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Some reflections on characterizing potential surfaces for gas-phase ionic reactions

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Abstract

Gas phase ionic chemistry has become an essential element in our general understanding of chemical reactivity. Obtaining experimental data and then extracting information about the potential surfaces for ionic reactions in the gas phase has been critical in making the connections between gas phase and solution ionic chemistry. In this paper we discuss insights that have been important in developing some of the methodologies that are currently used in analyzing gas phase data. (Int J Mass Spectrom 200 (2000) 591–595) © 2000 Elsevier Science B.V.

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1. Introduction

I am honored to be invited to contribute to this volume, but I am somewhat intimidated, since there is so much to say about this subject and so many people have made such important contributions. Rather than try either to summarize the field or to provide some special insight, I have chosen to provide some brief reflections on how we got where we are and where I think we might be going. I decided not to document or annotate this article, so it is clear that this is simply a collection of observations and opinions rather than a more conventional article.

One of the wonderful things about science is the ability ultimately to accomplish experiments that initially seem impossible. When I was a graduate student with Andy Streitwieser I studied hydrocarbon acidities. My experiments were carried out in cyclohexylamine solution, but we tried to analyze our data in terms of simple quantum calculations. Recognizing the problems of connecting theory and experiment, I noted in my thesis that it would be preferable to have gas phase data, but this seemed pretty hopeless. In fact, I pointed out that if electron affinities (EAs) of the conjugate radicals were known, one could in fact evaluate the acidities by combining the EAs with bond energies. It never occurred to me that one might actually measure relative acidities directly, to say nothing of determining EAs. As it happened, when John Baldeschwieler came to Stanford he developed ion cyclotron resonance (ICR) spectrometry, and when he invited me to participate in some of that work it was immediately apparent to me that one could begin to answer some of the questions that had seemed so difficult when I was a graduate student.

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At about the same time, many other important new kinds of instrumentation began to have a big impact. In particular the flowing afterglow (and its successors) and high pressure mass spectrometry could be used to study bimolecular (or higher order) reactions. In addition, the use of double focusing mass spectrometers to study metastable and other unimolecular decompositions was becoming widely used. And, molecular beams were beginning to provide spectacular insights into fine details of reactions. The result of all of this activity was that unusual and unexpected results could be verified in many laboratories, often with completely different experimental techniques.

2. Acidities and basicities

Acid–base chemistry dominates our thinking about many ionic processes. The measurements for reasonably acidic compounds are easily carried out, so we have lots of pK_a's and pK_b's available for correlations. A substantial amount of physical organic chemical "understanding" is based on this kind of solution measurement. Although it was well known that solvation can play a determining role in the thermodynamics of ionic solution chemistry, for example in the redox potentials of the alkali metals, the discovery that acid–base chemistry of some simple compounds such as alcohol acidities and amine basicities played an important role in sensitizing the more conventional chemical communities that gas-phase ion chemistry had something important to offer. The measurements themselves would play an important role in some analytical applications as well.

3. Association reactions

In many respects, although the thermodynamics of gas phase ionic reactions proved to be provocative, the dynamics are, in many respects, more interesting but much more difficult to deal with. Some of the reasons for this are discussed below, but it is interesting to see that the initial insights into understanding bimolecular reaction chemistry came out of an understanding of three-body association reactions. Third-body stabilized association reactions have played an extraordinary role in shaping the gas phase ion field. First, they provided a major bridge to understanding solvation. Measuring the association equilibria for addition of solvent molecules to ions has been a critical part of the understanding of how solvation works—step by step. Moreover, having these equilibrium data allows us to deal with the dynamics of the association process

$$A^+ + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [A^+ \cdot B]^* \xrightarrow{k_M[M]} [A^+ \cdot B] \tag{1}$$

The overall production of $[A^+ \cdot B]$ has the extremely interesting feature of a negative temperature dependence. This arises as a consequence of the easily understood temperature dependence of the three rate constants. k_1 and k_M are collision rate constants, which for ions, are rather independent of temperature. k_{-1} on the other hand is a unimolecular decomposition reaction of the complex $[A^+ \cdot B]$, and it increases with increasing temperature. Thus, the overall reaction slows as the temperature is raised. And, using some of the beautiful equilibrium and dynamic data that had been obtained in a variety of labs, we were able to reproduce essentially all of the temperature and pressure behavior of a number of association reactions. We quickly recognized that opening a chemical reaction channel for the complex $[A^+ \cdot B]$ would provide a way of understanding the overall dynamics of "real" chemical reactions.

4. Bimolecular reactions

One of the critical elements that makes gas-phase ion chemistry so relevant to solution chemistry is that the dynamics allow us to measure (or deduce) important information about the potential surface that can then be compared with what is seen in solution. Interestingly, for a long time it appeared that this would not be the case. In contrast to reactions in condensed phases where the rate of reactions can be controlled over a wide range by changing concentrations, and time for measurements can be varied over many orders of magnitude, gas phase ion chemistry is more limited. Thus bimolecular rate constants in solution can have a much wider range. In the gas phase, we observe only ions, we usually do not know the neutral products, and the range of rate constants that can be observed is fairly small. In fact, for a long time, it was felt that all exothermic ion-molecule reactions occurred at the collision limit. (It should be noted that only collision limited reactions were fast enough to be measurable). This problem is exacerbated by the relatively weak temperature dependence of gas-phase ionic reactions so we frequently cannot get the rate constants into a measurable range. Impurities significantly limit the range of rate constants that are accessible. For example, the reaction of Cl^- with some alkyl bromide RBr is always competing with the proton transfer reaction of Cl^- with HBr. If HBr is present in the sample at a level of 0.1%, then if the rate of reaction with RBr occurs only once in 10 000 collisions it will be a factor of 10 slower than the proton transfer reaction, and the rate that we thought we were measuring will be substantially in error. Many of us have been misled by this kind of result.

In spite of all of these difficulties it appeared that a wide and interesting range of reactions actually occurred in a rate regime that was slow enough to be interesting, but fast enough for the rate constant to be measured reliably. Many S_N2 reactions, proton transfer reactions, and carbonyl addition elimination reactions are in this group. If we consider the simple association model it is clear that a surface in which a complex is formed and then subsequently either reacts to give products or returns to reactants can accommodate most of the experimental observations. This gives rise to the general picture of the double minimum potential in Fig. 1.

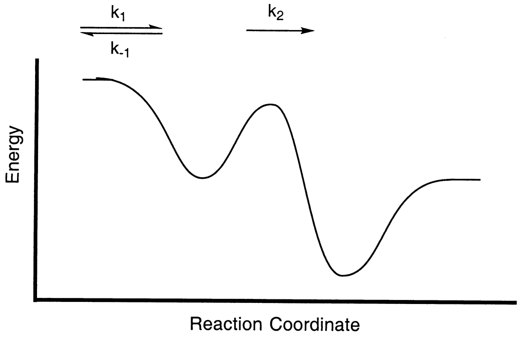

Fig. 1. Double minimum potential.

The reaction rate is then given by the rate at which the complex is formed (essentially a constant at some pressure) multiplied by the ratio of $k_2/(k_2 + k_{-1})$. That is, the efficiency is the fraction of complexes that go on to products. Even though the top of the barrier for k_2 is lower than the barrier for k_{-1}, k_2 is smaller than k_{-1}. This occurs because the overall free energy associated with k_2 is actually higher than that for k_{-1} owing to the decreased entropy, degrees of freedom, of its transition structure. The collision rate constant k_1 is relatively insensitive to temperature, to kinetic energy, and to the structure of the neutral. The rate constant k_{-1} is, however, the same unimolecular rate constant that we saw in Eq. (1), and it increases with temperature. Thus, the reaction goes slower as the temperature increases (just like the third-body stabilized association reaction).

5. Energy distribution functions

The entire analysis described above depends on two assumptions. First, that we know the energy distribution function that describes the system, and second that we know the relationship between that energy distribution function and the dynamics of the system. It is imaginable that if we could specify all of the quantum states involved and the behavior of each of them, then we could predict everything about the system's dynamics. In fact, we do not know all of that, and we make the assumption that the system behaves statistically. That is, that it explores all of the possible degrees of freedom consistent with the constraints of conservation of energy and angular momentum. This "assumption" takes on a life of its own, because if it is not true, predicting how fast the reaction will occur is daunting, and deducing what the potential surface must look like from simple rate measurements is extremely difficult, if not impossible. Consequently, we, and others, make this assumption, then see if its predictions can be tested for consistency with experiment. Translating the assumption into a model means choosing some theoretical model. We generally use Rice-Ramsperger-Kassel-Marcus (RRKM) theory. In brief, we make estimates of the frequencies in the complex and in the transition state, then calculate a microcanonical rate constant, $k(E)$, which we convolute with an energy distribution function $P(E)$. We can then calculate $\langle k \rangle$ for various values of the barrier heights, and choose values for the barrier heights to be consistent with the experiment. The check on this method is to see if the barrier heights obtained in this way correspond to those calculated quantum mechanically. Agreement has been surprisingly good in many cases. Philosophically, the use of a method such as this to obtain a barrier height is more or less the same as making an assumption about the pre-exponential factor in a thermal reaction in order to deduce the activation energy.

It is tempting to treat rates and product ratios by using the Arrhenius equation. Clearly this cannot be the correct way to treat the absolute rates, since the proper energy distribution is not a thermal one although it is derived from a Boltzmann distribution in the reactants. In contrast, branching ratios can be analyzed using a formulation that gives rise to an exponential dependence on energy differences. The "kinetic method" depends on this sort of treatment.

At the time this kind of analysis of ion–molecule reaction rates was first suggested, a number of people were concerned that the distribution of ion energies in an ICR instrument was likely to be very different from a Boltzmann distribution, and that trying to understand reactions quantitatively in this way was likely to lead to difficulties. Indeed, subsequent work showed that some ions can be formed quite hot, and a variety of methods for cooling the ions by relaxation have been developed. Smaller ions generally appear not to be problematic in this regard. Further, if it is slow reactions in which we are interested, most of the collisions of the ions with the neutral are nonreactive, and this provides an opportunity for the ions to cool. Thus, "hot" ions have not proven to be a problem in the context of analyzing bimolecular reaction rates for most systems that have been studied.

The most unexpected aspect of energy distributions has been the discovery that ions can absorb infrared blackbody radiation from the cell walls, ultimately reaching energies at which they can undergo unimolecular decomposition. This arises as a consequence of the low pressures and long trapping times in ICR instruments. This mechanism for unimolecular activation first suggested by Perrin had been largely dismissed, but it clearly plays a role and must be considered in analyzing ion reactivity. Ions can also absorb infrared energy from hot filaments, and this, too, can be important.

6. Statistical behavior

As noted above there is an important assumption that the energy in these complexes is distributed statistically. It is this assumption that makes it possible to use RRKM and similar theories to analyze these data. There are many reasons to believe that this assumption is not completely correct, and in some cases may be quite wrong. We know that collisional energy exchange is inefficient. For example, a hot ion colliding with a thermalized bath gas requires many collisions to become thermalized. Since the prereactive complexes that are formed in these ion-molecule reactions are not dissimilar structurally to those formed in collisions that lead to energy relaxation, it is unlikely that their internal energy distributions would be completely statistical. And, indeed, it has been shown clearly, both experimentally and in simulations, that for some small systems, e.g. $Cl^- + CH_3Br$, kinetic energy in Cl^- is not utilized statistically in the reaction. On the other hand, larger systems appear to behave more in accord with statistical predictions, with respect to their overall rates and the dependence of these rates on translational energy of the ionic reactants. Consequently, it appears that the use of statistical theory for analyzing and predicting the rates of thermal ion–molecule reactions around room temperature is a reasonable approach.

7. Summary

We have made a lot of progress in understanding gas-phase ion chemistry, and that in turn has led to much better understanding ionic chemistry in solution. It is clear that we still do not understand all of these issues completely. We know that our assumptions about energy redistribution are not completely right. Our models work nonetheless. I suspect this is a happy accident that results from folding together energy distributions that are themselves very similar. In any event, it is important to get some resolution of this problem or we will surely make the wrong predictions in other energy or temperature regimes. And, we will resolve it. Similarly, our analyses of collisions and long range interactions will get better.

It is now also quite obvious that we have a lot to learn about dynamics and chemistry of reactions of very large molecules and multiply charged ions. There have already been many beautiful studies of rather complex reactions, and we will see much more of that in the future as well.

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