NISTIR 5744

Report of the Workshop on Data Needs for Modeling Aqueous Chemical Kinetics for the Global Atmoshpere

November 1 - 2, 1994

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Report of the Workshop on Data Needs for Modeling Aqueous Chemical Kinetics for the Global Atmosphere, National Institute of Standards and Technology, Gaithersburg, Maryland, November 1-2, 1994.

International Union of Pure and Applied Chemistry

Commission on Atmospheric Chemistry and Commission on Chemical Kinetics

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Workshop on Data Needs for Modeling Aqueous Chemical Kinetics for the Global Atmosphere

Summary

A Workshop on Data Needs for Modeling Aqueous Chemical Kinetics for the Global Atmosphere, was held at the National Institute of Standards and Technology, Gaithersburg, Maryland, November 1-2, 1994. It was organized jointly by the Commission on Atmospheric Chemistry and the Commission on Chemical Kinetics of the International Union of Pure and Applied Chemistry. The goals of the workshop were to provide IUPAC with a blueprint for prioritizing reactions for inclusion in an evaluated data base for use by atmospheric modelers and laboratory scientists, and to provide a starting point for rationalizing and encouraging long range research into the problems of aqueous atmospheric chemistry.

The workshop featured a series of invited lectures, followed by breakout sessions organized on the basis of the two very general and not necessarily exclusive topic areas of inorganic chemistry and organic chemistry. Each panel prepared a series of recommendations which were then discussed by the workshop as a whole. From those deliberations and subsequent discussions with the participants, it was recommended that the data evaluation activity in its initial phase should focus on four topics:

1. Reactions in dilute solution. The logical ordering of the work should be evaluation of a core set of reactions related to H-O species, followed by evaluations based on adding species in the approximate order C1 organic compounds, SO_x, NO_x, Cl, CO_2, metals and C2 organic compounds.

2. Reactions of transition metal ions in strong acids.

3. Reductive dissolution of iron oxides.

4. Ancillary data including properties such as solubilities, Henrys Law coefficients, acid dissociation constants, hydration equilibria, reduction potentials, etc., for the individual species in the kinetics data base.

Workshop on Data Needs for Modeling Aqueous Chemical Kinetics for the Global Atmosphere

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Workshop on Data Needs for Modeling Aqueous Chemical Kinetics for the Global Atmosphere

1. Introduction

It is increasingly recognized that the development of predictive methodologies for chemical transformations in the atmosphere requires an understanding of heterogeneous reactions and reactions occurring in the aqueous phase in addition to a quantitative understanding of gas phase reactions. The importance of aqueous-phase transformations was recognized early in studies of sulfur dioxide oxidation, and most of the models incorporating aqueous-phase reactions are those constructed for understanding acid precipitation. The role of aqueous-phase chemical transformations in other areas, such as the global ozone budget, are subjects of increasing interest.

In order to address some of the data needs for modeling global atmospheric chemistry, including the aqueous component, the International Union of Pure and Applied Chemistry (IUPAC) initiated a new project to provide evaluated kinetic data for aqueous phase reactions. The involvement of IUPAC is based on the global impact of the problem, and also on the belief that the most cost effective approach to starting a new data evaluation activity is to bring together the international community of experts in this area to avoid costly duplication of effort.

Within IUPAC, the project was defined as follows:

> *"The objective of this project is to provide a set of evaluated chemical kinetic data for reactions taking place in aqueous phases needed for modeling atmospheric chemistry. It should be regarded as a companion activity for the gas kinetic data evaluation project for atmospheric chemistry ongoing in the Chemical Kinetics Commission."*

The idea is to do for solution kinetics of the atmosphere what is already being done for the gas kinetics part through the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, which is an activity of the Chemical Kinetics Commission.

This workshop is the first stage in that program. The goals of the workshop are twofold; first, to provide IUPAC with a blueprint for prioritizing reactions for inclusion in an evaluated data base and devising a mechanism for carrying out the evaluations, and secondly, providing a starting point for rationalizing and encouraging long range research into the problems of aqueous atmospheric chemistry.

2. Organization of the workshop

The workshop featured a series of invited lectures, followed by breakout sessions organized on the basis of two very general and not necessarily exclusive topic areas:

- Inorganic chemistry
    - Halogens
    - Inorganic sulfur chemistry
    - Inorganic nitrogen chemistry
    - Metal ions and metal oxides
- Organic chemistry
    - Organic acids
    - Organic sulfur/nitrogen compounds
    - Aldehydes, ketones, and other organics
    - Metal ion and metal oxide interactions

The members of the breakout groups were asked to create their own agendas, address the issues presented in the charge to the workshop given in the next section of the report, and report back to the meeting with recommendation.

In the last day of the meeting, the breakout panel recommendations were presented, discussed, and a final set of recommendations and policy statements agreed upon.

3. Charge to the Workshop

The major goals of the workshop were to provide answers to the following questions:

- What is the role of aqueous kinetics in global atmospheric chemistry?
- What reactions need to be included in models?
- What are the priorities?
- What information needs to be included in a data evaluation? What ancillary information (equilibrium constants, thermodynamic data) is needed?
- Who will do the evaluations?

- What are the mechanics of having a geographically dispersed group work on a joint evaluation?
- How can the evaluated data best be distributed in a timely fashion?
- What are the long-term or urgent research needs in aqueous phase atmospheric chemistry?

In the following, these questions and their answers are treated with varying degrees of success. The most important questions, which involve the needs and priorities for the chemical kinetics part received the greatest attention of the workshop and provide the core of this report. Some of the other questions having more to do with logistics and organization of effort, have been left to the discretion of those who may choose to become involved in a long term evaluation activity.

5. Synopsis of Talks and Discussion

The opening talk of the workshop, “Current Problems in the Heterogenous Chemistry of the Troposphere,” was presented by Dr. Daniel Jacob of Harvard University. In his talk, Dr. Jacob discussed data needs from the perspective of global tropospheric models, concentrating on four major problems currently of great interest in atmospheric chemistry: (1) what controls the concentration of greenhouse gases; (2) what controls the concentration of tropospheric ozone; (3) what controls the oxidizing power of the atmosphere; and (4) what is the origin and evolution of the atmospheric aerosol. Heterogeneous chemistry, which includes both the chemistry of the atmospheric aqueous phase and chemical reactions occurring on solid surfaces, is likely to be important in all of these areas. In this talk, possible effects of heterogeneous chemistry on chemical species central to these problems were discussed. More specifically, the talk addressed the question of the extent to which aerosols and clouds affected the gas-phase concentrations of NO_x, OH, Cl, O_3, and SO_2.

The main sink for NO_x in the global troposphere appears to result from the hydrolysis of N_2O_5. This species is thought to have a lifetime with respect to hydrolysis of a few hours, except in the upper troposphere. The greatest uncertainty in the determination of the atmospheric hydrolysis rate is an understanding of the nature of the background aerosol, particularly the extent to which this aerosol is aqueous and what the reactivity of N_2O_5 is on the surface layer of these aerosol particles. In the lower troposphere, the aerosol particles are primarily $(NH_4)_2SO_4$ or NH_4HSO_4, depending on the NH_3 concentration. The distinction between these two is important due to their different deliquescent points. In the upper troposphere, the aerosol probably is primarily H_2SO_4, which may exist as an aqueous phase, although some recent data suggest that it exists as solid $H_2SO_4{\cdot}4H_2O$.

The concentration of NO_x in the atmosphere can also be influenced by the reaction of NO_3 with the aerosol or within atmospheric droplets. Little is known, however, about the solubility of this species.

There is also a possible role for aerosols as sources of NO_x in the gas-phase. There is no direct evidence for this, but atmospheric models consistently under-predict NO_x in the remote troposphere. Possible mechanisms include the reaction of CH_2O with HNO_3 in acid aerosols to produce either $CH_2(NO_3)_2$ or CHOOH and HNO_2; the reaction of protonated nitric acid, $H_2NO_3^+$, with Cl^- to give $ClNO_2$; and the diffusion of OH into sulfuric acid aerosols which can react to give SO_4^-. which in turn can react with NO_3^- to yield NO_3.

The effect of atmospheric aerosols and the atmospheric aqueous phase on the gas-phase hydroxyl concentration appears to result primarily from the scavenging of HO_2 and the subsequent rapid reaction of HO_2 with O_2^-. In aerosols, this reaction might also be catalyzed by transition-metal ions. O_2^- may also react with O_3 to generate OH.

The aqueous phase of the atmosphere can also act on OH by removing formaldehyde. This possibility is supported by the apparent overestimation of CH_2O in the lower troposphere by atmospheric models. But the weak diurnal cycle for CH_2O suggests that loss to the aqueous phase is not very important.

The atmospheric aerosol may also serve as a source of OH. Indirectly, it can do so by promoting the decomposition of gas-phase HNO_4. More direct mechanisms include the photolysis of metal-ion complexes. Of potentially great importance are complexes involving organic acids, but there is very little information on the composition of the organic fraction of the aerosol. Finally, OH can be produced through photocatalysis involving semiconductors, although it is not apparent that this will take place in actual atmospheric aerosols.

There is indirect evidence that atmospheric aerosols may serve as sources of Cl atoms. These include an unexplained Cl^- deficit in the sea-salt aerosol, measurements of gas-phase inorganic chlorine other than HCl, and observed ratios of some hydrocarbons in the marine boundary layer consistent with a Cl-atom loss mechanism. The deficit in Cl^- was previously ascribed to acid displacement, but more recent studies indicate that this is not the case. Possible sources of Cl include the reaction of O_3 with Cl^- and the reactions of HOBr and $BrNO_3$ with NaCl.

Aerosols and clouds may also serve as sinks for ozone. A mechanism for the loss of ozone due to the processing of air by clouds has been proposed which involves the scavenging of HO_2 by cloud drops. This results in the separation of HO_2 and NO, which is very insoluble, and therefore prevents their reaction to yield NO_2. In addition, HO_2 in water dissociates to produce O_2^-, which reacts rapidly with O_3. Dr. Jacob pointed out that the importance of this process is somewhat controversial since there appears to be sufficient CH_3O_2 to react with NO in the clean troposphere. On the other hand, atmospheric aerosols might have a negative impact on atmospheric ozone if they prove to be sources of active halogen species.

The oxidation of SO_2 in clouds appears to be reasonably well understood, since there appears to be sufficient H_2O_2 for complete oxidation. Of less certainty is what may happen on the background aerosol. One possibility is oxidation by O_3 on sea-salt aerosols, which generally have a pH of about 8. An interesting point in this regard is that the oxidation of SO_2 in the aerosol prevents the formation of new aerosol from the gas-phase oxidation of SO_2.

Dr. Jacob strongly emphasized the importance of including in any data evaluation activity the chemistry taking place in the background aerosol, which means chemistry in concentrated sulfuric acid and high ionic strength solutions. Otherwise, the relevance to global atmospheric chemistry would be marginal. Cloud chemistry occurs in only a limited portion of the troposphere. He also recommended that the evaluation of phase equilibria data be given high priority in the recommendations of the workshop.

The second talk was presented by Dr. Rudi van Eldik, of the Institute for Inorganic Chemistry of the University of Erlangen-Nurmberg, Erlangen, Germany on "Metal Catalyzed Atmospheric Oxidation Processes: a Challenge to Inorganic Chemists."

His talk focussed on transition-metal ion catalysis of oxidation reactions of importance in the atmospheric aqueous phase from the point of view of a coordination chemist, emphasizing work from his laboratory on the metal-catalyzed oxidation of S(IV). In addition, he discussed the metal-catalyzed oxidation of NO_y species and of mixed SO_x/NO_y systems. The major question addressed in his work is the mechanism of the catalysis of these reactions by metal ions. The basic idea is that metal ions in a higher oxidation state can initiate a chain reaction by reacting with the SO_x (or NO_y) to produce free radicals. The reduced metal ion can then be reoxidized in some subsequent reaction step.

The oxidation of SO_2 can be catalyzed by a number of transition-metal ions. The systems seem simple, but are actually very complicated. At any particular pH, there will be acid-base equilibria of the metal ions and of the S(IV) species; there will be problems with the solubility of some of the species, particularly the metal ions in the higher oxidation states where oxides, hydroxides, and solid particles are formed; there will also be complex formation between the metal ions and S(IV). For example, for Fe(III) and S(IV), there are two distinct complex formation steps.

A particularly important observation in this work is that S(IV) can induce the oxidation of Fe(II) in an autocatalytic reaction. This means that there is redox cycling of the metal ions in the system. This is also true of manganese. In this case, Mn(III) is a necessary intermediate. This species is unstable except at high acidity. Organic acids, however, will help stabilize the Mn(III) and also improve its solubility.

The synergistic effects among the metal ions were also discussed, particularly of Mn on Fe , Co, and Cu.

This concept of redox cycling has been included in many other mechanisms used in modeling atmospheric processes, although this phenomenon is usually not recognized as such. In some examples, SO_2 is not even involved. The basic features are the same, however.

The question was raised about the possibility of redox cycling resulting from the interaction of NO_y species with transition-metal ions. It is known that many of the NO_y species interact with metal ions, the binding of NO by reduced metal ions is particularly well known. NO is also known to react with S(IV) in the presence of metal ions to give a range of N-S compounds. Although these species have not been observed in rainwater, their hydrolysis products are found.

Dr. van Eldik summarized his views of the major outstanding problems. The most important is the pH dependence of the various processes which have been studied, due to the need to extrapolate the laboratory data to conditions of environmental significance. The second is the possible role of photolysis on redox cycling. Finally, the need for more feedback from modelers to experimentalists was pointed out.

The final talk "Aqueous Phase Chemical Kinetics Seen from European Atmospheric Chemistry Point of View," was presented by Dr. Detlev Möller of the Fraunhofer institute for Atmospheric Environmental Research, Berlin. The theme of the talk was suggested by the organizers in order to acquaint other workers with the kinds of problems being addressed in the European Community with respect to tropospheric air pollution. Thus, his talk focused on regional modeling with a particular emphasis on the chemistry of the European atmosphere. Although there are no differences in the basic reactions which can take place, there are significant differences in atmospheric conditions and emission patterns between Europe and North America. In European cloud water samples, a bimodal pH distribution is observed, whereas at Whiteface Mountain in the north-eastern United States, a single maximum is found. The output of a model is strongly dependent on these initial conditions. Within Europe, there is a distinction between the atmospheric chemistry of Western Europe, which is representative of a more advanced industrial society, and Eastern Europe, which possesses a more classical polluted atmosphere. In East Germany, the emissions of SO_2 are much higher than in the west, but in West Germany NO_x emissions are higher. Correspondingly, sulfate deposition rates are higher in the east, reflecting differing source terms, but nitrate deposition is the same in both regions, reflecting the differences in the atmospheric chemistry of these species. The recent fall of the Communist regimes in Eastern Europe and, particularly, the reunification of Germany, has resulted in a dramatic reduction in emissions. This has provided a unique opportunity to improve our understanding of atmospheric chemical processes. Of particular importance may be the reduction in fly ash, which serves to neutralize atmospheric acidity.

Dr. Möller also spoke in some detail of the mechanics of modeling atmospheric aqueous phase chemistry. He pointed out that with a box model, there is no reason to reduce the chemical system that is employed. For transport models, however, there is a need to reduce the number of species and/or the number of reactions in the system. One result of this is that it is best to use reduced systems which are specific to the particular goal. For example, the chemical module of the model used to study sulfate formation would be different from the chemical module of the system used to study oxidant formation. This procedure, of course, can lead to errors -- a certain amount of art is involved.

The various chemical modules included in the model were discussed. A chlorine module was developed because there are chemical plants in middle Europe which emit Cl_2, but this system is probably not important in a typical polluted environment. More important is the NO_y system. The most important conclusion from an analysis of the model results is that most of the nitrate in cloud water comes from direct transport from the gas phase, either in the form of HNO_3 or as N_2O_5 (which hydrates to NO_3^-). Probably less than 5% of the NO_3^- is formed from the oxidation of NO_2^-.

SO_2 oxidation in cloud water is very important. The module employed excludes transition-metal ion catalyzed oxidation but includes oxidation by H_2O_2, O_3, and free radicals such as OH and NO_3. The model indicates that in the summer, most of the oxidation of SO_2 takes place by reaction with H_2O_2, corresponding to about 90% of the total. (During the day, about 10% is from gas-phase OH + SO_2 reaction.) At night, about 11% of the oxidation in the liquid phase is caused by NO_3. During the winter day, about 65% of the oxidation of SO_2 is due to reaction with O_3 in the aqueous phase, 27% due to reaction with H_2O_2, and 8% by reaction with radicals. At night, radical oxidation predominates at 41%, followed by reaction with H_2O_2 at 35%, and reaction with O_3 at 24%.

Cloud water chemistry has a significant effect on the chemistry of gas-phase oxidants. An understanding of gas-phase oxidant chemistry requires a consideration of the chemistry of the liquid phase. The big question is whether the liquid phase is a source or a sink of oxidants. In the oxidant module, transition-metal ion reactions must be included. Redox cycles involving the metal ions are very important in the formation and loss of H_2O_2. A very important reaction in cloud water is $O_3 + O_2^- + H^+ \rightarrow OH + 2O_2$. This is an important source of OH radicals, which can react with dissolved organics to regenerate HO_2 and, hence, H_2O_2. This cycle can be disturbed by the reaction of HSO_3^- with H_2O_2.

There are significant similarities and differences between the gas and liquid phase oxidant systems. Organics play the same role in both, but in the gas phase NO reacts with HO_2 to provide OH, whereas in the aqueous phase this role is played by O_3.

Aqueous-phase reactions of both O_2^- and of S(IV) provide sinks for gas-phase O_3. If the atmospheric concentration of SO_2 is decreased, the cloud scavenging of O_3 will be decreased, but only up to a point. This is because the decreased acidification of the cloud water favors O_2^-. The net result, according to the model, is that at 10 ppb [SO_2] and a 0.1 ppb the scavenging rates are about the same, while the scavenging rates are only 1/3 as large at 1.5-2 ppb [SO_2].

5. Reports of Breakout Panels

5.1. Inorganic Chemistry

Chairman: P. Warneck

The panel discussed not only the kinetics of transformations in the aqueous phase of the atmosphere, but also spent a considerable amount of time discussing sources and speciation of the compounds present and other properties which affect their reactivity.

An item of considerable concern to the panel was the importance of ionic strength on chemical reactions in atmospheric droplets. At low ionic strength, the effect of ionic strength on reactions involving ions is easily treated. However, the validity of the treatment is more questionable at high ionic strengths. In addition, an effect of ionic strength on the reactions of uncharged radicals has been reported. This effect could be important at high ionic strengths and is certainly important in evaluating laboratory kinetic data, but its importance on the reactions of atmospheric radicals is not well established. During the life cycle of a cloud droplet, the ionic strength can go through dramatic changes; as the droplet is formed and as it evaporates, the ionic strength is likely to be quite high. The tropospheric background aerosol also might be considered a high ionic strength solution. While recognizing the possible importance of high ionic strength effects, the panel recommended that the initial evaluation activities consider only reactions occurring in dilute solutions where ionic strength corrections are well understood, and leave the treatment of chemical reactions at high ionic strength for future evaluation. At the same time, additional experimental work should be carried out to resolve outstanding issues relating to the effect of ionic strength on important reactions, including the effect of ionic strength on reactions involving neutral species.

Since the importance of transformations in the atmospheric aqueous phase depends on the proportion of the substance which is in the aqueous phase, the panel recommended that the evaluation of Henry's Law coefficients be included in the evaluation activity. It was recommended further that the temperature dependence of these coefficients be provided, obtained preferably from data spanning at least the range 0 to 40°C.

Probably the most important difference between the aqueous phase and the gas phase chemistry is that electron-transfer reactions are possible in the former. This means that chemical transformations can take place rapidly in the aqueous phase which are slow, or do not take place at all, in the gas phase. Important atmospheric free radicals such as OH and NO_3 are strong one-electron oxidants; HO_2 is also an oxidant, but its deprotonated form, O_2^-, is a reductant. The rate constants for electron-transfer reactions are related to the difference in reduction potential between the reactants. For couples involving stable oxidation states, for example the couple Fe^{3+}/Fe^{2+}, reduction potentials have been measured by standard electrochemical techniques and are available in most chemical handbooks. For reduction couples involving a free radical, for example SO_3^{2-}/SO_3^-, standard electrochemical techniques are generally not adequate and reduction potentials must be obtained through kinetic techniques. For many of the couples of atmospheric interest, one-electron reduction potentials have been determined and there are two useful reviews which can serve as starting points.

Another important characteristic of a chemical substance in solution which should be included in a kinetic data evaluation relate to its acid/base properties. The panel recommends that pK_a values in water for the various substances reviewed for their kinetic properties be included where relevant. In addition, equilibrium constants for interactions among many species likely to be present are needed. Particularly important are those involving transition metal ions Although there are tables containing many of these data, a critical evaluation focused on atmospheric species is lacking. Other properties which are important in modeling and understanding aqueous atmospheric chemistry include solubilities, acid dissociation constants, hydration equilibria, reduction potentials, etc. be included in a long range plan for data evaluation.

As in the gas phase, the photolysis of species present in solution may prove to be an important phenomena in atmospheric chemistry. Absorption coefficients and quantum yield data are needed for many of the primary species likely to be present in atmospheric droplets. This is particularly true for species such as H_2O_2, HNO_2, and HNO_3 which are likely to be important OH radial sources. Absorption coefficients are also needed for metal complexes of these and other species, although these data are likely to be more sparse. Of greatest importance are the cross sections and quantum yields for hydroxy ferric complexes, which again are likely to be OH sources. Some of the important processes are indicated in Table 1.

Table 1. Some Photochemical Reactions Important in Aqueous Atmospheric Chemistry

$O_3 + hv \rightarrow O_2 + O(^1D)$
$H_2O_2 + hv \rightarrow 2OH$
$NO_2^- + hv \rightarrow NO + O^-$
$NO_3^- + hv \rightarrow NO_2 + O^-$
$FeOH^{2+} + hv \rightarrow Fe^{2+} + OH$
$FeSO_4^+ + hv \rightarrow Fe^{2+} + SO_4^-$
$Fe_3^+ + hv\ (+ H_2O) \rightarrow Fe^{2+} + OH + H^+$
$Fe(C_2O_4)_3^{3-} + hv \rightarrow Fe^{2+} + 2(C_2O_4)^{2-} + CO_2 + CO_2^-$

5.2. Organic Chemistry

Chairman: R. E. Huie

The discussion of the panel on organic chemistry centered on which compounds should be included in the initial data review. It was pointed out that a very large fraction of the organic component in atmospheric droplets may be humic material. This is a very complex organic system and it is unlikely that useful information could be gathered in the short term. The panel did recommend, however, that long-term research into the atmospheric chemistry of humic material be listed as a high priority.

After some discussion, it was agreed that the initial set of organic compounds to be considered should include the C_1 and C_2 acids, diacids, aldehydes, alcohols, and mixed compounds (containing differing functional groups). Due to their significance in degradation pathways for halogenated organics, kinetics involving halogenated acids should be included. For the acids and the aldehydes, hydrolysis equilibria should also be evaluated and included in the report.

From a consideration of the likely reactants, it was agreed that the evaluations should include reactions of the organic compounds with: OH, O_3, NO_3, H_2O_2, HO_2/O_2^-, SO_4^-, SO_5^-, Cl_2^-, HSO_5^-, CO_3^-, and RO_2. Table 2, based on a survey of standard data compilations, indicates the availability of data for reactions involving organic compound; a check meaning that some data exist, a blank cell meaning that nothing is available.

In addition to the reactions of the organic compounds with these simple oxidants, complex formation by the organic compounds, particularly the acids with transition metal ions, and the subsequent photolysis of these complexes should receive attention.

Finally, it was pointed out that reactions of organic oxidants formed in the gas phase could be important to the chemistry of atmospheric droplets. Specifically, reactions of peroxyacyl nitrate and organic hydroperoxides with and in atmospheric droplets should be part of the long-term plan for evaluation.

6. Discussion

Following the reports to the workshop by the two panel chairmen, there was a general discussion in which the various recommendations were considered and further recommendations for structuring future work or additional specific recommendations for items to be included were made.

The question of heterogeneous reactions was discussed in great detail (Heterogeneous reactions in this context are reactions within atmospheric droplets involving solid materials). It was pointed out that heterogeneous reactions on mineral phases were of great importance in long range transport. Of particular importance is the reductive dissolution, in which a reductant such as S(IV), is oxidized at the surface of a metal oxide, releasing reduced metal ions. Absorbed inorganic and organic compounds can be oxidized in this manner and metal ions carried into solution where they can react further. In view of the importance of this subject, it was suggested that this could be readily treated as a separable topic from the homogeneous part of the kinetics. There are extensive measurements available and the kinetics of these processes can be treated in terms of classical Langmuir-Hinshelwood theory.

Table 2. Availability of Data for Reactions of Organic Compounds.

	OH	Cl_2^-	Br_2^-	Cl	Br	O_3	O_3^-	CO_3^-	NO_3	SO_4^-	SO_5^-	RO_2	HO_2 $/O_2^-$
CH_3OH	✓	✓	✓	✓	✓	✓		✓	✓	✓			
CH_3CH_2OH	✓	✓		✓		✓	✓	✓	✓	✓			
$HOCH_2CH_2OH$	✓												
CH_2O	✓					✓			✓	✓			
CH_3CHO	✓					✓			✓				
CHOCHO	✓												
HCOOH	✓	✓				✓			✓	✓			
CH_3COOH	✓	✓		✓		✓			✓	✓			
$HOCH_2COOH$	✓												
CHOCOOH						✓							
$(COOH)_2$	✓												
$(CH_3)_2S$	✓	✓	✓						✓			✓	
$(CH_3)_2SO$	✓	✓		✓		✓			✓	✓			
$(CH_3)_2SO_2$	✓								✓				
$ClCH_2COOH$	✓												
$BrCH_2COOH$													

Other items related to heterogeneous kinetics were also considered: reactions on ice phases for example. The activities relating to these kinds of data in the NASA data base were described. It seemed clear that at this point the data is more of the nature of a compilation than an evaluation, but that progress in research in this area could lead to more and better data. The kinds of material in the NASA data base include accommodation coefficients, Henrys Law constants, and hydrolysis rates.

This led to a discussion of the scope of the proposed kinetics activity. There appeared to be a general consensus that all important aspects of the atmospheric chemistry problem must be identified and considered, but that because of the breadth of the field and the limits on resources, priorities must be established at the outset.

The question of who should be responsible for defining the importance of atmospheric reactions was raised, and the clear consensus was that it was the job of the modelers to define data needs, and the laboratory and data community to provide reliable data. This implies that data needs will change with time, and that any prioritizing by the workshop will be modified by the body which is subsequently charged with carrying out our recommendations.

The workshop then turned to the problem of prioritizing the kinetics needs. A key question which came up repeatedly was what reactions are important in any possible model or in the majority of models? It was agreed that probably the most important set of reactions was that involving hydrogen-oxygen species. A simple grid was drawn to identify the species and indicate which reactions between them were important. This is shown in Fig. 1.

The grid concept was recognized as an ideal way in which to prioritize further and to provide a “bookkeeping” mechanism for the proposed work. It was pointed out that gaps in such a grid provided modelers with a means to extend models by “inventing” chemistry, and to experimentalists to study unexamined chemical systems.

The discussion which followed was basically about the succeeding order of importance. Appendix A summarizes some of the important considerations which are the basis for the prioritization of reactions which follow.

Fig. 1. Core Grid for H-O Reactions

	OH^-	H^+	O_2	OH	HO_2	O_2^-	H_2O_2	O_3	O_3^-
OH^-									
H^+									
O_2									
OH									
HO_2									
O_2^-									
H_2O_2									
O_3									
O_3^-									

On the basis of the discussion, it was possible to derive an extended grid as shown in Fig. 2. Here, we have simplified the original "core" grid of Fig. 1, and added the other priority reactants. Thus, we have combined OH^-/H^+ as H_2O, HO_2/O_2^- as HO_2, and dropped O_3^-. Note the grid is not completely filled in, and all possible reactive species are not given. That will be the task of the evaluation group. Photolysis, which was recognized as an important process in all aspects of atmospheric chemistry is included in the grid explicitly.

The final part of the discussion concerned the kinds of ancillary data which should be included. Those quantities which received greatest attention from the workshop were Henrys Law constants, reduction potentials, and hydration equilibria. There are probably other important quantities that need to be included. It was recognized, however, that general data compilations were not required, but that this part of the data activity should be handled on a species specific basis, and data added only with the addition of a species to the data base.

Fig.2. Reaction Grid for Aqueous Kinetics for Atmospheric Chemistry

	hγ	H_2O	O_2	OH	HO_2	O_3	H_2O_2	C1	S(IV	SO_5^-	SO_4^-	NO_X	Cl^-	Cl	Cl_2^-	CO_2	CO_3^-	Metals	C2								
hγ																											
H_2O																											
O_2																											
OH																											
HO_2																											
O_3																											
H_2O_2																											
C1																											
S(IV)																											
SO_5^-																											
SO_4^-																											
NO_X																											
Cl^-																											
Cl																											
Cl_2^-																											
CO_2																											
CO_3^-																											
Metals																											
C2																											

7. Recommendations

The many issues raised in the original charge to the workshop were not addressed in equal detail. The main questions addressed were what are the specific data needs and how can these be organized in terms of long term and short term priorities.

The workshop recommendations can be broken down into four major categories, each of which may have short term and long term components:

1. Reaction in dilute solution. This was given the highest priority by the panel not only because of its importance to tropospheric chemistry, but also because the existing mass of data make it a prime target for an evaluation. The use of a reaction grid such as that shown in Fig. 2, to organize and track progress was also recommended. The logical ordering of the work should be:

    a. Evaluation of a core set of reactions related to H-O chemistry as indicated by the grid given in Fig. 1.

    b. Evaluation of succeeding augmentations in the approximate order C1 organic compounds, SO_x, NO_x, Cl, CO_2, metals and C2 organic compounds as illustrated by the grid shown in Fig. 2. This ordering is subject to modification by the evaluation group.

2. Reactions of transition metal ions in strong acids. There is an extensive body of data available, and this is an area of opportunity for an evaluation.

3. Reductive dissolution of iron oxides also was recognized to be a separate subcategory.

4. Ancillary data was recognized as a separate but essential category of data needs. These kinds of properties such as solubilities, Henrys law coefficients, acid dissociation constants, hydration equilibria, reduction potentials, etc. should be compiled and evaluated in terms of the individual species in the kinetics data base. Particularly important are properties for transition metal ions Although there are tables containing many of these data, a critical evaluation focused on atmospheric species is lacking.

These recommendations all focus on areas in which there exist sufficient data to justify compilation and/or evaluation. They are separable in terms of task, are definable and executable projects, and each would make a significant contribution to the advancement of atmospheric chemistry.

However, in addition to these specific tasks, the panel felt that there were other areas that needed to be considered in terms of more long term research; areas not yet ripe for a data project, but areas that must eventually become part of the data base.

An item emphasized throughout the workshop was the need to have kinetics and thermodynamic data over the range of temperature representative of the atmosphere, starting at least with the range 0 to 40°C.

The properties of solutions of high acidity or high ionic strength, representative of the atmospheric aerosol, are vital, yet we lack a viable body of data.

There is great need for characterization of aerosols in terms of speciation. In particular we need much more information on the nature of "humic" materials.

Photolysis has been explicitly included in the grid of Fig. 2, but the needs for fundamental data are great. We need information on absorption coefficients and quantum yields, for species such as H_2O_2, HNO_2, and HNO_3 which are likely to be important OH radial sources. Absorption coefficients are also needed for metal complexes of these and other species, although these data are likely to be more sparse. Of greatest importance are the cross sections and quantum yields for hydroxy ferric complexes, which again are likely to be OH sources.

Reactions of organic oxidants formed in the gas phase could be important to the chemistry of atmospheric droplets. Specifically, reactions of peroxyacyl nitrate and organic hydroperoxides with and in atmospheric droplets should be part of the long-term research activity.

8. Acknowledgments

This workshop would not have been possible without the support of our sponsors. We are grateful to the Physical Chemistry Division of the International Union of Pure and Applied Chemistry, the Atmospheric Chemistry and Modeling Program of the National Aeronautics and Space Administration, the Chemical Manufacturers Association, and the Chemical Kinetics and Thermodynamics Division of the National Institute of Standards and Technology. In addition to the organizations which sponsored the workshop, the organizers take pleasure in thanking the following for their help in providing support, sharing in the task of organization, or of otherwise supporting the goals of the meeting: Prof. Kozo Kuchitsu, Dr. Jack Kaye, Dr. Bruce Gay, Dr. Charles Kolb, and Dr. Sharon Lias.

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10. Appendix A.

Some Important Reactants in Aqueous Atmospheric Chemistry

1. Radical Oxidants

The most important radical, which also is the one for which there is the most kinetic information, is hydroxyl, OH. This radical can be formed in the gas phase and diffuse into the aqueous phase, or it can be formed directly in the aqueous phase. Interestingly, the most important source of OH in the gas phase, the photolysis of O_3 followed by the reaction of O^1D with H_2O

$$O_3 + h\nu \rightarrow O_2 + O^1D$$
$$O^1D + H_2O \rightarrow 2OH$$

will not take place in the aqueous phase because the reaction of O^1D with H_2O in water yields only H_2O_2. Other photolytic sources, however, may be important, including the photolysis of the nitrite anion and of ferric hydroxy complexes. In addition, some OH may result from the reaction of O_2^- with O_3

$$O_2^- + O_3 + H^+ \rightarrow OH + 2O_2$$

The OH radical reacts in the gas-phase by addition and abstraction. In the aqueous phase, these reaction modes are joined by electron transfer, which is particularly important in the case of inorganic anions.

Next in importance is HO_2/O_2^-. This pair is related through the proton equilibrium

$$HO_2 \rightleftharpoons H^+ + O_2^-$$

with $pK_a = 4.8$. HO_2 can diffuse into a droplet from the gas phase or be formed in the aqueous phase by a large number of processes. A possibly important example is through the decomposition of alcohol-peroxyl radicals. HO_2/O_2^- radicals are generally not highly reactive, but their reactions with other radicals, with ozone, and with transition metal ions are likely to be important.

The final radical likely to have a substantial gas-phase source is nitrate, NO_3. Although this radical can react by abstraction and addition, these are slow compared to its reactions as a one-electron oxidant. Recently, a substantial amount of work has been done on the reactivity of this radical, but there are important issues which remain to be resolved.

An important set of radicals formed only in the aqueous phase is that of the dihalide radical anions, X_2^-. These radicals are probably formed primarily as a result of strong oxidants such as OH, NO_3, or SO_4^-. As Cl^- is the dominant halide ion, Cl_2^- is likely to be the dihalide radical most often formed. It is also the most reactive. In the clean, marine troposphere, Br_2^- and I_2^-, which have lower reduction potentials, might also become important. Presently, there is little information on the mixed dihalide radical anions, such as $ClBr^-$.

In addition to the dihalide radical anions, halogen atoms might also be important in atmospheric droplets where the halide concentration is low. This should be true even for Cl, due to the favorable equilibrium constant for

$$Cl_2^- \rightleftharpoons Cl + Cl^-$$

In the past few years, kinetic information on the reactivity of halogen atoms in aqueous solution has become available.

The sulfate radical, SO_4^-, has been shown to be formed in the autoxidation of sulfite and bisulfite solutions, probably in the chain-propagation steps. It is a very strong one-electron oxidant, easily produced and monitored in the laboratory, and there is an extensive base of kinetic information on its behavior. The other key radicals in S(IV) oxidation are SO_3^- and SO_5^-, although there is less information on the reactivity of these radicals. The main fate of SO_3^- is expected to be the reaction with O_2 to form SO_5^-.

Of some interest is the CO_3^- radical, which can be produced from HCO_3^-. Both the reactions of OH and SO_4^- with HCO_3^- are slow, so that the production of this radical is not very efficient. On the other hand, in very pure atmospheric droplets there may be few other anions for OH to react with. There have been a large number of studies of the kinetics of this radical, few of which are of atmospheric significance.

Due to the large number of possible varieties, the organic peroxyl radicals, RO_2, will probably best be considered as a group. There is a great deal of information on the kinetic behavior of these radicals, including the effect of substituents on their reactivity. Most of this work has not been directed toward reactions of atmospheric significance, however, so additional measurements are probably needed.

2. Non-Radical Oxidants

The most important non-radical oxidant is probably hydrogen peroxide. This species is formed both in the gas phase and in the aqueous phase, primarily by the self-reaction of HO_2/O_2^-. It is important both as a direct two-electron oxidant, for example in the oxidation of bisulfite

$$H_2O_2 + HSO_3^- \rightarrow H_2O + HSO_4^-$$

and, in its reactions with reduced metal ions, as a source of OH radicals

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$

The reactions of H_2O_2 are not well represented in modern compilations, and a comprehensive evaluation is needed.

In spite of its low solubility, ozone still appears to be a potentially important reactant in the atmospheric aqueous phase. Although there have been a large number of studies of the reactivity of this species in solution, many key reactions of likely atmospheric importance have not been studied adequately.

PAN (peroxyacyl nitrate), and similar atmospheric oxidants, might also play a role in the chemistry of the aqueous phase. Presently, very little is known about the interactions of these compounds with water.

11. Appendix B.
Guidelines for Publication of Evaluated Data Using the IUPAC Data Evaluation Format

In order to provide the best possible service to the user community, and to generate evaluations compatible with the existing gas phase evaluations in atmospheric or combustion chemistry, we recommend that the general format used by the IUPAC atmospheric kinetics panel be adopted. That format is illustrated in the following.

Example Pages from the IUPAC Evaluation of Chemical Kinetic Data for Gas Phase Atmospheric Chemistry. (Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, Jr., R. F., Kerf, J. A., and Troe, J., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry. Supplement IV. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry", J. Phys. Chem. Ref. Data, 21, 1125, 1992.)

Using the original page numbering from the article, these pages illustrate some of the desirable features of any critical chemical kinetics data evaluation.

Page 1127. This is a summary table that appears in the front of the main body of the evaluation. It gives the page number for the detailed review of the reaction, the recommended values for rate parameters, the conditions of validity, and an estimate of reliability. It provides data users with a convenient access to the results of the evaluation.

Page 1472. This is a typical data sheet. It lists the known and in some cases only inferred reaction mechanism. It gives pertinent thermodynamic data, in this case data on reaction enthalpy. For solution kinetics this may differ. It gives the available data, reaction conditions, and citations to the literature. The most important part of the table is the comments section where the methodology is described, and any remarks as to experimental problems or interpretive complexities are described. This is followed by a statement of the recommended values and comments thereon.

There are no graphical displays in this data base. That might be a desirable feature for some reactions.

Page 1509. This is a typical data sheet for a photochemical process. The formatting is somewhat different, but basically the same features prevail as for the regular gas kinetics data sheets.

One of the key features of these data sheets is that each is self-contained. That makes their use remarkably easy and their subsequent revision also much simpler than if the data,

2. Summary of Reactions and Preferred Rate Data

Page number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K
	O_x Reactions						
1148	$O + O_2 + M \rightarrow O_3 + M$	6.0×10^{-34} [O_2]	(k_0)	±0.05	$6.0 \times 10^{-34}(T/300)^{-2.8}[O_2]$	100–300	Δn = ±0.5
		5.6×10^{-34} [N_2]	(k_0)	±0.05	$5.6 \times 10^{-34}(T/300)^{-2.8}[N_2]$	100–300	Δn = ±0.5
•	$O + O_2 \rightarrow O_3^*$	See previous evaluation					
•	$O_3^* + M \rightarrow O_3 + M$	See previous evaluation					
1149	$O + O_3 \rightarrow 2\,O_2$	8.0×10^{-15}		±0.08	$8.0 \times 10^{-12}\exp(-2060/T)$	200–400	±200
•	$O + O_3^* \rightarrow$ products	See previous evaluation					
1150	$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	4.0×10^{-11}		±0.05	$3.2 \times 10^{-11}\exp(67/T)$	200–350	±100
1151	$O(^1D) + O_3 \rightarrow O_2 + 2\,O(^3P)$	1.2×10^{-10}		±0.1	2.4×10^{-10}	100–400	$\Delta\log k$ = ±0.05
	$\rightarrow 2\,O_2(^3\Sigma_g^-)$	1.2×10^{-10}		±0.1			
1152	$O_2^* + O_3 \rightarrow O + 2\,O_2$	See data sheet					
1152	$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$	1.6×10^{-18}	($M = O_2$)	±0.2	$3.0 \times 10^{-18}\exp(-200/T)$	100–450	±200
		$\leq 1.4 \times 10^{-19}$	($M = N_2$)				
		5×10^{-18}	($M = H_2O$)	±0.3			
		$\leq 2 \times 10^{-20}$	($M = CO_2$)				
•	$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$	See previous evaluation					
•	$O_2(^1\Sigma_g^+) + O_3 \rightarrow$ products	See previous evaluation					
•	$O_2(^1\Sigma_g^+)^* + O_2 \rightarrow O_2(^1\Sigma_g^+) + O_2$	See previous evaluation					
1153	$O_2 + h\nu \rightarrow$ products	See data sheets					
1155	$O_3 + h\nu \rightarrow$ products	See data sheets					
	HO_x Reactions						
1157	$H + HO_2 \rightarrow H_2 + O_2$	5.6×10^{-12}		±0.5	5.6×10^{-12}	245–300	$\Delta\log k$ = ±0.5
	$\rightarrow 2\,HO$	7.2×10^{-11}		±0.1	7.2×10^{-11}	245–300	$\Delta\log k$ = ±0.1
	$\rightarrow H_2O + O$	2.4×10^{-12}		±0.5	2.4×10^{-12}	245–300	$\Delta\log k$ = ±0.5
1158	$H + O_2 + M \rightarrow HO_2 + M$	$6.2 \times 10^{-32}[N_2]$	(k_0)	±0.05	$6.2 \times 10^{-32}(T/300)^{-1.6}[N_2]$	200–600	Δn = ±0.6
		7.5×10^{-11}	(k_∞)	±0.3	7.5×10^{-11}	200–300	Δn = ±0.6
		$F_c = 0.55$		ΔF_c = ±0.15	$F_c = \exp(-T/498)$	200–300	
•	$H + O_3 \rightarrow HO + O_2$	See previous evaluation					
•	$H + O_3 \rightarrow HO^* + O_2$	See previous evaluation					
•	$O + H_2 \rightarrow HO + H$	See previous evaluation					
1159	$O + HO \rightarrow O_2 + H$	3.3×10^{-11}		±0.1	$2.3 \times 10^{-11}\exp(110/T)$	220–500	±100
1160	$O + HO_2 \rightarrow HO + O_2$	5.8×10^{-11}		±0.08	$2.7 \times 10^{-11}\exp(224/T)$	200–400	±100
1161	$O + H_2O_2 \rightarrow HO + HO_2$	1.7×10^{-15}		±0.3	$1.4 \times 10^{-12}\exp(-2000/T)$	250–390	±1000
1162	$O(^1D) + H_2 \rightarrow HO + H$	1.1×10^{-10}		±0.1	1.1×10^{-10}	200–350	±100
1163	$O(^1D) + H_2O \rightarrow 2\,HO$	2.2×10^{-10}		±0.1	2.2×10^{-10}	200–350	±100
1164	$HO + H_2 \rightarrow H_2O + H$	6.7×10^{-15}		±0.1	$7.7 \times 10^{-12}\exp(-2100/T)$	200–450	±200
•	$HO + H_2(v=1) \rightarrow H_2O + H$	See previous evaluation					
1165	$HO + HO \rightarrow H_2O + O$	1.9×10^{-12}		±0.15	$4.2 \times 10^{-12}\exp(-240/T)$	250–500	±240

$$ClO + NO_3 \rightarrow ClOO + NO_2 \quad (1)$$
$$\rightarrow OClO + NO_2 \quad (2)$$

$\Delta H°(1) = -36$ kJ·mol^{-1}
$\Delta H°(2) = -32$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.0 \pm 1.7) \times 10^{-13}$	296	Cox *et al.*, 1984[1]	(a)
$1.6 \times 10^{-12} \exp[-(420 \pm 200)/T]$	278–338	Cox *et al.*, 1987[2]	(b)
Reviews and Evaluations			
4.0×10^{-13}	298	IUPAC, 1989[3]	(c)
4.0×10^{-13}	200–300	NASA, 1990[4]	(d)

Comments

(a) Time dependent measurements of NO_3 in the photolysis of $Cl_2-ClONO_2-N_2$ mixtures. ClO assumed to be produced in presence of excess NO_3 by the reaction Cl + NO_3. [NO_3] calculated using $\sigma = 1.7 \times 10^{-17}$ cm^2 molecule^{-1} at 662 nm.

(b) Molecular modulation system with UV absorption. Photolysis of $Cl_2-ClONO_2-N_2$ mixtures. ClO monitored in UV at 277.2 nm ($\sigma = 7.2 \times 10^{-18}$ cm^2) and NO_3 at 662 nm ($\sigma = 1.7 \times 10^{-17}$ cm^2 molecule^{-1}). Rate coefficients obtained by computer modeling of absorption-time profiles for ClO in the presence of excess NO_3. Upper limit of $k_2/k_1 < 0.4$ based on absence of observable OClO.

(c) See Comments on Preferred Values.

(d) Based on Cox *et al.*,[1,2] but with recommended zero temperature dependence.

Preferred Values

$k = 4.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous eva ation, IUPAC, 1989.[3] The two studies[1,2] using a simi technique are in good agreement at 298 K. In view of uncertainty in the data, the temperature depende cannot be considered to be established and a tempe ture dependent expression for k is not recommen from this evaluation. The weight of evidence present suggests that channel (1) is the major pathway at T 300 K.

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[2] R. A. Cox, M. Fowles, D. Moulton, and R. P. Wayne, J. Phys. C 91, 3361 (1987).
[3] IUPAC, Supplement III, 1989 (see references in Introduction).
[4] NASA Evaluation No. 9, 1990 (see references in Introduction).

CF_2Cl_2 (CFC–12) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{\text{threshold}}$/nm
$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$	(1)	346	346
$\rightarrow CF_2 + 2\,Cl$	(2)	542	221

Preferred Values

Absorption cross-sections for CF_2Cl_2 photolysis at 295 K and 210 K

	$10^{20}\ \sigma$/cm^2			$10^{20}\ \sigma$/cm^2	
λ/nm	295 K	210 K	λ/nm	295 K	210 K
174	162	162	200	8.89	5.11
6	181	181	2	5.51	2.97
8	187	187	4	3.44	1.69
180	179	179	6	2.09	0.99
2	160	160	8	1.27	0.56
4	134	134	210	0.76	0.32
6	107	107	2	0.45	0.18
8	82.8	79.3	4	0.27	0.10
190	63.2	52.9	6	0.16	0.058
2	45.5	35.8	8	0.10	0.033
4	31.5	22.8	220	0.060	0.018
6	21.1	14.4	2	0.036	0.010
8	13.9	8.8	4	0.022	0.006
			6	0.013	0.003

Quantum Yields for CF_2Cl_2 Photolysis at 298 K

λ/nm	ϕ_1	ϕ_2	λ/nm	ϕ_1	ϕ_2
170	0.59	0.41	210	0.85	0.15
180	0.62	0.38	220	0.96	0.04
190	0.67	0.33	230	1.0	
200	0.74	0.26	240	1.0	

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are the values reported by Simon *et al.*[1] This recent publication reports the results of the most comprehensive study of the temperature dependence. The values at room temperature are in good agreement with those recommended in our previous evaluation, CODATA, 1980,[2] where a detailed discussion of earlier work can be found. The recommended quantum yield values are taken from Ref. 2, and are based on the results of Rebbert and Ausloos.[3]

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