STATE-TO-STATE CHEMISTRY

Philip R. Brooks
and
Edward F. Hayes
Editors

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State-to-State Chemistry

Philip R. Brooks and
Edward F. Hayes, EDITORS
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FOREWORD

The ACS Symposium Series was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing Advances in Chemistry Series except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. As a further means of saving time, the papers are not edited or reviewed except by the symposium chairman, who becomes editor of the book. Papers published in the ACS Symposium Series are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

One of the main goals of chemistry is to understand and predict chemical changes. Toward this end chemists have attempted to characterize reactive intermediates and to study the rates of various elementary chemical processes. A complete understanding of a chemical reaction requires knowledge of the microscopic rate constant for evolution of a system in a single reagent "quantum state" (translation, rotation, vibration, and electronic state) to a single product "quantum state." Conventional bulk rate studies are incapable of resolving these states and merely provide average rates. Although much has been learned from these average rates, further understanding demands less averaging. Fortunately, technological developments—such as molecular beams and lasers—are providing us with the tools necessary to probe these states, and the direct measurement of some of these fundamental microscopic "state-to-state" reaction rates has begun to be feasible.

The papers assembled in this volume represent the proceedings of a symposium held at the 173rd ACS National Meeting, March 21–23, 1977, in New Orleans. The purpose of the symposium and this book is to present a snapshot of the exciting and rapidly developing field of state-to-state chemistry. The papers represent early attempts to answer such questions as: "Which quantum states are most likely to react?" and "Which quantum states are most likely to be formed?" Few papers actually represent studies of the evolution of one quantum state into another (except some of the theoretical papers), attesting to the present difficulties in performing such experiments. Instead, collision processes (both chemical reactions and energy transfer collisions) are studied with varying groups of quantum states specified.

In the area of state-to-state chemistry the interaction between theory and experiment is strong, with theory suggesting new experiments and new approaches and experiment providing calibration for the theory. This marriage has been very productive in the generation of chemical "scope" or understanding, but some practical children have also been born. One past example of this is the infrared chemiluminescence experiments of Polanyi (1961) showing that HCl was preferentially formed in vibrationally excited states in the reaction of H atoms with Cl_2. These results were essential to Kasper and Pimentel in their development of the first HCl chemical laser (1965). While other studies have led to still other lasers, the emphasis has recently been reversed: lasers are being used to alter the course of reactions. This raises the tantalizing possibilities of laser chemistry where lasers are used to choose a quantum state of the reagents which may react faster or form different products from the ground state. Currently there is considerable interest in the possibility that laser-induced chemistry may be attractive for large-scale chemical processing.

The papers in this volume have been grouped under three main headings: Reactive Collisions, Energy Transfer Collisions, and Theory. In addition, Reactive Collisions has beeen further divided into Beam Studies and Bulk Studies. The assignment of a paper to a particular group in many cases was somewhat arbitrary. It should be recognized that there are strong complementary interactions between research activities in each of these areas.

The editors hope that this book will help the reader share in the exciting developments in state-to-state chemistry. It is a pleasure to thank the contributors and publishers for their excellent cooperation, without which this volume would not have been possible. A special note of thanks goes to Dorothy D. Butler for her assistance in assembling the manuscripts.

July 1977

PHILIP R. BROOKS
EDWARD F. HAYES

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Paul R. Brooks
Edward F. Hayes

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State-to-State Cross Sections and Rate Constants for Reactions of Neutral Molecules

RICHARD B. BERNSTEIN

Chemistry Department, The University of Texas, Austin, TX 78712

Recent experimental and theoretical advances have led to the development of a new field known as "state-to-state" chemistry. It is now becoming possible to measure directly (and interpret, on a sound theoretical basis) the relative probabilities of formation of nascent reaction products in specified internal states from reagents in selected states.

In addition to a number of important practical applications (e.g., the discovery of new laser-induced reactions and the development of improved chemical lasers) there are many fundamental implications for the field of gas-phase chemical kinetics. The basic components of the reaction rate constant are the state-to-state rate coefficients, say $k_{i\rightarrow f}(T)$, or, at a more fundamental level, the state-to-state reaction cross sections, $\sigma_{i\rightarrow f}(E)$. Here i and f denote initial (reagent) and final (product) states, respectively, T the translational temperature, and E the total energy.

The theoretical framework for dealing with state-to-state kinetics was laid down by Eliason and Hirschfelder (1) in 1959, who established the relationship between the transition probabilities, the detailed differential state-to-state cross sections, the reaction cross sections, state-to-state rate coefficients and the thermal rate constant. A number of subsequent fundamental papers have advanced the understanding of state-to-state reactions (2-4).

Reviewing briefly (5), the gas-phase bimolecular thermal rate constant can be expressed

$$k(T) = \sum_i P_i(T)k_i(T), \qquad (1)$$

where $P_i(T)$ represents the relative population of reagent state i at the given temperature T, and $k_i(T)$ is the total rate constant out of state i,

$$k_i(T) = \sum_f k_{i\to f}(T), \tag{2}$$

summing over all final states f.

Consider an experiment at a given translational energy distribution characterized by a certain value of the average relative translational energy $\bar{E}_{tr}$. The state-to-state rate constant is the expectation value of the product of the relative speed times the cross section, i.e.

$$k_{i\to f}(\bar{E}_{tr}) = \left\langle v_r \sigma_{i\to f}(v_r)\right\rangle_{\bar{E}_{tr}} \tag{3}$$

where $v_r = (2E_{tr}/\mu)^{\frac{1}{2}}$. Thus

$$k_{i\to f}(\bar{E}_{tr}) = \int v_r \sigma_{i\to f}(v_r)p(v_r|\bar{E}_{tr})dv_r \tag{4a}$$

$$= (2/\mu)^{\frac{1}{2}}\int \sigma_{i\to f}(E_{tr})E_{tr}^{\frac{1}{2}}\, P(E_{tr}|\bar{E}_{tr})dE_{tr} \tag{4b}$$

where p and P represent the normalized probability density functions (pdf's) for v_r and E_{tr}, respectively.

Considering the total rate constant out of state i,

$$k_i(\bar{E}) = (2/\mu)^{\frac{1}{2}}\int E^{\frac{1}{2}}\sigma_i(E)P(E|\bar{E})dE \tag{5}$$

where $\sigma_i(E) = \sum_f \sigma_{i\to f}(E)$ (6)

(dropping the subscript tr).

For the special case of a Maxwellian translation energy distribution (for which $\bar{E} = 3\underline{k}T/2$),

$$P(E|3\underline{k}T/2) = 2(E/\pi)^{\frac{1}{2}}(\underline{k}T)^{-3/2}\exp(-E/\underline{k}T) \tag{7}$$

so $k_i(T) = (\pi\mu)^{-\frac{1}{2}}(2/\underline{k}T)^{3/2}\int E\sigma_i(E)\exp(-E/\underline{k}T)dE$ (8)

from which k(T) is obtained via Eq. (1). For the limiting case of a line-of-centers cross section (rising from threshold at $E=E_\circ$, to a limiting value of πd^2), and assuming no state dependence, Eq. (8) yields the usual Arrhenius-like temperature dependence for the rate constant

$$k(T) = (8\underline{k}T/\pi\mu)^{\frac{1}{2}}\pi d^2\exp(-E_\circ/\underline{k}T). \tag{9}$$

Eq. (9) is not applicable to reactions of excited-state reagents and non-Maxwellian translational distributions; one must use Eq. (1), which requires a knowledge of P_i, together with Eq. (5), which requires both $P(E)$ and $\sigma_i(E)$ for all populated reagent states i. As will be seen later, for reactions with an energy barrier σ_i is extremely sensitive to the state of internal excitation of the reagent, and therefore so is k_i. For many practical situations involving laser excitation the translational distribution can be taken to be essentially Maxwellian and so Eq. (8) may be used.

In 1969 Parker and Pimentel (6) made a significant advance in connection with their chemical laser study dealing with the exothermic $F + H_2 \rightarrow HF^\dagger + H$ reaction, which gives rise to a vibrational population inversion in the HF product. (The dagger denotes internal excitation.) From the ratios of the rate constants for the formation of the various vibrational states of the $HF^\dagger$ (see Fig. 1), they deduced (via detailed balance) that the rate of the reverse, endothermic reaction would be strongly enhanced by vibrational excitation of the HF reagent. The possibility of preferential utilization of reactant internal excitation energy (vs. relative translational energy) had already been suggested on dynamical grounds by Polanyi (7) in 1959 (and, on the basis of trajectory calculations a decade later by Polanyi et al (8, 9) and Raff et al (10)).

In 1969 Anlauf et al (11) showed how to make use of microscopic reversibility to predict the vibrotational selectivity in endoergic reactions from the population-inversion data for the inverse (exoergic reaction), usually obtained from infrared chemiluminescence data (12).

Consider the state-to-state atom–diatomic exchange reaction, written in the exoergic direction:

$$A + BC\ (v,J) \underset{r}{\overset{f}{\rightleftarrows}} AB(v',J') + C; \qquad \Delta E_\circ < 0. \qquad \text{(I)}$$

At a given value of the total energy E, microscopic reversibility yields (2, 3, 11):

$$\frac{\sigma_f(vJ \rightarrow v'J'|E)}{\sigma_r(v'J' \rightarrow vJ|E)} = \left(\frac{\mu'}{\mu}\right) \times \left(\frac{E'_{tr}}{E_{tr}}\right) \times \left[\frac{2J'+1}{2J\ +1}\right] \qquad (10)$$

so $$\frac{k_f(vJ \rightarrow v'J'|E)}{k_r(v'J' \rightarrow vJ|E)} = \left(\frac{\mu'}{\mu}\right)^{3/2} \times \left(\frac{E'_{tr}}{E_{tr}}\right)^{\frac{1}{2}} \times \left(\frac{2J'+1}{2J+1}\right) . \qquad (11)$$

Several valuable reviews have been published (5, 13-16) dealing with experimental and theoretical-computational studies of nascent product state distributions for exoergic reactions (which are found to be almost always non-Boltzmann).

Recently, Levine et al (17-20) presented a theoretical analysis of the effect of reagent energy on reaction rates. They employed the information-theoretic method (21-25) to deal with the problem of the selectivity of energy requirements. In the course of their work they considered also the implication of detailed balance.

Kaplan et al (19) showed that for a Maxwellian translational distribution, detailed balance yields

$$\frac{k_f(vJ \rightarrow v'J'|T)}{k_r(v'J' \rightarrow vJ|T)} = \left(\frac{\mu'}{\mu}\right)^{3/2} \times \left(\frac{2J'+1}{2J+1}\right) \times \exp(-\delta_1 E/\underline{k}T) \qquad (12)$$

where $\delta_1 E \equiv \Delta E_\circ + G_{v'J'} - G_{vJ}$; (13)

here G_{vJ} is the vibrotational energy of the reagent vJ state, $G_{v'J'}$ that for the product v'J' state.

In the special case for which the rotational states of both reagent and product molecules are Boltzmannized, Eq. (12) leads to the detailed-balance result:

$$\frac{k_f(v \rightarrow v'|T)}{k_r(v' \rightarrow v|T)} = \frac{\sum_{J'}(2J'+1)\exp(-G_{J'}/\underline{k}T)}{\sum_{J}(2J+1)\exp(-G_J/\underline{k}T)} \times \left(\frac{\mu'}{\mu}\right)^{3/2} \times \exp(-\delta_2 E/\underline{k}T) \qquad (14)$$

where $\delta_2 E \equiv \Delta E_\circ + G_{v'} - G_v$; (15)

here G_v is the vibrational energy of the reagent in its rotationless state and $G_{v'}$ that of the product. Eq. (14) is essentially that used by Parker and Pimentel (6) in their analysis of the vibrational dependence of the "reverse rate constant", mentioned above.

On the experimental side, an early yet elegant experiment in the ion-molecule field played an important role in stimulating research involving excited neutral reagent molecules. This "textbook example" is the work of Chupka et al (26) in 1969 on the endoergic ion-molecule reaction $H_2^+(v) + He \rightarrow HeH^+ + H$, from which a direct comparison could be made (27), at constant total energy, of the comparative effect of reagent vibrational energy vs. relative translational energy upon the reaction cross section. Enhancements of more than two orders of magnitude were observed, which have been the subject of considerable theoretical attention (17, 28).

A number of other ion-molecule studies showed important vibrational energy effects, but in the field of neutral-neutral kinetics results on selectivity of energy requirements (14) were forthcoming with more difficulty. These are the subject of the review which follows. Not to be discussed are the closely related but well-reviewed (13-16) subjects of vibrotational and translational energy disposal in exoergic reactions, nor the large body of computer-simulation studies.

Early "bulk" experiments involving vibrationally excited reagents.

In 1970 Stedman et al (29) produced evidence from a discharge-flow experiment that the rate of the reaction $Cl + H_2$ is enhanced by H_2 vibrational excitation. In 1972 Heidner and Kasper (30) reported that the rate constant for the process (predominately reactive) $H + H_2(v=1) \rightarrow H_2(v=0) + H$ exceeded that of the H-exchange reaction with ground-state H_2 by a factor of ca.10^3. They attributed this to the efficient utilization of the 12 kcal mol^{-1} excitation energy in overcoming the barrier (corresponding to a 7.5 kcal mol^{-1} activation energy). On the other hand, Birely et al (31) in 1975 found in a similar discharge-flow experiment that vibrational excitation of the H_2 was ineffective in overcoming the barrier corresponding to the 10 kcal mol^{-1} activation energy for the reaction of H_2 with oxygen atoms.

Bauer et al (32) in 1973 reported observations of a laser-induced exchange reaction: $H_2 + D_2 \rightarrow 2HD$, interpreted in terms of a vibrational enhancement mechanism. They deduced from a computer analysis of their experimental data that the exchange reaction proceeds with a measureable rate for $H_2(v \geq 4)$. However, there is some doubt about the interpretation of the experi-