Development of a Chemical Kinetics Data Base for Plasma Chemistry. Part 1. SF_6/O_2.

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Abstract - We describe an approach to establishing a database of rate constants of elementary single step reactions of neutral species relevant to plasma processes. The approach is illustrated by compiling and evaluating data for the SF_6/O_2 system.

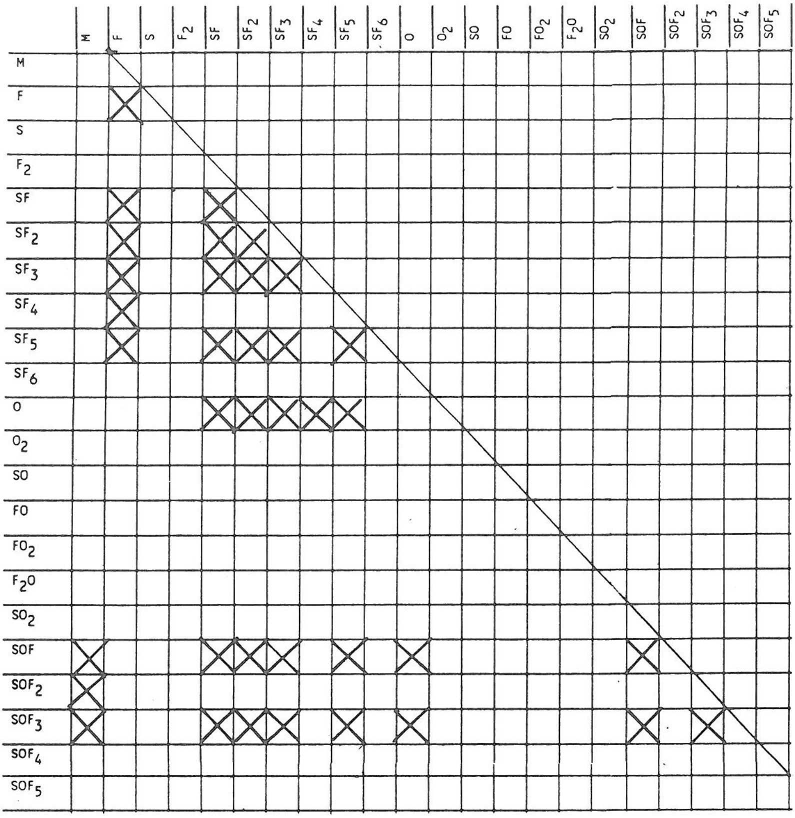
1. Introduction

A major goal of plasma chemistry is the quantitative description of plasma systems in terms of elementary chemical reactions. The value of that approach has been enhanced by recent advances in computer technology which now allow one to carry out modeling studies which simulate plasma processes using chemical kinetic data as input parameters. In this paper we describe an approach to establishing a database of rate constants of elementary single step reactions of neutral species relevant to plasma processes. The goal is to present in tabular form all published data on the relevant reactions, to provide recommended values for rate constants based on these data, to provide estimates of rate constants where no data exist, and to provide a critical discussion of the reaction mechanism. Gas phase chemical kinetics is largely the study of reactions of species containing C, H, O, N, and S. There are few kinetic studies of direct application to plasma chemistry. This makes not only the evaluation effort more difficult, but also provides only a tenuous basis for devising empirical estimation methods. However, as the data base grows our ability to estimate kinetic parameters also will improve. Here, we consider one system of interest to plasma chemistry, SF_6/O_2, outline an approach to setting up a data base, and illustrate the approach with data on selected reactions. The period covered is through about mid-1989.

2. Approach

The approach involves the identification of all potential reactive species and all possible reactions including multiple reaction product paths, calculation of reaction enthalpies, compilation and evaluation of experimental and theoretical kinetic data, and recommendation of rate constants based on reported data or by estimation. Since failure to provide an estimate is tantamount to setting the rate constant to zero, we provide an estimate for every relevant reaction for which no literature data exist. The basis for the estimate is given in the appropriate data sheet.

The identification of reactions is based on the concept of the reaction grid in which we start with a list of all possible reactant species and then consider the possible unimolecular reactions of each species, and all possible bimolecular reactions as defined by all possible reaction pairs. Fig.1 shows the reaction grid for the SF_6/O_2 reaction system.



	M	F	S	F_2	SF	SF_2	SF_3	SF_4	SF_5	SF_6	O	O_2	SO	FO	FO_2	F_2O	SO_2	SOF	SOF_2	SOF_3	SOF_4	SOF_5
M																						
F		X																				
S																						
F_2																						
SF		X			X																	
SF_2		X			X	X																
SF_3		X			X	X	X															
SF_4		X																				
SF_5		X			X	X	X		X													
SF_6																						
O					X	X	X	X	X													
O_2																						
SO																						
FO																						
FO_2																						
F_2O																						
SO_2																						
SOF	X				X	X	X		X		X							X				
SOF_2	X																					
SOF_3	X				X	X	X		X		X							X		X		
SOF_4																						
SOF_5																						

Fig. 1. Reaction grid for SF_6 decomposition and oxidation.
X, reactions covered in present work.

3. Data Sheets

Each reaction is treated by means of a self-contained data sheet. The heading of each sheet gives the reactants and the known or postulated products and the reaction enthalpy at 298 K. Enthalpies of formation for reactants and products are given in Table 1.

Table 1. Enthalpies of Formation at 298 K[a].

Species	$\Delta_f H$, kJ mol^{-1}	Ref.
F	78.91±1.67	5
S	276.98±0.21	2
S_2	128.49±0.29	2
SF	13.0±6.3	3
SF_2	-296.6±16.7	3
SF_3	-488.3±25	6
SF_4	-763.2±21	3
SF_5	-912.5±13.4	6
SF_6	-1220.5±0.8	3
S_2F	(-10±20)	6
SSF_2	-297±10	6
FSSF	-286±10	6
$SFSF_3$	-660±24	6
S_2F_6	(-1130±50)	6
S_2F_8	(-1570±50)	6
S_2F_9	(-1704±25)	6
S_2F_{10}	-2012±21	6
O	249.17±0.10	2
SO	5.0±1.3	2
FO	109±42	5
FO_2	12.6±21	5
F_2O	24.52±1.59	5
SO_2	-296.84±0.21	5
OSF	(-207±33)	6
OSF_2	(-494±32)	6
OSF_3	(-633±21)	6
OSF_4	(-954±16)	6
OSF_5	(-996±15)	6
O_2SF	(-428±15)	6
O_2SF_2	-758.6±8.4	4
O_2SF_5	-969±15	6
$(SF_5O)_2$	(-2148±25)	6
$SF_5O_3SF_5$	(-2069±21)	6

[a] All values in parentheses are estimated

The data sheet heading is followed by a table giving data from the literature and recommended values. Column 1 contains the reference code and notes relevant to the experimental procedure. The reference code consists of the last two digits of the year of publication, followed by the first three letters of the names of the first and second authors separated by a slash. Column 2 contains a two-character data type code: EX - experimentally measured absolute value; RL - experimentally measured relative value; RN - experimentally measured relative value normalized to an absolute value; TH - theoretical value; DE - derived from modeling study; SE - a recommended value from the literature. Column 3 gives the applicable temperature. If it gives a single temperature, e.g., 298, the value in Column 4 is k at that temperature; if it contains a temperature range, e.g., 200-500, the value in Column 4 is the Arrhenius A parameter. The units of k and A are cm^3 molec^{-1} s^{-1} and their values are given in exponential form. Column 5 and Column 6, respectively, contain, when applicable, the n and B parameters in the extended Arrhenius equation, $k=AT^n\exp(-B/T)$. The final entry is the recommendation of the present evaluation. Column 7 gives the overall uncertainty factors assigned to k.

Following the listing of data there is a secti "Comments and Recommendations", in which the basis for th recommended value is discussed, and the reaction mechanism is treated. Finally, we list the references cited in the dat sheet.

The approach is illustrated with reference to th reactions O + SF_2 and SF_5 + SF_5.

4. Sample Data Sheets

O + SF_2

$O + SF_2 \rightarrow SF + FO$ (a) $\Delta H(298)=169$ kj mol^{-1}
$\rightarrow SO + F_2$ (b) $\Delta H(298)=53$ kj mol^{-1}
$\rightarrow SOF + F$ (c) $\Delta H(298)=-81$ kj mol^{-1}
$\rightarrow SOF_2$ (d) $\Delta H(298)=-446$ kj mol^{-1}

Reference code, notes	Type	T/K	k,k/k(ref) A,A/A(ref)	n	B, B-B(ref)	k err. factor
86PLU/RYA	EX	295	1.08E-10			
Discharge flow-mass spectrometry.						
Recommended (c)		300-1000	1E-10			2

Comments and Recommendations

Within the limits of the reliability of the thermochemical data, only reactions (c) and (d) can be of any importance. Plumb and Ryan (86PLU/RYA) studied the reaction at low pressure (0.3 kPa) and observed that the decay of SF_2 was accompanied by the formation of a transient SOF species which in turn reacted to give ultimately SO and SO_2. Under these conditions, reaction (c) is probably the only important channel, and the recommended value is taken from 86PLU/RYA. There should be little if any temperature dependence. At high pressure channel (d) may become important.

References

86PLU/RYA Plumb, I. C. and K. R. Ryan, Plas. Chem. Plas. Process., 6, 247 (1986).

SF_5 + SF_5

$SF_5 + SF_5 \rightarrow SF_6 + SF_4$ (a) $\Delta H(298)=-159$ kj mol^{-1}
$\rightarrow S_2F_{10}$ (b) $\Delta H(298)=-187$ kj mol^{-1}

Reference code, notes	Type	T/K	k,k/k(ref) A,A/A(ref)	n	B, B-B(ref)	k err. factor
75TAI/HOW	EX	153-233	1.7E-11		850	
Electron spin resonance. Solvents: c-C_3H_6, CCl_2F_2.						
87HER (b)	SE		1.7E-11		850	
Recommended (a)		150-500	1.7E-10		2250	5
(b)		150-500	1.7E-11		850	3

Comments and Recommendations

There has been only one direct determination of the overall rate of reaction (75TAI/HOW), and no new data have been reported since the last review (87HER). The 87HER recommendation in which the overall reaction at low temperature was attributed entirely to reaction (b) is accepted. However, it should be noted that Schumacher and co-workers (79CZA/SCH, 81GON/SCH) have argued that both (a) and (b) are slow. These arguments are discussed more fully in 87HER.

87HER also proposed a value for the rate constant for reaction (a) which is also adopted here. However, estimates of the combination to disproportionation ratio, k(b)/k(a), are derived from modeling complex systems, such as the pyrolysis of S_2F_{10} (52TRO/MCI, 69BEN/BOT), and are highly unreliable.

References

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5. References

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