

**FINAL REPORT TO IUPAC PHYSICAL AND BIOPHYSICAL CHEMISTRY
DIVISION (I)**

Project Number: 1999-037-2-100

Title: EVALUATED KINETIC DATA FOR ATMOSPHERIC CHEMISTRY

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Objective

The primary objective of this project was to enhance the accessibility and availability of the evaluated kinetic data base, which has been assembled by the IUPAC Subcommittee for Gas Kinetic Data Evaluation for Atmospheric Chemistry, by placing the material in a database on an interactive site on the www. A second objective is to develop and implement a scheme for updating the material on the website. The work covers development of a linked, interactive website, retyping and posting of new updated data sheets and other information relating to the evaluation, and creation of a mirror site at the IUPAC HQ website in North Carolina.

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The work on this project was conducted in two phases. The first phase was funded for 2 years commencing in July 2001 and the second phase which started in 2004 was completed in 2006. Progress reports have been produced regularly. In the year since the last progress report (2006) work has continued on the project to develop the website (<http://www.iupac-kinetic.ch.cam.ac.uk/>) with support from the EU project 'Network Of Excellence on Atmospheric Composition Change', ACCENT, and from UK NERC Knowledge Transfer funds. This report covers the whole period up to July 2007.

Use of Funds

A total of \$56500 was allocated to the project, consisting of \$30,000 for phase 1, \$20,000 for phase 2 and \$6500 for a meeting for the Task Group, which was consolidated with the project in 2006. A total of \$10,563.57 was used for Task Group Meeting expenses (reimbursed directly from IUPAC office) and the residual was used mainly for website set up and maintenance. This work was done by Dr G. Carver (Cambridge) and Dr R.G. Hynes (Cambridge/CSRIO) who created the database and managed/implemented the website. In addition funds were used for preparation, editing and archiving of the datasheets produced by the Evaluation Panel. This was done by Siglin Hoff and Inge Dreger at Gottingen under the supervision of Prof. Troe, and by Dr Barbara Cox and Dr Hannah Barjat at Cambridge, under the supervision of Dr Cox. Assistance with checking of summary sheets was provided by Dr Sandra Saunders at University of Western Australia and Dr Paola Cassinelli at Cambridge.

The IUPAC Subcommittee for Gas Kinetic Data Evaluation

The IUPAC Subcommittee for Gas Kinetic Data Evaluation for Atmospheric Chemistry (formerly the CODATA Task Group on Chemical Kinetics) was originally tasked to produce an evaluation of the existing chemical kinetics data in 1977. This was in response to the need to provide an internationally judged data set for modelling the emerging problem of the depletion of atmospheric ozone due to man made pollutants. Since that time the Subcommittee has continued to expand and update the evaluations, which have been published in a series of nine peer reviewed articles in *J. Phys. Chem. Ref. Data.*, and three peer reviewed article in *Atm. Chem. Phys.*(see list in Appendix 1).

The published evaluations contain two elements. Firstly a summary table which contains a list of recommended rate parameters giving recommended values for rate coefficients, for use in models representing atmospheric chemistry/explicitly as a system of elementary chemical reactions. Secondly each reaction was discussed in a separate data sheet, in which the key experimental data are summarised and the basis of the recommendation together with its uncertainty given. These data sheets provide details which are of interest to atmospheric modellers and experimental scientists conducting

investigations of kinetics and mechanisms of atmospheric reactions, and chemical kinetics generally.

The utility of the evaluations has always been limited by the cost and availability of the *J. Phys. Chem. Ref. Data* volumes. To overcome this, the summary tables have been published from time to time in more widely subscribed Journals (*Int. Journal of Chemical Kinetics; Atmospheric Environment*). The data base now contains over 650 chemical reactions relevant to the chemistry of the stratosphere and the troposphere and, as the number of reactions has expanded, the size of the evaluation and effort needed for updates has become greater, such that the later volumes focussed only on specific categories of reactions. In order to improve access to this data, the IUPAC panel created in 1998 a website at the Centre for Atmospheric Science in the Department of Chemistry, University of Cambridge, UK, (<http://www.iupac-kinetic.ch.cam.ac.uk>). The panel has recently completed a project supported by IUPAC Physical Chemistry Division to update and display the entire database on this website.

The online database

The strategy for developing online database has been to maintain a similar style to the earlier publications, i.e. a summary table plus a series of data sheets. Initially the website only displayed the summary tables containing the recommended values for the rate coefficients, their temperature dependence and estimates of the uncertainties. The main purpose of the project has been to substantially expand the content of the website to include the data sheets for photochemical reactions (absorption cross sections, quantum yields), heterogeneous reactions (kinetic uptake coefficients for atmospheric gases on a range of surfaces) and the individual data sheets for each of the 600 gas phase reactions, for which the data have been evaluated, since the first publication by the Group in 1980. In addition to expansion, the website is continually being modified to give improved access, including a simple search facility and implemented hyperlinks between the summary table and the data sheets.

The data sheets are grouped in a series of categories which include:

- 1) Gas phase and photolysis reactions of Ox, HOx, NOx and SOx species.
- 2) Gas-phase and photolysis reactions of organic species (including reactions with HOx, NO₃ and halogen radicals.
- 3) Reactions of organic peroxy radicals, organic alkoxy radicals and other organic radicals with oxygen.
- 4) Gas phase and photolysis reactions of inorganic FOx, ClOx, BrOx and IOx species.
- 5) Gas phase and photolysis reactions of organic halogen species.
- 6) Uptake coefficients for non-reactive and reactive heterogeneous processes.

In the first phase of the project which finished in 2003, data sheets for Ox, HOx, NOx, SOx, organic species were updated and displayed on the website. In the second phase of the project, which is now completed, the remaining data sheets for inorganic and organic

halogen (F, Cl, Br, I) species have been updated, and an updated compilation of data for heterogeneous reactions, have been incorporated into the website. In addition some rearrangement and increased facilities have been added to the website to aid access to the data.

Technical details

At the time the idea of the kinetic data website was conceived, new internet and publishing technologies had been developed which significantly reduced the amount of effort required to create the website. What's more, freely available open source software provided the backbone of the website: the Apache webserver, MySQL database software and PHP scripting language. One of the difficulties initially was how best to present the datasheets on the website. Rather than try to convert each datasheet, authored in MS Word, to HTML which would have presented problems in representing special characters, it was decided to convert the datasheets to Adobe PDF format. This has a number of advantages: the formatting of the original Word document was exactly preserved; printing quality was not compromised; special characters were preserved; by making use of the internet aware nature of PDF files active links would be put in the PDF documents which linked back to the main website. The disadvantage was that this approach relied on users having the Adobe Acrobat plugin for the web browser, but this was becoming commonplace (though it did cause a few problems for some users with older browsers).

The other key aspect to the technical side of the website was to make maintenance as easy as possible. To that end it has been constructed to be as automatic as possible. Although the website consists of many webpages, most of these are automatically generated using PHP scripts extracting the required information from MySQL database tables. In these tables are stored information about each category of datasheet, the location of the datasheets and a list of each reaction. Only a few pages on the website are actually edited and maintained by hand. In addition, the addition of new datasheets to the database and other administrative tasks can be carried out via the website itself again using PHP embedded in the Apache webserver to do the work behind the scenes. This supports the distributed nature of the IUPAC kinetic data team who administer the website as well as preventing mistakes occurring that might cause loss or damage to part of the website.

The technical aspects of the website were successful largely due to the timing of the project; at a time when many internet technologies were mature enough to be made use of to create the website rapidly with a minimum of development cost.

Provision of kinetic data

The website contains up-to-date evaluated kinetic and photochemical data in the form of a summary table and datasheets with experimental reaction rate data stored as individual files. The current version of the summary table contains the latest (2006) recommended

kinetic data. The summary table is updated every six months, and past editions dating back to January 1999 are accessible for reference. All data can be accessed directly in pdf or Word format using the hyperlinks on the Home Page. The datasheets are divided into specific categories, and users can use the simple "search and view" facility to examine the list of the different categories and to select a specific reaction category (i.e., O_x, NO_x, HO_x or SO_x). Each category contains a current list of datasheets of the reactions that are available, along with information on the date when the reactions were placed on the web, and the date of the last alteration. Hyperlinks from the summary table allow the specific data sheet to be displayed.

The format of the data sheets allows traceability of the new sources of experimental data and new analyses, including theoretical treatment. Data is freely available but with restriction that it cannot be reproduced elsewhere. Citation of any material from the data base should follow the usual web reference format: IUPAC Evaluation, [http://www.iupac-kinetic.ch.cam.ac.uk.\(current year\)](http://www.iupac-kinetic.ch.cam.ac.uk.(current year))

The website also provides links to a "recent changes" service, which gives detailed information on recent changes, due to updates of datasheets, errors report by colleagues, and information on the posting up of new datasheets on the IUPAC website. This facility allows the updating process of the website to be carried out quickly, and for users to have access to the best available rate coefficient data in the field. Furthermore, a "mailing list" is offered to users who would like to be notified when the information on the website is updated. A limited personal "help" service is offered via e-mail to the web master (G. Carver) or data manager (R.G. Hynes), who can refer questions to the sub-committee members. The Chairman, R.A. Cox, is the arbiter in the case of disputes

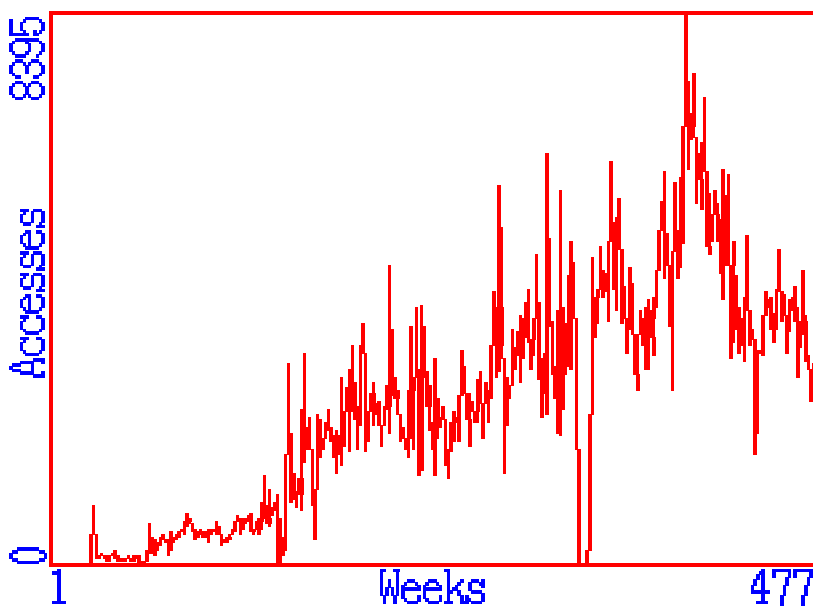
"Supplementary information", accessed by hotlinks on the home page, is presented to users as background information on the evaluation of the kinetic data. This includes a comprehensive "guide to the data sheets" (for gas phase and photochemical reactions), "the introduction to the heterogeneous datasheets", notes on a list of the "thermochemical data" which has been taken from the evaluations, and "the ordering of chemical reactions within a family", as used in the summary table.

Access to the website

The Cambridge IUPAC website has attracted very significant interest since its expansion in 2001. In 2002 a mirror site was created at the IUPAC HQ website in North Carolina, USA. Provision of kinetic data is available by both the Cambridge (master) site and the mirror site at the IUPAC HQ website in North Carolina, USA. The mirror site is automatically updated with the contents of the master web pages, thus allowing all users fast access to the online evaluated data. In 2007, the website mirror was moved to a new IUPAC server in Berlin with a new domain name under the main IUPAC domain (iupac.org).

The graph below shows the history of accesses to the IUPAC website since going 'live'. The chart shows peaks at times of announcements of new summary table releases. There is typically a decrease in accesses after this time. The graph does show a lower level of usage approximately over the last year. However, this does not mean the website is being

used less by real users. The graph below does NOT account for accesses to the mirror site. Also, a very large fraction of accesses are from automated system from web search sites. Therefore, this chart is a very unreliable measure of real usage of data from the website. A more reliable measure of the interest the website generates is subscriptions to the mailing list associated with the website. At the time of writing there are 395 genuine email addresses on this list. The number of subscriptions to the list continues to see a increase of ~ 10% year on year.



In late 2005 a user consultation exercise was initiated as part of the ACCENT activity. A questionnaire was prepared and sent out and 38 replies were received. A summary of the replies has been prepared and discussed with a view to implementation of website improvements.

Future work

In the future the efforts of laboratory kineticists will continue to provide new data in response to new scientific and societal issues in the field of Atmospheric Chemistry. The Group is seeking a more effective way of updating and extending the portfolio of recommended rate coefficients, which will be necessary to maintain an effective and ongoing communication between laboratory scientists and atmospheric modellers. The establishment of web-based material allows for the first time the opportunity of near continuous update of the evaluation. The development and implementation of protocols for the updating of the evaluation, both web-based and archived hard copy will be addressed in the future development of the project.

The protocols for future updating and addition of new reactions decided at the June 2007 Sub-committee meeting are being implemented. This includes creation of new datasheets with recommended kinetic parameters for selected heterogeneous reactions. The new

datasheets for heterogeneous reactions will be added to the website in a completely new database. The gas phase reaction rate data will continue to be updated by the Panel as new data appears. The Panel are considering expansion of the atmospheric degradation reactions of organic compounds to include higher alkanes, aromatics and perfluoro-compounds

The website is being restructured to allow automatic electronic download of data from the summary tables. A major change is the creation of a duplicate IUPAC website for development purposes as part of the NERC funded Knowledge Transfer project. This duplicate is unavailable for public use. However, no further development will be made to the existing website as the duplicate will eventually replace it.

A new project linking the IUPAC database with the Master Chemical Mechanism has been funded by UK NERC. This is a very exciting project which will significantly enhance the useability of the site and provide a pathway to added value for the data provided. A new page describing the Knowledge Transfer project has been added to the IUPAC website.

Work on improved access to the IUPAC data is also being carried out within the framework of ACCENT. New funds to support the Sub-Committee's work in updating and maintaining the database have been sought from IUPAC Physical Chemistry Division. \$15,000 has been awarded in a new project covering the period up to end of 2008.

Publications listing

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