text{O}$	$(1.8 \pm 0.2) \times 10^4$	var	22 ± 2	0-2	pr	$G(\text{H}_2) = 3.8$ at pH 0-2.	Cohe.74-1142
<i>Cr(II) reactions (includes only those measured by radiolytic methods).</i>								
<i>Cr²⁺_{aq}</i>								
5.4	$\text{Cr}^{2+} + \text{Br}_2^- \rightarrow \text{CrBr}^{2+} + \text{Br}^-$	$(1.9 \pm 0.2) \times 10^9$	0.2	22 ± 3	1	pr	Reaction occurs by inner sphere diffusion controlled mechanism. $G(\text{CrBr}^{2+}) = 2.4$ in γ -radiolysis experiments.	Laur.74-1104
5.5	$\text{Cr}^{2+} + \text{Cl}_2^- \rightarrow \text{CrCl}^{2+} + \text{Cl}^-(\text{a}) \text{ or } \text{Cr}^{2+} + 2\text{Cl}^-(\text{b})$	$(2.4 \pm 0.3) \times 10^9$	0.2	22 ± 3	1	pr	Reaction occurs by parallel mechanisms involving inner-sphere (path a) and outer sphere (b) diffusion control with approximately equal probability. $G(\text{CrCl}^{2+}) = 1.4$ in γ -radiolysis experiments.	Laur.74-1104
5.6	$\text{Cr}^{2+} + \text{I}_2^- \rightarrow \text{CrI}^{2+} + \text{I}^-$	$(1.5 \pm 0.2) \times 10^9$	0.2	22 ± 3	1	pr	Reaction occurs by inner sphere diffusion controlled mechanism. CrI^{2+} characterised by flash photolysis and γ -radiolysis experiments. $G(\text{CrI}^{2+}) = 0.85$ at 0°C .	Laur.74-1104
5.7	$\text{Cr}^{2+} + \text{MnO}_4^- (\text{et})$	3.7×10^9	ca.0.01	20	nat	pr	Measured by the rate of depletion of the MnO_4^- absorption.	Baxe..65-0385
5.8	$\text{Cr}^{2+} + \text{N}_2\text{O}$	$< 10^6$	-	25	nat	γ	Estimated from the values of $G(\text{N}_2)$ measured in the γ -radiolysis of $\text{Cr}^{2+} + \text{N}_2\text{O}$ solutions.	Sell72-0844

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions — Continued

No.	Reaction	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹ *	<i>I</i>	<i>t</i> /°C	pH	Method	Comments	Ref.
5.9	$\text{Cr}^{2+} + \text{O}_2 \rightarrow \text{CrO}_2^{2+}$	$(1.6 \pm 0.2) \times 10^8$	—	25±2	2.6–4.3	pr	Measured from the rate of formation of CrO_2^{2+} in the presence of 0.5 mol dm ⁻³ 2-methyl-2-propanol. Product characterised by its absorption spectrum and by conductivity measurements.	Sell.76-1134
		$(1.6 \pm 0.2) \times 10^8$	—	RT	1–3	pr	Measured from the rate of formation of CrO_2^{2+} .	Ilan..75-1215
		$(1.9 \pm 0.3) \times 10^8$	—	25±2	3.4	pr (comp)	Measured by competition with 1,4-benzoquinone taking $k(\text{Cr}^{2+} + \text{C}_6\text{H}_4\text{O}_2) = 3.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.	Sell.76-1134
5.10	$\text{Cr}^{2+} + \cdot\text{CONH}_2 \rightarrow \text{CrCONH}_2^{2+}$	$(6.5 \pm 0.7) \times 10^8$	—	22±2	0–4.5	pr	Measured by the rate of formation of the product in the presence of 1 mol dm ⁻³ formamide. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74-1146
5.11	$\text{Cr}^{2+} + \cdot\text{CH}_3\text{OH} \rightarrow \text{CrCH}_3\text{OH}^{2+}$	1.6×10^8	—	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74-1146
5.12	$\text{Cr}^{2+} + \text{CO}_2^- \rightarrow \text{CrCO}_2^+$	$(1.1 \pm 0.1) \times 10^9$	ca. 0.04	25±2	1.4	pr	Measured by rate of formation of the product in the presence of 1 mol dm ⁻³ formic acid. Product characterised by its spectrum and decay kinetics.	Elli....73-1057
5.13	$\text{Cr}^{2+} + \cdot\text{CH}_2\text{CHO} \rightarrow \text{CrCH}_2\text{CHO}^{2+}$ or $\text{CrCH}_2\text{CH}(\text{OH})_2^{2+}$	3.5×10^8	—	22±2	0–1	pr	Measured by the rate of formation of the product, which may be in the form of an acetal.	Cohe.74-1146
5.14	$\text{Cr}^{2+} + \cdot\text{CH}_2\text{COOH} \rightarrow \text{CrCH}_2\text{COOH}^{2+}$	2.5×10^8	—	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74-1146
5.15	$\text{Cr}^{2+} + \cdot\text{CHOH.COOH} \rightarrow \text{CrCHOH.COOH}^{2+}$	1.4×10^8	—	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74-1146

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
5.16	$\text{Cr}^{2+} + \text{CH}_3\text{CHOH} \rightarrow \text{CrCH}(\text{CH}_3)\text{OH}^{2+}$	7.9×10^7	—	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.17	$\text{Cr}^{2+} + \cdot\text{CHOHCH}_2\text{OH} \rightarrow \text{CrCH}_2\text{CHO}^{2+}$ or $\text{CrCH}_2\text{CH}(\text{OH})_2^{2+}$	1.5×10^8	—	22 ± 2	3.0–4.5	pr	Measured by the rate of formation of the product. Product is identical to that formed in the reaction $\text{Cr}^{2+} + \text{CH}_3\text{CHO}$ (see entry 5.13).	Cohe.74–1146
5.18	$\text{Cr}^{2+} + \cdot\text{CH}(\text{COOH})_2 \rightarrow \text{CrCH}(\text{COOH})_2^{2+}$	6.0×10^7	—	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.19	$\text{Cr}^{2+} + \text{CH}_3\text{CHCOOH} \rightarrow \text{CrCH}(\text{CH}_3)\text{COOH}^{2+}$	1.1×10^8	—	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.20	$\text{Cr}^{2+} + \text{CH}_3\text{C}(\text{OH})\text{COOH} \rightarrow \text{CrCOH}(\text{CH}_3)\text{COOH}^{2+}$	9.2×10^7	—	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.21	$\text{Cr}^{2+} + \cdot\text{CH}_2\text{N}(\text{CH}_3)\text{CHO} \rightarrow (\text{1.1} \pm 0.1) \times 10^8 \text{ CrCH}_2\text{N}(\text{CH}_3)\text{CHO}^{2+}$	$(\text{1.1} \pm 0.1) \times 10^8$	—	22 ± 2	0–4.5	pr	Measured by the rate of formation of the product in the presence of 1 mol dm^{-3} $\text{CH}_2\text{N}(\text{CH}_3)\text{CHO}$. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.22	$\text{Cr}^{2+} + (\text{CH}_3)_2\text{COH} \rightarrow \text{CrCOH}(\text{CH}_3)_2^{2+}$	5.1×10^7	—	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.23	$\text{Cr}^{2+} + \cdot\text{R} \rightarrow \text{CrR}^{2+}$ ·R = radical from dioxane (H abstraction)	1.0×10^8	—	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.24	$\text{Cr}^{2+} + \cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH} \rightarrow \text{CrCH}_2\text{C}(\text{CH}_3)_2\text{OH}^{2+}$	1.0×10^8	—	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ *	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
5.25	$\text{Cr}^{2+} + \text{CH}_3\text{CHOCH}_2\text{CH}_3 \rightarrow \text{CrCH}(\text{CH}_3)\text{OCH}_2\text{CH}_3^{2+}$	3.4×10^7	—	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.26	$\text{Cr}^{2+} + \text{CH}_3\text{C}(\text{CH}_3)_2\text{COOH} \rightarrow \text{CrCH}_2\text{C}(\text{CH}_3)_2\text{COOH}^{2+}$	1.1×10^8	—	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.27	$\text{Cr}^{2+} + \text{anthraquinone}-2,6\text{-disulphonate} \rightarrow \text{Cr}^{2+} + (\text{anthraquinone}-2,6\text{-disulphonate})^-$	$(2.8 \pm 0.3) \times 10^9$	—	<i>ca.</i> 22	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of <i>ca.</i> 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.75–1032
5.28	$\text{Cr}^{2+} + 1,4\text{-benzo-quinone} \rightarrow \text{Cr}^{2+} + (1,4\text{-benzoquinone})^-$	$(3.2 \pm 0.3) \times 10^8$	—	25 ± 2	3.4	pr	Measured by the rate of formation of the semiquinone in the presence of 0.5 mol dm^{-3} 2-methyl-2-propanol.	Sell.76–1134
		$(3.5 \pm 0.4) \times 10^9$	—	<i>ca.</i> 22	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of <i>ca.</i> 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.75–1032
5.29	$\text{Cr}^{2+} + \text{tetra-nitromethane} \rightarrow \text{Cr}^{2+} + \text{NO}_2 + \text{C}(\text{NO}_2)_3^-$	$(1.2 \pm 0.2) \times 10^8$	—	25 ± 2	3.4	pr	Measured by the rate of formation of the nitroform anion in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Sell.76–1134
5.30	$\text{Cr}(\text{V}) \text{ (from } \text{CrO}_4^{2-} + e_{\text{aq}}^-)$ $\text{Cr}^{\text{V}} + \text{Cr}^{\text{V}} \text{ (dis or af)} \quad 2k/\epsilon_{400} = (7 \pm 3) \times 10^6 \text{ cm s}^{-1}$		0.003	25	nat	pr	—	Sell72–0844

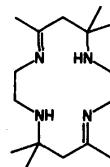
*If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 6. Copper(I) and copper(III) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
6.1	$\text{Cu}_{\text{aq}}^{+}$ $\text{Cu}^{+} + \text{Cu(OH)}_2^{+} (\text{et})$	$(1.8 \pm 0.6) \times 10^0$ $(1.6 \pm 0.5) \times 10^0$	0.003 0.003	25 25	4.8 6	pr pr	See comments under entry 6.37. See comments under entry 6.37.	Sell72-0844 Sell72-0844
6.2	$\text{Cu}^{+} + \text{MnO}_4^{-} (\text{et})$	$(3.6 \pm 1.2) \times 10^0$ 5×10^0 $ca.$ 0.08	0.002 RT 20	nat 2	pr pr	-	Measured by the rate of depletion of the MnO_4^{-} absorption. Dependence of k on $[\text{Cu}^{2+}]$ detected. Measured by the rate of depletion of the MnO_4^{-} absorption.	Meye71-0174 Baxe..65-0385 Sell72-0844
6.3	$\text{Cu}^{+} + \text{N}_2\text{O}$	$< 10^0$	-	25	nat	γ	Estimated from N_2 yields in the γ -radiolysis of $\text{Cu}^{2+} + \text{N}_2\text{O}$ solutions.	Sell72-0844
6.4	$\text{Cu}^{+} + \cdot\text{CH}_2\text{OH} \rightleftharpoons \text{CuCH}_2\text{OH}^{+}$	$k_t \text{ ca. } 10^{10}$ $k_r \text{ ca. } 10^6 \text{ s}^{-1}$	-	RT	4.5	pr	Identity of product inferred from its absorption spectrum.	Buxt.77-1500
6.5	$\text{Cu}^{+} + (\text{CH}_3)_2\text{COH} \rightarrow \text{CuCOH}(\text{CH}_3)_2^{+}$	$ca. 6 \times 10^0$	-	RT	4.5	pr	Identity of product inferred from its absorption spectrum.	Buxt.77-1500
6.6	$\text{CuCOH}(\text{CH}_3)_2^{+} + \text{H}^{+} \rightarrow \text{Cu}^{+} + \text{products}$	3.2×10^7	-	RT	3-4.5	pr	Estimated from dependence of decay of absorption attributed to $\text{CuOH}(\text{CH}_3)_2^{+}$ on $[\text{H}^{+}]$ (see entry 6.5).	Buxt.77-1500
6.7	$\text{Cu}^{+} + \cdot\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{OH}^{-} + \text{Cu}^{2+}$	1.9×10^{10}	-	RT	4.5	γ	Estimated from yields of Cu^I in γ -radiolysis of $\text{Cu}^{2+} + \text{C}_2\text{H}_4$ solutions. Products inferred from data for entry 6.8.	Buxt.77-1500
6.8	$\text{Cu}^{+} + \cdot\text{CH}_2(\text{CH}_3)_2\text{COH} \rightarrow \text{CuCH}_2(\text{CH}_3)_2\text{COH}^{+}$	2.6×10^0	-	RT	4.5	γ	Product inferred from its absorption spectrum. Estimated from yields of Cu^I in the γ -radiolysis of $\text{Cu}^{2+} + 2$ -methyl-2-propanol + C_2H_4 solutions. Final product is $\text{CH}_2=\text{C}(\text{CH}_3)_2$.	Buxt.77-1500
6.9	$\text{Cu}^{+} + \text{acrylamide} \rightleftharpoons \text{Cu-acrylamide}^{+}$	$K = (2.1 \pm 0.1) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ $k_t = 2 \times 10^0$ $k_r = 1.1 \times 10^5 \text{ s}^{-1}$	-	25 ± 2	4	pr	Measured from the effect of [acrylamide] on the yield and rate of formation of Cu-acrylamide^{+} .	Buxt.76-1186
6.10	$\text{Cu}^{+} + \text{benzoquinone}$	$< 10^0$	-	25 ± 2	4.9	pr	Estimated from the non-formation of benzosemiquinone in the pulse radiolysis of $\text{Cu}^{2+} + \text{benzoquinone}$ solutions.	Sell.76-1134

TABLE 6. Copper(I) and copper(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
6.11	$\text{Cu}^+ + \text{ethylene} \rightleftharpoons \text{Cu-ethylene}^+$	$K = (2.22 \pm 0.1) \times 10^8 \text{ dm}^3 \text{ mol}^{-1}$	-	25 ± 2	4	γ	Measured from the effect of admitting ethylene to solutions of Cu-acrylamide ⁺ (see entry 6.9).	Buxt..76-1186
6.12	$\text{Cu}^+ + \text{fumaric acid} \rightleftharpoons \text{Cu-fumaric acid}^+$	$k_f = (1.7 \pm 0.4) \times 10^9$ $k_r = (2.4 \pm 0.4) \times 10^8 \text{ s}^{-1}$ $K = (7.1 \pm 2.0) \times 10^8 \text{ dm}^3 \text{ mol}^{-1}$ $K = (9.0 \pm 2.0) \times 10^8 \text{ dm}^3 \text{ mol}^{-1}$	-	22 ± 2	3.65	pr	Measured from the rate of formation of the product in the presence of 1 mol dm^{-3} methanol.	Meye75-1092
6.13	$\text{Cu}^+ + \text{iso-butene} \rightleftharpoons \text{Cu-iso-butene}^+$	$K = (2.7 \pm 0.1) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$	-	25 ± 2	4	γ	Measured from the effect of admitting iso-butene to solutions of Cu-acrylamide ⁺ .	Buxt..76-1186
6.14	$\text{Cu}^+ + \text{maleic acid} \rightleftharpoons \text{Cu-maleic acid}^+$	$k_f = (2.0 \pm 0.4) \times 10^9$ $k_r = (1.8 \pm 0.4) \times 10^8 \text{ s}^{-1}$ $K = (1.1 \pm 0.3) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ $K = (1.3 \pm 0.2) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$	-	22 ± 2	3.65	pr	Measured from the rate of formation of the product in the presence of 1 mol dm^{-3} methanol.	Meye75-1092
6.15	$\text{Cu}^+ + \text{tetranitro-methane} \rightarrow \text{Cu}^{2+} + \text{NO}_2 + \text{C}(\text{NO}_2)_3^-$	$(4.2 \pm 0.4) \times 10^8$ $(4.7 \pm 0.5) \times 10^8$	-	RT	-	pr	Measured from the rate of formation of the nitroform anion.	Asmu...64-0133
			-	25 ± 2	4.9	pr	Measured from the rate of formation of the nitroform anion.	Sell.76-1134
6.16	$\text{CuL}^+ + \text{Co}(\text{bpy})_3^{2+}$ (et)	$(1.2 \pm 0.1) \times 10^7$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76-1039
6.17	$\text{CuL}^+ + \text{CoL}'(\text{OH}_2)(\text{OH})^{2+}$	$< 10^8$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76-1039

Cu(I) Complexes CuL^+ ($L = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene}$)

(L' = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene).

TABLE 6. Copper(I) and copper(III) reactions — Continued

No.	Reaction	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹ ^a	<i>I</i>	<i>t</i> /°C	pH	Method	Comments	Ref.
6.18	CuL ⁺ + Co(en) ₃ ³⁺	< 10 ³	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
6.19	CuL ⁺ + Co(NH ₃) ₆ ³⁺	< 10 ³	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
6.20	CuL ⁺ + CoL'(OH) ₂ ⁺	< 10 ³	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
6.21	(L' = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,7,10-tetraene). CuL ⁺ + Cr(bpy) ₃ ³⁺ (et)	(3.7 ± 0.4) × 10 ⁶	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
6.22	CuL ⁺ + Fe(bpy) ₃ ³⁺	< 10 ³	0.016– 0.028	RT	7.0	pr	Estimated in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
6.23	CuL ⁺ + H ₃ O ⁺ (pt)	(5.0 ± 0.5) × 10 ⁶	0.06– 0.3	RT	<1.25	pr	Reaction may involve proton transfer to the metal centre to give a hydrido complex.	Tait..76–1039
6.24	CuL ⁺ + H ₂ PO ₄ ⁻	< 10 ⁴	0.01– 0.1	RT	5.50	pr	—	Tait..76–1039
6.25	CuL ⁺ + N ₂ O (et or O at)	(1.7 ± 0.2) × 10 ⁶	—	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Reaction possibly involves two electron oxidation to Cu(III) complex.	Tait..76–1039
6.26	CuL ⁺ + O ₂ → CuLO ₂ ⁺	(2.6 ± 0.3) × 10 ⁷	—	RT	7.0	pr	Product does not transfer an electron to 1,4-benzoquinone, and identified therefore as O ₂ adduct.	Tait..76–1039
6.27	CuL ⁺ + Ru(NH ₃) ₆ ³⁺ (et)	(7.2 ± 0.7) × 10 ⁶	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
6.28	CuL ⁺ + Ru(NH ₃) ₆ NO ₃ ³⁺	< 10 ³	0.016– 0.028	RT	7.0	pr	Estimated in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
6.29	CuL ⁺ + acetic acid	< 10 ⁴	0.015– 0.06	RT	4.85	pr	Estimated in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
6.30	CuL ⁺ + 9,10-anthra-quinone-2,6-disulphonate (et)	(4.3 ± 0.4) × 10 ⁶	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039

TABLE 6. Copper(I) and copper(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
6.31	$\text{CuL}^+ + 9,10\text{-anthra-quinone-2-sulphonate (et)}$	$(1.1 \pm 0.1) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76-1039
6.32	$\text{CuL}^+ + 1,4\text{-benzo-quinone (et)}$	$(2.6 \pm 0.3) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76-1039
6.33	$\text{CuL}^+ + 3\text{-benzoyl-pyridine}$	no reaction observed	0.004	RT	7.0	pr	—	Tait..76-1039
6.34	$\text{CuL}^+ + \text{eosin Y}$	no reaction observed	0.004	RT	7.0	pr	—	Tait..76-1039
6.35	$\text{CuL}^+ + \text{fluorescein}$	no reaction observed	0.004	RT	7.0	pr	—	Tait..76-1039
6.36	$\text{CuL}^+ + \text{methyl iodide (et or S}_N^2)$	$(3.1 \pm 0.3) \times 10^8$	0.01	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76-1039
<i>Cu(III) Reactions</i>								
<i>Cu(III) aquo ion (Cu(OH)_3, Cu(OH)_2^+ and CuOH^{2+})^b</i>								
6.37	$\text{CuOH}^{2+} \rightleftharpoons \text{Cu(OH)}_2^+ + \text{H}^+$	$\text{pK} = 2.4 \pm 0.2$	var	25	0.6	pr	Degree of hydrolysis deduced from conductivity experiments (see ref. 70-0512). Note: pK of this value is also in keeping with the data of Baxendale <i>et al</i> (ref. 65-0394) and of Meyerstein (ref. 71-0174) taking into account equilibrium 6.39.	Sell72-0844
6.38	$\text{Cu(OH)}_2^+ \rightleftharpoons \text{CuOH}^+ + \text{OH}$	$\text{pK} = 3.05 \pm 0.05$ $k_t = (4.2 \pm 1.4) \times 10^4 \text{ s}^{-1}$ and $K = 1.3 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1}$ $k_t = (2.8 \pm 1.0) \times 10^4 \text{ s}^{-1}$ and $K = 9.0 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1}$	var var	RT RT	2-7 3.50	pr pr	— Estimated from decay of Cu^{III} in the presence of Br^- , CH_3OH , H_2O_2 etc. Values of k_t taken to be same as $k(\text{Cu}^{2+} + \text{OH})$.	Baxe..65-0394 Baxe..65-0394
6.39	$\text{Cu(OH)}_2^+ \rightleftharpoons \text{Cu}(\text{OH})_3 + \text{H}^+$	$\text{pK} > 6$	var	25	0-6	pr	—	Sell72-0844
6.40	$\text{Cu}(\text{OH})_2^+ + \text{Cu}^+$ (et)	$(1.8 \pm 0.6) \times 10^8$ $(1.6 \pm 0.5) \times 10^8$ $(3.6 \pm 1.2) \times 10^8$	0.003 0.003 0.002	25 25 RT	4.8 6 nat	pr pr pr	Estimated from decay of Cu^{III} in deaerated solutions. Possibly some contribution from $\text{Cu}(\text{OH})_3 + \text{Cu}^+$. Possibly some contribution from $\text{Cu}(\text{OH})_2^+ + \text{Cu}^+$.	Sell72-0844 Sell72-0844 Meye71-0174
6.41	$\text{Cu}(\text{OH})_2^+ + \text{Cu}(\text{gly})^+$ (et?)	$(8.1 \pm 0.5) \times 10^7$	0.004	RT	5.5	pr	—	Meye71-0775

TABLE 6. Copper(I) and copper(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^a	I	t/°C	pH	Method	Comments	Ref.
6.42	$\text{Cu(OH)}_2^+ + \text{Cu(OH)}_2^+$ (af)	$2k = (4.6 \pm 0.6) \times 10^7$	0.002	RT	6	pr	Estimated from the decay of Cu^{III} in N_2O saturated solutions.	Meye71-0174
		$2k < 5 \times 10^7$	0.004	25	6	pr	Possibly some contribution from $\text{Cu(OH)}_2^+ + \text{Cu(OH)}_2$ and $\text{Cu(OH)}_2 + \text{Cu(OH)}_3^-$.	Sell72-0844
6.43	$\text{Cu(OH)}_2^+ + \text{CuNO}_2^+$ (et)	ca. 3×10^9	ca. 0.002	RT	5.2	pr	Estimated from decay of Cu^{III} in presence of NO_2^- .	Meye71-0174
6.44	$\text{Cu(OH)}_2^+ + \text{mena-quinone} (?)$	$(2.0 \pm 0.2) \times 10^9$	—	RT	9.0, 10.6	pr	40% of Cu^{III} claimed to react by electron transfer. Cu^{III} formed by $\text{OH} + \text{Cu}(\text{ClO}_4)_2$.	Rao.73-1047
		—	—	RT	8.0	pr	20.3% electron transfer. Cu^{III} formed by $\text{OH} + \text{CuSO}_4$.	Rao.73-1047
		—	—	10.6	pr	39% electron transfer. Cu^{III} formed by $\text{OH} + \text{CuSO}_4$.	Rao.73-1047	
<i>Cu(III) Complexes.</i> (The precise nature of these complexes is uncertain: all were formed by OH oxidation of the corresponding Cu^{II} complex).								
6.45	$\text{Cu}^{III}(\text{NH}_3)_n + \text{Cu}^{III}(\text{NH}_3)_n$ (af?)	$2k = (3.0 \pm 0.5) \times 10^7$	<0.008	RT	11.1	pr	—	Meye71-0775
6.46	$\text{Cu}^{III}(\alpha\text{-alanine})_2$ (int et?)	$(8.0 \pm 2.4) \times 10^8 \text{ s}^{-1}$	<0.002	RT	6.3	pr	—	Meye71-0775
6.47	$\text{Cu}^{III}(\beta\text{-alanine})_2$ (int et?)	$(7.0 \pm 2.1) \times 10^8 \text{ s}^{-1}$	<0.002	RT	5.8	pr	—	Meye71-0775
6.48	$\text{Cu}^{III}(\alpha\text{-amino-n-butryic acid})_2$ (int et?)	$(5.0 \pm 1.5) \times 10^8 \text{ s}^{-1}$	<0.002	RT	6.1	pr	—	Meye71-0775
6.49	$\text{Cu}^{III}(\beta\text{-amino-n-butryic acid})_2$ (int et?)	$(4.5 \pm 1.3) \times 10^8 \text{ s}^{-1}$	<0.002	RT	6.0	pr	—	Meye71-0775
6.50	$\text{Cu}^{III}(\gamma\text{-amino-n-butryic acid})_2$ (int et?)	$(1.2 \pm 0.4) \times 10^8 \text{ s}^{-1}$	<0.002	RT	4.8	pr	—	Meye71-0775
6.51	$\text{Cu}^{III}(\alpha\text{-amino-iso-butyric acid})_2$ (int et?)	$(1.5 \pm 0.5) \times 10^8 \text{ s}^{-1}$	<0.002	RT	6.2	pr	—	Meye71-0775
		$(2.5 \pm 0.8) \times 10^8 \text{ s}^{-1}$	<0.002	RT	7.3	pr	—	Meye71-0775
6.52	$\text{Cu}^{III}(\text{en})_n$ (int et?)	$< 3 \text{ s}^{-1}$ 120 s^{-1}	0.002 0.002	RT RT	5.8 11.6	pr pr	— —	Meye71-0775 Meye71-0775
6.53	$\text{Cu}^{III}(\text{en})_n + \text{Cu}^{III}(\text{en})_n$ (af?)	$2k = 5.5 \times 10^8$	0.002	RT	5.8	pr	—	Meye71-0775
6.54	$\text{Cu}^{III}(\text{gly})_2$ (int et?)	$2k = 3.9 \times 10^7$	0.002	RT	11.6	pr	—	Meye71-0775
		$(6.0 \pm 2.0) \times 10^8 \text{ s}^{-1}$	<0.002	RT	6.1	pr	—	Meye71-0775
		$(2.2 \pm 0.7) \times 10^4 \text{ s}^{-1}$	<0.002	RT	7.5	pr	—	Meye71-0775

^aIf the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).^bThe form of Cu^{III} reacting reinterpreted from original references according to equilibria 6.37 and 6.39.

TABLE 7. Europium(II) reactions

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
<i>Eu²⁺</i> (Includes only those rate constants measured by pulse radiolysis).							
<i>Eu²⁺</i> + BrO_3^-	$< 10^4$	ca. 0.01	RT	nat	pr	—	Fara.72-0065
<i>Eu²⁺</i> + $\text{Co}(\text{NH}_3)_6\text{Cl}^{2+}$ (et-is)	90 ± 9 $(4.7 \pm 0.5) \times 10^3$	0.06 1.0 (NaClO_4)	25 25 6	6	pr pr	— —	Fara.73-0107 Fara.73-0107
<i>Eu²⁺</i> + $\text{Co}(\text{NH}_3)_6\text{CN}^{2+}$	$(5.3 \pm 0.5) \times 10^3$	1.0 (NaCl)	25	6	pr	—	Fara.73-0107
<i>Eu²⁺</i> + $\text{Co}(\text{NH}_3)_6\text{F}^{2+}$ (et-is)	$(2.8 \pm 0.3) \times 10^3$ $(1.5 \pm 0.2) \times 10^4$	0.06 1.0 (NaClO_4)	25 25 6	6	pr pr	— —	Fara.73-0107 Fara.73-0107
<i>Eu²⁺</i> + $\text{Co}(\text{NH}_3)_6\text{OH}^{2+}$ (et-is)	$(2.4 \pm 0.2) \times 10^4$	1.0 (NaCl) ca. 0.3	25 25 25	6	pr	—	Fara.73-0107 Fara.73-0107
<i>Eu²⁺</i> + $\text{Co}(\text{NH}_3)_6\text{N}_3^{2+}$	< 30	0.06	25	6	pr	—	Fara.73-0107
<i>Eu²⁺</i> + $\text{Co}(\text{NH}_3)_6\text{NCS}^{2+}$	< 10	0.06	25	6	pr	—	Fara.73-0107
<i>Eu²⁺</i> + Cu^{2+}	$< 10^4$	ca. 0.01	RT	nat	pr	—	Fara.72-0065
<i>Eu²⁺</i> + BaO_2	$< 10^4$	ca. 0.01	RT	nat	pr	—	Fara.72-0065
<i>Eu²⁺</i> + IO_3^-	$< 10^4$	ca. 0.01	RT	nat	pr	—	Fara.72-0065
<i>Eu²⁺</i> + MnO_4^- (et)	6.5×10^4	ca. 0.01	RT	nat	pr	—	Fara.72-0065
<i>Eu²⁺</i> + NO_3^- (et)	6.2×10^4	ca. 0.01	RT	nat	pr	—	Fara.72-0065
<i>Eu²⁺</i> + NO_2^-	$< 10^4$	ca. 0.01	RT	nat	pr	—	Fara.72-0065
<i>Eu²⁺</i> + N_2O	$< 10^4$	ca. 0.01	RT	nat	pr	—	Fara.72-0065
<i>Eu²⁺</i> + O_2	$< 10^4$	ca. 0.01	RT	nat	pr	—	Fara.72-0065
<i>Eu²⁺</i> + OH (et)	9×10^4	—	RT	nat	pr	Measured from the rate of decay of Eu^{2+} in the absence of OH scavengers. Major competing reaction is $\text{OH} + \text{OH}$.	Fara.72-0065
<i>Eu²⁺</i> + $\text{Ru}(\text{NH}_3)_6\text{Br}^{2+}$ (et-is)	$(1.3 \pm 0.2) \times 10^4$ 3.8×10^4 ca. 3×10^4	— — 0.06 25	RT RT nat 6	25	pr pr pr	— — —	Pika..73-1084 Gord65-0799 Fara.73-0107
<i>Eu²⁺</i> + $\text{Ru}(\text{NH}_3)_6\text{Cl}^{2+}$ (et-is)	$(1.5 \pm 0.2) \times 10^4$	0.06	25	6	pr	—	Fara.73-0107
<i>Eu²⁺</i> + $\text{Ru}(\text{NH}_3)_6\text{H}_2\text{O}^{2+}$	$< 2 \times 10^4$	0.3	25	2	pr	—	Fara.73-0107
<i>Eu²⁺</i> + $\text{Ru}(\text{NH}_3)_6^{2+}$ (et-is)	ca. 1×10^4 $(2.3 \pm 0.2) \times 10^4$	0.06 1.0 (NaClO_4)	25 25 6	6	pr pr	— —	Fara.73-0107 Fara.73-0107
<i>Eu²⁺</i> + $\text{Ru}(\text{NH}_3)_6\text{OH}^{2+}$ (et-is)	$(1.5 \pm 0.2) \times 10^4$	1.0 (NaCl)	25	6	pr	—	Fara.73-0107
	$(6.0 \pm 0.6) \times 10^4$ $(1.0 \pm 0.1) \times 10^4$	0.06 0.3	25 25	6	pr pr	— —	Fara.73-0107 Fara.73-0107

Data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for 24).

TABLE 8. Iron(II) and iron(III) radical complex reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	τ	$t/^\circ\text{C}$	pH	Method	Comments	Ref
8.1	$\text{FeH}^{2+} + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$	$(1.06 \pm 0.1) \times 10^4$	0.1– 1.0	19–24	0.1– 1.0	pr	H_2 product characterised by vpc; Fe^{2+} by its absorption spectrum.	Jaya... ^c
8.2	$\text{FeHO}_2^{2+} \rightarrow \text{Fe}^{2+} + \text{HO}_2^-$	$(1.8 \pm 0.1) \times 10^4$	1.0 ($\text{HClO}_4/\text{NaClO}_4$)	20,25	0.1– 0.3	pr	Fe^{2+} detected as product.	Jaya... ^c
8.3	$\text{FeHO}_2^{2+} + \text{Fe}^{2+} \rightleftharpoons \text{FeHO}_2\text{Fe}^{2+}$	$E_a = 8.8 \pm 0.8 \text{ kJ mol}^{-1}$ $K = 22 \pm 2 \text{ dm}^3 \text{ mol}^{-1}$ $K = 27 \pm 2 \text{ dm}^3 \text{ mol}^{-1}$ $K = 33 \pm 1 \text{ dm}^3 \text{ mol}^{-1}$ $K = 37.5 \text{ dm}^3 \text{ mol}^{-1}$	1.0 ($\text{HClO}_4/\text{NaClO}_4$) 1.0 ($\text{HClO}_4/\text{NaClO}_4$) 1.0 ($\text{HClO}_4/\text{NaClO}_4$)	20 25 30 40	0.1– 0.3 0.1– 0.3 0.1– 0.3	pr pr pr pr	Measured from the effect of $[\text{Fe}^{2+}]$ on the absorption of $\text{FeHO}_2\text{Fe}^{2+}$.	Jaya... ^c
8.4	$\text{FeHO}_2^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{FeHO}_2\text{SO}_4^-$	$K = 90 \pm 20 \text{ dm}^3 \text{ mol}^{-1}$	1.0 ($\text{HClO}_4/\text{NaClO}_4$)	22±1	0.1– 0.3	pr	Measured from the effect of $[\text{SO}_4^{2-}]$ on the absorption of $\text{FeHO}_2\text{Fe}^{2+}$.	Jaya... ^c
8.5	$\text{FeHO}_2\text{Fe}^{2+} \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{Fe}^{2+}$	$(1.8 \pm 0.1) \times 10^4$ $(2.5 \pm 0.1) \times 10^4$	1.0 ($\text{HClO}_4/\text{NaClO}_4$) 1.0 ($\text{HClO}_4/\text{NaClO}_4$)	20 25	0.1– 0.3 0.1– 0.3	pr pr	Fe^{2+} detected as product.	Jaya... ^c
8.6	$\text{FeHO}_2\text{Fe}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{FeHO}_2\text{FeSO}_4^{2+}$	$K = 100 \pm 20 \text{ dm}^3 \text{ mol}^{-1}$	1.0 ($\text{HClO}_4/\text{NaClO}_4$)	22±1	0.1– 0.3	pr	Measured from the effect of $[\text{SO}_4^{2-}]$ on the absorption of $\text{FeHO}_2\text{Fe}^{2+}$.	Jaya... ^c
8.7	$\text{FeHO}_2\text{SO}_4^- \rightarrow \text{FeSO}_4^{2+} + \text{HO}_2^-$	$\text{ca. } 10^4 \text{ s}^{-1}$	—	22±1	0.1– 0.3	pr	FeSO_4^{2+} characterised by its absorption spectrum.	Jaya... ^c
8.8	$\text{FeHO}_2\text{FeSO}_4^{2+} \rightarrow \text{FeSO}_4^{2+} + \text{HO}_2^-$	$\text{ca. } 10^4 \text{ s}^{-1}$	—	22±1	0.1– 0.3	pr	FeSO_4^{2+} characterised by its absorption spectrum.	Jaya... ^c

^aIf the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 9. Mercury(0) and mercury(I) reactions

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	T	t/°C	pH	Method	Comments	Ref.
$\text{Hg}^0 + \text{Hg}^{2+} \rightarrow \text{Hg}_{\text{ss}}^{2+}$	$(5.9 \pm 0.6) \times 10^8$	—	RT	3–4	pr	Measured from the pH dependence of the formation of $\text{Hg}_{\text{ss}}^{2+}$.	Fuji..73–1080
$\text{Hg}^0 + \text{HgOH}^+ \rightarrow \text{Hg}_{\text{ss}}^{2+} + \text{OH}^-$	$(5.0 \pm 0.5) \times 10^8$	—	RT	3–4	pr	Measured from the pH dependence of the formation of $\text{Hg}_{\text{ss}}^{2+}$.	Fuji..73–1080
$\text{Hg}^0 + \text{Hg(OH)}_2 \rightarrow \text{Hg}_{\text{ss}}^{2+} + 2\text{OH}^-$	$< 5 \times 10^7$	—	RT	3–4	pr	Measured from the pH dependence of the formation of $\text{Hg}_{\text{ss}}^{2+}$. See also comments for entry 6.	Fuji..73–1080
$\text{Hg}_{\text{ss}}^{2+}$ $\text{Hg}_{\text{ss}}^{2+} + \text{Hg}^+ (\text{et?})$	$2k = (1.4 \pm 0.2) \times 10^{10}$	< 0.017	RT	1.9	pr	Rate constant calculated taking $\epsilon_{\text{ss}} = 9000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Fara.72–0290
$\text{Hg}(\text{I})$ $\text{Hg}_{\text{ss}}^{2+}$ (and hydrolysed forms)	$\text{pK} = 5.1$	var	RT	4–7	pr	Measured from the effect of pH on the absorption spectrum of Hg^+ .	Fuji..75–1044
$\text{Hg}^+ + \text{Hg}^+ \rightarrow \text{Hg}^0 + \text{Hg}^{2+}$	$2k = (4.9 \pm 0.5) \times 10^9$	$\rightarrow 0$	RT	2.0	pr	Transient product formed, whose decay is dependent on $[\text{Hg}^+]$, and which gives $\text{Hg}_{\text{ss}}^{2+}$. These results taken to indicate that $\text{Hg}^+ + \text{Hg}^+$ results in dismutation. Rate constants calculated taking $\epsilon_{\text{ss}} = 1.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Fuji..73–1080
$\text{Hg}^+ + \text{Hg}^+ (\rightarrow \text{Hg}_{\text{ss}}^{2+})$	$2k = (8.0 \pm 1.0) \times 10^9$	< 0.017	RT	1.9	pr	Products not characterised, but reaction considered to involve dimerisation. Rate constant calculated taking $\epsilon_{\text{ss}} = 7800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Fara.72–0290
$\text{HgOH} + \text{HgOH} \rightarrow \text{Hg}_2\text{O} + \text{H}_2\text{O}$ or $\text{Hg}_2(\text{OH})_2$	$2k = (4.4 \pm 0.4) \times 10^9$	< 0.1	RT	—	pr	Products identified from pH dependence of their absorption spectra. Rate constant calculated taking $\epsilon_{\text{ss}} = 5300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Fuji..75–1044
$\text{Hg}^{\text{I}} + \text{Hg}^{\text{I}}$	$2k = (4.9 \pm 1.0) \times 10^9$	—	RT	1.2	pr	—	Pika..75–1218
	$2k = (5.1 \pm 1.0) \times 10^9$	—	RT	3.15	pr	—	Pika..75–1218
	$2k = (3.5 \pm 0.7) \times 10^9$	—	RT	4.8	pr	—	Pika..75–1218
	$2k = \text{ca. } 1.1 \times 10^{10}$	—	RT	10.2	pr	—	Pika..75–1218

TABLE 9. Mercury(0) and mercury(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	T	t/°C	pH	Method	Comments	Ref.
9.8	$\text{Hg}^{\text{I}} + \text{Hg}^{\text{I}}$	$2k = ca. 1.5 \times 10^{10}$	—	RT	11.0	pr	—	Pika..75-
		$2k = (7.0 \pm 1.4) \times 10^9$	1(KOH)	RT	14	pr	—	Pika..75-
9.9	$\text{Hg}^{\text{I}} + \text{O}_2$ (ct or af)	$(4.0 \pm 0.6) \times 10^8$ $(1.2 \pm 0.2) \times 10^9$ $(1.6 \pm 0.2) \times 10^9$	—	RT	2.7	pr	—	Pika..75-
			1(KOH)	RT	11.2	pr	—	Pika..75-
			1(KOH)	RT	14	pr	—	Pika..75-
	Note: A change in mechanism of the decay of Hg^{I} aquo ions is observed on increasing the pH. There appears to be no good understanding of why this should be, and we suggest, therefore, that the reaction mechanisms written above should be viewed with caution. Note also that the spectral data for Hg^{I} obtained by Faraggi and Amozig (ref. 72-0290) and by Fujita <i>et al.</i> (ref. 73-1080) do not correspond.							
	<i>Hg(I) Complexes</i>							
<i>HgBr and related species</i>								
9.10	$\text{HgBr} + \text{HgBr} \rightarrow \text{Hg}_2\text{Br}_2$	$2k = 8 \times 10^8$	—	RT	—	pr	Product characterised by its absorption spectrum.	Jung..76
		$2k = (1.0 \pm 0.1) \times 10^{10}$	—	RT	—	pr	—	Fuji..76-
9.11	$\text{HgBr} + \text{O}_2 \rightarrow \text{HgBrO}_2$	$> 10^9$	—	RT	—	pr	Product characterised by conductivity experiments and non-formation of $\text{O}_2^-/\text{HO}_2^-$ absorption.	Jung..76
9.12	$\text{HgBr} + 1,4\text{-benzoquinone} \rightarrow \text{HgBr}^+ + (1,4\text{-benzoquinone})^-$	$> 10^9$	—	RT	5-5.5	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76
9.13	$\text{HgBr} + \text{tetranitromethane} \rightarrow \text{HgBr}^+ + \text{C}(\text{NO}_2)_3^- + \text{NO}_2$	2.2×10^8	—	RT	—	pr	Nitroform anion product characterised by its absorption spectrum.	Jung..76
9.14	$\text{HgBrO}_2 + 1,4\text{-benzoquinone} \rightarrow \text{HgBr}^+ + \text{O}_2^- + (1,4\text{-benzoquinone})^-$	7×10^8	—	RT	—	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76
9.15	HgCl $\text{HgCl} + \text{HgCl} \rightarrow \text{Hg}_2\text{Cl}_2$	$2k = (8.0 \pm 0.5) \times 10^8$	—	RT	—	pr	Product characterised by its absorption spectrum, and gravimetrically giving $G(\text{Hg}_2\text{Cl}_2) = 3.0$ in solutions containing 2-propanol.	Nazh.7
9.16	$\text{HgCl} + \text{O}_2 \rightarrow \text{HgClO}_2$	$(1.0 \pm 0.3) \times 10^8$	—	RT	—	pr	Product characterised by conductivity experiments and non-formation of $\text{O}_2^-/\text{HO}_2^-$ absorption.	Nazh.7
9.17	$\text{HgCl} + \text{OH}^- \rightarrow \text{HgCl} + \text{OH}^-$	$ca. 10^{10}$	—	RT	—	pr	Products characterised by conductivity experiments.	Nazh.7
9.18	$\text{HgCl} + 1,4\text{-benzoquinone} \rightarrow \text{HgCl}^+ + (1,4\text{-benzosemiquinone})^-$	3.0×10^8 $(3.9 \pm 0.4) \times 10^8$	—	25±2	5.1	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76 Sell.76-
9.19	$\text{HgCl} + \text{tetranitromethane} \rightarrow \text{HgCl}^+ + \text{C}(\text{NO}_2)_3^- + \text{NO}_2$	$(4.5 \pm 0.3) \times 10^8$	—	RT	5-5.5	pr	Nitroform anion product characterised by its absorption spectrum.	Nazh.7

TABLE 9. Mercury(0) and mercury(I) reactions — Continued

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	f	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
$\text{HgClO}_4 + 1,4\text{-benzoquinone} \rightarrow \text{HgCl}^+ + \text{O}_2 + (1,4\text{-benzoquinone})^-$	7×10^9	—	RT	—	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76-1042
HgCN							
$\text{HgCN} + \text{HgCN} \rightarrow \text{Hg}_2(\text{CN})_2$	$2k = (3.4 \pm 0.5) \times 10^9$	< 0.2	RT	—	pr	Product characterised by its absorption spectrum and decay to give Hg^0 and $\text{Hg}(\text{CN})_2$. Rate constant calculated taking $\epsilon_{250} = 3800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Fuji..75-1203
$\text{HgCN} + \text{O}_2 \rightarrow \text{HgCN}^+ + \text{O}_2^-$	$2k = 1.2 \times 10^{10}$	4×10^9	—	RT RT	pr pr	O_2^- product characterised by its absorption spectrum, lifetime in neutral solution, and conductivity measurements.	Jung..76-1042 Jung..76-1042
$\text{HgCN} + \text{OH (et)}$	3.1×10^9	—	RT	—	pr	Estimated from initial decay of HgCN in the absence of OH scavengers.	Fuji..75-1203
$\text{HgCN} + \text{CH}_3\text{OH}$	4.0×10^9	—	RT	—	pr	Estimated from initial decay of HgCN in the presence of methanol.	Fuji..75-1203
$\text{HgCN} + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{Hg}^0 + \text{CN}^- + \text{CH}_3\text{COCH}_3 + \text{H}^+$	2.4×10^9	—	RT	—	pr	Estimated from initial decay of HgCN in the presence of ethanol.	Fuji..75-1203
$\text{HgCN} + \text{CH}_3\text{C}(\text{CH}_3)_2\text{OH (af?)}$	1.6×10^9	—	RT	—	pr	Estimated from initial decay of HgCN in the presence of 2-methyl-2-propanol. $G(\text{acetone}) = 3.0$ measured.	Fuji..75-1203
$\text{HgCN} + 1,4\text{-benzoquinone} \rightarrow \text{HgCN}^+ + (1,4\text{-benzoquinone})^-$	3.5×10^9	—	RT	—	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76-1042
$\text{HgCN} + \text{tetranitromethane} \rightarrow \text{HgCN}^+ + \text{C}(\text{NO}_2)_2^- + \text{NO}_2$	3.1×10^9	—	RT	—	pr	Nitroform anion product characterised by its absorption spectrum.	Jung..76-1042
HgI							
$\text{HgI} + \text{HgI} \rightarrow \text{Hg}_2\text{I}_2$	$2k = 5.0 \times 10^9$	—	RT	—	pr	Product characterised by its absorption spectrum.	Jung..76-1042

TABLE 9. Mercury(0) and mercury(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ *	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
9.31	$\text{HgI} + \text{O}_2 \rightarrow \text{HgIO}_2$	$> 10^6$	—	RT	—	pr	Product characterised by conductivity experiments and non-formation of O_2^-/HO_2 absorption.	Jung..76
9.32	$\text{HgI} + 1,4\text{-benzoquinone} \rightarrow \text{HgI}^+ + (1,4\text{-benzoquinone})^-$	$> 10^6$	—	RT	—	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76
9.33	$\text{HgI} + \text{tetranitromethane} \rightarrow \text{HgI}^+ + \text{C}(\text{NO}_2)_3^- + \text{NO}_2$	1.4×10^6	—	RT	—	pr	Nitroform anion product characterised by its absorption spectrum.	Jung..76
9.34	HgSCN $\text{HgSCN} + \text{HgSCN} \rightarrow \text{Hg}_2(\text{SCN})_2$	$2k = 6.0 \times 10^6$	—	RT	—	pr	Product characterised by its absorption spectrum.	Jung..76
9.35	$\text{HgSCN} + \text{O}_2 \rightarrow \text{HgSCNO}_2$	$> 10^6$	—	RT	—	pr	Product characterised by conductivity experiments and non-formation of O_2^-/HO_2 absorption.	Jung..76
9.36	$\text{HgSCN} + 1,4\text{-benzoquinone} \rightarrow \text{HgSCN}^+ + (1,4\text{-benzoquinone})^-$	$> 10^6$	—	RT	—	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76
9.37	$\text{HgSCN} + \text{tetranitromethane} \rightarrow \text{HgSCN}^+ + \text{C}(\text{NO}_2)_3^- + \text{NO}_2$	2.8×10^6	—	RT	—	pr	Nitroform anion product characterised by its absorption spectrum.	Jung..76
9.38	$\text{HgSCNO}_2 + 1,4\text{-benzoquinone} \rightarrow \text{HgSCN}^+ + \text{O}_2 + (1,4\text{-benzoquinone})^-$	1.0×10^6	—	RT	—	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76

*If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 10. Indium(II) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^a	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
10.1	$\text{In}^{2+}_{\text{aq}} + \text{In}^{2+}$ (et or af)	$2k = ca. 1.2 \times 10^9$ $2k = (1.6 \pm 0.2) \times 10^9$	0.7 (LiClO_4) 0.0075	RT 25	3 3.6	pr pr	Reinterpreted from data in ref. 76-1087. Measured in the presence of 1 mol/dm ³ 2-methyl-2-propanol taking $\epsilon_{250} = 7000$ dm ³ mol ⁻¹ cm ⁻¹ .	Tayl69-0971 R.M. Sellers, unpub. data
10.2	$\text{In}^{2+} + \text{OH}$ (et)	$2k = (4.9 \pm 0.7) \times 10^9$	-	25	3.6	pr	Measured from the initial decay of In^{2+} in the absence of OH scavengers.	R.M. Sellers, unpub. data
10.3	$\text{In}^{2+} + \text{N}_2\text{O}$	$< 10^6$	-	25	nat	γ	Estimated from the values of $G(\text{N}_2)$ measured in the γ -radiolysis of $\text{In}^{2+} + \text{N}_2\text{O}$ solutions.	Sell72-0844

^aIf the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 11. Iridium(II) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^a	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
11.1	$\text{Ir}^{II} (\text{from } e_{\text{aq}}^- + \text{IrCl}_6^{3-}) + \text{Ir}^{II}$ (dis)	$2k = (3.3 \pm 0.4) \times 10^6$	0.0018	RT	-	pr	-	Bros73-1066

^aIf the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 12. Manganese(I) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^a	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
12.1	$\text{Mn}^{+}_{\text{aq}} + \text{Cu}^{2+}$ (et?)	$k_{\text{rel}} = 1.6 \pm 0.2$	2.0 (MnSO_4)	RT	5-8	γ	Measured by competition kinetics using NO_3^- as competitor in the presence of 0.5 mol dm ⁻³ MnSO_4 . Rate constant relative to $k(\text{Mn}^+ + \text{NO}_3^-)$.	Fiti70-0117
12.2	$\text{Mn}^+ + \text{IO}_3^-$ (et?)	$k_{\text{rel}} = 1.4 \pm 0.1$	2.0 (MnSO_4)	RT	5-8	γ	Measured by competition kinetics using NO_3^- as competitor in the presence of 0.5 mol dm ⁻³ MnSO_4 . Rate constant relative to $k(\text{Mn}^+ + \text{NO}_3^-)$.	Fiti70-0117
12.3	$\text{Mn}^+ + \text{NO}_3^-$ (et?)	see entries 12.1 and 12.2.						

^aIf the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 13. Molybdenum reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
$[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]^-$ (from $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4 + e^-$ in methanol)								
13.1	$[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]^- + [\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]^-$ (dis?)	$'k' = (4.5 \pm 1.0) \times 10^8$ $'k' = (2.5 \pm 1.0) \times 10^8$	-	RT	-	pr	Measured from decay of Mo(1 1/2) species in methanol. Two decay processes observed, one of which believed to be a dismutation reaction. Rate constant (unclear whether k or $2k$) calculated taking $\epsilon_{780} = 2600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Note that if the slower process does not involve the Mo(1 1/2) species, the value of ϵ , and hence k , is incorrect.	Baxe...76-1003
13.2	$[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]^- + \text{O}_2$ (af?)	$(5.9 \pm 0.3) \times 10^9$	-	RT	-	pr	Measured in Methanol. Starting material $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]$ not regenerated, so reaction does not involve electron transfer.	Baxe...76-1003

*If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 14. Nickel(I) and nickel(III) reactions

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
$\text{Ni}^{+} + \text{BrO}_3^-$	$< 8.4 \times 10^6$	0.08	RT	nat	pr	-	Meye..68-0855
$\text{Ni}^{+} + \text{Cd}^{2+}$	$< 10^7$	-	RT	nat	pr	-	Baxe..66-0848
$\text{Ni}^{+} + \text{Co(en)}_3^{2+}$	$< 5 \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Cl}^-$	$(5.9 \pm 0.9) \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co(en)}_2\text{Cl}_2^{+}$ (et)	$(8.3 \pm 2.1) \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{trans}-\text{Co(en)}_2\text{Cl}_2^{+}$ (et)	$(8.3 \pm 2.1) \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co(en)}_2\text{CO}_3^{2+}$	$< 5 \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{cis}-\text{Co(en)}_2\text{F}_3^{+}$	$< 5 \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co(en)}_2\text{FH}_3\text{O}^{2+}$	$< 5 \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{cis}-\text{Co(en)}_2\text{NH}_3\text{Cl}^{+}$ (et)	$(4.7 \pm 0.7) \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{cis}-\text{Co(en)}_2\text{N}(\text{H}_3)\text{NO}_3^{2+}$ (et)	$(3.3 \pm 0.8) \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co}(\text{NH}_3)_2\text{Br}^{2+}$ (et)	$< 5 \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co}(\text{NH}_3)_2\text{Cl}^{2+}$ (et)	$(1.05 \pm 0.2) \times 10^6$	0.08	RT	4.0	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co}(\text{NH}_3)_2\text{CN}^{2+}$ (et)	$(6.5 \pm 1.0) \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co}(\text{NH}_3)_2\text{F}^{2+}$ (et)	$(3.3 \pm 0.8) \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co}(\text{NH}_3)_2\text{O}^{2+}$	$< 5 \times 10^6$	0.08	RT	5-6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co}(\text{NH}_3)_2\text{OH}^{2+}$ (et)	$(1.3 \pm 0.3) \times 10^6$	0.08	RT	7.6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co}(\text{NH}_3)_2\text{Na}^{2+}$ (et)	$(5.8 \pm 1.5) \times 10^6$	0.08	RT	7.6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co}(\text{NH}_3)_2\text{N}(\text{H}_3)^+$	$(4.1 \pm 1.0) \times 10^6$	0.08	RT	7.6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co}(\text{NH}_3)_2\text{NCS}^{2+}$ (et)	$< 5 \times 10^6$	0.08	RT	5.6	pr	-	Meye..69-0428
$\text{Ni}^{+} + \text{Co}(\text{NH}_3)_2\text{OOCCH}_2^{2+}$	$< 5 \times 10^6$	0.08	RT	5.6	pr	-	Baxe..66-0848
$\text{Ni}^{+} + \text{Cr}^{2+}$	$< 10^7$	-	RT	nat	pr	-	Meye..68-0855
$\text{Ni}^{+} + \text{H}_2\text{O}_2 \rightarrow$	$< 2.4 \times 10^7$	0.08	RT	nat	pr	-	Buxt..76-1072
$\text{Ni}^{+} + \text{H}_2\text{O}_2 \rightarrow$	$(3.2 \pm 0.3) \times 10^7$	-	25	nat	pr	-	Meye..68-0855
$\text{Ni}^{2+} + \text{OH}^- + \text{OH}^-$	$(4.3 \pm 0.6) \times 10^7$	-	RT	nat	pr	-	Buxt..67-0062
		2.1×10^8	-				
Products identified in γ -radiolysis studies (see ref. 73-0039).							
$\text{Ni}^{+} + \text{H}_2\text{O}_4^+$	$< 10^6$	0.08	RT	nat	pr	-	Meye..68-0855
$\text{Ni}^{+} + \text{IO}_3^-$ (et)	$(2.2 \pm 0.3) \times 10^6$	0.08	RT	nat	pr	-	Meye..68-0855
$\text{Ni}^{+} + \text{MnO}_4^-$ (et)	7.5×10^6	0.005	RT	nat	pr	Measured by the rate of depletion of the MnO_4^- absorption.	Baxe..65-0385
$\text{Ni}^{+} + \text{Ni}^{+}$	slow ($< 10^6$)	var	RT	nat	pr	Estimated from decay of Ni^{+} in presence and absence of OH scavengers.	Kelm..74-1037
$\text{Ni}^{+} + \text{NO}_3^-$ (et)	$(1.5 \pm 0.2) \times 10^6$	0.08	RT	nat	pr	-	Meye..68-0855
$\text{Ni}^{+} + \text{NO}_3^-$	$< 1.4 \times 10^6$	0.08	RT	nat	pr	-	Meye..68-0855
$\text{Ni}^{+} + \text{N}_2\text{O} \rightarrow$	6.3×10^6	-	RT	nat	pr	Measured in the presence of 1 mol dm ⁻³ NiSO_4 .	Meye..68-0855
$\text{NiO}^{+} + \text{N}_2$	$(9.1 \pm 0.9) \times 10^6$	-	25 + 2	nat	pr	Measured in the presence of 0.5 mol dm ⁻³ NiSO_4 .	Buxt..76-1072
	5.1×10^7	-	RT	nat	pr	-	Buxt..67-0062
	5.1×10^7	-	1-30	nat	pr	-	Buxt..67-0062
$E_a = 40.6 \pm 3.8 \text{ kJ mol}^{-1}$							
Products inferred from γ -ray induced chain reaction in the system $\text{Ni}^{2+} + \text{HCO}_3^- + \text{N}_2\text{O}, G(\text{Na})$ also measured in $\text{Ni}^{2+} + \text{N}_2\text{O}$ solutions. (see ref. 73-0039).							

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
14.31	$\text{Ni}^+ + \text{OH} \rightarrow \text{Ni}^{2+} + \text{OH}^-$	2×10^{10}	—	RT	nat	pr	Measured from a computer fit of the decay of Ni^+ in the absence of OH scavengers assuming competing reactions to $\text{OH}^- + \text{OH}^+$ and $\text{Ni}^+ + \text{H}_2\text{O}_2$. Product identified by conductivity measurements (but see ref. 75–1027).	Kelm...74-
14.32	$\text{Ni}^+ + \text{O}_2 \rightarrow \text{NiO}_2^+$	$(1.4 \pm 0.2) \times 10^8$ 2.2×10^8	—	RT RT	nat nat	pr pr	Product characterised by its absorption spectrum (ref. 76–1072), reactivity with tetranitromethane and lack of reactivity with 1,4-benzoquinone (ref. 76–1134).	Meye..68- Baxe..66-
14.33	$\text{Ni}^+ + \text{Ph}^{2+}$	$\leq 10^7$	—	RT	nat	pr	—	Baxe..66-
14.34	$\text{Ni}^+ + \text{Ru}(\text{NH}_3)_6^{3+}$ (et)	$(4.0 \pm 0.6) \times 10^8$	0.08	RT	nat	pr	—	Navo..70-
14.35	$\text{Ni}^+ + \text{S}_2\text{O}_4^{2-} \rightarrow \text{Ni}^{2+} + \text{SO}_4^{2-} + \text{SO}_4^{2-}$	$(1.5 \pm 0.2) \times 10^8$	0.049	25 ± 2	nat	pr	SO_4^{2-} product characterised by its absorption spectrum and decay kinetics.	Tait..76-
14.36	$\text{Ni}^+ + \text{Zn}^{2+}$	$\leq 10^7$	—	RT	nat	pr	—	Baxe..66-
14.37	$\text{Ni}^+ + \text{CH}_3\text{OH} \rightarrow \text{NiCH}_3\text{OH}^+$	4.2×10^8	—	RT	nat	pr	Product characterised by its absorption spectrum and conductivity measurements.	Kelm...74-
14.38	$\text{Ni}^+ + \text{CO}_2^- \rightarrow \text{NiCO}_2$	6.6×10^8	4×10^{-4}	RT	nat	pr	Product characterised by its absorption spectrum and conductivity measurements.	Kelm...74-
14.39	$\text{Ni}^+ + \cdot\text{C}_2\text{H}_4\text{OH} \rightarrow \text{NiC}_2\text{H}_4\text{OH}^+$	2.8×10^8	4×10^{-4}	RT	nat	pr	Product characterised by its absorption spectrum and conductivity measurements.	Kelm...74-
14.40	$\text{Ni}^+ + \text{CH}_3\text{COHCH}_3 \rightarrow \text{NiCOH(CH}_3)_2$	1.4×10^8	4×10^{-4}	RT	nat	pr	Product characterised by its absorption spectrum and conductivity measurements.	Kelm...74-
14.41	$\text{Ni}^+ + \text{H}_2\text{C}(\text{CH}_3)_2\text{OH} \rightarrow \text{Ni}^{2+} + \text{OH}^- + \text{CH}_2=\text{C}(\text{CH}_3)_2$	2×10^8	4×10^{-4}	RT	nat	pr	Isobutene detected as product; OH^- detected by conductivity measurements.	Kelm...74-
14.42	$\text{Ni}^+ + \cdot\text{C}_5\text{H}_9 \rightarrow \text{NiC}_5\text{H}_9^+$ ($\cdot\text{C}_5\text{H}_9$ = cyclopentyl radical)	2.8×10^8	4×10^{-4}	RT	nat	pr	Product characterised by its absorption spectrum and conductivity measurements.	Kelm...74-

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	T	t/°C	pH	Method	Comments	Ref.
3 $\text{Ni}^+ + \text{allyl alcohol} \rightarrow \text{Ni-allyl alcohol}^+$	ca. 10^8	—	25 ± 2	nat	pr	—	Buxt..76-1072
4 $\text{Ni}^+ + 1,4\text{-benzo-quinone} \rightarrow \text{Ni}^{2+} + (1,4\text{-benzoquinone})^-$	(2.3 ± 0.5) × 10 ⁸	—	25	6.0	pr	Measured by the rate of formation of the semiquinone in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Sell..76-1134
5 $\text{Ni}^+ + \text{menaquinone} \rightarrow \text{Ni}^{2+} + (\text{menaquinone})^-$	2.4 × 10 ⁸ (2.5 ± 0.3) × 10 ⁸	— ca. 25 RT	7.0 7.0	pr pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol.	Rao..75-1032 Rao..73-1047	
6 $\text{Ni}^+ + \text{tetranitro-methane} \rightarrow \text{Ni}^{2+} + \text{C}(\text{NO}_2)_3^- + \text{NO}_2$	(1.4 ± 0.2) × 10 ⁸	—	25 ± 2	5.9	pr	Measured by the rate of formation of the nitroform anion in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Sell..76-1134
<i>Ni(I) Complexes</i>							
Ni ^I -cyano complexes							
$\text{Ni}(\text{CN})_{\text{s}}^{2-} + \text{Ni}(\text{CN})_{\text{s}}^{2-} \rightarrow \text{Ni}_2(\text{CN})_{\text{s}}^{2-}$	2k = (1.5 ± 0.2) × 10 ⁸	0.1 (HCO ₂ Na)	20 ± 2	—	pr	Product characterised by its absorption spectrum.	Mula....74-1072
$\text{Ni}(\text{CN})_{\text{s}}^{2-} \rightarrow \text{Ni}(\text{CN})_{\text{s}}^{2-} + \text{CN}^-$	(8.1 ± 1.0) × 10 ⁸ s ⁻¹	0.1 (HCO ₂ Na)	20 ± 2	—	pr	Ni(CN) _s ²⁻ characterised by its absorption spectrum.	Mula....74-1072
<i>NiL⁺</i> (<i>L</i> = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).							
$\text{NiL}^+ + \text{Co(bpy)}_3^{2+}$	(1.3 ± 0.1) × 10 ⁸	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1039
$\text{NiL}^+ + \text{CoL}'(\text{OH})_2^{2+}$ (et)	(1.1 ± 0.1) × 10 ⁸	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1039
(L' = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene).							
$\text{NiL}^+ + \text{Co(en)}_3^{2+}$ (et)	(1.1 ± 0.1) × 10 ⁸	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1039
$\text{NiL}^+ + \text{Co}(\text{NH}_3)_6^{2+}$ (et)	(1.9 ± 0.2) × 10 ⁸	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1039
$\text{NiL}^+ + \text{CoL}'(\text{OH})_2^{2+}$ (et)	(1.7 ± 0.2) × 10 ⁸	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-1039
(L' = 2,2,0,10-tetramethyl-1,4,9,11-tetraazacyclotetradeca-1,2,9,10-tetracne).							

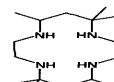


TABLE 14. Nickel(I) and nickel(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	f	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
14.54	$\text{NiL}^+ + \text{Cr(bpy)}_3^{3+}$ (et)	$(7.7 \pm 0.8) \times 10^8$	0.016— 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-
14.55	$\text{NiL}^+ + \text{Fe(bpy)}_3^{3+}$ (et)	$(6.4 \pm 0.6) \times 10^7$	0.016— 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-
14.56	$\text{NiL}^+ + \text{H}_2\text{O}_2$ (pt)	$(1.1 \pm 0.1) \times 10^8$	0.06— 0.3	RT	<1.25	pr	Reaction may involve proton transfer to the metal centre to give a hydrido complex.	Tait..76-
14.57	$\text{NiL}^+ + \text{H}_2\text{PO}_4^-$ (pt)	$< 10^4$	0.01— 0.1	RT	5.50	pr	—	Tait..76-
14.58	$\text{NiL}^+ + \text{NaO}$ (et or O at)	$(3.9 \pm 0.4) \times 10^7$	—	RT	7.0	pr	Reaction possibly involves two electron oxidation to Ni(III) complex.	Tait..76-
14.59	$\text{NiL}^+ + \text{O}_2 \rightleftharpoons \text{NiL}^{3+} + \text{O}_2^-$	$(1.6 \pm 0.2) \times 10^8$	—	RT	7.0	pr	Product transfers an electron to 1,4-benzoquinone but not menaquinone, and identified therefore as O_2^- , although O_2 adduct, NiLO_2^{3+} could conceivably react in same way.	Tait..76-
14.60	$\text{NiL}^+ + \text{Ru}(\text{NH}_3)_6^{3+}$ (et)	$(3.8 \pm 0.4) \times 10^8$	0.016— 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-
14.61	$\text{NiL}^+ + \text{Ru}(\text{NH}_3)_6\text{NO}_3^{3+}$ (et)	$(7.4 \pm 0.7) \times 10^7$	0.016— 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-
14.62	$\text{NiL}^+ + \text{acetic acid}$ (pt)	$(1.2 \pm 0.1) \times 10^4$	0.015— 0.06	RT	4.85	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-
14.63	$\text{NiL}^+ + 9,10\text{-anthra-quinone-2,6-disulphonate}$ (et)	$(4.8 \pm 0.5) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-
14.64	$\text{NiL}^+ + 1,4\text{-benzo-quinone}$ (et)	$(4.8 \pm 0.5) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-
14.65	$\text{NiL}^+ + 3\text{-benzoyl-pyridine}$ (et)	$(2.5 \pm 0.3) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-
14.66	$\text{NiL}^+ + \text{fluorescein}$ (et)	$(3.2 \pm 0.3) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-
14.67	$\text{NiL}^+ + \text{methyl iodide}$ (et or S _N 2)	$(4.6 \pm 0.5) \times 10^8$	0.01	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76-

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	f	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
NiL^+ ($L = 5,7,7,12,14,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene).							
$\text{NiL}^+ + \text{Co(bpy)}_3^{2+}$ (et)	$(1.3 \pm 0.1) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
$\text{NiL}^+ + \text{CoL}'(\text{OH}_2)(\text{OH})^{2+}$ (et)	$(2.6 \pm 0.3) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
$(L' = 5,7,7,12,14,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene).							
$\text{NiL}^+ + \text{Co(en)}_3^{2+}$ (et)	$(1.1 \pm 0.1) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
$\text{NiL}^+ + \text{Co(NH}_3)_6^{2+}$ (et)	$(1.9 \pm 0.2) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
$\text{NiL}^+ + \text{CoL}'(\text{OH})_2^{2+}$ (et)	$(3.6 \pm 0.4) \times 10^7$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
$(L' = 2,3,9,10$ -tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene).							
$\text{NiL}^+ + \text{Cr(bpy)}_3^{2+}$	$(1.1 \pm 0.1) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
$\text{NiL}^+ + \text{Fe(bpy)}_3^{2+}$ (et)	$(2.2 \pm 0.2) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
$\text{NiL}^+ + \text{H}_2\text{O}_2$ (pt)	$(1.3 \pm 0.1) \times 10^6$	0.06–0.3	RT	<1.25	pr	Reaction may involve proton transfer to the metal centre to give a hydrido complex.	Tait..76–1039
$\text{NiL}^+ + \text{H}_2\text{PO}_4^-$ (pt)	$(2.4 \pm 0.2) \times 10^6$	0.01–0.1	RT	5.50	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–1039
$\text{NiL}^+ + \text{NaO}$ (et or O at)	$(1.8 \pm 0.2) \times 10^7$	—	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Reaction possibly involves two electron oxidation to Ni^{III} complex. Product transfers an electron to 1,4-benzoquinone but not menaquinone, and is identified therefore as O_2^- , although O_2 adduct NiLO_2^{2+} , could conceivably react in same way.	Tait..76–1039
$\text{NiL}^+ + \text{O}_2 \rightarrow \text{NiL}^{2+} + \text{O}_2^-$	$(1.7 \pm 0.2) \times 10^6$	—	RT	7.0	pr		Tait..76–1039

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
14.79	$\text{NiL}^+ + \text{Ru(NH}_3)_6\text{NO}_3^+$ (et)	$(4.5 \pm 0.5) \times 10^8$	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–
14.80	$\text{NiL}^+ + \text{Ru(NH}_3)_6\text{NO}_3^+$ (et)	$(3.5 \pm 0.4) \times 10^7$	0.016– 0.028	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–
14.81	$\text{NiL}^+ + \text{acetic acid}$ (pt)	$(1.9 \pm 0.2) \times 10^8$	0.015– 0.06	RT	4.85	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–
14.82	$\text{NiL}^+ + 9,10\text{-anthra-quinone-2,6-disulphonate}$ (et)	$(5.0 \pm 0.5) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–
14.83	$\text{NiL}^+ + 1,4\text{-benzoquinone}$ (et)	$(3.8 \pm 0.4) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–
14.84	$\text{NiL}^+ + 3\text{-benzoylpyridine}$ (et)	$(7.5 \pm 0.8) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–
14.85	$\text{NiL}^+ + \text{eosin Y}$ (et)	$(2.7 \pm 0.3) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–
14.86	$\text{NiL}^+ + \text{fluorescein}$ (et)	$(3.3 \pm 0.3) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–
14.87	$\text{NiL}^+ + \text{methyl iodide}$ (et or $\text{S}_{\text{N}}2$)	$(1.3 \pm 0.1) \times 10^8$	0.01	RT	9.2	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol.	Tait..76–
14.88	<i>Ni(I) radical complexes</i> $\text{NiCH}_3\text{OH}^+ + \text{H}_2\text{O} \rightarrow$ $\text{Ni}^{3+} + \text{CH}_3\text{OH} + \text{OH}^-$	7 s ⁻¹	—	RT	nat	pr	Products characterised by conductivity experiments.	Kelm...74
14.89	$\text{NiCH}_3\text{OH}^+ + \text{H}_2\text{O}_2$ (et?)	7.3×10^8	—	RT	nat	pr	—	Kelm...74
14.90	$\text{NiCO}_3^+ + \text{H}_2\text{O}$	$< 1 \text{ s}^{-1}$	—	RT	nat	pr	—	Kelm...74
14.91	$\text{NiC}_6\text{H}_5\text{OH}^+ + \text{H}_2\text{O} \rightarrow$ $\text{Ni}^{3+} + \text{C}_6\text{H}_5\text{OH} + \text{OH}^-$	5 s ⁻¹	—	RT	nat	pr	Products characterised by conductivity experiments.	Kelm...74
14.92	$\text{NiC}_6\text{H}_5\text{OH}^+ + \text{H}_2\text{O}_2$ (et?)	2.3×10^4	—	RT	nat	pr	—	Kelm...74
14.93	$\text{NiCOH}(\text{CH}_3)_2^+ + \text{H}_2\text{O}$	$< 1 \text{ s}^{-1}$	—	RT	nat	pr	—	Kelm...74
14.94	$\text{NiCOH}(\text{CH}_3)_2^+ + \text{H}_2\text{O}_2$	1.1×10^4	—	RT	nat	pr	—	Kelm...74
14.95	$\text{NiC}_6\text{H}_5\text{OC}_6\text{H}_5^+ + \text{H}_2\text{O}$	$< 1 \text{ s}^{-1}$	—	RT	nat	pr	—	Kelm...74
14.96	$\text{NiC}_6\text{H}_5\text{OC}_6\text{H}_5^+ + \text{H}_2\text{O}_2$	1.3×10^8	—	RT	nat	pr	—	Kelm...74
14.97	$\text{NiC}_6\text{H}_5^+ + \text{H}_2\text{O} \rightarrow$ $\text{Ni}^{3+} + \text{C}_6\text{H}_5^- + \text{OH}^-$	49 s ⁻¹	—	RT	nat	pr	Products characterised by conductivity experiments.	Kelm...74
14.98	$\text{NiC}_6\text{H}_5^+ + \text{H}_2\text{O}_2$ (C_6H_5^- = cyclopentyl radical)	$< 5 \times 10^8$	—	RT	nat	pr	—	Kelm...74
14.99	$\text{NiO}_2^+ \rightarrow \text{Ni}^{3+} + \text{O}_2^-$	$780 \pm 80 \text{ s}^{-1}$	—	25 ± 2	5.7	pr	Measured from the rate of formation of the nitroform anion in solutions containing tetra-nitromethane and 1 mol dm ⁻³ 2-methyl-2-propanol.	Sell.76

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	f	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
0 $\text{NiO}_2^{+} + \text{H}^{+} \rightleftharpoons \text{NiO}_2\text{H}^{2+}$	$K = 2000 \pm 1200 \text{ M}^{-1}$ (i.e. $\text{p}K_a = 3.2 \pm 0.3$)	0.04	25 ± 2	3.0— 5.7	pr	Measured from the pH dependence of the rate of formation of the nitroform anion in solutions containing tetranitromethane and 1 mol dm^{-3} 2-methyl-2-propanol.	Sell.76-1134
1 $\text{NiO}_2\text{H}^{2+} \rightarrow \text{Ni}^{2+} + \text{HO}_2$	$> 2800 \text{ s}^{-1}$	—	25 ± 2	3.0	pr	Estimated from the rate of formation of the nitroform anion in solutions containing tetranitromethane and 1 mol dm^{-3} 2-methyl-2-propanol.	Sell.76-1134
2 $\text{Ni}^{III}(\text{NH}_3)_n + \text{N}_2\text{H}_4$	$(4 \pm 1) \times 10^6$	—	RT	11.3	pr	—	Lati.72-0460
3 $\text{Ni}^{III}(\text{NH}_3)_n + \text{Ni}^{III}(\text{NH}_3)_m$	$2k < 3.5 \times 10^7$	—	RT	11.3	pr	—	Lati.72-0460
Rate constants for the decay of $\text{Ni}^{III}(\text{en})_n$ and $\text{Ni}^{III}(\text{gly})_n$ are given in tables III and IV respectively of ref. 72-0461. These rate constants cannot be attributed to any specific reaction.							

data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 15. Lead(I) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	γ	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
	Pb^{+2}							
15.1	$\text{Pb}^{+2} + \text{Cd}^{2+}$	$< 10^7$	—	RT	nat	pr	—	Baxe..66
15.2	$\text{Pb}^{+2} + \text{Cr}^{3+}$	$< 10^7$	—	RT	nat	pr	—	Baxe..66
15.3	$\text{Pb}^{+2} + \text{Ni}^{2+}$	$< 10^7$	—	RT	nat	pr	—	Baxe..66
15.4	$\text{Pb}^{+2} + \text{O}_2 \rightarrow \text{Pb}^{2+} + \text{O}_2^-$	3.9×10^9	—	RT	nat	pr	Product transfers an electron to 1,4-benzoquinone and tentatively identified as O_2^- . (Ref. 76-1134).	Baxe..66
15.5	$\text{Pb}^{+2} + \text{OH}^- (\text{et})$	7.7×10^8	—	RT	nat	pr	Reinterpreted from data in ref. 66-0848 on decay of Pb^{+2} in the absence of OH scavengers. Principal competing reaction, $\text{Pb}^{+2} + \text{Pb}^{+2}$, not taken into account.	Baxe..66
15.6	$\text{Pb}^{+2} + \text{Zn}^{2+}$	$< 10^7$	—	RT	nat	pr	Lead(II) acetate salt used. Pb^{+2} may be complexed to acetate. Measured from the rate of formation of the benzoquinone product in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	—
15.7	$\text{Pb}^{+2} + 1,4\text{-benzoquinone} \rightarrow \text{Pb}^{2+} + (1,4\text{-benzoquinone})^-$	$(4.1 \pm 0.8) \times 10^9$	—	25 ± 2	6.3	pr	Lead(II) acetate salt used. Pb^{+2} may be complexed to acetate. Measured from the rate of formation of the benzoquinone product in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Sell..76
15.8	$\text{Pb}^{+2} + \text{menaquinone} \rightarrow \text{Pb}^{2+} + (\text{menaquinone})^-$	$(3.7 \pm 0.4) \times 10^9$	—	RT	7.2	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao..7 Rao..7

*If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 16. Praseodymium(IV) reactions

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	γ	$\varepsilon/^\circ\text{C}$	pH	Method	Comments	Ref.
$\text{Pr}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{PrOH}^{3+} + \text{H}^+$	$K = (7 \pm 1) \times 10^{-4}$ or $\text{p}K_s = 3.1 \pm 0.1$	var	RT	1.95– 5.87	pr	Measured from effect of pH on absorption of $\text{Pr}(\text{IV})$.	Fara.72–0066
$\text{Pr}^{4+} + \text{Br}^-$ (et or af)	$(1.2 \pm 0.4) \times 10^6$	0.75	RT	nat	pr	—	Fara.72–0066
$\text{Pr}^{4+} + \text{H}_2\text{O}_2$ (H at ?)	$(8 \pm 1) \times 10^6$	[$\text{Pr}_2(\text{SO}_4)_2$] 0.75	RT	nat	pr	—	Fara.72–0066
$\text{Pr}^{4+} + \text{HSO}_4^-$ (et or H at?)	$(2.0 \pm 0.3) \times 10^6$	[$\text{Pr}_2(\text{SO}_4)_2$] —	RT	2–3.8	pr	—	Fara.72–0066
$\text{Pr}^{4+} + \text{NO}_3^-$ (et?)	$(3 \pm 1) \times 10^7$	0.75	RT	nat	pr	—	Fara.72–0066
$\text{Pr}^{4+} + \text{Pr}^{4+}$ (see comments)	$2k = (1.6 \pm 0.8)$ $\times 10^6$	—	RT	5.8	pr	Stable products of reaction suggested to be Pr^{III} and Os . Initial product possibly an oxo or hydroxo bridged diprasedymium species.	Fara.72–0066

data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 17. Platinum(I) and platinum(III) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	f	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
<i>Pt^I Reactions</i>								
17.1	$\text{Pt}^{\text{I}} \text{ from } \text{PtCl}_4^{2-} + e_{\text{aq}}$	$< 4 \times 10^8$	—	RT	nat	pr	—	Ghos.66
17.2	$\text{Pt}^{\text{I}} + \text{NaO}$ (et or O at)	$< 2 \times 10^7$	—	RT	nat	pr	—	Ghos.66
17.3	$\text{Pt}^{\text{I}} + \text{O}_2$ (et or af)	$'k' = (4.1 \pm 0.5) \times 10^8$	0.003	RT	nat	pr	Unclear whether rate constants refer to k or $2k$. Measured in the presence of 0.1 mol dm ⁻³ KCl.	Ghos.66
	$\text{Pt}^{\text{I}} + \text{Pt}^{\text{I}} \rightarrow \text{Pt}^{\text{o}} + \text{Pt}^{\text{II}}$	$'k' = (3.15 \pm 0.15) \times 10^8$	0.013	RT	nat	pr	—	Ghos.66
		$'k' = ca. 2.5 \times 10^8$	0.018	RT	2	pr	Products identified in γ -radiolysis experiments (see ref. 62-0164).	Ghos.66
17.4	$\text{Pt}^{\text{I}} \text{ from } \text{Pt}(\text{CN})_4^{2-} + e_{\text{aq}}$	$(1.8 \pm 0.25) \times 10^7$	—	RT	nat	pr	—	Ghos.66
17.5	$\text{Pt}^{\text{I}} + \text{O}_2$ (et or O at)	$(3.5 \pm 0.5) \times 10^8$	—	RT	nat	pr	—	Ghos.66
17.6	$\text{Pt}^{\text{I}} \text{ from } \text{PtLCl}^+$ ($L = \text{diethylenetriamine}$)	$2k = (4.6 \pm 2.0) \times 10^8$	2×10^{-4}	ca. 25	nat	pr	Rate constant represents decay of second transient produced from $\text{Pt}^{\text{II}} + e_{\text{aq}}$. First transient decays by a first order reaction with $(2.3 \pm 1.3) \times 10^8$ s ⁻¹ , probably associated with the substitution of Cl^- by H_2O .	Stor...75- 62-0164
	$\text{Pt}^{\text{I}} + \text{Pt}^{\text{I}}$ (?) see comments)							
17.7	$\text{Pt}^{\text{I}} \text{ from } \text{PtLCl}^+ + H$ ($L = \text{diethylenetriamine}$)	$2k = (6.8 \pm 0.8) \times 10^8$	—	ca. 25	2-3	pr	—	Stor...75- 62-0164
17.8	$\text{Pt}^{\text{I}} \text{ from } \text{Pt}(\text{en})_3^{2+} + e_{\text{aq}}$	$2k = (0.0 \pm 0.0) \times 10^8$	4×10^{-4}	ca. 25	nat	pr	—	Stor...75- 62-0164
17.9	$\text{Pt}^{\text{I}} \text{ from } \text{Pt}(\text{en})_3^{2+} + H$	$2k = (2.8 \pm 0.6) \times 10^8$	—	ca. 25	2-3	pr	—	Stor...75- 62-0164
17.10	$\text{Pt}^{\text{I}} \text{ from } \text{PtLCl}^+ + H$ ($L = \text{tetraethylidioethylenetriamine}$)	$2k = (1.3 \pm 0.6) \times 10^{11}$ (?)	—	ca. 25	2-3	pr	—	Stor...75- 62-0164
<i>Pt^{III} Reactions</i>								
17.11	$\text{Pt}^{\text{III}} \text{ from } \text{PtCl}_4^{2-} + \text{Cl}_2^-$ ($\text{Pt}^{\text{III}} \rightarrow (\text{Pt}^{\text{III}})^n$ (see comments for mechanism))	$(3 \pm 1) \times 10^8 \text{ s}^{-1}$	—	ca. 25	0.3	pr	Reaction probably associated with change in number of chloride ligands and/or substitution of Cl^- by H_2O . Measured in the presence of 0.5 mol dm ⁻³ HCl.	Stor...75- 62-0164
17.12	$\text{Pt}^{\text{III}} + \text{Cu}^{\text{II}}$ (et)	$(1.5 \pm 0.2) \times 10^8$	0.5 (HCl)	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm ⁻³ HCl. Cu^{II} in the form of chloro complex.	Stor...75- 62-0164

TABLE 17. Platinum(II) and platinum(III) reactions — Continued

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	f	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
$\text{Pt}^{\text{III}} + \text{Pt}^{\text{III}}$ (dis)	$2k = \text{ca. } 2 \times 10^6$	0.5 (HCl)	ca. 25	0.3	pr	Rate constant is for the decay of the second transient Pt ^{IV} species, (Pt^{IV}_2) ⁿ in entry 17.11. Measured in the presence of 0.5 mol dm ⁻³ HCl.	Stor...75-1188
Pt^{III} from $\text{PtCl}_6^{2-} + h\nu$							
$\text{Pt}^{\text{III}} + \text{Fe}^{2+}$ (ct)	$(2.8 \pm 0.3) \times 10^6$	2×10^{-2}	—	—	f.ph.	From dependence of rate constant for this reaction on ionic strength charge on Pt^{III} is -1, and identified therefore as PtCl_6^{2-} . Brozskiewicz and Grodzowski (ref. 76-1055) suggest however that the reaction observed under the conditions employed was $\text{Cl}_2^- + \text{Fe}^{2+}$. Other experiments give $k = (4.0 \pm 0.6) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{Cl}_2^- + \text{Fe}^{2+}$.	Wrig.72-7088
$\text{Pt}^{\text{III}} + \text{Pt}^{\text{III}}$ (dis)	$2k = (4.6 \pm 0.4) \times 10^6$	10^{-2}	ca. 20	5.8	f.ph.	Rate constant calculated taking $\epsilon_{410} = 3.7 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Wrig.72-7088
Pt^{III} from $\text{PtCl}_6^{2-} + \text{OH}$							
							
	$1.8 \times 10^6 \text{ s}^{-1}$	—	RT	nat	pr	Rate constant measured from decay of reactant at 450 nm.	Adam..68-0169
	$2.0 \times 10^6 \text{ s}^{-1}$	—	RT	nat	pr	Rate constant measured from decay of reactant at 450 nm.	Ghos.69-0144
	$2.0 \times 10^6 \text{ s}^{-1}$	—	RT	nat	pr	Rate constant measured from build-up of product at 400 nm. Ligand reorganization mechanism implied from similarity of products of $\text{PtCl}_6^{2-} + \text{OH}$ and $\text{PtCl}_6^{2-} + e_{\text{aq}}$ (ref. 68-0169).	Adam..68-0169
Pt^{III} from $\text{Pt(en)}_2^{2+} + \text{Cl}_2^-$ $(\text{Pt}^{\text{III}})^n \rightarrow (\text{Pt}^{\text{III}})^n$	$(1.3 \pm 0.1) \times 10^6 \text{ s}^{-1}$	—	ca. 25	0.3	pr	Decay approximates to two consecutive first orders (see also 17.18). Measured in the presence of 0.5 mol dm ⁻³ HCl.	Stor...75-1188

TABLE 17. Platinum(II) and platinum(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	f	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
17.18	$(\text{Pt}^{\text{III}})^{\text{II}} \rightarrow (\text{Pt}^{\text{III}})^{\text{II}}$	$7.7 \pm 0.8 \text{ s}^{-1}$	—	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm^{-3} HCl. See also comments under 17.17.	Stor...75
17.19	$\text{Pt}^{\text{III}} + \text{Cu}^{\text{II}}$ (ct)	$(3.2 \pm 0.7) \times 10^8$	0.5 (HCl)	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm^{-3} HCl.	Stor...75
17.20	$\text{Pt}^{\text{III}} + \text{Fe}^{\text{II}}$ (ct)	$(2.5 \pm 0.4) \times 10^8$	0.5 (HCl)	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm^{-3} HCl.	Stor...75
17.21	$\text{Pt}^{\text{III}} \text{ from } \text{Pt}(\text{en})_2^{2+} + \text{OH}^-$ $(\text{Pt}^{\text{III}})^{\text{I}} \rightarrow (\text{Pt}^{\text{III}})^{\text{II}}$ + H^+	$(2.5 \pm 0.2) \times 10^8$ s^{-1}	—	RT	4.0–7.0	pr	—	Brod...76
		$(2.4 \pm 0.3) \times 10^8$ s^{-1}	—	RT	7.0–9.6	pr	—	Brod...76
17.22	$(\text{Pt}^{\text{III}})^{\text{I}} + \text{OH}^- \rightarrow$ $(\text{Pt}^{\text{III}})^{\text{II}} + \text{H}_2\text{O}$	$(3.1 \pm 0.5) \times 10^{10}$	—	RT	7.0–9.6	pr	—	Brod...76
17.23	$(\text{Pt}^{\text{III}})^{\text{I}} + \text{H}^+ \rightarrow$ $(\text{Pt}^{\text{III}})^{\text{II}}$	$(4.2 \pm 0.9) \times 10^8$	—	RT	4.0–7.0	pr	—	Brod...76
17.24	$(\text{Pt}^{\text{III}})^{\text{II}} +$ $(\text{Pt}^{\text{III}})^{\text{IV}}$ (ct?)	$(1.5 \pm 0.4) \times 10^8$	—	RT	2.9–8.5	pr	Measured in the presence of $(0.2) \times 10^{-2} \text{ mol dm}^{-3}$ Cl^- .	Brod...76
		$(4.3 \pm 2.8) \times 10^8$	—	RT	4.0–9.1	f.ph.	Measured in the presence of $(0.1) \times 10^{-2} \text{ mol dm}^{-3}$ Cl^- . Unclear whether these rate constants refer to k or $2k$.	Brod...76
17.25	$(\text{Pt}^{\text{III}})^{\text{II}} + \text{Cu}^{\text{II}}$	$< 10^4$	—	RT	6.3–6.6	pr	—	Brod...76
17.26	$(\text{Pt}^{\text{III}})^{\text{II}} +$ $\text{Fe}(\text{CN})_6^{4-}$ (ct)	$(2.3 \pm 0.2) \times 10^8$	—	RT	6.3–6.6	pr	—	Brod...76
17.27	$(\text{Pt}^{\text{III}})^{\text{II}} + \text{O}_2$	$< 10^8$	—	RT	6.3–6.6	pr	—	Brod...76
17.28	$(\text{Pt}^{\text{III}})^{\text{II}} \rightarrow$ $(\text{Pt}^{\text{III}})^{\text{IV}}$	$(6.6 \pm 1.8) \times 10^8$ or $\text{pK}_{\text{a}} = 6.8 \pm 0.2$	—	RT	2.8–4.3	pr	Cf. entry 17.23	Brod...76
17.29	$(\text{Pt}^{\text{III}})^{\text{II}} + \text{H}^+$ $(\text{Pt}^{\text{III}})^{\text{IV}} \rightarrow$	$2.8 \pm 0 \text{ s}^{-1}$	—	RT	2.8–4.3	pr	Reaction may be second order.	Brod...76
17.30	$(\text{Pt}^{\text{III}})^{\text{II}} + \text{Cl}^- \rightarrow$ $(\text{Pt}^{\text{III}})^{\text{IV}}$	$(1.11 \pm 0.09) \times 10^8$	—	RT	3–4, 5.1	pr	—	Brod...76
17.31	$(\text{Pt}^{\text{III}})^{\text{IV}} + \text{Cu}^{\text{II}}$ (ct?)	$(2.7 \pm 1.0) \times 10^8$	—	RT	2.1	pr	Measured in the presence of $5 \times 10^{-2} \text{ mol dm}^{-3}$ Cl^- . Measured in the presence of 0–0.5 mol dm^{-3} 2-methyl-2-propanol. Mechanism of reaction may be complex as the rate constants were appreciably higher (25–50%) at the lower $[\text{Cu}^{\text{II}}]$ employed.	Brod...76
17.32	$(\text{Pt}^{\text{III}})^{\text{IV}} +$ $(\text{Pt}^{\text{III}})^{\text{IV}}$ (dis?)	$'k' = (5.7 \pm 1.0) \times 10^7$	—	RT	3.4	pr	Measured in the presence of 10^{-2} mol dm^{-3} Cl^- . Rate constant calculated taking $\epsilon_{\text{so}} (\text{Pt}^{\text{III}})^{\text{IV}} = 0.070 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Brod...76

TABLE 17. Platinum(II) and platinum(III) reactions — Continued

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	T	t/°C	pH	Method	Comments	Ref.
Cont. $'k' = (4.9 \pm 1.9) \times 10^7$	—	RT	2.0	f.ph.	Measured in the presence of (O-1) $\times 10^{-6} \text{ mol dm}^{-3}$ Cl ⁻ and 0.01 mol dm ⁻³ 2-methyl-2-propanol. Rate constant calculated taking $\epsilon_{\text{so}}(\text{Pt}^{III})^{\text{IV}} = 9490 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Unclear whether these rate constants refer to k or $2k$.	Brod...76-1093	
Pt^{III} from $\text{trans-Pt(en)}_2\text{Cl}_2^{2+} + \text{en}^-$ or $\text{CH}_3\text{COHCH}_3$	$2k = (5.8 \pm 1.0) \times 10^7$	—	ca. 25	—	pr	Measured in the presence of 2.6 mol dm ⁻³ 2-methyl-2-propanol.	Stor...75-1188
Pt^{III} from $\text{trans-Pt(en)}_2\text{Cl}_2^{2+} + \text{H}$	$2k = (8.8 \pm 1.0) \times 10^7$	—	ca. 25	2	pr	Measured in the presence of 0.11-2 mol dm ⁻³ 2-methyl-2-propanol.	Stor...75-1188
Pt^{III} from $\text{trans-Pt(en)}_2\text{Cl}_2^{2+} + \text{CH}_3\text{OH}$	$2k = (1.04 \pm 0.38) \times 10^8$	—	ca. 25	—	pr	Measured in the presence of 2-4 mol dm ⁻³ methanol.	Stor...75-1188
Pt^{III} from $\text{Pt(dien)}\text{Cl}^+$ + Cl_2^-	$(3.2 \pm 0.7) \times 10^8$	—	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm ⁻³ HCl.	Stor...75-1188
$\text{Pt}^{III} + \text{Pt}^{III}$ (dis)	$2k = (6.8 \pm 1.6) \times 10^8$	—	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm ⁻³ HCl.	Stor...75-1188
Pt^{III} from $\text{Pt(dien)}\text{Cl}^+ + \text{OH}$	$(4.8 \pm 0.8) \times 10^8$	—	RT	nat	pr	Rate constant for initial decay of Pt^{III} transient. This process is followed by (i) an intermediate process exhibiting mixed order kinetics, and (ii) a slow second order decay with $2k = (7.6 \pm 0.6) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.	Brod...76-1093
Pt^{III} from PtLCl^+ + Cl_2^- ($L = \text{tetraethyldiethylenetriamine}$)	$(1.5 \pm 0.4) \times 10^7$	—	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm ⁻³ HCl.	Stor...75-1188
$\text{Pt}^{III} + \text{Pt}^{III}$	$2k = \text{ca. } 8 \times 10^8$	—	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm ⁻³ HCl.	Stor...75-1188
Pt^{III} from PtLCl^+ + OH ($L = \text{tetraethyldiethylenetriamine}$)	$1.8 \pm 0.6 \text{ s}^{-1}$	—	ca. 25	nat	pr	—	Brod...76-1093
<i>ata source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).</i>							

TABLE 18. Rhodium(II) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ *	T	t/°C	pH	Method	Comments	Ref
18.1	$\text{Rh}(\text{NH}_3)_6^{2+}$ and related complexes $\text{Rh}(\text{NH}_3)_6^{2+} + \text{H}_2\text{O} \rightarrow \text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}^{2+} + \text{NH}_3$	$3.5 \times 10^3 \text{ s}^{-1}$	—	RT	4.0	pr	Rate constant measured by change in conductivity resulting from $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$. Solutions contained also 0.5 mol dm ⁻³ 2-methyl-2-propanol.	Lili..75
18.2	$\text{Rh}(\text{NH}_3)_6\text{H}_2\text{O}^{2+} + \text{H}_2\text{O} \rightarrow \text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})_2^{2+} + \text{NH}_3$	40 s ⁻¹	—	RT	4.0	pr	Rate constant measured by change in conductivity resulting from $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$. Solutions contained also 0.5 mol dm ⁻³ 2-methyl-2-propanol.	Lili..75
18.3	$\text{Rh}(\text{NH}_3)_6^{2+} + \text{O}_2 \rightarrow \text{O}_2\text{Rh}(\text{NH}_3)_6^{2+}$	3.1×10^6	—	RT	4.0	pr	Product characterised by conductivity measurements. Measured in the presence of 0.5 mol dm ⁻³ 2-methyl-2-propanol.	Lili..75
18.4	$\text{Rh}(\text{NH}_3)_6^{2+} + \text{Rh}(\text{NH}_3)_6^{2+}$ (dis?)	$2k = \text{ca. } 1.2 \times 10^7$	—	RT	4.0	pr	Estimated from dependence of chain length in the $\text{Rh}(\text{NH}_3)_6^{2+} + \text{Rh}(\text{NH}_3)_6\text{Br}_2^{2+}$ reaction on dose rate.	Lili..75
18.5	$\text{Rh}(\text{NH}_3)_6^{2+} + \text{Rh}(\text{NH}_3)_6\text{Br}_2^{2+} \rightarrow \text{Rh}(\text{NH}_3)_5^{2+} + \text{Rh}(\text{NH}_3)_5\text{Br}_2$	ca. 1.4×10^6	—	RT	4.0	pr	Estimated from initial conductivity change. Measured in the presence of 0.5 mol dm ⁻³ 2-methyl-2-propanol. Products inferred from chain reaction which ensues.	Lili..75

*If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 19. Ruthenium(I), (II), (III) and (IV) reactions

Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
Ru^I $\text{Ru}(\text{NH}_3)_6\text{N}_3^+$ $\text{Ru}(\text{NH}_3)_6\text{N}_3^+ + \text{Ru}(\text{NH}_3)_6\text{N}_3^+ (\text{dis})$	$2k = 2.7 \times 10^6$	$< 6 \times 10^{-4}$	20 ± 2	nat	pr	Deposit of metallic ruthenium and molecular nitrogen ($\text{C}(\text{N}_3)$) was observed as stable products. Immediate products of reaction unknown.	Baxe..71-0234
Ru^{II} $\text{Ru}(\text{NH}_3)_6\text{Cl}^+ + \text{H}_2\text{O} \rightarrow \text{Ru}(\text{NH}_3)_6\text{H}_2\text{O}^{2+} + \text{Cl}^-$	$4.7 \pm 0.4 \text{ s}^{-1}$	—	20	nat	pr	Product characterised by its absorption spectrum. Products inferred from fact that radiation brings about complete aquation of $\text{Ru}(\text{NH}_3)_6\text{Cl}^+$.	Baxe..70-0178
$\text{Ru}(\text{NH}_3)_6\text{H}_2\text{O}^{2+} + \text{Ru}(\text{NH}_3)_6\text{Cl}^+ \rightarrow \text{Ru}(\text{NH}_3)_6\text{Cl}^+ + \text{Ru}(\text{NH}_3)_6\text{H}_2\text{O}^{2+}$	1.0×10^6	3×10^{-4}	20	nat	pr	Products inferred from fact that radiation brings about complete aquation of $\text{Ru}(\text{NH}_3)_6\text{Cl}^+$.	Baxe..70-0178
$\text{Ru}(\text{NH}_3)_6\text{NO}^{2+} + \text{O}_2$ (et or et) $\text{Ru}(\text{NH}_3)_6\text{NO}^{2+} + \text{H}_2\text{CC}(\text{CH}_3)_2\text{OH} \rightarrow \text{Ru}(\text{NH}_3)_6\text{NO} \cdot \text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}^{2+}$	7.6×10^6	—	RT	—	pr	Measured in the presence of 0.1–2.0 mol dm^{-3} 2-methyl-2-propanol. Product characterised by elemental microanalysis, ion exchange chromatography, and uv-visible, ir and nmr spectroscopy.	Armo..75-1049
$\text{Ru}(\text{NH}_3)_6\text{NO}^{2+} + \text{O}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ (af or et)	3×10^6	—	RT	nat	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Armo..75-1077
Ru^{III} $\text{Ru}(\text{NH}_3)_6\text{N}_3^+ + \text{H}_2\text{O} \rightarrow \text{Ru}(\text{NH}_3)_6\text{OH}^{2+} + \text{H}^+ + \text{N}_2$	$250 \pm 20 \text{ s}^{-1}$	—	20 ± 2	nat	pr	Measured from decay of $\text{Ru}(\text{NH}_3)_6\text{N}_3^+$ absorption.	Baxe..71-0234
	$270 \pm 20 \text{ s}^{-1}$	—	20 ± 2	nat	pr	Measured from the formation of $\text{Ru}(\text{NH}_3)_6\text{OH}^{2+}$. Ru product characterised by its absorption spectrum $\text{C}(\text{N}_2) = 0.7 (= 2 \text{ C}_{\text{aa}} + \text{C}_{\text{m}})$ measured in γ -radiolysis experiments with NaO^- saturated solutions.	Baxe..71-0234

TABLE 19. Ruthenium(I), (II), (III) and (IV) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
19.8	Ru^{IV} (The precise nature of these complexes is uncertain; all were formed by OH oxidation of the corresponding Ru^{III} complex). $\text{Ru}(\text{NH}_3)_6^{4+} +$ $\text{Ru}(\text{NH}_3)_6^{4+}$ (dis)	4.5×10^6	3×10^{-3}	20	nat	pr	Unclear whether rate constant refers to k or $2k$. A product of dissociation (possibly $\text{Ru}(\text{NH}_3)_6^{4+}$) decays by a first order process with $k = 0.75 \text{ s}^{-1}$. Further, slower reactions ensue before the formation of the stable products, and these presumably are due to aquation and hydrolysis reactions.	Baxc..70—
19.9	$\text{Ru}(\text{NH}_3)_6\text{Cl}^{3+} \rightarrow$ products	$2.5 \times 10^6 \text{ s}^{-1}$	3×10^{-3}	20	nat	pr	The product of this reaction undergoes two further unimolecular reactions with rate constants of 44 and 0.45 s^{-1} . These are probably associated with aquation and hydrolysis reactions.	Baxc..70—

*If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 20. Samarium(II) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^a	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
20.1	$\text{Sm}^{2+}_{\text{aq}}$ $\text{Sm}^{2+} + \text{BrO}_3^-$ (et)	7.1×10^6 (7.0 ± 0.5) $\times 10^7$	0.015 0.0375	RT RT	nat 6	pr pr	- -	Fara.72-0065 Pika..73-1084
20.2	$\text{Sm}^{2+} + \text{Co}(\text{en})_3^{3+}$	$< 1 \times 10^6$	0.06-	RT	6	pr	-	Fara.73-0107
20.3	$\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ (et)	3.5×10^7 1.6×10^8 2.5×10^8	0.06 1.0 1.0	RT RT RT	6 6 6	pr pr pr	- - -	Fara.73-0107 Fara.73-0107 Fara.73-0107
20.4	$\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ (et)	3.8×10^7 1.7×10^8 2.3×10^8	0.06 1.0 1.0	RT RT RT	6 6 6	pr pr pr	- - -	Fara.73-0107 Fara.73-0107 Fara.73-0107
20.5	$\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{CN}^{2+}$	$< 3.0 \times 10^6$	0.06	RT	6	pr	-	Fara.73-0107
20.6	$\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{F}^{2+}$ (et)	2.5×10^7 1.1×10^8	0.06 1.0	RT RT	6 6	pr pr	- -	Fara.73-0107 Fara.73-0107
				(NaClO_4)				
20.7	$\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (et)	6.0×10^8 8.8×10^8 2.6×10^7	0.3 1.0 1.0	RT RT RT	- - -	pr pr pr	- - -	Fara.73-0107 Fara.73-0107
				(NaClO_4)				
20.8	$\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{I}^{2+}$ (et)	5.8×10^7	0.06	RT	6	pr	-	Fara.73-0107
20.9	$\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{N}_5^{2+}$ (et)	7.8×10^7 2.5×10^8	0.06 0.5	RT RT	6 6	pr pr	- -	Fara.73-0107 Fara.73-0107
				(NaClO_4)				
20.10	$\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$	$< 1.0 \times 10^6$ $< 1.0 \times 10^6$	0.06 0.5	RT RT	6 6	pr pr	- -	Fara.73-0107 Fara.73-0107
				(NaClO_4)				
20.11	$\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_6^{3+}$ (et)	$< 1.0 \times 10^6$	0.06	RT	6	pr	-	Fara.73-0107
				5.0×10^6	1.0	pr	-	Fara.73-0107
20.12	$\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_6\text{OH}^{2+}$ (et)	1.5×10^7	0.3	RT	-	pr	-	Fara.73-0107
				5.0×10^7	1.0	pr	-	Fara.73-0107
				5.0×10^7	1.0	pr	-	Fara.73-0107
				(NaClO_4)				
20.13	$\text{Sm}^{2+} + \text{CrO}_4^{2-}$ (et)	$(4.0 \pm 0.5) \times 10^9$	0.375	RT	6	pr	-	Pika..73-1084
20.14	$\text{Sm}^{2+} + \text{Cu}^{2+}$ (et)	8.3×10^7	0.015	RT	nat	pr	-	Fara.72-0065
20.15	$\text{Sm}^{2+} + \text{H}_2\text{O}_2$ (et)	3.5×10^7	0.015	RT	nat	pr	-	Fara.72-0065
		$(6.7 \pm 0.3) \times 10^7$	0.375	RT	6	pr	-	Pika..73-1084
20.16	$\text{Sm}^{2+} + \text{Eu}^{3+}$ (et)	7.5×10^6	0.015	RT	nat	pr	-	Fara.72-0065
20.17	$\text{Sm}^{2+} + \text{IO}_3^-$ (et)	4.9×10^7	0.015	RT	nat	pr	-	Fara.72-0065
20.18	$\text{Sm}^{2+} + \text{MnO}_4^-$ (et)	$(4.7 \pm 0.5) \times 10^9$	0.375	RT	6	pr	-	Pika..73-1084
		6.5×10^9	0.015	RT	nat	pr	-	Fara.72-0065
20.19	$\text{Sm}^{2+} + \text{NO}_2^-$ (et)	1.1×10^8	$\rightarrow 0$	RT	nat	pr	-	Fara.72-0065
		$(1.3 \pm 0.2) \times 10^9$	0.375	RT	6	pr	-	Pika..73-1084
20.20	$\text{Sm}^{2+} + \text{NO}_3^-$ (et)	$(1.5 \pm 0.2) \times 10^9$	0.375	RT	6	pr	-	Pika..73-1084
		2.0×10^8	0.015	RT	nat	pr	-	Fara.72-0065
20.21	$\text{Sm}^{2+} + \text{NaO}$ (et?)	2.0×10^8	0.015	RT	nat	pr	-	Fara.72-0065

TABLE 20. Samarium(II) reactions — Continued

No.	Reaction	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹ ^a	<i>I</i>	<i>t</i> /°C	pH	Method	Comments	Ref.
20.22	Sm ²⁺ + O ₂ (af or et)	3.9 × 10 ⁸ (4.2 ± 0.5) × 10 ⁸	0.015 0.375	RT RT	nat 3–6	pr pr	— —	Fara.72-0065 Pika..73-1084
20.23	Sm ²⁺ + OH (et)	6 × 10 ⁸ (6.2 ± 0.8) × 10 ⁸	— 0.375	RT RT	nat 3–6	pr pr	— —	Fara.72-0065 Pika..73-1084
20.24	Sm ²⁺ + Ru(NH ₃) ₆ Br ²⁺ (et)	1.5 × 10 ⁸	0.06	RT	6	pr	—	Fara.73-0107
20.25	Sm ²⁺ + Ru(NH ₃) ₆ Cl ²⁺ (et)	1.5 × 10 ⁸ 4.3 × 10 ⁸ 6.5 × 10 ⁸	0.06 1.0 1.0	RT (NaClO ₄) RT (NaCl)	6 6 6	pr pr pr	— — —	Fara.73-0107 Fara.73-0107 Fara.73-0107
20.26	Sm ²⁺ + Ru(NH ₃) ₆ H ₂ O ²⁺ (et)	6.5 × 10 ⁷ 1.8 × 10 ⁸ 1.3 × 10 ⁸	0.3 1.0 1.0	RT (NaClO ₄) RT (NaCl)	2 2 2	pr pr pr	— — —	Fara.73-0107 Fara.73-0107 Fara.73-0107
20.27	Sm ²⁺ + Ru(NH ₃) ₆ I ²⁺ (et)	ca. 10 ⁸	0.06	RT	6	pr	—	Fara.73-0107
20.28	Sm ²⁺ + Ru(NH ₃) ₆ OH ²⁺ (et)	4.0 × 10 ⁷ 2.2 × 10 ⁸ 6.0 × 10 ⁸	0.06 1.0 1.0	RT (NaClO ₄) RT (NaCl)	6 6 6	pr pr pr	— — —	Fara.73-0107 Fara.73-0107 Fara.73-0107
20.29	Sm ²⁺ + Ru(NH ₃) ₆ s ⁺ (et)	2.5 × 10 ⁷ 2.0 × 10 ⁸ 8.0 × 10 ⁸	0.06 1.0 1.0	RT (NaClO ₄) RT (NaCl)	6 6 6	pr pr pr	— — —	Fara.73-0107 Fara.73-0107 Fara.73-0107
20.30	Sm ²⁺ + Yb ³⁺ (et)	3.0 × 10 ⁸	0.015	RT	nat	pr	—	Fara.72-0065

^aIf the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for 2*k*).

TABLE 21. Thallium(0) and (II) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
21.1	$\text{Tl}^0 + \text{H}_2\text{O}_2 \rightarrow \text{Tl}^{+} + \text{OH} + \text{OH}^-$	5×10^8	-	RT	0.1,5,2	γ	Rate constant and products deduced from H_2O_2 and H_2 yields in γ -irradiated Tl^0 solutions.	Fara..71-0036
21.2	$\text{Tl}^0 + \text{HO}_2 \rightarrow \text{Tl}^{+} + \text{HO}_2^-$	$< 10^7$	-	RT	nat	pr γ	Rate constant and products deduced from H_2O_2 and H_2 yields in γ -irradiated Tl^0 solutions.	Fara..71-0036 Fara..71-0036
21.3	$\text{Tl}^0 + \text{O}_2 \rightarrow \text{Tl}^{+} + \text{O}_2^-$	$(1.0 \pm 0.2) \times 10^7$	-	RT	nat	pr	-	Fara..71-0036
21.4	$\text{Tl}^0 + \text{O}_2^- \rightarrow \text{Tl}^{+} + \text{O}_2^{2-}$	1.4×10^8	-	RT	5.2	γ	Rate constant and products deduced from H_2O_2 and H_2 yields in γ -irradiated Tl^0 solutions.	Fara..71-0036
21.5	$\text{Tl}^0 + \text{Tl}^{+} \rightleftharpoons \text{Tl}_2^+$	$K = 2.3 \times 10^8 \text{ M}^{-1}$ $k_f > 10^{10}$	-	RT	6.5	pr	Measured from the effect of $[\text{Tl}^{+}]$ on the absorption due to Tl_2^+ .	Cerc..66-0097
21.6	$\text{Tl}^0 + \text{Tl}^{II} \rightarrow \text{Tl}^{+} + \text{Tl}^{II}$	$(4.5 \pm 1) \times 10^8$	-	RT	nat	pr	Products deduced from H_2O_2 and H_2 yields in γ -irradiated Tl^0 solutions. No account taken of the hydrolysis of Tl^{II} (see entry 21.19). No account taken of competing reaction $\text{Tl}_2^+ + \text{Tl}^{II}$ (see entry 21.12).	Fara..71-0036
21.7	$\text{Tl}^0 (?) + 1,4\text{-benzo-quinone} \rightarrow \text{Tl}^{+} + (1,4\text{-benzo-quinone})^-$	2.8×10^8	-	ca. 25	7.0	pr	Semiquinone product identified by its absorption spectrum.	Rao..75-1032
21.8	$\text{Tl}_2^+ + \text{H}_2\text{O}_2 \rightarrow 2\text{Tl}^{+} + \text{OH} + \text{OH}^-$	$(7 \pm 2) \times 10^8$	-	RT	nat	pr	Products deduced from H_2O_2 and H_2 yields in γ -irradiated Tl^0 solutions.	Fara..71-0036
21.9	$\text{Tl}_2^+ + \text{N}_2\text{O}$ (O at or et)	$(1.4 \pm 0.2) \times 10^7$	-	25	nat	pr	γ -radiolysis studies indicate that N_2 is one of the products of this reaction.	Sell72-0844
21.10	$\text{Tl}_2^+ + \text{O}_2 \rightarrow 2\text{Tl}^{+} + \text{O}_2^-$	$(1.0 \pm 0.2) \times 10^7$ 1.2×10^7	-	RT	nat	pr γ	Rate constant and products deduced from H_2O_2 and H_2 yields in γ -irradiated Tl^0 solutions.	Fara..71-0036 Fara..71-0036
21.11	$\text{Tl}_2^+ \rightleftharpoons \text{Tl}^0 + \text{Tl}^{+}$	see entry 21.5						
21.12	$\text{Tl}_2^+ + \text{Tl}^{II} \rightarrow 3\text{Tl}^{+}$	$(4.4 \pm 0.9) \times 10^8$ $(4.5 \pm 1) \times 10^8$	$\rightarrow 0$ 0.0006	RT	nat	pr	Products deduced from H_2O_2 and H_2 yields in γ -irradiated Tl^0 solutions.	Cerc..66-0097 Fara..71-0036
		$(7.5 \pm 1) \times 10^8$	0.015	RT	nat	pr	No account taken of the hydrolysis of Tl^{II} (see entry 21.19).	

TABLE 21. Thallium(0) and (II) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
21.13	$\text{Tl}_2^+ + 1,4\text{-dicyano-}$ $\text{benzene} \rightarrow 2\text{Tl}^+ +$ $(1,4\text{-dicyanobenzene})^-$	2.7×10^6	—	RT		pr	Organic product characterised by its absorption spectrum.	Robi..73-0121
21.14	$\text{Tl}^{2+} + \text{Co}^{3+} \rightleftharpoons$ $\text{Tl}^+ + \text{Co}^{2+}$	$k_t = (6.2 \pm 0.5) \times 10^3$	0.75	25	0.6	f.ph.	Evidence for products and equilibrium from conventional kinetic studies.	Falc..74-7625
21.15	$\text{Tl}^{2+} + \text{Co}^{3+} \rightarrow$ $\text{Tl}^+ + \text{Co}^{2+}$	$(9.5 \pm 0.5) \times 10^6$	0.55	22 ± 2	0.3	f.ph.	Evidence for products from conventional kinetic studies.	Falc..75-7093
21.16	$\text{Tl}^{2+} + \text{Fe}^{2+} \rightarrow$ $\text{Tl}^+ + \text{Fe}^{3+}$	$(2.42 \pm 0.1) \times 10^6$	0.30	14.7	0.6	f.ph.	Evidence for products from conventional kinetic studies.	Falc..75-7093
		$(2.50 \pm 0.1) \times 10^6$	0.30	18.3	0.6	f.ph.		Falc..75-7093
		$(2.53 \pm 0.1) \times 10^6$	0.30	20.7	0.6	f.ph.		Falc..75-7093
		$(2.60 \pm 0.1) \times 10^6$	0.30	24.8	0.6	f.ph.		Falc..75-7093
		$(2.70 \pm 0.1) \times 10^6$	0.30	29.0	0.6	f.ph.		Falc..75-7093
		$(2.73 \pm 0.1) \times 10^6$	0.30	33.9	0.6	f.ph.		Falc..75-7093
		$(2.81 \pm 0.1) \times 10^6$	0.30	36.0	0.6	f.ph.		Falc..75-7093
		$(2.91 \pm 0.1) \times 10^6$	0.30	39.6	0.6	f.ph.		Falc..75-7093
		$E_a = 48 \pm 2 \text{ kJ mol}^{-1}$	0.30	14-40	0.6	f.ph.		Falc..75-7093
		$(6.7 \pm 0.7) \times 10^6$	1	23	0	pr		Schw..74-1017
21.17	$\text{Tl}^{2+} + \text{Fe}^{2+} \rightleftharpoons$ $\text{Tl}^+ + \text{Fe}^{3+}$	$(1.1 \pm 0.15) \times 10^6$	0.30	25	0.6	f.ph.	Evidence for products and equilibrium from conventional kinetic studies.	Falc..74-7625
21.18	$\text{Tl}^{2+} + \text{HO}_2 \rightarrow$ $\text{Tl}^+ + \text{H}^+ + \text{O}_2$	$(2.5 \pm 1) \times 10^6$	—	RT	1	pr	Estimated from initial decay of Tl^{II} in aerated solutions.	Cerc..66-0097
21.19	$\text{Tl}^{2+} + \text{H}_2\text{O} \rightleftharpoons$ $\text{TIOH}^+ + \text{H}^+$	$pK = 4.6 \pm 0.2$ $k_t = 3.5 \times 10^6 \text{ s}^{-1}$ $k_r = (1.4 \pm 0.5) \times 10^{10}$	var	21	2-7	pr	Evidence for equilibrium from optical and conductivity measurements.	O'Ne..75-1130
21.20	$\text{Tl}^{2+} + \text{H}_2\text{O}_2 \rightarrow$ $\text{Tl}^+ + \text{HO}_2 + \text{H}^+$	$(2.8 \pm 0.8) \times 10^7$	—	RT	1	pr	Evidence for products from H_2O_2 and H_2 yields in γ -irradiated Tl^I solutions. (see ref. 71-0036).	Cerc..66-0097
21.21	$\text{Tl}^{2+} + \text{Mn}^{2+} \rightarrow$ $\text{Tl}^+ + \text{Mn}^{3+}$	$(1.9 \pm 0.2) \times 10^6$	0.75	22 ± 3	0.3	f.ph.	Evidence for products from conventional kinetic studies etc. (see ref. 75-7093).	Falc..75-7093
21.22	$\text{Tl}^{II} + \text{O}_2^- \rightarrow$ $\text{Tl}^I + \text{O}_2$	2×10^{10}	—	RT	5.2	γ	Rate constant and products deduced from H_2O_2 and H_2 yields in γ -irradiated Tl^I solutions. No account taken of hydrolysis of Tl^{2+} (see entry 21.19).	Fara..71-0036
21.23	$\text{Tl}^{II} + \text{Tl}^0$	see entry 21.6						
21.24	$\text{Tl}^{II} + \text{Tl}_2^+$	see entry 21.12						

TABLE 21. Thallium(0) and (II) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^a	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
21.25	$\text{Tl}^{2+} + \text{Tl}^{2+}$ (dis)	$2k = (3.8 \pm 0.6) \times 10^8$	1 (HClO_4)	23	0	pr	Measured from decay of Tl^{2+} monitored at 280 nm. Value of ϵ_{280} used to calculate rate constant not given, but is <i>ca.</i> 3200 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Schw...74-1017
		$2k = (5.2 \pm 0.5) \times 10^8$	0.25	25	1	f.ph.	Measured from decay of Tl^{2+} monitored at 270 nm. Rate	Falc...74-7625
		$2k = (5.5 \pm 0.5) \times 10^8$	0.25	25	0.6	f.ph.		
		$2k = (9.2 \pm 0.9) \times 10^8$	0.50	25	0.6	f.ph.		
		$2k = (1.3 \pm 0.1) \times 10^9$	1.0	25	0.6	f.ph.	constant calculated	
		$2k = (1.2 \pm 0.1) \times 10^9$	1.0	25	0.3	f.ph.	taking $\epsilon_{270} = 5500$	
		$2k = (1.3 \pm 0.1) \times 10^9$	1.0	25	0	f.ph.	$\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. This value was obtained by interpolation from the measured spectrum of Tl^{2+} and the value of $\epsilon_{280} = 5400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ measured by Cercek <i>et al</i> (ref. 66-0097).	
		$E_a = 7.9 \pm 1.5 \text{ kJ mol}^{-1}$	-	15-45	-	f.ph.	Note however that this latter value was measured in solutions at pH <i>ca.</i> 6.5 and refers therefore to TiOH^+ (see entry 21.19).	
		$2k/\epsilon_{270} = (6.1 \pm 0.6) \times 10^4 \text{ cm s}^{-1}$	1 (HClO_4)	25 ± 2	0	f.ph.	Measured in the presence of $5 \times 10^{-3} \text{ mol dm}^{-3}$ Ti^{III} and $1 \times 10^{-4} \text{ mol dm}^{-3}$ Ti^I .	Burc.70-7309
		$2k/\epsilon_{270} = (1.3 \pm 0.2) \times 10^6 \text{ cm s}^{-1}$	1 (HClO_4)	25 ± 2	0	f.ph.	Measured in the presence of $5 \times 10^{-3} \text{ mol dm}^{-3}$ Ti^{III} and $5 \times 10^{-2} \text{ mol dm}^{-3}$ 2-propanol.	Burc.70-7309
21.26	$\text{TiOH}^+ + \text{TiOH}^+$ (dis)	$2k = (4.6 \pm 1.6) \times 10^9$	<i>ca.</i> 0	RT	6.5	pr	Measured from decay of TiOH^+ monitored at 260 nm. Rate constant calculated taking $\epsilon_{260} = 5400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Cerc..66-0097
		$2k = 5 \times 10^9$	-	RT	> 5.5	pr	Extinction coefficient used to calculate rate constant not given.	O'Ne.75-1130
21.27	$\text{Tl}^{2+} + \cdot\text{CH}_3\text{OH}$ (et or af)	$(1.2 \pm 0.3) \times 10^4$	-	23 ± 2	0.43	γ	Estimated from the γ -ray induced chain reaction in Tl^{II} + methanol solutions, taking $k(\text{Tl}^{II} + \text{Tl}^{II}) = 5.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see entry 21.25).	Burc.70-0336
21.28	$\text{Tl}^{2+} + \text{CH}_3\text{C HOH}$ (et or af)	$(1.5 \pm 0.4) \times 10^4$	-	23 ± 2	0.43	γ	Estimated from the γ -ray induced chain reaction in Tl^{II} + ethanol solutions, taking $k(\text{Tl}^{II} + \text{Tl}^{II}) = 5.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see entry 21.25).	Burc.70-0336

TABLE 21. Thallium(0) and (II) reactions — Continued

No.	Reaction	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹ *	<i>I</i>	<i>t</i> /°C	pH	Method	Comments	Ref.
21.29	Tl ²⁺ + CH ₃ COHCH ₃ (et or af)	(9.4 ± 2.3) × 10 ⁸	—	23 ± 2	0.43	γ	Estimated from the γ-ray induced chain reaction in Tl ^{II} + 2-propanol solutions. taking <i>k</i> (Tl ^{II} + Tl ^{II}) = 5.5 × 10 ⁸ dm ³ mol ⁻¹ s ⁻¹ (see entry 21.25).	Burc.70-0336
21.30	Tl ²⁺ + anisole → Tl ⁺ + (anisole) ⁺	(5.0 ± 0.5) × 10 ⁸	—	20 ± 2	4	pr	Radical cation pro- duct characterised by its absorption and esr spectra.	O'Ne..75-1171
21.31	Tl ²⁺ + 1,2-dimeth- oxybenzene → Tl ⁺ + (1,2-dimethoxybenzene) ⁺	(6.0 ± 0.6) × 10 ⁸	—	20 ± 2	4	pr	Radical cation pro- duct characterised by its absorption and esr spectra.	O'Ne..75-1171 O'Ne..75-1086
21.32	TlOH ⁺ + 1,2-dimethoxy- benzene → Tl ⁺ + OH ⁻ + (1,2-dimethoxybenzene) ⁺	1.2 × 10 ⁸	—	RT	> 4.7	pr	Radical cation pro- duct characterised by its absorption and esr spectra.	O'Ne..75-1086
21.33	Tl ²⁺ + 1,3-dimethoxy- benzene → Tl ⁺ + (1,3- dimethoxybenzene) ⁺	(8.0 ± 0.8) × 10 ⁸	—	20 ± 2	4	pr	Radical cation pro- duct characterised by its absorption and esr spectra.	O'Ne..75-1171
21.34	Tl ²⁺ + 1,4-dimethoxy- benzene → Tl ⁺ + (1,4-dimethoxybenzene) ⁺	(6.5 ± 0.7) × 10 ⁸	—	20 ± 2	4	pr	Radical cation pro- duct characterised by its absorption and esr spectra.	O'Ne..75-1086 O'Ne..75-1171
21.35	TlOH ⁺ + 1,4-dimethoxy- benzene → Tl ⁺ + OH ⁻ + (1,4-dimethoxybenzene) ⁺	4.5 × 10 ⁸	—	RT	> 4.7	pr	Radical cation pro- duct characterised by its absorption and esr spectra.	O'Ne..75-1086
21.36	TlOH ⁺ + menaquinone	slow	—	RT	6.8	pr	—	Rao.73-1047
21.37	Tl ²⁺ + 1,2,3-trimethoxy- benzene → Tl ⁺ + (1,2,3- trimethoxybenzene) ⁺	(3.2 ± 0.3) × 10 ⁸	—	20 ± 2	4	pr	Radical cation pro- duct characterised by its absorption and esr spectra.	O'Ne..75-1171
21.38	Tl ²⁺ + 1,2,4-trimeth- oxybenzene → Tl ⁺ + (1,2,4-trimethoxybenzene) ⁺	(6.8 ± 0.7) × 10 ⁸	—	20 ± 2	4	pr	Radical cation pro- duct characterised by its absorption and esr spectra.	O'Ne..75-1171
21.39	Tl ²⁺ + 1,3,5-trimeth- oxybenzene → Tl ⁺ + (1,3,5-trimethoxybenzene) ⁺	(7.0 ± 0.7) × 10 ⁸	—	20 ± 2	4	pr	Radical cation pro- duct characterised by its absorption and esr spectra.	O'Ne..75-1171

TABLE 21. Thallium(0) and (II) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^a	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
<i>Tl^{II} chloro-complexes</i>								
21.40	$\text{Tl}^{2+} + \text{Cl}^- \rightleftharpoons \text{TlCl}^+$	$K = (6.2 \pm 0.7) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$	1 (HClO_4)	23	0	pr	Measured from effect of $[\text{Cl}^-]$ on absorption spectrum of Tl^{II} .	Dods.74-1038
		$k_f = 9 \times 10^9$	1 (HClO_4)	23	0	pr	Measured from rate of attainment of equilibrium.	Dods.74-1038
		$k_r = 1.4 \times 10^5 \text{ s}^{-1}$	1 (HClO_4)	23	0	pr		
21.41	$\text{TlCl}^+ + \text{Cl}^- \rightleftharpoons \text{TlCl}_2$	$K = (1.9 \pm 0.4) \times 10^8 \text{ dm}^3 \text{ mol}^{-1}$	1 (HClO_4)	23	0	pr	Measured from effect of $[\text{Cl}^-]$ on absorption spectrum of Tl^{II} .	Dods.74-1038
21.42	$\text{TlCl}_2 + \text{Cl}^- \rightleftharpoons \text{TlCl}_3^-$	$K = 13 \pm 3 \text{ dm}^3 \text{ mol}^{-1}$	1 (HClO_4)	23	0	pr	Measured from effect of $[\text{Cl}^-]$ on absorption spectrum of Tl^{II} .	Dods.74-1038
21.43	$\text{Tl}^{II} + \text{Tl}^{II}$ (dis)	$2k = 5.38 \times 10^9$	1	23	0	pr	$[\text{Cl}^-] = 1 \times 10^{-3} \text{ mol dm}^{-3}$	Dods.74-1038
		$2k = 5.58 \times 10^9$	1	23	0	pr	$[\text{Cl}^-] = 9.7 \times 10^{-3} \text{ mol dm}^{-3}$	Dods.74-1038
		$2k = 4.74 \times 10^9$	1	23	0	pr	$[\text{Cl}^-] = 0.1 \text{ mol dm}^{-3}$	Dods.74-1038
		$2k = 3.70 \times 10^9$	1	23	0	pr	$[\text{Cl}^-] = 0.98 \text{ mol dm}^{-3}$	Dods.74-1038
Plus data at intermediate chloride concentrations.								

^aIf the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 22. Thulium(II) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^a	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
<i>Tm²⁺</i>								
22.1	$\text{Tm}^{2+} + \text{OH}^- (\text{et})$	$(7 \pm 1) \times 10^9$	-	RT	3-6	pr	-	Pika..73-1084

^aIf the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 23. Ytterbium(II) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
<i>Yb²⁺</i> (Rate constants from pulse radiolysis studies only).								
23.1	$\text{Yb}^{2+} + \text{BrO}_3^-$	< 10 ⁸	0.015	RT	nat	pr	-	Fara.72-0065
23.2	$\text{Yb}^{2+} + \text{Co}(\text{en})_3^{2+}$	< 5 x 10 ⁸	0.06-1.0	RT	6	pr	-	Fara.73-0107
23.3	$\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_6\text{Br}^{2+}$ (et)	3.0 x 10 ⁸	0.06	RT	6	pr	-	Fara.73-0107
		1.4 x 10 ⁷	1.0	RT	6	pr	-	Fara.73-0107
		2.5 x 10 ⁷	1.0	RT	6	pr	-	Fara.73-0107
		(NaClO ₄)						
23.4	$\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_6\text{Cl}^{2+}$ (et)	4.3 x 10 ⁸	0.06	RT	6	pr	-	Fara.73-0107
		1.9 x 10 ⁷	1.0	RT	6	pr	-	Fara.73-0107
		2.3 x 10 ⁷	1.0	RT	6	pr	-	Fara.73-0107
		(NaClO ₄)						
23.5	$\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_6\text{CN}^{2+}$ (et)	3.0 x 10 ⁸	0.06	RT	6	pr	-	Fara.73-0107
23.6	$\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_6\text{F}^{2+}$ (et)	1.1 x 10 ⁷	0.06	RT	6	pr	-	Fara.73-0107
		6.0 x 10 ⁷	1.0	RT	6	pr	-	Fara.73-0107
		1.0 x 10 ⁸	1.0	RT	6	pr	-	Fara.73-0107
23.7	$\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_6\text{H}_2\text{O}^{2+}$ (et)	2.2 x 10 ⁸	0.3	RT	2	pr	-	Fara.73-0107
		6.4 x 10 ⁸	1.0	RT	2	pr	-	Fara.73-0107
		(NaClO ₄)						
23.8	$\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_6\text{N}_3^{2+}$ (et)	1.6 x 10 ⁷	0.06	RT	6	pr	-	Fara.73-0107
		2.6 x 10 ⁷	0.5	RT	6	pr	-	Fara.73-0107
		(NaClO ₄)						
23.9	$\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_6\text{NCS}^{2+}$	< 5.0 x 10 ⁴	0.5	RT	6	pr	-	Fara.73-0107
		(NaClO ₄)						
23.10	$\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_6\text{S}^{2+}$	< 5.0 x 10 ⁴	0.06	RT	6	pr	-	Fara.73-0107
23.11	$\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_6\text{OH}^{2+}$ (et)	7.7 x 10 ⁴	0.3	RT	5.5	pr	-	Fara.73-0107
		1.9 x 10 ⁷	1.0	RT	5.5	pr	-	Fara.73-0107
		(NaClO ₄)						
		2.9 x 10 ⁷	1.0	RT	5.5	pr	-	Fara.73-0107
		(NaCl)						
23.12	$\text{Yb}^{2+} + \text{Cu}^{2+}$ (et)	1.2 x 10 ⁷	0.015	RT	nat	pr	-	Fara.72-0065
23.13	$\text{Yb}^{2+} + \text{H}_2\text{O}_2$ (et)	9.1 x 10 ⁸	0.015	RT	nat	pr	-	Fara.72-0065
23.14	$\text{Yb}^{2+} + \text{IO}_3^-$ (et)	2.1 x 10 ⁸	0.015	RT	nat	pr	-	Fara.72-0065
23.15	$\text{Yb}^{2+} + \text{MnO}_4^-$ (et)	8.3 x 10 ⁷	0.015	RT	nat	pr	-	Fara.72-0065
23.16	$\text{Yb}^{2+} + \text{NO}_3^-$ (et)	4.7 x 10 ⁷	0.015	RT	nat	pr	-	Fara.72-0065
23.17	$\text{Yb}^{2+} + \text{NO}_2^-$ (et)	3.6 x 10 ⁸	0.015	RT	nat	pr	-	Fara.72-0065
23.18	$\text{Yb}^{2+} + \text{N}_3\text{O}$ (et?)	ca. 10 ⁴	0.015	RT	nat	pr	-	Fara.72-0065
23.19	$\text{Yb}^{2+} + \text{O}_3$ (et or af)	(6.3 ± 1) x 10 ⁷	0.375	RT	2	pr	-	Pika..73-1084
		6.5 x 10 ⁷	0.015	RT	nat	pr	-	Fara.72-0065
23.20	$\text{Yb}^{2+} + \text{OH}$ (et)	3 x 10 ⁹	0.015	RT	nat	pr	-	Fara.72-0065
		(3.2 ± 0.3) x 10 ⁸	0.375	RT	2	pr	-	Pika..73-1084
23.21	$\text{Yb}^{2+} + \text{Ru}(\text{NH}_3)_6\text{Br}^{2+}$ (et)	3.3 x 10 ⁷	0.06	RT	6	pr	-	Fara.73-0107
23.22	$\text{Yb}^{2+} + \text{Ru}(\text{NH}_3)_6\text{Cl}^{2+}$ (et)	1.5 x 10 ⁷	0.06	RT	6	pr	-	Fara.73-0107
		1.8 x 10 ⁸	1.0	RT	6	pr	-	Fara.73-0107
		(NaClO ₄)						
		2.8 x 10 ⁸	1.0	RT	6	pr	-	Fara.73-0107
		(NaCl)						

TABLE 23. Ytterbium(II) reactions — Continued

No.	Reaction	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹ *	<i>I</i>	<i>t</i> /°C	pH	Method	Comments	Ref.
23.23	Yb ²⁺ + Ru(NH ₃) ₆ H ₂ O ²⁺ (et)	1.0 × 10 ⁷	0.3	RT	2	pr	—	Fara.73-0107
		2.9 × 10 ⁷	1.0	RT	2	pr	—	Fara.73-0107
		3.2 × 10 ⁸	1.0 (NaClO ₄)	RT	2	pr	—	Fara.73-0107
23.24	Yb ²⁺ + Ru(NH ₃) ₆ I ²⁺ (et)	ca. 10 ⁸	0.06	RT	6	pr	—	Fara.73-0107
23.25	Yb ²⁺ + Ru(NH ₃) ₆ ²⁺ (et)	5.0 × 10 ⁶	0.06	RT	6	pr	—	Fara.73-0107
		4.5 × 10 ⁷	1.0 (NaClO ₄)	RT	6	pr	—	Fara.73-0107
		3.0 × 10 ⁸	1.0 (NaCl)	RT	6	pr	—	Fara.73-0107
23.26	Yb ²⁺ + Ru(NH ₃) ₆ OH ²⁺ (et)	1.3 × 10 ⁷	0.06	RT	6	pr	—	Fara.73-0107
		2.3 × 10 ⁷	0.3	RT	6	pr	—	Fara.73-0107
		5.0 × 10 ⁷	1.0 (NaClO ₄)	RT	6	pr	—	Fara.73-0107
		1.4 × 10 ⁸	1.0 (NaCl)	RT	6	pr	—	Fara.73-0107

*If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for 2 *k*).

TABLE 24. Zinc(I) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
24.1	$\text{Zn}^{+}_{\text{aq}}$							
24.1	$\text{Zn}^{+} + \text{BrO}_3^- (\text{et})$	$(2.1 \pm 0.3) \times 10^9$	0.08	RT	nat	pr	-	Meye.68-0855
24.2	$\text{Zn}^{+} + \text{Cd}^{2+} (\text{et?})$	$< 1 \times 10^7$	0.08	RT	nat	pr	The reason for the discrepancy between these two values is not clear.	Meye.68-0855
		8.3×10^8	-	RT	nat	pr		Baxe..66-0848
24.3	$\text{Zn}^{+} + \text{ClO}_3^-$	$< 3 \times 10^6$	0.08	RT	nat	pr	-	Meye.68-0855
24.4	$\text{Zn}^{+} + \text{Co}^{2+}$	$< 3 \times 10^6$	0.08	RT	nat	pr	-	Meye.68-0855
24.5	$\text{Zn}^{+} + \text{Co(bpy)}_3^{3+} (\text{et})$	2.6×10^9	-	RT	nat	pr	-	Baxe..72-0381
24.6	$\text{Zn}^{+} + \text{Co(en)}_3^{2+} (\text{et})$	$(2.5 \pm 0.4) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
24.7	$\text{Zn}^{+} + \text{cis-Co(en)}_2\text{Cl}_2^{+}$ (et)	$(1.91 \pm 0.3) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
24.8	$\text{Zn}^{+} + \text{trans-Co(en)}_2\text{Cl}_2^{+}$ (et)	$(2.3 \pm 0.3) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
24.9	$\text{Zn}^{+} + \text{Co(en)}_2\text{CO}_3^{+}$ (et)	$(4.7 \pm 0.7) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
24.10	$\text{Zn}^{+} + \text{cis-Co(en)}_2\text{F}_2^{+}$ (et)	$(5.4 \pm 0.8) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
24.11	$\text{Zn}^{+} + \text{Co(en)}_2\text{FH}_2\text{O}^{2+}$ (et)	$(4.7 \pm 0.7) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
24.12	$\text{Zn}^{+} + \text{cis-Co(en)}_2\text{NH}_3\text{Cl}^{2+}$ (et)	$(1.47 \pm 0.2) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
24.13	$\text{Zn}^{+} + \text{cis-Co(en)}_2\text{NH}_3\text{NO}_2^{2+}$ (et)	$(2.7 \pm 0.7) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
24.14	$\text{Zn}^{+} + \text{Co(NH}_3)_6^{3+}$ (et)	$(8.4 \pm 1.3) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0248
24.15	$\text{Zn}^{+} + \text{Co(NH}_3)_6\text{Br}^{2+}$ (et)	$(2.6 \pm 0.4) \times 10^9$	0.08	RT	4.0	pr	-	Meye.69-0428
24.16	$\text{Zn}^{+} + \text{Co(NH}_3)_6\text{Cl}^{2+}$ (et)	$(2.2 \pm 0.3) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
24.17	$\text{Zn}^{+} + \text{Co(NH}_3)_6\text{CN}^{2+}$ (et)	$(1.30 \pm 0.2) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
24.18	$\text{Zn}^{+} + \text{Co(NH}_3)_6\text{F}^{2+}$ (et)	$(8.2 \pm 1.2) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
24.19	$\text{Zn}^{+} + \text{Co(NH}_3)_6\text{fumarate}^{+}$ (et)	$(1.2 \pm 0.3) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
24.20	$\text{Zn}^{+} + \text{Co(NH}_3)_6\text{H}_2\text{O}^{2+}$ (et)	$(1.56 \pm 0.2) \times 10^9$	0.08	RT	4.0	pr	-	Meye.69-0428
24.21	$\text{Zn}^{+} + \text{Co(NH}_3)_6\text{OH}^{2+}$ (et)	$(1.10 \pm 0.2) \times 10^9$	0.08	RT	6.6	pr	-	Meye.69-0428
24.22	$\text{Zn}^{+} + \text{Co(NH}_3)_6\text{N}_3^{2+}$ (et)	$(1.49 \pm 0.2) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
24.23	$\text{Zn}^{+} + \text{Co(NH}_3)_6\text{NCS}^{2+}$ (et)	$(1.65 \pm 0.2) \times 10^9$	0.08	RT	5-6	pr	-	Meye.69-0428
24.24	$\text{Zn}^{+} + \text{Co(NH}_3)_6\text{OOCCCH}_3^{2+}$ (et)	$(5.0 \pm 0.8) \times 10^8$	0.08	RT	5-6	pr	-	Meye.69-0428
24.25	$\text{Zn}^{+} + \text{Cr}^{3+}$	$< 10^7$	-	RT	nat	pr	-	Baxe..66-0848
24.26	$\text{Zn}^{+} + \text{Cr}_2\text{O}_7^{2-} (\text{et})$	$(1.6 \pm 0.2) \times 10^{10}$	0.020*	25±2	nat	pr	-	Buxt..76-1072
24.27	$\text{Zn}^{+} + \text{Cu}^{2+} (\text{et})$	$(2.5 \pm 0.4) \times 10^8$	0.08	RT	nat	pr	-	Meye.68-0855
		$(9.5 \pm 2.0) \times 10^9$	0.4	RT	5-8	γ	Measured by competition with NO_3^- . Rate constant calculated taking $k(\text{Zn}^{+} + \text{NO}_3^-) = 2.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see entry 24.33).	Fiti70-0117
				(ZnSO_4)				
24.28	$\text{Zn}^{+} + \text{H}_2\text{O}_2 \rightarrow$ $\text{Zn}^{2+} + \text{OH}^- + \text{OH}^-$	$(1.80 \pm 0.3) \times 10^9$ $(2.3 \pm 0.2) \times 10^9$	-	RT	nat	pr	-	Meye.68-0855
			-	25±2	nat	pr	Products inferred from γ -radiolysis experiments (see ref. 73-0039).	Buxt..76-1072
	$E_a = 10.5 \pm 1.0$ kJ mol^{-1}	-	-		nat	pr	-	Buxt..76-1072

TABLE 24. Zinc(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
24.29	$\text{Zn}^+ + \text{H}_3\text{O}^+$	$< 10^4$	0.08	RT	—	pr	—	Meye..68-0855
24.30	$\text{Zn}^+ + \text{IO}_3^- (\text{et})$	$(3.6 \pm 0.5) \times 10^9$ $(1.7 \pm 0.3) \times 10^{10}$	0.08 0.4	RT RT	nat 5-8	pr γ	Measured by competition with NO_3^- . Rate constant calculated taking $k(\text{Zn}^+ + \text{NO}_3^-) = 2.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see entry 24.33).	Meye..68-0855 Fitj70-0117
24.31	$\text{Zn}^+ + \text{Ni}^{2+} (\text{et})$	$< 5 \times 10^4$ 5×10^7	0.08	RT	nat	pr	—	Meye..68-0855
24.32	$\text{Zn}^+ + \text{NO}_2^- (\text{et})$	$(2.2 \pm 0.3) \times 10^9$	0.08	RT	nat	pr	—	Baxe..66-0848
24.33	$\text{Zn}^+ + \text{NO}_3^- (\text{et})$	$(2.1 \pm 0.3) \times 10^9$	0.08	RT	nat	pr	—	Meye..68-0855
24.34	$\text{Zn}^+ + \text{N}_2\text{O} \rightarrow$ $\text{ZnO}^+ + \text{N}_2$	$< 1.3 \times 10^7$ $(3.7 \pm 0.4) \times 10^7$ $E_a = 35.5 \pm 1.4 \text{ kJ mol}^{-1}$	—	RT 25±2	nat	pr pr	Products characterised by their absorption spectrum (see ref. 76-1072) and in γ -radiolysis experiments (see ref. 73-0039).	Meye..68-0855 Buxt..76-1072
24.35	$\text{Zn}^+ + \text{O}_2 \rightarrow$ $\text{Zn}^{2+} + \text{O}_2^-$	$(2.4 \pm 0.4) \times 10^9$ 3.3×10^9	—	RT RT	nat nat	pr pr	Products characterised by their absorption spectrum (see ref. 76-1072) and reactivity with 1,4-benzoquinone (see ref. 76-1134).	Meye..68-0855 Baxe..66-0848
24.36	$\text{Zn}^+ + \text{OH} (\text{et})$	5.7×10^9 <i>ca.</i> 8×10^9	—	RT	nat	pr	No correction made for competing reaction $\text{Zn}^+ + \text{Zn}^+$.	Baxe..66-0848
			—	25±2	nat	pr	Estimated from decay of Zn^+ in the absence of OH scavengers taking into account competing reactions such as $\text{Zn}^+ + \text{Zn}^+$, $\text{Zn}^+ + \text{H}_2\text{O}_2$, $\text{OH} + \text{OH}$ etc.	Buxt..75-1027
24.37	$\text{Zn}^+ + \text{Pb}^{2+} (\text{et})$	4.0×10^8	—	RT	nat	pr	—	Baxe..66-0848
24.38	$\text{Zn}^+ + \text{Ru}(\text{bpy})_3^{2+} (\text{et})$	2.5×10^9	—	RT	nat	pr	—	Baxe..72-0381
24.39	$\text{Zn}^+ + \text{Ru}(\text{NH}_3)_6^{2+} (\text{et})$	$(2.2 \pm 0.3) \times 10^9$	0.08	RT	nat	pr	—	Navo..70-1229
24.40	$\text{Zn}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow$ $\text{Zn}^{2+} + \text{SO}_4^{2-} + \text{SO}_4^{2-}$	$(1.3 \pm 0.1) \times 10^9$	0.02*	25±2	nat	pr	—	Buxt..76-1072
24.41	$\text{Zn}^+ + \text{Zn}^+$	$2k < 8 \times 10^8$	0.4	25±2	nat	pr	Estimated from rate of decay of Zn^+ in the presence of 2-methyl-2-propanol. Major competing reaction is $\text{Zn}^+ + \cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$.	Buxt..75-1027
24.42	$\text{Zn}^+ + \text{allyl alcohol} \rightarrow$ $(\text{Zn} - \text{allyl alcohol})^+$	<i>ca.</i> 10^8	—	25±2	nat	pr	Product characterized by its absorption spectrum.	Buxt..76-1072

TABLE 24. Zinc(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	I	t/°C	pH	Method	Comments	Ref.
24.43	$\text{Zn}^+ + \text{benzophenone} \rightarrow \text{Zn}^{2+} + (\text{benzophenone})^-$	2.5×10^9	-	RT	7.0	pr	Measured in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol. Ketyl radical product characterised by its absorption spectrum.	Rao.75-1032
24.44	$\text{Zn}^+ + 1,4\text{-benzoquinone} \rightarrow \text{Zn}^{2+} + (1,4\text{-benzoquinone})^-$	$(3.0 \pm 0.6) \times 10^9$	-	25±2	5.7	pr	Measured in the presence of 1 mol dm ⁻³ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption spectrum.	Sell.76-1134
		4.8×10^9	-	RT	7.0	pr	Measured in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption spectrum.	Rao.75-1032
24.45	$\text{Zn}^+ + \text{menaquinone} \rightarrow \text{Zn}^{2+} + (\text{menaquinone})^-$	$(3.8 \pm 0.4) \times 10^9$	-	RT	7.1	pr	Measured in the presence of ca. 1 mol dm ⁻³ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption spectrum.	Rao.73-1047, Rao.75-1032
<i>Zn^I Complexes</i>								
	ZnL^+ (from $\text{ZnL}^{2+} + \text{CH}_3\text{CO}^- \text{CH}_3$), L = hematoporphyrin (ix) (no reference made to number of protons involved with complex).							
24.46	$\text{ZnL}^+ + \text{ZnL}^+ \rightarrow (\text{ZnL})_2^{2+}$	$'k' = (2.1 \pm 0.4) \times 10^8$	0.1	RT	13	pr	Unclear whether k or $2k$. Measured in the presence of 1 mol dm ⁻³ 2-propanol. Dimerisation mechanism implied from subsequent reactions (see entry 24.47) and comparison with the products of reduction of ZnL^{2+} in aprotic solvents.	Hare.74-1040
24.47	$(\text{ZnL})_2^{2+} \rightarrow \text{P}$	$17 \pm 2 \text{ s}^{-1}$	0.1	RT	13	pr	Reaction suggested to involve internal rearrangement.	Hare.74-1040
	$\text{P} \rightarrow \text{dihydroporphyrin product}$	$< 0.14 \text{ s}^{-1}$	0.1	RT	13	pr	Reaction presumed to involve splitting of dimer.	Hare.74-1040

^aIf the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for $2k$).

TABLE 25. Intramolecular electron transfer reactions for some metal complexes^a

No.	Reaction	<i>k/s</i> ⁻¹ ^b	<i>I</i>	<i>t/°C</i>	pH	Method	Comments	Ref.
<i>Electron adducts</i>								
25.1	(NH ₃) ₅ Co ^{III} (<i>p</i> -OOCC ₆ H ₄ NO ₂) ⁻ → (NH ₃) ₅ Co ^{II} (<i>p</i> -OOCC ₆ H ₄ NO ₂)	2.6 × 10 ³	-	RT	7.0	pr	-	Simi.77-1027
25.2	(NH ₃) ₅ Co ^{III} (<i>m</i> -OOCC ₆ H ₄ NO ₂) ⁻ → (NH ₃) ₅ Co ^{II} (<i>m</i> -OOCC ₆ H ₄ NO ₂)	1.5 × 10 ²	-	RT	7.0	pr	-	Simi.77-1027
25.3	(NH ₃) ₅ Co ^{III} (<i>o</i> -OOCC ₆ H ₄ NO ₂) ⁻ → (NH ₃) ₅ Co ^{II} (<i>o</i> -OOCC ₆ H ₄ NO ₂)	4.0 × 10 ⁵	-	RT	7.0	pr	-	Simi.77-1027
25.4	(NH ₃) ₅ Co ^{III} (<i>o</i> -OOCC ₆ H ₄ NO ₂ H) → (NH ₃) ₅ Co ^{II} (<i>o</i> -OOCC ₆ H ₄ NO ₂) + H ⁺	9.5 × 10 ³	-	RT	0.8	pr	-	Simi.77-1027
25.5	(NH ₃) ₅ Co ^{III} [2,4-OOCC ₆ H ₄ (NO ₂) ₂] ⁻ → (NH ₃) ₅ Co ^{II} [2,4-OOCC ₆ H ₄ (NO ₂) ₂]	3.5 × 10 ⁴	-	RT	7.0	pr	-	Simi.77-1027
25.6	(NH ₃) ₅ Co ^{III} [3,5-OOCC ₆ H ₄ (NO ₂) ₂] ⁻ → (NH ₃) ₅ Co ^{II} [3,5-OOCC ₆ H ₄ (NO ₂) ₂]	1.3 × 10 ²	-	RT	7.0	pr	-	Simi.77-1027
25.7	Cu ^{II} (gluthathione) ⁻ → Cu ^I (gluthathione)	(3.6 ± 0.3) × 10 ³	-	RT	11	pr	Rate constant independent of [Cu ^{II}]: [glutathione] ratio in range 1:2 to 1:5 and of [Cu ^{II}] in the range (1-10) × 10 ⁻⁴ mol dm ⁻³ .	Fara.76-1016
25.8	Cu ^{II} (gly) ₂ (gly) ⁻ → Cu ^I (gly) ₂	(1.7 ± 0.3) × 10 ⁴	-	RT	9	pr	Rate constant independent of [Cu ^{II}]: [gly] ratio in range 1:6 to 1:15 and of [Cu ^{II}] in the range (1-10) × 10 ⁻⁴ mol dm ⁻³ .	Fara.76-1016
<i>Hydroxyl radical adducts</i>								
25.9	(NH ₃) ₅ Co ^{III} OOCC ₆ H ₅ OH → (NH ₃) ₅ Co ^{II} OOCC ₆ H ₅ OH + H ⁺	< 10 ²	-	RT	6.0	pr	-	Cohe.71-0282
<i>Hydrogen atom adducts</i>								
25.10	(NH ₃) ₅ Co ^{III} OOCC ₆ H ₅ H → (NH ₃) ₅ Co ^{II} OOCC ₆ H ₅ H + H ⁺	< 10 ²	-	RT	1	pr	-	Cohe.71-0282

^aIntramolecular electron transfer reactions of metallo-proteins and related systems not included..^bN.B. First order rate constants.

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