General introduction

A Definition and coverage

In the following tables rate constants for reactions of free radicals in liquids are collected. The species covered are mostly paramagnetic molecules deriving their paramagnetism from a single unpaired valence electron. They are neutral molecular fragments or ions with positive of negative charges. Emphasis is on polyatomic organic free radicals. Excluded are some small species like the hydrated electron, the hydrogen and other atoms and a variety of polyatomic inorganic radicals. For reaction rates of these in aqueous solutions recent other compilations are available [88Bux and earlier tables]. A table on organic biradicals is included since their reactions are similar to those of monoradicals, and of carbenes, nitrenes and related compounds which also have similar reactivities.

The volume is divided grossly into sections dealing with individual types of free radicals such as carbon-centered radicals, nitrogen-centered radicals, nitroxy radicals, oxygen-centered radicals and radicals centered on other heteroatoms. These sections deal mainly with irreversible reactions. In addition, there are sections on proton transfer processes and their equilibria and a chapter on radicals reacting in excited states. An index of radicals formulae will facilitate data retrieval.

The reactions covered involve bimolecular processes between like and unlike radicals and between radicals and molecules via atom, group or electron transfer, or addition and unimolecular processes like fragmentations or rearrangements. Within the chapters dealing with special radical types a subdivision according to the types of reaction is applied. In such subdivisions the entries are organized according to the molecular formula of the radical involved, and formulae are in the order of increasing number of C, H atoms and then all other elements (except D, listed with H) in alphabetical order.

The main subject of the volume is the compilation of absolute rate constants for established reactions. In part they were deduced from published relative rate data if the absolute rate constants of the reference reactions were known. Relative rate constants of qualitative data as reaction half-lifes are included occasionally, in particular for important classes of radicals or radical reactions for which absolute data are not yet available. Thus, the tables do not represent a comprehensive compilation of all reactions known to date, yet of all those with sufficiently characterized reaction kinetics.

For details on subdivision into subvolumes, chapters and ordering within chapters, see Table of contents and the introductory sections of individual chapters. The literature is generally covered from the date of appearance of the precursor volumes Landolt-Börnstein New Series II/13a-e and 1993.

B Arrangement and contents of tables

As indicated by the general table headings there is one separate entry for each specific reaction or each set of competing reactions. Besides specifying the reaction the entry contains information on the technique of radical generation, the method of rate determination, and experimental conditions such as solvent and temperature. It lists the rate constants, the equilibrium constants and other rate data, such as activation parameters of the reactions, and gives the pertinent reference plus additional references. Further relevant information is given in footnotes. The following explanations apply to the individual parts of the entries.

REACTION: The reaction or the competing reactions are written in stoichiometric form starting with the reacting radical. For reactions between different radicals the radical appearing first in the adopted ordering of substances (see above) is written first and specifies the location of that entry. A cross reference to this reaction is entered at that later position of the tables which corresponds to the order of the second radical. The same principle is obeyed in the ordering of the substrates in competing radical molecule reactions. Where deviations from this scheme occur the reader is referred to the introduction of the individual chapters. Where necessary, structural formulae of radicals, reactants and products are written out in full detail. Repeatedly occuring structures are abbreviated by capital bold letters and an entry R = group may specify a substituent within the general structure. Self-evident structures of products are also abbreviated occasionally as OO- or NN-dimers of otherwise. Product structures are not given if they could not be identified from the original literature.
RADICAL GENERATION: The technique of radical production is outlined in short using abbreviations given in the *List of symbols and abbreviations*.

METHOD: The methods in use for the determination of reaction rate data are manifold, and a variety of abbreviations had to be introduced (see also *List of symbols and abbreviations*). Whereas earlier literature mostly applied the rather indirect techniques of measurements of product ratios (PR), the consumption of inhibitors (inh. cons.), rates of oxygen absorption (ROA) or consumption of other reactants (RRC) the progress of time resolved spectroscopy is evident more recently, and the most accurate rate data for irreversible processes are now obtained from kinetic absorption spectroscopy (KAS), kinetic electron spin resonance spectroscopy (KESR) or conductometry (cond.) in conjugation with pulsed radical generation. For reversible processes steady-state techniques of absorption spectroscopy (SAS) or electron spin resonance (ESR) or line-shape analyses in magnetic resonance (ESRLA, NMRLA) are common. For details of methods, the reader is referred to the original literature.

SOLVENT: Where possible the solvent is given by its molecular formula or name. Special conditions such as pH or solvent composition are indicated.

TEMPERATURE T [K]: The temperature of the sample during the rate measurement is given in K. RT stands for an unspecified room temperature. Where activation parameters of rate constants were measured, the column temperature indicates the temperature range of measurement.

RATE DATA: Rate constants of uni- and bimolecular processes are given in their usual dimensions s⁻¹ and M⁻¹s⁻¹, equilibrium constants in their corresponding appropriate dimensions. The same applies to ratios of rate constants. All rate constants k are defined for product appearance. Consequently, 2k governs the rate of radical disappearance in bimolecular self-reactions of radicals. Since the rate of radical disappearance is often measured in these cases, the value of 2k is displayed. If available the Arrhenius activation parameters, i.e. the parameters of the equation \( k = A \cdot \exp(-E_a/RT) \) are also listed with A given in logarithmic form and \( E_a \) in kJ mol⁻¹. The column rate data may also give enthalpies (\( \Delta H^* \)), entropies (\( \Delta S^* \)), and volumes (\( \Delta V^* \)) of activation in SI-units. For acid-base equilibria pK-values are listed. Errors are given in units of the last digit displayed for the data.

REFERENCE/ADDITIONAL REFERENCE: The first entry specifies the reference from which the data were extracted with the first two numbers for the year of appearance (92 = 1992), the following three letters for the family name of the first author and the last number ordering the publications in the year of publication. Additional references contain earlier less reliable work on the same subject, theoretical treatments of rate data or other relevant information.

The following list of symbols and abbreviations is common for all chapters. Additional symbols and abbreviations may appear as necessary in individual chapters. For these and additional information on contents and coverage, on arrangements and ordering and on special data display the reader is referred to the introductory sections of the individual chapters.