Liquid-Phase Reaction Rate Constants

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Е.Т. Денисов

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PREFACE

The past 25 years in chemical kinetics have seen major advances in studying the mechanisms of complex chemical reactions, in particular free radical reactions. Many different methods have been developed for quantitative studies of elementary chemical reactions. Thousands of rate constants have been measured, for hundreds of diverse chemical reactions. It is becoming more and more difficult for the chemist to orient himself in the voluminous and rapidly growing literature of chemical reaction kinetics. This leads to major expenditures of time in searching out, collecting, and evaluating quantitative kinetic data; to unnecessary repetition (duplication) of research; and to a situation in which the rich material already accumulated in the field of chemical kinetics is very often not fully utilized in comparing, interpreting, and analyzing new experimental data. There is a pressing need for the creation of a series of handbooks on reaction rate constants. Such work was begun several years ago at the initiative of V. N. Kondrat'ev, and is now going forward under his direction at the Institute of Chemical Physics of the USSR Academy of Sciences.

This book is devoted to liquid-phase, homolytic reactions. Part One contains data on monomolecular reactions in which molecules decompose to form radicals, as well as data on bimolecular and trimolecular reactions that form free radicals. Also collected in Part One are data on the probability of radical escape into the bulk volume from a "cage" of solvent with various initiators, as well as values of the stoichiometric inhibition coefficients for various phenols and aromatic amines that are used as free radical acceptors. In Part Two, rate constants are collected for reactions of decomposition, substitution, and addition of radicals to molecules, as well as radical recombination and disproportionation reactions. Part Three contains data on ion--molecule reactions that are accompanied by radical formation, as well as reactions of

free radicals with metal ions and acid anions, reactions of ion-radicals and solvated electrons, and ionic oxidation-reduction reactions with electron transfer. In this book, rate constant values are presented along with a statement of the conditions and a brief characterization of the method of measurement.

I wish to express deep gratitude to Academician V. N. Kondrat'ev for having inspired me to this not easy but useful task, and for having aided me with counsel. The last chapter of this book was written by V. N. Berdnikov. For assistance in collecting the reaction rate constants, I thank A. L. Buchachenko, R. L. Vardanyan, S. S. Ivanchev, N. F. Kazanskaya, G. M. Nazin, A. A. Shteinman, and V. Ya. Shlyapintokh. I also wish to express gratitute to Z. A. Denisova for painstaking work in preparing the manuscript for publication.

E. T. Denisov

SYMBOLS

Reaction rate constant, expressed in sec^{-1} for first-order reaction, liter/mole·sec for second-order reaction, and $liter^2/mole^2 \cdot sec$ for third-order reaction

Equilibrium constant

Activation energy, kcal/mole

Temperature in degrees Celsius

Temperature in degrees Kelvin
$\theta = 4.575\ T/1000$

Preexponential factor, with dimensionality corresponding to that of k for the reaction

Rate of chain reaction

Chain propagation rate constant in chain reaction

Rate constant for reaction between two radicals

Respectively, rate and rate constant for reaction of radical formation from molecules. If radicals $R\cdot$ are formed at a rate W_i and are destroyed only by reaction with each other (rate constant k_t), then in the stationary regime $W_i = 2k_t[R\cdot]^2$

Probability of escape of radicals into the bulk volume from a "cage" of solvent; if k is the rate constant for decomposition of initiator into two radicals, then $k_i = 2\ ek$

Concentration, mole/liter

InH	Inhibitor or acceptor of free radicals
f	Inhibition coefficient, equal to the number of radicals successively reacted with one molecule of inhibitor and conversion products from the inhibitor molecule

ABBREVIATIONS

The following abbreviations, which denote methods for measuring rate constants, are not listed in the original Russian text but have been compiled here for convenience. Abbreviations used here (in the English translation) are listed in the left-hand column; abbreviations used in the original Russian text are transliterated and listed in the right-hand column for reference.

Catal.	Ionic catalytic reactions	Kataliz
CINH	Inhibited chain reaction	TsING
CL	Chemiluminescence	KhL
CSM	Consumption of starting material	RIV
DP	Degree of polymerization	SP
EP	Emulsion polymerization	ÉP
EPR	Electron paramagnetic resonance	ÉPR
FM	Flash method	FM
ICA	Initial consumption of (radical) acceptor	NRA
IIM	Intermittent illumination method	PO
IIP	Introduction of initiator fragments into polymer	VIP
IM	Isotope method	IM
JM	Jet method	JM
KEPF	Kinetics of end product formation	KOKP
KICR	Kinetics of initiated chain reaction	KTsIR
Kin. Racem.	Kinetics of racemization	Kin. Ras.
KNP	[not identified]	KNP
KRAC	Kinetics of radical acceptor consumption	KRAR
KRR	[not identified]	KRR
MCR	Method of competing reactions	MKR
NK	[not identified]	NK
NKR	Nonstationary kinetics of radical chain reaction	NKR

NMR	Nuclear magnetic resonance	YaMR
NR	[not identified]	NR
Pol.	Polarographic method	Pol.
POL	[not identified]	POL
PR	Pulse radiolysis	IP
PSD	Photochemical space discontinuity	FPP
RICR	Rate of initiated chain reaction	STsIR
RRC	Products of radical recombination in cage	PR
RUCR	Rate of unbranched chain reaction	STsNR
SUNR	[not identified]	SUNR
TIM	Tritium isotope method	ITM
TJ	Temperature jump	TS
TsINR	[not identified]	TsINR

Note: For a listing of abbreviations for names of ligands in metal complexes, see Chapter X, p. 482.

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