

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

EQUILIBRIUM CONSTANTS OF
LIQUID-LIQUID DISTRIBUTION
REACTIONS

INTRODUCTION, AND PART 1:
ORGANOPHOSPHORUS EXTRACTANTS

Compiled by

Y. MARCUS, A. S. KERTES and E. YANIR

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON EQUILIBRIUM DATA

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INTRODUCTION

1. General introduction

The Commission on Equilibrium Data of the Analytical Chemistry Division of the International Union of Pure and Applied Chemistry decided in 1963 to supplement the tables of *Stability Constants**, then going into a second edition, with constants for distribution equilibria of metal complexes. Extraction equilibria of both chelates and non-chelating systems were to be included. It soon transpired that the job of compiling these data was rather large, and also that the necessarily different organization of the material would make impractical the indiscriminate inclusion of these data in the Supplement to the second edition of *Stability Constants*, planned for publication in 1968 (later delayed to 1971). It was then decided that D. Dyrssen and H. Freiser would take care of the compilation of data for chelating systems, while Y. Marcus and A. S. Kertes would do the same for non-chelating ones. The latter authors obtained for this purpose financial assistance from the United States National Bureau of Standards, which was very helpful in advancing the work vigorously.

An examination of the literature published in 1965 revealed that about three quarters of the relevant data deal with organophosphorus extractants. This was assumed to be the case for the period between 1955 and 1967, and also earlier these extractants constituted a large portion of those reported. Thus, a compilation of these data would be a significant portion of the whole effort, and it was decided to prepare it as a separate publication, in order to avoid finished work being unduly held up.

2. Scope

Very few papers with equilibrium constants for distribution reactions involving metal complexes were published prior to 1947. The literature search for the compilation therefore generally covers the period 1947-1968 inclusive. Some more recent publications (1969) are also included. For certain extractants, however, such as ethers and esters, significant publications are known to predate 1947. For these the literature search has started at as early a date as deemed suitable in each case.

The main access to the information is through *Chemical Abstracts*, complemented by data obtained from *Nuclear Science Abstracts*, *Citation Index*, review articles, conference proceedings and the references of the papers scanned. Following the practice in the compilation of *Stability Constants*, it has been the policy of the compilers to attempt to read each paper in the original, after it had been located in one of the sources listed above.

* *Stability Constants of Metal-Ion Complexes*, Second Edition, compiled by L. G. Sillén (inorganic ligands) and A. E. Martell (organic ligands), The Chemical Society, London, Special Publication No. 17 (1964).

It was decided that the compilation would be of greatest utility if it were limited to include only commonly used extractants, rather than try to include every system that has been reported in the literature. The aim, thus, is to obtain all the available information on a selected number of systems. The authors' judgement is hereby involved, and they will welcome any suggestions of glaring omissions. It was found that for several organophosphorus extractants, although used in practical extraction work, no equilibrium constants have been reported, nor could they readily be obtained by the compilers from the original publications. Thus, the list of extractants which are actually presented in the Tables is considerably shorter than the list which serves as the basis for the literature search. This latter list constitutes Appendix I of this Introduction.

Distribution equilibria involving metal ions often depend on other equilibria, involving the extractant and/or the inorganic ligand accompanying the metal ion. Thus, the partition of water, of acids and of the extractant itself are important reactions. So are also the equilibrium data on ionic dissociation of the extractant (mainly in the aqueous phase), its dimerization or further aggregation, and its association with other solvents. Therefore, in addition to the heterogeneous equilibria of the metal distribution, other heterogeneous and homogeneous equilibria which are relevant to the overall extraction reaction are also included in the compilation.

3. General arrangement

The great success of *Stability Constants* has encouraged the authors to follow its general arrangement as far as practical. The deviation from that practice is dictated by the nature of the systems dealt with in this compilation. The main difference devolves on the participation of *two* reactants associating with the metal ion: the extractant and the inorganic ligand, rather than the *one* reactant involved in the equilibria of chelate systems. In distribution equilibria, of course, it is the extractant which is of major interest, while the inorganic ligand is often of secondary importance only. Therefore, the primary classification of the present Tables is according to the extractants, and for each, after the equilibria which do not involve a ligand are dealt with, subclassification is made according to the ligands. For neutral* extractants an anionic ligand is required for charge neutralization when the metal ion is extracted. Acidic extractants usually act themselves as the anionic ligands, though under certain conditions they act as solvating extractants as well. It is then difficult to generalize about the role of the potentially involved inorganic anion. In all cases, therefore, distribution reactions are subclassified under the inorganic anion present, which belongs to the major constituent of the aqueous phase, whether or not it actually acts as a ligand.

The information given for each distribution system is the chemical reaction, the equilibrium constant, the temperature, the composition of the aqueous phase, the composition of the organic phase and the reference to the

* Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, London (1969).

EQUILIBRIUM CONSTANTS OF LIQUID-LIQUID DISTRIBUTION REACTIONS

original paper. Contrary to the practice in *Stability Constants* the method of measurement is not given, since in the great majority of cases it simply is the analysis of the equilibrium phases, often radiometrically. The literature referred to follows the compilation of the data for each extractant separately.

4. Order of extractants, ligands and metal ions

Since only a limited number of extractants (about ninety) are considered in these Tables, they were ordered according to their chemical nature and the chemistry of the extraction reaction, as listed in Appendix 1, rather than according to their empirical formulae, as used in the organic ligand section of *Stability Constants*.

For each extractant, the following equilibria are listed in the order given, as far as they apply and as far as data are available.

- (a) Distribution of the extractant.
- (b) Dissociation of the extractant.
- (c) Dimerization and further aggregation of the extractant.
- (d) Reactions of the extractant with diluents and other solvents.
- (e) Extraction of water.
- (f) Homogeneous equilibria of the extractant with metal ions.
- (g) Extraction of metal ions with the extractant as the sole ligand.
- (h) Extraction of metal ions with other ligands (potential or actual).

The ligands in (h) are ordered according to the order established in *Stability Constants*, with organic ligands, if present (other than the extractant), following the inorganic ligands. The metal ions mentioned in (f), (g) and (h) follow the order established in *Stability Constants*, Inorganic Section.

5. Reactions

Distribution equilibria usually involve two reactants with the metal ion, in various proportions, and these may be in different states of protonations. Therefore, a system of subscripts and generalized symbols, such as β_2 or $\star K_3$ used in *Stability Constants*, cannot cope with the complexities of these equilibria. In order to avoid uncertainties and ambiguities, the actual equilibrium reaction to which the equilibrium constant pertains has been given in each case. The following symbolism is used.

S represents the extractant if it does not dissociate ionically, otherwise it is written as HS, SA, etc. as is appropriate. The symbol used is given at the head of the table near the name of the extractant.

A represents the inorganic ligand in the solution, and is defined in each subsection of each table, near the name of the anion it represents.

M represents the metal ion appearing in the first column of the table.

Other reactants are represented by their chemical formula, except that other extractants participating in the equilibria are represented either by S', defined in the next line below the reaction, for those extractants used only occasionally, or by their common abbreviation. These abbreviations are listed in Appendix 2. [Cf. also Y. Marcus, E. Hoffmann and A. S. Kertes, *J. Inorg. Nucl. Chem.* 33, 853 (1971).]

A bar over chemical symbols signifies that this species is in the organic phase.

6. Equilibrium constants

Under the heading 'log K ' are given the logarithms to base ten of the equilibrium constants for the reactions listed. The molar (mole litre⁻¹) concentration scale is understood, and exceptions are specifically noted. The following convention is used to express the limits of confidence of these entries (as estimated by the authors of the original papers). If the relative error in the constant is ≤ 0.07 in log K , two figures are given after the decimal point; if it is > 0.07 but ≤ 0.2 , one figure after the decimal point is given; and if it is beyond that, the two extreme limits are listed. Following *Stability Constants*, '?' denotes the authors' doubt of the values given in the source, while '(?)', used very occasionally, denotes the compilers' doubt. Its absence, naturally, does not constitute endorsement by the compilers.

In a few cases a reaction has been examined, but found to proceed only to a completely negligible extent. Then, $K \sim 0$ is used to express this finding.

In some cases the temperature variation of the equilibrium constants enabled the authors of the original papers to calculate the enthalpy and the entropy changes of the reactions quoted. These, with the Gibbs free energy changes, are given in kcal mol⁻¹ for ΔH and ΔG , and cal deg⁻¹ mol⁻¹ for ΔS , for the reaction as written. No attempt was made to assess the precision of these data, and they are reproduced as published.

7. Temperature

Under this heading are given the temperatures in °C at which the distribution reactions were studied. 'rt' denotes room temperature, and '?' is used if the value was not found by the compilers. Unfortunately, this is the case for distribution equilibria more often than for homogeneous complex formation studies.

8. Conditions

Under the heading 'aq.' appears the composition of the aqueous phase, which sometimes is kept as a constant ionic medium, e.g. a constant molality. The salt or acid present is designated (as HA, etc., if the ligand A⁻ has been defined), and its molar concentration is given. If the ionic strength has been kept constant at a given value, this is given, preceded by $\mu =$. Often the composition of the aqueous phase has been varied considerably, and then the range, or the upper value of the concentration is given. In dilute aqueous solutions, the pH is given where appropriate. The figures given pertain, in every case, to the 'initial' composition of the aqueous phase, and not to its equilibrium composition. The latter is generally very difficult to derive from the published data, while the former permits, at least, reproduction of the experimental conditions to which the equilibrium data pertain.

The entries under the heading 'org.' give the relevant information for the composition of the organic phase. The diluent used is specified, and the molar concentration, or concentration range (or wt. per cent if so given by the authors), of the extractant in the diluent is given. The nature and concentration of any additives used in the organic phase are also given. The neat, undiluted extractant, when used as the organic phase, is designated by S undil. or 100% S. Again, the 'initial' rather than the equilibrium composition of the

EQUILIBRIUM CONSTANTS OF LIQUID-LIQUID DISTRIBUTION REACTIONS

organic phase is specified.

9. References

The entries under this heading follow the usage of *Stability Constants*. Each reference is characterized by two figures denoting the year of publication, a capital letter denoting the (first) author's name, and a lower-case letter, distinguishing references with the same year and capital letter. The following conventions are used:

64D conclusions of 64D from data in 64D or other sources

64D, 67D conclusions and data of 64D and of 67D are substantially the same

64D/57D conclusions of 64D from data in 57D

/64D conclusions of compiler from data in 64D

APPENDIX 1. LIST OF EXTRACTANTS FOR WHICH THE LITERATURE WAS SEARCHED FOR DISTRIBUTION EQUILIBRIUM CONSTANTS

I Organophosphorus extractants

Phosphoric and pyrophosphoric acids

Dibutylphosphoric acid $(C_4H_9O)_2POOH$

Bis(2-ethylhexyl)phosphoric acid $(2-C_2H_5-C_6H_{12}O)_2POOH$

Diisopentylphosphoric acid $(2-CH_3-C_4H_9O)_2POOH$

Diocetylphosphoric acid $(C_8H_{17}O)_2POOH$

Butylphosphoric acid $(C_4H_9O)PO(OH)_2$

2-Ethylhexylphosphoric acid $(2-C_2H_5-C_6H_{12}O)PO(OH)_2$

Diocetylpyrophosphoric acid* $(C_8H_{17}O)P(O)(OH)OP(O)(OH)(OC_8H_{17})_2$

Di-*p*-chlorophenylphosphoric acid $(p-ClC_6H_4O)_2POOH$

Phosphonic and phosphinic acids

Diisopentylphosphonic acid* $(2-CH_3-C_4H_9O)(2-CH_3-C_4H_9)POOH$

Diocetyl methylenediphosphonic acid*
 $(C_8H_{17}O)P(O)(OH)CH_2P(OC_{18}H_{17})OOH$

Phosphates

Tri-*n*-butyl phosphate $(n-C_4H_9O)_3PO$

Triisobutyl phosphate $(i-C_4H_9O)_3PO$

Tris(butoxyethyl)phosphate* $(C_4H_9OC_2H_4O)_3PO$

Tri-*n*-octyl phosphate $(C_8H_{17}O)_3PO$

Tetrabutyl pyrophosphate* $(C_4H_9O)_2P(O)OP(O)(OC_4H_9)_2$

*Equilibrium constants searched for, but none found.

Phosphonates, phosphinates

Dibutyl butylphosphonate $(C_4H_9O)_2(C_4H_9)PO$
 Dibutyl phenylphosphonate* $(C_4H_9O)_2(C_6H_5)PO$
 Diisopentyl methylphosphonate $(2-CH_3-C_4H_9O)_2(CH_3)PO$
 Tetraethyl methylenediphosphonate* $(C_4H_9O)_2P(O)CH_2P(O)(OC_2H_5)_2$
 Tetrahexyl methylenediphosphonate* $(C_6H_{13}O)_2P(O)CH_2P(O)(OC_6H_{13})_2$
 Octyl dioctylphosphinate $(C_8H_{17}O)(C_8H_{17})_2PO$

Phosphine oxides

Tributylphosphine oxide $(C_4H_9)_3PO$
 Trioctylphosphine oxide $(C_8H_{17})_3PO$
 Triphenylphosphine oxide $(C_6H_5)_3PO$
 Methylene bis(di-hexylphosphine) oxide $CH_2[P(C_6H_{13})_2(O)]_2$
 Methylene bis(di-2-ethylhexylphosphine) oxide*
 $CH_2[P(2-C_2H_5-C_6H_{13})_2(O)]_2$

Sections II to V to be published subsequently

II Amines, ammonium and other 'onium' compounds

Amines

Primene JMT
 Amberlite LA-2
 Diisononylamine $(i-C_9H_{19})_2NH$
 Didecylamine $(C_{10}H_{21})_2NH$
 Trioctylamine $(n-C_8H_{17})_3N$
 Triisooctylamine $(i-C_8H_{17})_3N$
 Trinonylamine $(C_9H_{19})_3N$
 Tridodecyl (lauryl) amine $(C_{12}H_{25})_3N$
 Alamine 336 $(C_{8-10}H_{17-21})_3N$

Quaternary ammonium and other 'onium' salts

Aliquat 336 $(C_{8-10}H_{17-21})_3(CH_3)N^+$
 Trilaurylmethylammonium $(C_{12}H_{25})_3(CH_3)N^+$
 Dimethyl octyl benzyl ammonium $(C_8H_{17})(C_6H_5CH_2)(CH_3)_2N^+$
 Dimethyl hexadecyl benzyl ammonium $(C_{16}H_{33})(C_6H_5CH_2)(CH_3)_2N^+$
 Tetraheptylammonium $(C_7H_{15})_4N^+$
 Tetraphenylarsonium $(C_6H_5)_4As^+$
 Tetraphenylphosphonium $(C_6H_5)_4P^+$

III Carboxylic and sulfonic acids, phenols

Octanoic acid (caprylic) $C_7H_{15}COOH$
 Decanoic acid (capric) $C_9H_{19}COOH$

* Equilibrium constants searched for, but none found.

EQUILIBRIUM CONSTANTS OF LIQUID-LIQUID DISTRIBUTION REACTIONS

Dodecanoic acid (lauric) $C_{11}H_{23}COOH$

Naphthenic acid(s)

Dodecylbenzene sulfonic acid $C_{12}H_{23}C_6H_4SO_3H$

Dinonylnaphthalene sulfonic acid $(C_9H_{19})_2C_{10}H_5SO_3H$

p-Cumyl phenol $p-(i-C_3H_7)C_6H_4-C_6H_4OH$

4-sec-Butyl-2-(α -methylbenzyl)phenol

$4-(sec-C_4H_9)_2-(C_6H_5CH(CH_3))C_6H_3OH$

IV Inert solvents

Heptane C_7H_{16}

Octane C_8H_{18}

Decane $C_{10}H_{22}$

Kerosene $C_{12-20}H_{26-42}$

Cyclohexane cyc- C_6H_{12}

Benzene C_6H_6

Toluene $C_6H_5CH_3$

Xylene $C_6H_4(CH_3)_2$

Carbon tetrachloride CCl_4

Chloroform $CHCl_3$

1,1,2-Trichloroethane Cl_2CHCH_2Cl

Chlorobenzene C_6H_5Cl

V Monofunctional oxygen derivatives

Alcohols

n-Butanol $n-C_4H_9OH$

iso-Butanol $i-C_4H_9OH$

iso-Pentanol (isoamyl alcohol) $(2-CH_3)C_4H_8OH$

Benzyl alcohol $C_6H_5CH_2OH$

n-Octanol $n-C_8H_{17}OH$

Ethers

Diethyl ether $(C_2H_5)_2O$

Di-n-propyl ether $(n-C_3H_7)_2O$

Diisopropyl ether $(i-C_3H_7)_2O$

Di-n-butyl ether $(n-C_4H_9)_2O$

β,β' -Dichlorodiethyl ether $(ClC_2H_4)_2O$

Dibutylcellosolve $C_4H_9OC_2H_4OC_4H_9$

Dibutyl carbitol $(C_4H_9OC_2H_4)_2O$

Diisopropyl carbinol $(i-C_3H_7)_2CHOH$

Pentaether $C_4H_9(OC_2H_4)_4OC_4H_9$

Ketones

Diisopropyl ketone $(i-C_3H_7)_2CO$

Methyl isobutyl ketone $CH_3CO-i-C_4H_9$

Cyclohexanone cyc- $(CH_2)_5C(O)-$

1-Methylcyclohexanone cyc- $(CH_2)_4CH(CH_3)C(O)-$

Esters

Ethyl acetate $C_2H_5OCOCH_3$
 n-Butyl acetate $n-C_4H_9OCOCH_3$
 Isopentyl acetate $i-C_5H_{11}OCOCH_3$

Others

Triphenylarsine oxide $(C_6H_5)_3AsO$
 Trioctylarsine oxide $(C_8H_{17})_3AsO$
 Nitrobenzene $C_6H_5NO_2$
 Nitromethane CH_3NO_2

APPENDIX 2. LIST OF ABBREVIATIONS

BDB'P	butyl dibutylphosphinate
B(DHx'PO)M'	methylene bis(diethylphosphine oxide)
DAM'P	diisopentyl methylphosphonate
DBB'P	dibutyl butylphosphonate
DBE	dibutyl ether
D(pCl-Ph)Ph'P	di-(p-chlorophenyl) phenylphosphonate
DiPE	diisopropyl ethers
DPhPh'P	diphenyl phenylphosphonate
EDB'P	ethyl dibutylphosphinate
(H)iAM'P	isopentyl methylphosphonic acid
(H)DiAP	diisopentylphosphoric acid
(H)DBP	dibutylphosphoric acid
(H)DpCl-PhP	di-p-chlorophenylphosphoric acid
(H)DE-HP	di-(2-ethylhexyl)phosphoric acid
(H)DiPP	diisopropylphosphoric acid
(H)OPh'P	octyl phenylphosphonic acid
HxOH	hexanol
MiBC	methyl isobutyl carbitol
MiBK	methyl isobutyl ketone
OcOH	octanol
TBP	tributyl phosphate
TiBP	triisobutyl phosphate
TB'PO	tributylphosphine oxide
TH'PO	triethylphosphine oxide
TOA	trioctylamine
TOP	trioctyl phosphate
TO'PO	trioctylphosphine oxide
TPP	tripropyl phosphate
TPhP	triphenyl phosphate

CONTENTS

Introduction

1. General introduction	vii
2. Scope	vii
3. General arrangement	viii
4. Order of extractants, ligands and metal ions	ix
5. Reactions	ix
6. Equilibrium constants	x
7. Temperature	x
8. Conditions	x
9. References	xi
Appendix 1 (List of extractants)	xi
Appendix 2 (Abbreviations)	xiv

Tables

Phosphates

1. Tri-n-butyl phosphate (TBP)	1
2. Triisobutyl phosphate (TiBP)	70
3. Trioctyl phosphate (TOP)	71

Phosphoric and pyrophosphoric acids

1. Dibutylphosphoric acid ((H)DBP)	72
2. Diethylhexylphosphoric acid ((H)DE-HP)	101
3. Diisopentylphosphoric acid ((H)DiAP)	123
4. Dioctylphosphoric acid ((H)DOP)	125
5. Mono-butylphosphoric acid ((H ₂)MBP)	130
6. Mono-(2-ethylhexyl)phosphoric acid ((H ₂)ME-HP)	131
7. Di- <i>p</i> -chlorophenylphosphoric acid ((H)DpCl-PhP)	132

Phosphonates and phosphinates

1. Dibutyl butylphosphonate (DBB'P)	137
2. Diisopentyl methylphosphonate (DAM'P)	144
3. Octyl dioctylphosphinate (ODO'P)	150

Phosphine oxides

1. Tributylphosphine oxide (TB'PO)	151
2. Trioctylphosphine oxide (TO'PO)	157
3. Triphenylphosphine oxide (TPh'PO)	166
4. Methylene bis(dihexylphosphine oxide) B(DHx'PO)M'	168

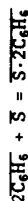
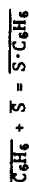
Extractant Class: Phosphates
Extractant Class: Phosphates

Extractant: Tri-n-butylphosphate (TBP), S

Dimerization



Reactions with diluents and other solvents



S 0.01 in cyclohexane

S 0.01 in dodecane

S 0.01-1.0 in hexane

0.1<S<0.5 in CS₂

0.1<S<0.7 in CCl₄

0.5<S<1.0 in CS₂

0.7<S<1.2 in CCl₄

S 0-100% in benzene

S 0-100% in CCl₄

—

—

—

H₂O

H₂O

H₂O

H₂O

—

—

22

22

22

25

25

25

25

?

?

?

0.39

0.41

0.46

0.95

0.54

0.53

4.2

-1.30
(mole fract.)

-0.7
(mole fract.)

-1.0
(mole fract.)

68P

68P

67P

68R

68R

68R

68R

63Rb

63Rb

63Rb

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Reactions with diluents and other solvents (cont.)						
	$2\text{CHCl}_3 + \text{S} = \text{S} \cdot 2\text{CHCl}_3$	-0.8 (mole fract.)	?			63Rb
	$\text{CHCl}_3 + \text{S} = \text{S} \cdot \text{CHCl}_3$	0.8 (mole fract.)	20	—	S < 0.7 in CHCl_3	62Pa
	$\text{CHCl}_3 + \text{S} = \text{S} \cdot \text{CHCl}_3$	0.78 (mole fract.)	?	—	S 0-100% in CHCl_3	63Rb
	$2\text{CHCl}_3 + \text{S} = \text{S} \cdot 2\text{CHCl}_3$	1.20 (mole fract.)	?	—		63Rb
	$\text{CHCl}_3 + \text{S} = \text{S} \cdot \text{CHCl}_3$	0.0	?	—	S 0-1.6 CDCl_3	64P
	$\text{ClCH}_2\text{CH}_2\text{Cl} + \text{S} = \text{S} \cdot \text{ClCH}_2\text{CH}_2\text{Cl}$	-0.22 (mole fract.)	20	—	S > 0.7 in $\text{ClCH}_2\text{CH}_2\text{Cl}$	62Pa
	$(\text{H})\text{DBP} + \text{S} = (\text{H})\text{DBP} \cdot \text{S}$	1.93	25	H_2SO_4 0.1	S + (H)DBP in benzene	68La
		2.8	25	HNO_3 1.0	S < 3.43 + (H)DBP 10^{-4} in CCl_4	60Da
		2.87	25	HNO_3 0.1	(H)DBP < 0.5 + S in CCl_4	64D/57D, 60Da
		2.7	?	HNO_3 0.1 + NaNO_3 0.9	(H)DBP < 0.03 + S < 0.5 in CCl_4	67K
		2.63	25	H_2SO_4 0.1	(H)DBP + S in CCl_4	66L, 67L, 68La
		1.60	25	HClO_4 1.0	S < 0.4 in CHCl_3 + (H)DBP $3.3 \cdot 10^{-5}$	57D

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Reactions with diluents and other solvents (cont.)						
		1.19	25	HNO ₃ 0.1	(H) DBP < 0.5 + S in CHCl ₃	64D/ 57D, 60Da
		3.77	25	HNO ₃ 0.1	(H) DBP < 0.5 + S in hexane	64D/ 57D, 60Da
		2.90	25	H ₂ SO ₄ 0.1	(H) DBP + S in hexane	66L, 67L, 68La
		2.83	25	HNO ₃ 1.0	S < 0.3 + (H) DBP 10 ⁻⁵ in kerosene	59H
		4.2 to 3.1	?	HNO ₃ 1.0	(H) DBP 10 ⁻⁵ + TBP 0.7-0.3 in kerosene	64H/59Hc
	$\frac{1}{2} [(H) DBP]_2 + \bar{S} = (H) DBP \cdot \bar{S}$	-0.38	25	HCl 0.3, 0.5	(H) DBP < 0.001 + S < 0.3 in benzene	67M
		-0.4	25	HNO ₃ 0.1	(H) DBP < 10 ⁻⁴ + S 0.01-3.4 in CCl ₄	63B/60Da
		0.11	25	HCl 0.3, 0.5	(H) DBP < 0.008 + S < 0.3 in heptane	67M
		-0.05	25	HNO ₃ 0-15	(H) DBP 10 ⁻⁶ -0.05 + S 0.1-100% in kerosene	63B/59H
	$(H) DBP + 2\bar{S} = (H) DBP \cdot 2\bar{S}$	3.30	25	H ₂ SO ₄ 0.1	(H) DBP < 0.1 + S < 1.0 in hexane	66L, 67L, 68La
	$[(H) DBP]_2 + \bar{S} = [(H) DBP]_2 \cdot \bar{S}$	0.2	25	HNO ₃ 0.1	(H) DBP < 10 ⁻⁴ + S 0.01-3.4 in CCl ₄	63B/60Da

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
<u>Reactions with diluents and other solvents (cont.)</u>						
	$\frac{[(H)DBP]_2 + \bar{S}}{[(H)DBP]_2 \cdot S}$	-0.75	25	HNO ₃ 0.1	(H)DBP 0.5 + S in CCl ₄	64D/ 57D, 60Da
		0.22	25	H ₂ SO ₄ 0.1	(H)DBP<0.1 + S 0.01-0.1 in CCl ₄	67L, 68La
		-0.5	25	HNO ₃ 0.1	(H)DBP 0.5 in CHCl ₃	64D/ 57D, 60Da
		1.08	25	HNO ₃ 0.1	(H)DBP<0.5 + S in hexane	64D/ 57D, 60Da
		1.23	25	H ₂ SO ₄ 0.1	(H)DBP<0.1 + S 0.01-0.1 in hexane	66L, 67L, 68L
		0.6	25	HNO ₃ 0-15	(H)DBP 10 ⁻⁶ -0.05 + S 0.1-100% in kerosene	63B/59H
	$\frac{(H)DE-HP + \bar{S}}{(H)DE-HP \cdot S}$	0.78	25	HClO ₄ 0.2	(H)DE-HP 1.4 · 10 ⁻³ + S<1.3 in benzene	66S
		1.12	25	HClO ₄ 0.2	(H)DE-HP 1.4 · 10 ⁻³ + S<1.3 in CCl ₄	66S
		0.9	25	HNO ₃ 0.1	(H)DE-HP<7 · 10 ⁻⁴ + S<2 · 10 ⁻³ in toluene	68Ld
	$\frac{1}{2} \frac{[(H)DE-HP]_2 + \bar{S}}{(H)DE-HP \cdot S}$	-0.6	25	—	S<0.5 + (H)DE-HP<0.4 in benzene	63B/59Ba
		-0.52	25	—	S<0.5 + (H)DE-HP<0.5 in CCl ₄	63B/59Ba
		-0.22	25	—	S<0.5 + (H)DE-HP<0.4 in hexane	63B/59Ba

METAL ION, M	REACTION	LOG K	TEMP.	CONDITIONS, AQ.	CONDITIONS, ORG.	REF.
Reactions with diluents and other solvents (cont.)						
	$\frac{1}{2} \frac{[(H)DE-HP]_2 + \bar{S}}{[(H)DE-HP]_2 + \bar{S}} = \frac{[(H)DE-HP]_2 + \bar{S}}{[(H)DE-HP]_2 + \bar{S}}$	0.0	25	—	$S < 0.5 + (H)DE-HP < 0.4$ in kerosene	63B/59Ba
	$(H)DE-HP + 2S = (H)DE-HP \cdot 2S$	1.13	25	HClO ₄ 0.1	$S + (H)DE-HP$ in CCl ₄	68La
		1.1	25	HClO ₄ 0.1	$(H)DE-HP < 1.0 + S < 0.4$ in CCl ₄	68Ld
		1.5	25	HClO ₄ 0.1	$(H)DE-HP < 6 \cdot 10^{-5} + S < 1.3$ in hexane	68Ld
		1.2	25	HNO ₃ 0.1	$(H)DE-HP < 7 \cdot 10^{-4} + S < 2 \cdot 10^{-3}$ in toluene	68Ld
	$\frac{[(H)DE-HP]_2 + \bar{S}}{[(H)DE-HP]_2 + \bar{S}} = \frac{[(H)DE-HP]_2 + \bar{S}}{[(H)DE-HP]_2 + \bar{S}}$	1.17	?	HNO ₃ 0.05	$(H)DE-HP 0.1 + S < 1.0$ in CCl ₄	66Z
		2.92	25	HClO ₄ 0.1	$S + (H)DE-HP$ in CCl ₄	68La, 68Ld
		0.72	?	H ₂ O	$(H)DE-HP + S$ undil.	69Y
	$\frac{[(H)DE-HP]_9 + \bar{S}}{[(H)DE-HP]_9 + \bar{S}} = \frac{[(H)DE-HP]_9 + \bar{S}}{[(H)DE-HP]_9 + \bar{S}}$	5.4	25	HClO ₄ 0.1	$(H)DE-HP < 1.0 + S < 0.4$ in CCl ₄	68Ld
	$\frac{TPP + \bar{S}}{TPP + \bar{S}} = \frac{TPP + \bar{S}}{TPP + \bar{S}}$	0.38	25	H ₂ O	$SO-1.5 + TPP 0-8.5$ in hexane	65Da
	$\frac{[(H)OPh]_2 + \bar{S}}{[(H)OPh]_2 + \bar{S}} = \frac{[(H)OPh]_2 + \bar{S}}{[(H)OPh]_2 + \bar{S}}$	1.95	?	HNO ₃ 0.05	$HS' 0.1 + S < 1.0$ in CCl ₄	66Z
	$\frac{(H)DpCl-PhP + \bar{S}}{(H)DpCl-PhP + \bar{S}} = \frac{(H)DpCl-PhP + \bar{S}}{(H)DpCl-PhP + \bar{S}}$	3.28	?	HClO ₄ 0.1	$(H)DpCl-PhP < S < 0.01$ in CCl ₄	67Kd, 68Ka