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Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry

by Michel J. Rossi

Atmospheric chemistry is the study of the complex network of thermal and photochemical processes occurring in the gas and condensed (cloud droplets, aerosol particles, ice crystals) phase as well as in multiphase processes. Chemical kinetic modeling is required to interpret observations in the field. This necessitates the availability of a robust, reliable, and regularly updated database of elementary reactions for use in chemical-radiative-transport models. Combustion chemistry and plasma processing for semiconductor applications require the same type of database.

Historical Background

In 1980, the original set of critically evaluated kinetic and photochemical rate parameters for atmospheric chemistry was published in the *Journal of Physical and Chemical Reference Data* by members of the CODATA Task Group on Gas Phase Chemical Kinetics under the auspices of the International Council of Scientific Unions. Cumulative updates were published in 1982 and 1984 as Supplements I and II, respectively. The original evaluation and Supplements I and II were primarily intended to furnish a kinetic database for modeling the chemistry of the middle atmosphere, which is between 10 and 50 km in altitude. In 1985, IUPAC set up a group to continue and enlarge upon work initiated by CODATA. The Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry was chaired by J. Alistair Kerr until the end of 1999. R. A. Cox took over the chairmanship thereafter. The subcommittee produced Supplements III, IV, and V in 1989, 1992, and 1997, respectively, which were all cumulative as they contained the complete but ever-increasing database that now mainly addresses the chemistry of the troposphere as well as the lower stratosphere. Supplement V included for the first time a database of heterogeneous chemical reactions.

After Supplement V it was no longer possible to cope with updating the very large number of chemical reactions involved in tropospheric chemistry. Therefore, the subcommittee decided to limit Supplements VI, VII, and VIII, published in 1997, 1999, and 2000, respectively, only to a subset of the more than 700 gas phase and heterogeneous reactions comprising the database last presented in cumulative form as Supplement V. The database met the approval of the scientific community and the number of citations has grown steadily over the past 10 years, reaching 800 for Supplement IV published in 1992. In 2000, it was decided to change the mode of publication by setting up the database on the primary website associated with the Center for Atmospheric Chemistry at the University of Cambridge, UK, and a mirror site on the IUPAC server. This represented a break with long-standing tradition, and a radical change from the peer-reviewed system of publication in JPCRD.

Structure of the Database

The database is accessible free of charge at <www.iupac-kinetic.ch.cam.ac.uk>. It is broadly structured into Summary Tables for families of reactions, Data Sheets, and Supplementary Information.

- **The Summary Tables** display the recommended kinetic data. It has to be emphasized that this list comprises critically evaluated data—in contrast to a mere compilation of experimental kinetic data—that are organized into five categories of atmospherically relevant reactions. These also include photochemical reactions in each category:
  (1) O_x, HO_x, NO_x, SO_x (inorganic) reactions
  (2) organic reactions
  (3) ClO_x reactions
  (4) FO_x, BrO_x, IO_x reactions
  (5) heterogeneous reactions
  The tables are designed so that allow users can conduct a rapid survey, with the preferred value of the rate constant at 298K displayed, as well as the Arrhenius representation of its temperature dependence (if available), the relevant temperature range of validity, and the associated uncer-

tainties. Past editions of the Summary Tables, starting with January 1999, are available to enable tracking of changes in the database over the years.

- **The Data Sheets** are brief summaries of available experimental data, with notes that provide details of the experimental procedures. For each thermal reaction a preferred value of the rate coefficient at 298K is given together with its temperature dependence, if available. The selection of the preferred value is discussed in some detail, and estimates of the accuracies of the rate coefficients and temperature coefficients have been given for each reaction depending on the number of studies and their quality. For each photochemical reaction, the data sheets list the preferred values of the photoabsorption cross-sections and the quantum yields of the photochemical reactions, together with comments on how these were selected. As of June 2006, a full list of 27 sets of data sheets are available representing just under 1 000 reactions. Each individual data sheet may be downloaded as either a Adobe PDF document or Microsoft Word file for individual use.
- **Supplementary Information** given at the bottom of the homepage includes a brief guide to the data sheets comprising key definitions of kinetic parameters and a glossary of terms; an introduction to the heterogeneous data sheets; a reference list of thermodynamic data of relevant atoms, free radicals, and closed shell molecules; and the order of chemical reactions within a family.

In addition, the home page affords easy access to additional information, including recent changes (displayed in chronological order), a list of members (providing a way to get in touch with the evaluators), a sign-up form to join the mailing list, and a list of publications, including Supplements I to VIII published to date.

Converting an extensive database from a hard copy volume to a website comes at a price: the well-known volatility of the electronic record is somewhat opposed to the need for unfailing documentation that is the hallmark of serious scientific work. Just imagine a climate modeler 10 years from now who inquires about the exact time at which the value of a crucial rate constant was changed due to a change in recommendation! In addition to the historical record of past versions of the Summary Table (vide supra), the subcommittee decided some time ago to take a "snapshot" of the kinetic database at a given moment in time by publishing subsets in the peer-reviewed literature. Three large subsets have already been published in electronic form in *Atmospheric Chemistry and Physics Discussions*, which provides the basis for the final hardcopy edition in *Atmospheric Chemistry and Physics*, two volumes of which have already been published, in 2004 (*Atmos. Chem. Phys.*, 4, 1461–1738) and 2006 (*Atmos. Chem. Phys.*, 6, 3625–4055).

Previously, the updating process of the database was conducted on a semiannual basis, but more recently this has occurred on a yearly basis. Updating involves intense discussions among members, and usually implies a meeting of the entire task group. The 32nd meeting of the group took place in June 2006.

Summary

The advantages of the kinetic database may be summarized as follows:

- extensive database, accessible free of charge
- critical evaluation as opposed to mere compilation of literature data
- rational path to recommended values based on highlighted experimental or theoretical values
- frequent updates
- hard copy "snapshots" of the state of the database at a given point in time for easier traceability of recommendation changes

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www.iupac.org/projects/1999/1999-037-2-100.html
www.iupac-kinetic.ch.cam.ac.uk

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