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Fortschritte der chemischen Forschung

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68

Theory

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This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

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Reactivity and Structure

Concepts in Organic Chemistry

Editors: K. Hafner, J.-M. Lehn, C. W. Rees, P. v. R. Schleyer, B. M. Trost, R. Zahradník

Volume 1: J. Tsuji
Organic Synthesis
by Means of Transition Metal Complexes
A Systematic Approach
4 tables. IX, 199 pages. 1975
This book is the first in a new series, *Reactivity and Structure: Concepts in Organic Chemistry,* designed to treat topical themes in organic chemistry in a critical manner. A high standard is assured by the composition of the editorial board, which consists of scientists of international repute. This volume deals with the currently fashionable theme of complexes of transition-metal compounds. Not only are these intermediates becoming increasingly important in the synthesis of substances of scientific appeal, but they have already acquired great significance in large-scale chemical manufacturing. The new potentialities for synthesis are discussed with examples. The 618 references bear witness to the author's extensive coverage of the literature.

Volume 2: K. Fukui
Theory of Orientation and Stereoselection
72 figures, 2 tables. VII, 134 pages. 1975
(Parts of this book have been published in "Topics in Current Chemistry", Vol. 15)
The 'electronic theory' has long been insufficient to interpret various modern organic chemical facts, in particular those of reactivity. The time has come for a book which shows clearly what is within, and what is beyond, the reach of quantum-chemical methods. Graduate students and young researchers in chemistry, both theoretical and experimental, will find this book an invaluable aid in helping them to become accustomed to the quantum-chemical way of thinking. Theory produces new experimental ideas, and, conversely, a host of experimental data opens new theoretical fields. A book such as the present one will constantly maintain its value, although the quantum-chemical approach to the theory of reactivity is, of course, still in the developmental stage.

Volume 4: H. Kwart, K. King
D-Orbital Involvement in the Organo-Chemistry of Silicon, Phosphorous and Sulfur
In Vorbereitung
Valence shell expansion has often been invoked in explanation of all sorts of unexpected effects in the spectra, bond lengths and angles, and the chemical reactivity of organic compounds of sulfur, phosphorous and silicon. The evidence cited in nearly 1,000 references for d-orbital participation in bonding in these third row elements and for alternative explanations is critically examined.

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Contents

Theoretical Chemical Dynamics: A Tool in Organic Chemistry

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* The Laboratoire de Chimie Théorique is associated to the C. N. R. S. (ERA n° 549).

Foreword

Obtaining the rate of a chemical reaction from the knowledge of the collisional elementary processes governing it, defines approximately the field of Chemical Dynamics. In most cases the investigation is restricted to molecular systems including a few atoms for the following reasons:

(i) the experiments for analyzing a flux of molecules in various intramolecular states are limited for technical reasons;

(ii) it is only in the case of small systems that "ab initio" potential energy surfaces can be computed over a wide range of coordinates where the dynamic can be studied rigorously.

The present article is a contribution for extending the scope of Chemical Dynamics in Organic Chemistry. In the first Chapter (A), previous trajectory studies in Chemical Dynamics are reviewed. The second Chapter (B) presents a general but elementary method for undertaking the dynamical study of any chemical reaction. This method seems to be applicable in a straightforward way to rather large molecular systems in Organic Chemistry. An application of this method is presented in the third Chapter (C): the optical and geometrical isomerizations of cyclopropane are treated dynamically[a]. It makes use of an ab initio potential energy surface[2-4]. The results are, as far as possible, compared with experimental results[b].

It should be emphasized that classical trajectories methods at present can be considered as fairly standard techniques for studying the dynamical behaviour of small molecular systems (either triatomic or tetraatomic). As a consequence many technical points have already been discussed in great detail in the literature[7-9] and they will not be discussed here. Such technical questions are, for instance:

(i) should a parameter defining an initial state be either scanned or sampled in a random way (Monte-Carlo methods)? ;

(ii) should the sampled points have uniform density or be distributed according to some weighting function?;

(iii) should quantized values of the initially observable quantities be exclusively selected? etc . . .

Other important topics related to the technology of trajectories will not be discussed either, for instance:

(iv) which integrator should be used to obtain the best compromise between stability and efficiency?[10-12];

(v) what are suitable tests to stop a trajectory integration according to the type of outcome produced?[7]

(vi) what type of semi-empirical potential should be preferentially used for a given reaction?[8] etc . . .

We will restrict this article to developing in detail our original contribution to the study of Chemical Dynamics in the field of Organic Chemistry. Consequently we will not say much about the connection between our work and semi-empirical statis-

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a) This study was previously published in the Journal of the American Chemical Society[1, 2].

b) More details on the subject can be found in our two "Thèses de Doctorat d'Etat": Yves Jean, Orsay (1973)[5] and Xavier Chapuisat, Orsay (1975)[6].

tical methods of chemical reactivity, such as the transition state method or the Rice-Ramsperger-Kassel-Marcus (RRKM) theory of unimolecular reactions[13–15]. The two points of view, dynamical and semi-empirical, differ greatly. Once again, the comparison is only meaningful in the case of small molecular systems for which complete and rigorous results have been obtained within both methodologies.

Finally, in view of all the restrictions above, the title of this article could as well be: "What can we do with trajectories in Organic Chemical Dynamics and under what kind of restrictions (drastic or not) is it possible?"

A. Trajectory Studies in Chemical Dynamics

1. Introduction

In this chapter we define the scope of this article, mention some studies relevant to it and give references where these studies are dealt with.

It is quite simple to say that this article deals with Chemical Dynamics. Unfortunately, the simplicity ends here. Indeed, although everybody feels that Chemical Dynamics lies somewhere between Chemical Kinetics and Molecular Dynamics, defining the boundaries between these different fields is generally based more on surmisal than on knowledge. The main difference between Chemical Kinetics and Chemical Dynamics is that the former is more empirical and the latter essentially mechanical. For this reason, in the present article we do not deal with the details of kinetic theories. These are reviewed excellently elsewhere[16–21]. The only basic idea which we retain is the reaction rate. Thus the purpose of Chemical Dynamics is to go beyond the definition of the reaction rate of Arrhenius (activation energy and frequency factor) for interpreting it in purely mechanical terms.

This field of research is subject to rapid expansion at present because the improvement of sophisticated experimental methods coincides with an increase of the computational possibilities for the theoretical investigation of both the mechanical study of the nuclear motion and the quantum mechanical study of the electron potential governing this motion.

The experimental situation has been the subject of several recent review papers, either general[22–24] or more specialized (molecular beams[25–32], infrared chemiluminescence[33], reactions of small molecules in excited states[34], etc . . .). The quantum mechanical theoretical approaches of Chemical Dynamics were also reviewed recently[8, 35, 36].

Since the scope of this article is purely theoretical, we just outline below the state of the experimental situation. The ideal experiment in Chemical Dynamics would be that in which starting with reactants in definite intramolecular quantum-states and running towards each other in a definite way (relative velocity and orbital angular momentum) the distribution of the products over the various intramolecular quantum-states and the state of the relative motion (direction and velocity) would be measured. Such an experiment would show whether there is a preferential molecular orientation at the heart of the collision, what the lifetime of the intermediate complex is, how the excess energy is distributed over the various degrees of freedom of

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this complex, etc. . . Unfortunately, this experiment has not been carried out yet, but there are experiments which fulfill one part or the other of the ideal experiment. In crossed-molecular-beams experiments, the reactants are prepared in perfectly defined states[37–53]. For instance a laser can select a given rotation-vibration intramolecular state[54, 55]. The products are analyzed by means of one of the following techniques:

(i) the laser-induced fluorescence[56–58];
(ii) the infrared chemiluminescence[33, 59–63];
(iii) the electric resonance spectroscopy[64–67] and
(iv) the chemical laser[59, 68–74].

We do not insist on stating details of these experiments. Let us just mention the recent work of Herschbach and collaborators which is a very impressive achievement[75, 76]. These authors have studied, by means of molecular beams, the very details of "termolecular" reactions involving van der Wall's bonds among halogen molecules, such as:

$$Cl_2 \ldots Cl_2 + Br_2 \longrightarrow (1)\ Cl_2 + 2\ BrCl;$$
$$(2)\ BrCl \ldots Cl_2 + BrCl \text{ and}$$
$$(3)\ Br_2 \ldots Cl_2 + Cl_2.$$

In particular, to channel (1) and (2) mechanisms involving formations of the same cyclic six-center intermediate complex can be attributed whereas channel (3) only requires Br_2 to interact with the nearer Cl_2 molecule of the dimer within a noncyclic molecular conformation. Thus channel (3) dominates at low collision energies (< 9 kcal/mol), but declines rapidly at higher collision energies and becomes much less probable than collision-induced dissociation to form $Br_2 + 2\ Cl_2$, this applies also to both channels (1) and (2).

In Chemical Dynamics the direct comparison between experiments (more precise than simple kinetic measurements of reaction rates) and theoretical results is in general rather subtle. As far as we know, it has been restricted to reactions in which a halide is produced. The most studied reaction, both theoretically[77, 80] and experimentally[47, 48, 69, 81], is

$$F + D_2 \longrightarrow DF + D,$$

or its isotopic variants

$$F + H_2 \longrightarrow HF + H \text{ and}$$
$$F + HD \longrightarrow HF + D.$$

Thus the activation energy for the formation of DF is minimal when F and D_2 collide colinearly. At low collision energy most molecules DF are observed backwards, in vibrational states $v = 2$, 3 and 4, at weak total angular momentum, etc. . . All the theoretical studies of this reaction, but one[80], use classical trajectories.

2. Trajectory Studies of Small Molecular Systems

Since theoretical Chemical Dynamics resort practically to classical trajectories, we briefly review below some previous works in this field[c].

The first chemical reaction studied by means of classical trajectories was $H_2 + H \longrightarrow H + H_2$ within the *collinear collision model*[84–87]. This pioneering work states the following: For any system driven by a bent potential valley, the reaction proceeds through a gradual transformation of the collision energy into vibrational energy of the product molecule. The first 3-dimensional trajectories were for the same reaction[88]. Since then, much important work has been undertaken. For instance, the way in which an empirical modification of the potential modifies the reaction-probability, the intramolecular states of the products, the deflection angle, etc. . . all these were the subject of many studies[89–95] and also of a review article[96].

The first "a priori" study (by Karplus, Porter and Sharma) of a chemical reaction undertaken on a large scale was again for $H_2 + H$, described by a London-Eyring-Polanyi-Sato (LEPS)-type potential[97–100]. All the standard concepts and techniques were introduced for this investigation[101]: 3-dimensional model, restricting the intramolecular states of the reactants to quantized states, obtaining the reaction total cross-section[d] as a function of the collision energy and of the intramolecular states of the reactants by averaging over the impact parameter (pseudo-random Monte-Carlo method), integrating these cross-sections with the collision energy to obtain the *rate constant* of the reaction, etc. . .

The main results of this study are[101]:

(i) the total reaction cross section is an increasing function of the collision energy that rises smoothly from a threshold to an asymptotic value;

(ii) the zero-point vibrational energy of the molecule contributes to the energy required for reaction, but the rotational energy does not;

(iii) the reaction probability is a smoothly decreasing function of the impact parameter;

(iv) for temperatures between 300 °K and 3000 °K the theoretical rate constant can be expressed by the form $K(T) = AT^{\alpha} \exp\{-E^{\ddagger}/kT\}$ where A, $E^{\ddagger}$ and α (= 1.18) are constants;

(v) there is no evidence of a long-lived intermediate complex.

The model was extended to the general atom-diatom exchange reaction $A + BC \longrightarrow AB + C$[102, 103], for which Polanyi and Wong studied in *3 dimensions* the relative influence of both initial translational energy and vibrational energy. This depends largely on the location of the top of the potential barrier, either along the approach coordinate (case I) or along the retreat coordinate (case II). In case I translation is more effective than vibration in promoting reaction. Moreover, at low collision energy, a major part of the available energy transforms into vibration of the product molecule (at higher collision energy this fraction decreases). In case II the opposite situation is observed: vibration is more effective than translation. Moreover, for low vibra-

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c) There are several more detailed review articles on the subject[7–9, 82, 83].

d) The cross section of an elementary collision process is roughly a measure of the reaction efficiency of this process.

tional energy of the reactants only a small part of the available energy appears as vibration in the product (at higher vibrational energy this fraction increases). This confirms the conclusion obtained within the collinear collision model. In both cases I and II most product molecules are scattered backwards at low collision energy (the peak of the distribution shifts forward at increased reactant energy, even in case II for an increase of reactant vibration).

Then the Karplus *et al.* model was extended to more complex reactions[104, 105], such as

$$K + CH_3I \longrightarrow KI + CH_3$$ [92, 93, 99, 100, 106]

and finally to the general *thermal bimolecular* reaction in the gas-phase: $A + B \rightleftharpoons C + D$[107, 114]. For the latter it is possible to obtain the forms for the theoretical rate constants[19, 82, 101, 115–120] for the forward ($\vec{K}$) and the backward ($\overleftarrow{K}$) reactions [defined by[e]: $-d(A)/dt = \vec{K}(A)(B) - \overleftarrow{K}(C)(D)$] as functions of the temperature. If the gas phase is homogeneous the temperature is introduced through maxwellian distribution functions. The result is:

$$\vec{K} = \sum_{\chi_A, \chi_B, \chi_C, \chi_D} F_A(\chi_A) F_B(\chi_B) \int d\vec{v}_A F_A(\chi_A; \vec{v_A}) \int d\vec{v}_B F_B(\chi_B; \vec{v_B})$$

$$v\, \sigma(\chi_A, \chi_B, \chi_C, \chi_D; E_{col})$$

$$\overleftarrow{K} = \sum_{\chi_A, \chi_B, \chi_C, \chi_D} F_C(\chi_C) F_D(\chi_D) \iint d\vec{v}_A\, d\vec{v}_B\, F_C(\chi_C; \vec{v}_C) F_D(\chi_D; \vec{v}_D)$$

$$v\, \sigma(\chi_A, \chi_B, \chi_C, \chi_D; E_{col})$$

where χ_I (I = A, B, C, D) denotes the set of all the quantum numbers defining the intramolecular state of molecule I (rotations and vibrations) $F_I(\chi_I)$ is the distribution function of the intramolecular quantum states of molecule I, $\vec{v}_I$ is the velocity of molecule I, $F_I(\chi_I; \vec{v}_I)$ is the normalized distribution function of the velocity of molecule I in the state χ_I, v is the initial relative velocity and E_{col} the collision energy:

$$v = |\vec{v}_A - \vec{v}_B| = (2E_{col}/\mu)^{1/2}$$

where μ is the reduced mass of A and B.

$$\sigma(\chi_A, \chi_B, \chi_C, \chi_D; E_{col})$$

is the reaction cross section of the elementary collision process $[A(\chi_A) + B(\chi_B) \longrightarrow C(\chi_C) + D(\chi_D)]$ at collision energy E_{col}. It is this quantity which is obtained by means of trajectories.

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e) This definition is for low concentrations and implies that the rate constants depend neither on the concentrations nor on the time.

This result is purely statistical. Replacing the distribution function by particular expressions, depending on the temperature, is the last operation[f]. When a dynamical process occurs the equilibrium distribution function (maxwellian) should be modified, and the greater the reaction rate compared to the relaxation rates of both the velocities and the intramolecular states, the greater the modification[121–123]. Thus it is only for low reaction rates that equilibrium distribution functions can be inserted in the formulas above, and that the reaction rate depends on the temperature, but neither on the time nor on the concentrations.

Now a question must be raised: which connection is there between classical trajectories results and results obtained through Quantum Mechanical calculations?

The Quantum Mechanical study of molecular collisions and of the chemical reaction is itself an important topic[124]. There are several review papers[35, 36, 125–129] and textbooks[130–139] on the subject. Unfortunately, there are no exact quantum results within a realistic model of a chemical reaction yet, not even for the simplest 3-atoms exchange. Thus the comparison is limited to particular cases.

For instance, $H + H_2 \longrightarrow H_2 + H$ was studied in 3-dimensions within a model where the vibrational states were reduced to a single one for each of the three possible product molecules[140]. At low collision energy (less than the classical energy threshold) the reaction cross section is non zero because of tunnelling. For the same reaction studied colinearly the following conclusions emerge[141–143]:

(i) for great values of the collision energies the quantum mechanical reaction probability slightly oscillates around the classical probability, because of the gradual "opening of excited vibrational states" in the products;

(ii) the reaction probability extends below the threshold by tunnelling. Thus, at low temperature and for the phenomenon of a pronounced quantum nature (such as the exchange of a light atom between two heavy groups), the classical trajectory reaction rate may be an underestimated approximation of the true reaction rate.

On the basis of such results and, more convincingly, on the strength of semi-classical investigations (classical S-matrix of Miller and Marcus[144–150]) it can be asserted that the classical description of the nuclear motion in the course of a molecular collision (either reactive or not) is not in itself a severe restriction. Thus, McCullough and Wyatt[151–152] have shown that for collinear $H + H_2 \rightarrow H_2 + H$ the agreement is quite good between the classical and the time-dependent quantum-mechanical descriptions during the greatest part of the reaction. A slight discrepancy appears only near the end of the reaction; the classical reaction is completed somewhat faster than the quantum-mechanical one. Nevertheless, all the dynamical effects such as the centrifugal force pushing the representative point of the reaction towards the outer part of the bent reaction valley and the whirlpool turbulence effects close to the saddle point, are surprisingly well described classically.

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[f] In the case of a complete equilibrium distribution, the result is:

$$K(T) = (8/\pi\mu kT)^{1/2}/kT \int_0^\infty dE_{\mathrm{col}}\, \sigma'(E_{\mathrm{col}})\, E_{\mathrm{col}} \exp(-E_{\mathrm{col}}/kT),$$

where: $\sigma'(E_{\mathrm{col}}) = \sum_{x_A, x_B, x_C, x_D} F_A(x_A)\, F_B(x_B)\, \sigma(x_A, x_B, x_C, x_D; E_{\mathrm{col}})$.

To wind up this chapter, we enumerate below the various fields of application of classical trajectories in Chemical Dynamics.

Many trajectories were integrated to obtain either total reaction cross sections for comparison with molecular beams experiments[79, 105, 153–171], or rotational and vibrational relaxation times of the products of chemical reactions, or intermolecular energy transfers[103, 107–111, 172–185], etc. . .

As seen previously, the chemical reactions studied most often are the exchange ones. Those requiring several potential energy surfaces of excited states (diabatic reactions) are worth special mention, since they most certainly define a domain of application with a future for classical trajectories. An electron jump from one surface to another requires either to be given a statistical probability of occurence by the Landau Zener formula[186, 187] (or one of its improved versions[188–192]) or to be described by means of complex-valued classical trajectories as a direct and gradual passage in the complex-valued extension of the potential surfaces (generalization of the classical S-matrix[193–197]).

Some atomic recombinations catalized by a rare gas atom[198–205] and some reactions involving a long-lived intermediate complex[112, 113, 206–208] were also studied classically. *Unimolecular* reactions are quite advantageous for trajectory studies since the potential is generally easy to express and the total energy is sufficiently great for reasonably neglecting the discreteness of vibrational levels of the reactant[7]. Until recently only triatomic decomposition has been studied extensively: $ABC \longrightarrow AB + C$[209–211]. The main concern is for the distribution of molecular lifetimes (the time elapsed before decomposition occurs) and for the variation of this distribution when varying the total energy and the particle mass. This can be compared directly with semiempirical predictions. Thus, it is well established for triatomic systems that the RRKM rate coefficients[13] satisfactorily agree with trajectory results. Another important advantage of trajectory methods is to provide the final energy partitioning between AB and C.

More recently, the unimolecular isomerization $CH_3NC \longrightarrow CH_3CN$ gave rise to elaborated studies by Bunker and collaborators[212–215]. The pressure dependence of the thermal reaction rate constant is well explained by the RRKM theory, applying the simple concept of the geometry and vibrations of the activated molecule[216]. However, the fact that the hot-atom displacement reactions

$$T^* + CH_3NC \longrightarrow CH_2TNC + H$$

and

$$T^* + CH_3CN \longrightarrow CH_2TCN + H$$

both result at the very end in CH_2TCN (observed by trajectories) is indicative of a failure of the RRKM theory for the unimolecular isomerization of nascent molecules[217]. In particular, CH_3NC is not a good RRKM molecule under non-thermal conditions, because the vibrational modes of CH_3NC are too far from being equally coupled to one another and also to the mode of isomerization. For unimolecular reactions it should be kept in mind that, since many vibrations (and not only the single translation) may play important roles, trajectory studies are always delicate and require much caution.

There have been a number of interesting trajectory studies of organic reactions that have used *empirical* potential energy surfaces. $CH_3NC \longrightarrow CH_3CN$ is the first example. The second example is

$K + C_2H_5I \longrightarrow KI + C_2H_5$ (studied by Raff)[218]

where the ethyl group is treated as a two-body system. The main results are:

(i) the total reaction cross section for this reaction is less than that for $K + CH_3I \longrightarrow KI + CH_3$, due to the increased steric hindrance;

(ii) KI is predominantly scattered backwards;

(iii) the C–C stretch of the ethyl absorbs an important part (15%) of the heat of reaction;

(iv) the reaction can occur by two mechanisms, either directly or through formation of a collision complex.

In the first mechanism most of the reaction energy transforms into rotation-vibration energy of KI, while in the second mechanism the energy distribution between the products is more random. A third example of organic reaction studied dynamically is that of a "hot" tritium atom on a methane molecule (studied by Polanyi and collaborators[219] on the one hand and by Bunker and collaborators[220–221] on the other hand). The main findings of several studies (using various potential energy surfaces) are:

(i) both abstraction of H by T ($T^* + CH_4 \longrightarrow TH + CH_3$) and T-for-H substitution ($T^* + CH_4 \longrightarrow H + CH_3T$) are direct (non complex) and concerted (non sequential) reactions;

(ii) substitution is favoured at intermediate collision energy (90–160 kcal/mol collision energy);

(iii) substitution with Walden inversion is an important fraction of overall substitution at low collision energy (40–100 kcal/mol);

(iv) the greatest part of the collision energy transforms into translational energy of the products;

(v) at 45–90 kcal/mol the product molecule is scattered sideways, following abstraction and backwards following substitution;

(vi) for abstraction, replacing T by D, the abstracted H by D, or CH_3 by a heavier radical results in a decrease of the reaction cross section;

(vii) for substitution, replacing T by D or the abstracted H by D results in a decrease of the reaction cross section while the latter increases when replacing CH_3 by a heavier radical.

We have kept the dynamical study of organic reactions by means of classical trajectories and based on semi-empirical and ab initio potential energy surfaces for the end. These studies are rare and constitute most likely a research subject with a future. The difficulty is to obtain forces acting on a large numbers of atoms. Constructing a potential whose partial derivatives provide reasonable forces is more and more difficult when the number of atoms and the directionality of valence forces increase[7, 9]. Except for the reaction study presented in the 3rd chapter of the present article, (in which an ab initio potential energy surface is interpolated and differentiated to give the forces) and as far as we know, these studies are reduced to a single one by Wang

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