IUPAC in the (real) clouds

40 years of evaluating atmospheric chemistry data

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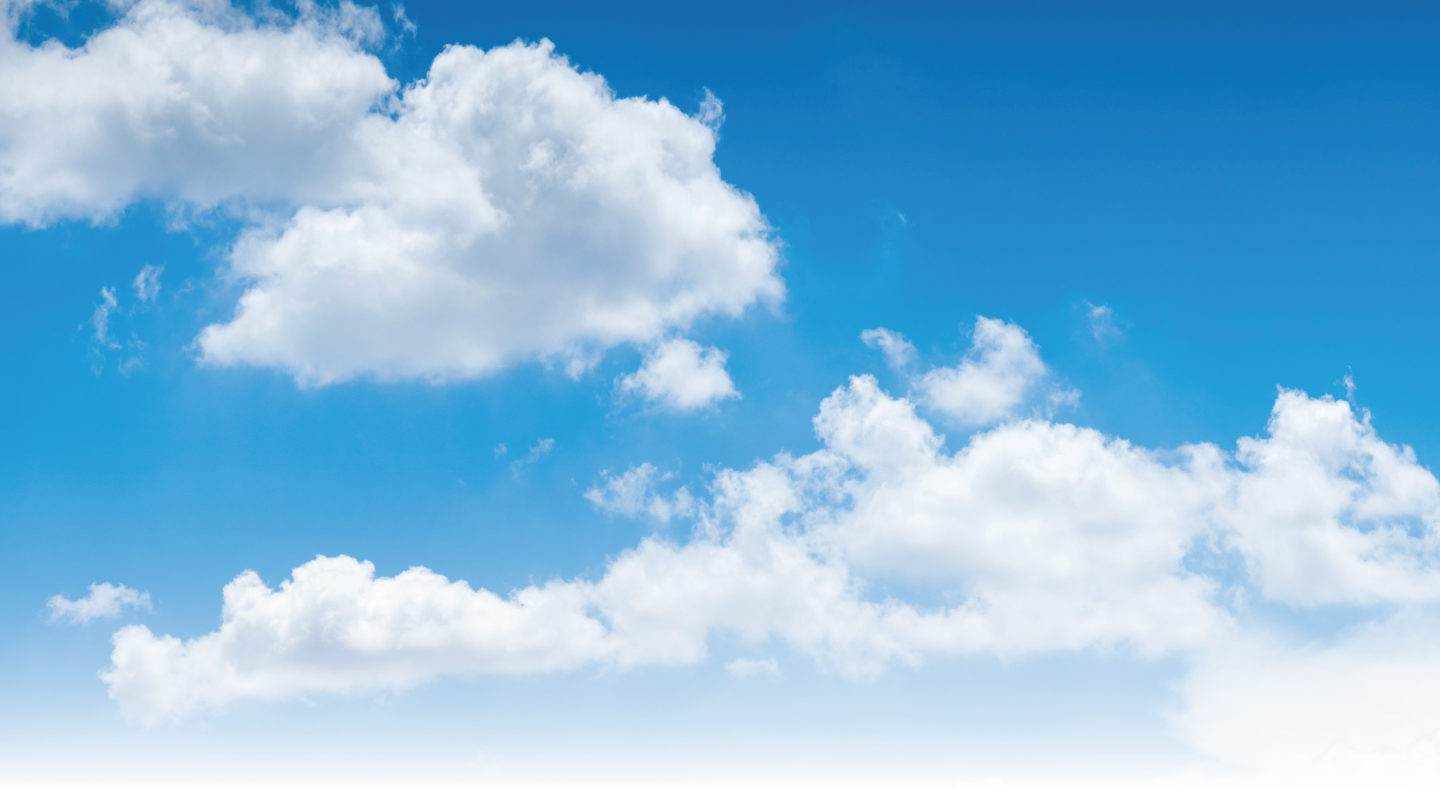
As we approach the end of the second decade of the 21st century, changes in atmospheric chemical composition due to anthropogenic pollution continue to challenge the well-being of society. The IUPAC effort in atmospheric chemistry data evaluation can be traced back over 40 years. Global concerns over potentially catastrophic stratospheric ozone depletion resulting from emissions of chlorofluorocarbons (CFCs) led to the creation of the CODATA Task Group on Chemical Kinetics in 1977. The task of the CODATA group was to provide the evaluated kinetic data for atmospheric reactions needed to assess the threat to stratospheric ozone. In 1989, sponsorship of the data evaluation effort was transferred to IUPAC, leading to the formation of the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation.

Despite greatly improved scientific knowledge of emissions and atmospheric processes over the past 30-40 years, gas-phase and particulate pollution of the atmosphere on local, regional, and global scales continues to be a serious problem. Climate and air quality computer models are important tools which integrate our knowledge of emissions, observations, atmospheric chemistry, and meteorology. Atmospheric models are a critical tool in the formulation of effective policies to address air pollution on all spatial and temporal scales. The IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation provides the evaluated chemical data for atmospheric chemistry used in these models [1].

Depletion of the stratospheric ozone layer by degradation products of CFCs and other halocarbons has been a focus of the IUPAC data evaluation group since the 1980s. The need to determine the impact of regulation strategies of emissions of ozone depleting halocarbons, under the provisions of the globally agreed Montreal Protocol and its follow-up treaties, has stimulated continued interest in CFCs and other long-lived halocarbons. Accurate and reliable chemical kinetics and photochemical data from laboratory measurements are needed to calculate the atmospheric lifetimes of the CFCs, CFC substitutes, and other long-lived halocarbons which continue to be released to the atmosphere. This is necessary for assessment of future ozone trends.

Halocarbons are efficient greenhouse gases, particularly the highly fluorinated halocarbons (*e.g.,* the perfluorocarbons, which do not contain Cl or Br and hence do not deplete ozone), have very long lifetimes, absorb strongly in the infrared, and consequently have large global warming potentials. Hydrofluorocarbons (HFCs) are widely used and can have long atmospheric lifetimes and large global warming potentials. In October 2016 the Kigali Agreement extended the Montréal Protocol to curtail release of long-lived HFCs to help reduce future damaging climate change. This development was assisted by a comprehensive review of the atmospheric chemistry of these compounds [2] which was built in part on IUPAC's work on the kinetics of halocarbon reactions [3]. This contribution was possible because of the extension in the scope of the



IUPAC evaluation to cover the new trace gases such as HFCs released to the atmosphere from a variety of applications. These data are available at the IUPAC atmospheric kinetics website [1].

In 2014, the International Global Atmospheric Chemistry project (IGAC) initiated a new scientific assessment of Tropospheric Ozone (TOAR). Prior to the 1970s, it was believed that ozone in the troposphere originated from downward transport of ozone from the stratosphere, where it was produced from photolysis of molecular oxygen. However, there are several key reactions involving nitrogen oxides which produce ozone in the troposphere. This phenomenon was discovered by chemists working on the problem of photochemical smog in Southern California. Its significance for influencing tropospheric ozone on a global scale was pointed out by Paul Crutzen in 1973 [4]. The key process involves the oxidation of nitric oxide to nitrogen dioxide, in the gas phase with hydroperoxyl (HO_2) or organic peroxy radicals (RO_2):

$$RO_2 + NO \rightarrow NO_2 + RO$$
(R = organic group)

NO_2 then undergoes photolysis by near UV light to form atomic oxygen, which combines with O_2 molecules to produce ozone:

$$NO_2 + (\text{UV light}) \rightarrow NO + O$$
$$O + O_2 (+ M) \rightarrow O_3$$
(M = any air molecule)

These chemical processes, together with the inputs and removal of ozone by physical processes such as transfer from the stratosphere and removal at land and water surfaces, determine ozone amounts in the troposphere. Ozone is, directly and indirectly, central to the rate of oxidation of most trace pollutants in the troposphere, a process that prevents the build-up in air of toxic pollutants. Hence, there has been an enormous effort by the scientific community to define the kinetics and related photochemistry of the mechanisms of tropospheric ozone production, involving hydroxyl radicals, organic peroxy radicals, and nitrogen oxides, in tropospheric conditions.

By the end of the 1980s there was a large body of experimental data on atmospheric oxidation processes and the role of hydroxyl radical [5]. This enabled the IUPAC group to provide an evaluated data set [6] allowing models of tropospheric ozone production and loss to be assembled. This work highlighted the importance of complex forming bimolecular reactions at the higher pressures encountered in the troposphere, and a treatment of the pressure dependence of rate constants was developed to assist the parameterization of atmospheric rates [7]. This work continues to be expanded today because field observations have revealed the huge amount and variety of volatile organic compounds (VOCs) present in the atmosphere. Oxidation of these compounds produces peroxy radicals that can influence ozone production. The IUPAC task group has provided an extensive evaluation of the elementary reactions of peroxy radicals of atmospheric importance [1].

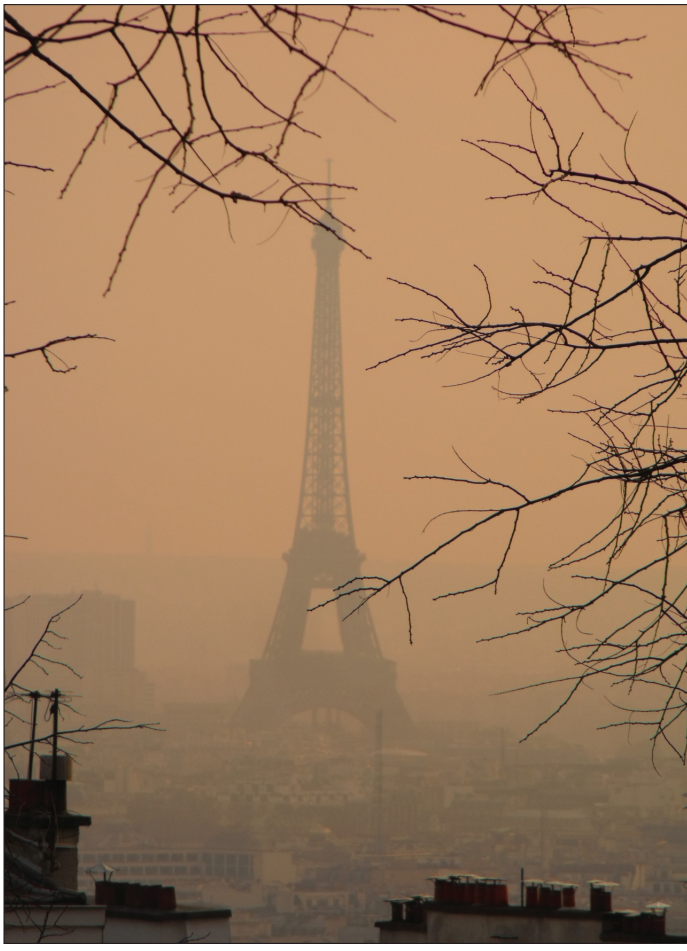
One of the first reactions studied in the context of atmospheric oxidation was the reaction of ozone with alkenes. This reaction proceeds via highly reactive diradical species, known as Criegee Intermediates, after

their discovery by Rudolf Criegee in the 1950s. Cox and Penkett [8] proposed that these intermediates could be responsible for oxidation of atmospheric SO_2. It was not until 2012 that quantitative measurements of the reaction kinetics of these elusive species were obtained, creating more definitive descriptions of their role in atmospheric oxidation [9]. The IUPAC panel completed an evaluation of some 25 elementary reactions of Criegee intermediates in 2018. This evaluation allows the non-photochemical atmospheric formation of hydroxyl radicals and key aerosol precursors such as SO_3 and organic acids, resulting from ozonolysis of a suite of unsaturated organics to be reliably formulated in atmospheric models.

Aerosol particles produced during oxidation of VOCs, nitrogen, and sulfur compounds have a fundamental influence on atmospheric radiation, due to backscatter of incoming sunlight and several indirect effects. Thus, global climate models need a capability to represent aerosol production and loss as well as gas-phase chemistry. Tropospheric ozone itself also acts as a greenhouse gas, in addition to its central role in tropospheric chemistry. Chemistry-climate models with detailed, explicit chemical schemes are being used increasingly to explore the future trends in climate change and atmospheric composition. Fine particulate matter with an aerodynamic diameter less than 2.5 µm (PM2.5) has been associated with premature mortality in epidemiological studies. The human health impacts of exposure to particulate matter in air pollution indoors and outdoors is an area of great research interest [10].

In the past two decades, the occurrence of heterogeneous reactions taking place on the surface of atmospheric particles has become recognized as a significant process causing changes in the gas phase composition of the atmosphere [11]. These reactions have a profound effect, particularly in the polar stratosphere where surface reactions can dramatically enhance concentrations of halogen oxides which catalytically destroy ozone. Lower in the atmosphere, aerosols of diverse composition, including partially oxidised organics, have effects on the chemistry of nitrogen oxides, the sulphur cycle and marine derived halogen gases. Atmospheric fine particulate matter (PM2.5) is implicated in adverse human health effects and is a topic of great societal interest.

Evaluated data for the rates of heterogeneous reactions in the atmosphere were first provided by the IUPAC group approximately 10 years ago, and dimensionless uptake coefficients (gamma values) and Langmuir adsorption parameters have been presented on



the IUPAC website since 2008. The website also presents an introduction to atmospheric heterogeneous processes, a description of the parameterization used to describe the rate processes using the resistance model, and summary sheets containing the recommended uptake parameters. Publications have been provided in 2010 [12] covering reactions on solid surfaces (ice, mineral dust, soot, sulfuric acid hydrate and nitric acid hydrate surfaces) and in 2013 [13] covering reactions following transfer to aqueous water surfaces, deliquesced halide salts, other aqueous electrolytes, and sulfuric acid. These publications cover most of the important fine particulate present in the atmosphere. The most recent additions in this category are evaluated data for heterogeneous reaction of NO_3 and HO_2 radicals on aqueous tropospheric aerosols and organic aerosols, also available on the website. The evaluation of heterogeneous reactions on mineral dust is also relevant for the assessment of potential influence on stratospheric chemistry of climate geo-engineering schemes involving aerosol injection into the stratosphere for solar radiation management [14].

These evaluations, made through interpretation of measurements from field campaigns, have enabled important advances in our knowledge of atmospheric chemical processes. For example, the heterogeneous hydrolysis of N_2O_5 transfers gas-phase NO_x into particle-phase HNO_3 and may limit the abundance of NO_3 available to oxidize organic trace gases. This complements the extensive evaluation of the rate constants for NO_3 reaction kinetics with VOCs undertaken by the IUPAC panel. The multiphase reaction of N_2O_5 with particulate chloride also provides a route for additional oxidation capacity through the formation of nitryl chloride ($ClNO_2$) which is rapidly photolysed to highly reactive Cl atoms, leading to enhanced hydrocarbon oxidation rates and production of tropospheric ozone [15].

The IUPAC group expanded the scope of its work by adding aqueous-phase reactions in 2017. This new category of rate constant data covers the kinetics of atmospherically relevant reactions occurring in cloud droplets, fog and haze, and water-containing aerosol particles. It was established in the 1980s that aqueous phase oxidation of SO_2 plays an important role in the atmospheric formation of sulphuric acid. In the last decade it has been realized that aqueous phase reactions are also important in secondary organic aerosol formation [16,17]. Representation of aerosol formation in atmospheric models requires accurate data for aqueous phase chemical reactions. Datasheets and recommendations for more than 100 aqueous-phase reactions involving HO and NO_3 radicals, H_2O_2 and O_3, and organic accretion, have been produced and integrated into the website (http://iupac.pole-ether.fr/).

The past 40 years have seen exciting advances in our chemical understanding of processes related to stratospheric ozone loss, tropospheric ozone formation, acid rain, urban air pollution, aerosol formation, and climate change. The IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation is playing an important role in evaluating the chemical data used to understand and develop policies to address these critical societal challenges. The scope of the IUPAC group's work has grown and now includes over 1400 gas-phase, heterogeneous, and aqueous-phase reactions of importance in atmospheric chemistry. The datasheets describing the reactions and recommendations are available to the global technical community on a website which provides easy and intuitive access to the recommended data, grouped according to reaction phase and category. Work is progressing to extend the coverage and to convert the reaction datasheets into machine-readable files. These files will facilitate more effective communication with the international chemistry community by allowing automated transfer of IUPAC recommended data into atmospheric models. Atmospheric chemistry is a relatively young field with fascinating discoveries awaiting. We look forward to future discovery, innovation, and the application of fundamental chemistry to protect the atmosphere that is vital to our, and our children's, well-being.

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