

# Critical Review of Rate Constants for Reactions of Transients from Metal Ions and Metal Complexes in Aqueous Solution

**George V. Buxton**

*University of Leeds,  
Cookridge Radiation Research Centre,  
Leeds, LS16 6QB, U.K.*

**Quinto G. Mulazzani**

*Istituto di Fotochimica e Radiazioni d'Alta Energia,  
Consiglio Nazionale delle Ricerche,  
Via P. Gobetti 101, 40129 Bologna, Italy*

**Alberta B. Ross**

*Radiation Chemistry Data Center,  
Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556*

Kinetic data for transient metal species in aqueous solution have been critically reviewed. The compilation covers over 2000 measurements of rate constants involving 660 metal ions and metal complexes from Groups 4-15; lanthanides and actinides are not included. Most of the data have been obtained by the methods of pulse radiolysis or flash photolysis. Data have been collected from 500 publications through 1993.

Key words: aqueous solution; chemical kinetics; critical review; data compilation; flash photolysis; metal ions; pulse radiolysis; rate constants; transients.

## 1. Introduction.

A wealth of information on the rates of fast reactions of metal ions has been obtained in the last 30 years, but there has been no systematic review of the data since the first tables of rate constants were published in 1978.<sup>1</sup> Such information is valuable in the fields of homogeneous catalysis, radio-sensitisation and solar energy conversion.

The present compilation, which supersedes the previous one,<sup>1</sup> comprises critically reviewed rate constants for the reactions of metal ions and their complexes in aqueous solution, together with pertinent data on their spectral properties and acid dissociation constants.

Rate constants are recorded for reactions where the metal species has a transient existence. Thus the compilation contains not only those species that are inherently unstable (e.g.  $\text{Cd}^+$ ,  $\text{Tl}^{2+}$ ), but also stable ions which react so rapidly under the given conditions that they have to be generated in situ, usually by the fast time-resolved methods of pulse radiolysis or flash photolysis. To keep the compilation within reasonable bounds we have generally omitted the vast amount of data that has been obtained by the slower time-resolved method of stopped-flow. Nevertheless, a few stopped-flow data have been included when we judge them to be particularly relevant to the pulse radiolysis or flash photolysis data. Finally, a small number of

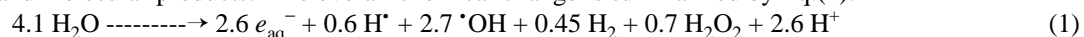
rate constants obtained from competition kinetics studies using  $\gamma$ -radiolysis and other steady-state methods are listed when they are the only available data.

A number of review articles have been published which deal with the mechanistic roles of metal ions<sup>2,3,4</sup> and the kinetic data compiled here are complementary to this mechanistic information.

## 2. Methods of Generation and Detection of Transients.

### 2.1. Pulse Radiolysis.

When moderately dilute ( $\leq 1 \text{ mol L}^{-1}$ ) aqueous solutions are exposed to ionizing radiation, such as  $^{60}\text{Co}$   $\gamma$ -rays or fast electrons from an accelerator, energy is predominantly absorbed by the solvent to create radical and molecular products. The overall chemical change is summarized by Eq.(1):



where the numbers represent the radiation chemical yields,  $G$ -values, in units of molecules per 100 eV of absorbed energy. These units are converted to SI units of  $\text{mol J}^{-1}$  by multiplying by  $1.036 \times 10^{-7}$ .

The hydrated electron,  $e_{\text{aq}}^-$ , and the hydrogen atom are powerful reducing agents and the hydroxyl radical is a strong oxidant.<sup>5</sup> Because of these properties they are very effective in bringing about one-electron changes in the oxidation states of metal ions, so radiolysis, and particularly pulse radiolysis, has been widely exploited for this purpose. Reactions (2)-(4) below are some illustrative examples of how oxidation states, which are not generally accessible by ordinary chemical means, can be generated in aqueous solution:



Data for the reactions of these free radicals with other metal species can be found in reference 6, and details of the conditions used to separate the radicals are described in reference 5.

It is sometimes desirable to convert the primary radicals of water radiolysis (reaction (1)) to secondary radicals so that redox changes can be controlled. For example, the reactions of  $^\bullet\text{OH}$  with metal ions are generally believed to result in the formation of hydroxo-adduct (e.g. reaction (4)) because simple outer-sphere electron transfer is unlikely on energetic grounds. On the other hand, outer-sphere electron transfer is more common with inorganic radicals such as  $\text{SO}_4^{\bullet-}$  and  $\text{N}_3^\bullet$ . Judicious choice of the redox agent becomes important when metal ions have ligands which can also be oxidized or reduced. Data for the reactions of these secondary radicals with metal ions and their complexes can be found in reference 7.

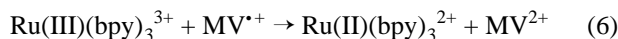
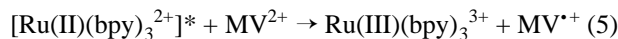
## 2.2. Photolysis.

### 2.2.1. Photoionization and Photoexcitation.

In this case energy is imparted directly to the metal ion or complex when it absorbs a photon. The result may be loss of an electron (photoionization) or excitation of an electron to a higher orbital (photoexcitation). In the first case one-electron oxidation of the metal species occurs, but in the second case the excited state may be quenched oxidatively or reductively by electron transfer to an acceptor or from a donor, respectively. Extensive kinetic data and details of these redox quenching processes can be found in reference 8.

### 2.2.2. Oxidative Quenching of Tris(2,2'-bipyridine)ruthenium(II) ion.

The oxidative quenching of  $\text{Ru(II)(bpy)}_3^{2+*}$  by 1,1'-dimethyl-4,4'-bipyridinium ion ( $\text{MV}^{2+}$ ) (reaction (5)) provides an illustrative example of the type of process that is relevant to this compilation, namely the back electron transfer reaction (6) between the oxidation product  $\text{Ru(III)(bpy)}_3^{3+}$  and the one-electron reduced quencher  $\text{MV}^{*+}$ :



We highlight reaction (6) here because its rate constant has been measured many times under a wide range of conditions of pH and ionic strength. Figure 1 shows data for  $I < 1 \text{ mol L}^{-1}$  which form a self-consistent set. The solid line is given by the empirical expression:

$$k = \{3.1 \times 10^9 [1 - \exp(-5.3I)] + 2.7 \times 10^9\} \text{ L mol}^{-1} \text{ s}^{-1} \quad (7)$$

## 3. Explanation of the Tables.

### 3.1. Scope of the Compilation.

The compilation contains data published by the end of 1993; data from a few papers received early in 1994 have also been included. The data were located through literature searches of the bibliographic database maintained by the Radiation Chemistry Data Center, and by examination of reviews.

Rate constants have not been recorded when the metal species is in the form of a macromolecule, a polymer or a colloid, or is contained in a micellar system, or in non-aqueous ( $\leq 50\% \text{ v/v H}_2\text{O}$ ) solvent. Intramolecular electron transfer reactions have also been omitted.

### 3.2. Data Selection.

In order to be included in this compilation, values of the rate constants had to be reported in published papers, including proceedings of conferences, or communicated to us in the detail appropriate for a paper in a refereed journal. Preference has been given to data obtained under well defined experimental conditions for well characterized chemical species. However, data for which the conditions are poorly defined, or even unstated, have been included when no others are available on the grounds that they are better than no data at all. The reader is given sufficient information in each entry to judge the quality of the result.

### 3.3. Uncertainties and Sources of Error.

In many cases authors have quoted the uncertainty of their data but the method of evaluation is not always specified. In others single values are reported to three significant figures. We have decided, therefore, not to report any errors and, since values of rate constants obtained in independent measurements are unlikely to have uncertainties of less than 5-10%, we have reported data to a maximum of two significant figures. In cases where the uncertainty is in the first figure or the data represent upper or lower limit values, only the first figure is recorded. Where the data have an uncertainty of more than 40-50%, they have been prefixed with '~'. When discrepant values of a rate constant have been reported we have endeavoured to judge which is correct from the information available and report only that one. In a few cases where it has not been possible to make this choice, the data have been marked to indicate that there is an unexplained discrepancy.

For some reactions there is uncertainty about the mechanism and even the structure of the reactant. Where different authors have presented different interpretations we have noted them in a comment along side the entries. In those cases where subsequent work has shown an earlier identification of the transient reactant to be in error, the correct identification has been used in the entry from the earlier work.

One of the main sources of error in measuring rate constants is the failure to take proper account of temperature. Many measurements are reported without reference to the temperature at which they were made, although the ambient temperature can vary by several °C. Where the measuring temperature is reported we have recorded it in the entry in the column headed “*t* (°C)”, otherwise this column is left blank.

Another source of error in data for reactions between charged species is due to measurement having been made at different, but unspecified, ionic strengths. Accordingly ionic strength is included in an entry only when it is specified by the authors. Lack of pH control can also be a source of error and again the pH has been recorded only if it is reported by the authors, or when it can be calculated from the *stated concentration* of H<sup>+</sup> or OH<sup>-</sup>.

### 3.4. Spectral Properties and p*K*<sub>a</sub>'s of the Metal Transients

We have collected data on the optical absorption spectra and values of ε (molar absorptivity) of transient metal species in separate tables for each metal. The species are arranged in order of ascending oxidation number. When the oxidation number is not known it is listed as, for example, Pt(II/?), to indicate that the oxidation number of the starting material is (II) but that of the product is uncertain. The entry numbers in Tables 1-28 to which the data refer are included in these tables; also reported there are values of acid dissociation constants (p*K*<sub>a</sub>).

For reactions between like species where the measured parameter is *k*/ε (or 2*k*/ε) discrepancies arise through the use of differing values of ε. If divergent values of *k* have been reported using different values of the molar absorptivity, the latter have been reassessed and values of *k* recalculated if appropriate.

### 3.5. Nomenclature.

Each chemical species has been named according to IUPAC rules whenever possible. The names of the reacting species appear as headings for the entries. An index of chemical names and synonyms is provided (Sec. 9), as well as a molecular formula index (Sec. 8), as aids in locating reactants which are present in Tables 1-28.

When it is not clear where the redox change occurs in the generation of a transient metal complex, the name used combines those of the starting material and the redox agent e.g. “Tris(5-chloro-1,10-phenanthroline)chromium(III), carboxyl radical adduct”. “Bis(ethylenediamine)platinum(II), H reaction product” and “Nitriloacetatonickelate(II), H-abstraction product”.

Abbreviations are used in writing the reactions, and these are listed separately in Sec. 4. Generally the metal appears as the first symbol, but where it is clear that a free radical bonds to a metal centre that is bonded to other ligands, the radical symbol precedes that of the metal, e.g. HOCH(CH<sub>3</sub>)Co(4,11-dieneN<sub>4</sub>)<sup>2+</sup>.

In some cases symbols of different ligands are contained in parentheses for the sake of clarity, e.g. HOCH<sub>2</sub>CoHEDTA(H<sub>2</sub>O)<sup>-</sup>.

A roman numeral is used to indicate the oxidation state of the metal when it is not obvious from the formula of the complex. Water of hydration has generally been omitted from the formulae. In some cases, free radical species are enclosed in square brackets with a superscripted dot for the sake of clarity, e.g. [Co(bpy)<sub>2</sub>(bpyOH)]<sup>3+</sup> and [2-CH<sub>3</sub>NQ]<sup>•-</sup>.

## 4. List of Abbreviations and Symbols

### *Methods and Other Symbols*

c.k.	competition kinetics
condy.	conductivity
d.k.	decay kinetics
$\Delta G^\ddagger$	free energy of activation
$\Delta H^\ddagger$	enthalpy of activation
$\Delta S^\ddagger$	entropy of activation
$\epsilon$	extinction coefficient (molar absorptivity)
$E_a$	activation energy
e.d.	discharge
esr	electron spin resonance
f.p.	flash photolysis
f.p./rq	flash photolysis/reductive quenching
f.p./oq	flash photolysis/oxidative quenching
f.p./pi	flash photolysis/photoionization
$G$	radiation yield (molecules per 100 eV)
$\gamma$ -r.	gamma radiolysis
$I$	ionic strength
$K$	equilibrium constant
$k$	specific rate of the forward reaction
$k_r$	specific rate of the reverse reaction
OQ	oxidative quencher
$pK_a$	negative logarithm of the acid dissociation constant, e.g. where $AH + H_2O \rightleftharpoons A^- + H_3O^+$
phot.	photolysis
p.b.k.	product buildup kinetics
p.r.	pulse radiolysis
RQ	reductive quencher
satd.	saturated
soln.	solution
s.f.	stopped flow

### *Chemical Species and Ligands*

ABTS	2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate)
Ac	acetyl
acac	acetylacetonato (2,4-pentanedionato)
Ala	alanine
aneN <sub>4</sub>	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
[13]aneN <sub>4</sub>	1,4,7,10-tetraazacyclotridecane
[15]aneN <sub>4</sub>	1,4,8,12-tetraazacyclopentadecane
[16]aneN <sub>5</sub>	1,4,7,10,13-pentaazacyclohexadecane
AQ	9,10-anthraquinone
AZAcapten	8-methyl-1,3,13,16-tetraaza-6,10,19-trithiabicyclo[6.6.6]eicosane
bpm	2,2'-bipyrimidine
bpy	2,2'-bipyridine
4,4'-bpy	4,4'-bipyridine
bpz	2,2'-bipyrazine
bth	2,2'-bithiazole
BuOH	butanol

<i>tert</i> -BuOH	<i>tert</i> -butyl alcohol (2-methyl-2-propanol)
chxn	<i>trans</i> -1,2-cyclohexanediamine
Cp	cyclopentadienyl
cyclam	1,4,8,11-tetraazacyclotetradecane
CysSH	cysteine
diamsar	1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
dien	diethylenetriamine
4,11-dieneN <sub>4</sub>	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
4,13-dieneN <sub>4</sub>	2,2,4,11,11,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-4,13-diene
4,14-dieneN <sub>4</sub>	5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene
10,13-dieneN <sub>4</sub>	11,13-dimethyl-1,4,7,10-tetraazacyclotetradeca-10,13-diene
diHOamsar	1,8-bis(hydroxyamino)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
dinosar	1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
DMCH	6,7-dihydro-5,8-dimethyldibenzo[ <i>b,j</i> ][1,10]phenanthroline
dmg	dimethylglyoxime
DMSO	dimethyl sulfoxide
DP	deuteroporphyrin
dppz	dipyrido[3,2- <i>a</i> :2',3'- <i>c</i> ]phenazine
DQ	duroquinone
DTPA	diethylenetriaminepentaacetate ion
EDDA	ethylenediaminediacetate ion
EDTA	ethylenediaminetetraacetate ion
en	ethylenediamine
Et <sub>4</sub> dien	tetraethyldiethylenetriamine
EtOH	ethanol
Fc	ferrocene
HEDTA	<i>N</i> -(2-hydroxyethyl)- <i>N,N,N'</i> -ethylenediaminetriacetate ion
HypO <sup>-</sup>	hydroxyprolinato
Gly <sup>-</sup>	glycinato
IDA	iminodiacetate ion
Im	imidazole
In	indole
isn	isonicotinamide
mbpy	1-methyl-4,4'-bipyridinium
Me	methyl
Me <sub>6</sub> [14]aneN <sub>4</sub>	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
Me <sub>4</sub> cyclam	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
Me <sub>10</sub> cyclam	1,4,8,11-decamethyl-1,4,8,11-tetraazacyclotetradecane
MeNH <sub>2</sub> [18]aneN <sub>6</sub>	8-Amino-8-methyl-1,3,6,10,13,15-hexaazatricyclo[13.1.1.1 <sup>13,15</sup> ]octadecane
MeNO <sub>2</sub> [18]aneN <sub>6</sub>	8-Methyl-8-nitro-1,3,6,10,13,15-hexaazatricyclo[13.1.1.1 <sup>13,15</sup> ]octadecane
MeOH	methanol
Me <sub>2</sub> pyo[14]aneN <sub>4</sub>	α-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene
Me <sub>2</sub> pyo[14]hexaeneN <sub>4</sub>	α-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,6,11,13,15-hexaene
Me <sub>2</sub> pyo[14]trieneN <sub>4</sub>	α-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene
Me <sub>4</sub> tetraeneN <sub>4</sub>	1,3,8,10-tetraamethyl-1,4,8,11-tetraazacyclodeca-1,3,8,10-tetraene
MV <sup>2+</sup>	1,1'-dimethyl-4,4'-bipyridinium (methyl viologen)
na	nicotinamide
NAD	nicotinamide adenine dinucleotide
NTA	nitrilotriacetate ion
NQ	naphthoquinone
PFP	tetra( <i>N</i> -methylisonicotinamidophenyl)phosphine
Ph	phenyl
phen	1,10-phenanthroline

pm	pyrimidine
PP	protoporphyrin
PrOH	propanol
pts	trisulfophthalocyanine
py	pyridine
pytda	2-(1,2,4-thiadiazol-5-yl)pyridine
pyth	2-(2-thiazolyl)pyridine
pz	pyrazine
Q	1,4-benzoquinone
QH <sub>2</sub>	hydroquinone
sar	3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane
SDS	sodium dodecylsulfate
sep	1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane
tacn	1,4,7-triazacyclononane
TAP	1,4,5,7-tetraazaphenanthrene
TAPP	tetra(4-trimethylammoniophenyl)porphine
TCP	tetra(4-carboxyphenyl)porphine
TCP	tetra(2,6-dichloro-3-sulfonatophenyl)porphine
TEOA	triethanolamine
terpy	2,2':2',2''-terpyridine
tetraen	tetraethyldiethylenetriamine
tetraeneN <sub>4</sub>	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene
tetren	tetraethylenepentamine
TFPPS	tetra(2-fluoro-3-sulfonatophenyl)porphine
tim	2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene
TMpyP	tetra(1-methyl-4-pyridyl)porphine
2-TMpyP	tetra(1-methyl-2-pyridyl)porphine
3-TMpyP	tetra(1-methyl-3-pyridyl)porphine
TPP	tetraphenylporphine
TPPS	tetra(4-sulfonatophenyl)porphine
TpyP	tetra(4-pyridyl)porphine
2-TpyP	tetra(2-pyridyl)porphine
3-TpyP	tetra(3-pyridyl)porphine
trien	triethylenetetramine
TrpH	tryptophan
tspc	3,10,17,24-tetrasulfophthalocyanine
TTP	tetra(4-methylphenyl)porphine
TxOH <sup>-</sup>	6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylate ion (Trolox C anion)
TyrOH	tyrosine
TZP	tetra[4- <i>N</i> -(3-sulfonatopropyl)pyridyl]porphine
U	uracil

## 5. Acknowledgements

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