DYNAMICS AND REACTION MECHANISMS OF ORGANIC IONS IN THE GAS PHASE
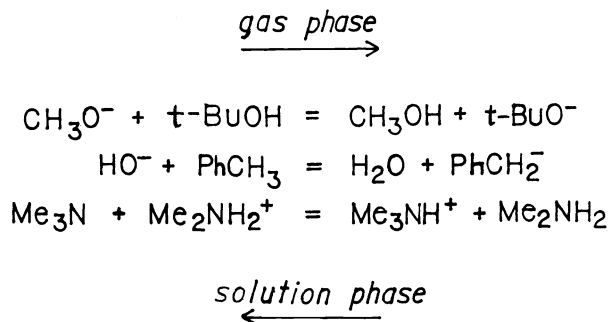
Andrew T. Barfknecht, James A. Dodd, Karen E. Salomon, William Tumas and
John I. Brauman

Department of Chemistry, Stanford University, Stanford, California 94305, USA

Abstract - Major advances have been made in the measurement and analysis
of gas phase ionic organic reactions. The dynamics can be interpreted in
terms of statistical reaction rate theory. The activation parameters and
rates have been interpreted in terms of Marcus theory. Infrared multiple
photon absorption has been used to activate ions which may be inter-
mediates in these ion-molecule reactions. The results provide information
about bimolecular dynamics.

INTRODUCTION

In 1972, at the time of the first IUPAC Conference on Physical Organic Chemistry, a great
deal of interest centered on measurements of ionic equilibria in the gas phase and the
relationship of these measurements to those for the same reactions in solution. Making use
of new instrumental techniques, particularly ion cyclotron resonance (ICR) spectroscopy,
flowing afterglow, and high pressure mass spectrometry, it had become possible to determine
values for simple gas phase ionic equilibria, and the dramatic effects of solvation on ionic
reactions was clearly demonstrated (ref. 1 & 2). Consider, for example, the following
equilibria:

$$gas\ phase \longrightarrow$$

$$CH_3O^- + t\text{-}BuOH = CH_3OH + t\text{-}BuO^-$$
$$HO^- + PhCH_3 = H_2O + PhCH_2^-$$
$$Me_3N + Me_2NH_2^+ = Me_3NH^+ + Me_2NH_2$$

$$solution\ phase \longleftarrow$$

At that time it was well known that a variety of complex bimolecular ion-molecule reactions
could occur, and, of course, many unimolecular fragmentation and rearrangement reactions of
ions were well documented in electron impact mass spectrometry studies. Bimolecular (or
higher order) reactions had not been studied extensively, however, since the ability to
measure rate constants with a significant degree of accuracy was still somewhat under-
developed. Consequently, there were relatively little data available and no straightforward
formalism existed for interpreting bimolecular rate constants.

Subsequently, a number of factors have changed this picture. First, instrumentation
development has continued at a rapid pace. As a result, it has become possible to study
reactions with a reasonable (see below) range of rate constants. Molecules containing a
wide variety of structural features can be examined, and temperature or even translational
or vibrational energy specifically can be varied to probe their effects on the reaction
dynamics. Second, making use of experimental data it has been possible to begin the
development of conceptual models which rationalize these data and allow predictions for new
reactions (ref. 3). Thus, significant progress has been made in our understanding of the
dynamics and mechanisms of gas phase ionic chemistry, and through it, implications for
chemistry in solution as well.

In this paper we report briefly on some of our current work in this area: first, the analysis of structure-reactivity relationships in bimolecular reactions through the application of Marcus theory; second, the use of unimolecular decompositions of possible intermediates in bimolecular reactions to probe the bimolecular reaction potential energy surface.

GENERAL ASPECTS OF REACTION DYNAMICS

Before proceeding with a detailed look at the chemistry, it is necessary to note some of the more general aspects of gas phase ionic reactions. Ions and neutral molecules have a long range, r^{-4} attractive potential which arises from the ion-induced dipole interaction and depends on the polarizability of the neutral. As a consequence, the potential surface is attractive at distances which are long compared with typical "chemical" interaction distances, and collisions are governed by "physical" forces. Especially if higher order effects such as permanent dipoles are taken into account, one can calculate a collision rate constant with rather good accuracy (ref. 4). The value of the collision rate constant is, typically, about a factor of ten larger than gas kinetic, that is $\sim 10^{-9}$ molecule·cm^{-3}· sec^{-1} = 10^{11} $\underline{M}^{-1}$. Since the collision rate constant depends only on these long range interactions, it is useful to characterize the reaction rate constant in terms of the fraction of collisions which result in reaction: efficiency = $k_{observed}/k_{collision}$.

Current instrumentation allows measurement of efficiencies in the range of ca. 10^{-4} to 1. Typically, measurements at the lower end of the scale are limited by unreactive ion loss or by reaction with impurities which themselves may have reaction efficiencies of close to unity. While many exothermic reactions have been observed to be near unit efficient, we now know that many others are inefficient.

For the reactions in which we have been interested, generally those involving medium sized organic molecules at thermal or near-thermal energies, we assume that once a collision has occurred, the system can be treated within the context of statistical reaction rate theory, with its usual assumptions including energy partitioning equally into all available degrees of freedom, subject to constraints of angular momentum, etc.

In view of the long range attractive interactions of ions and neutral molecules, one expects to find "inverted" potential surfaces such as shown in Fig. 1.
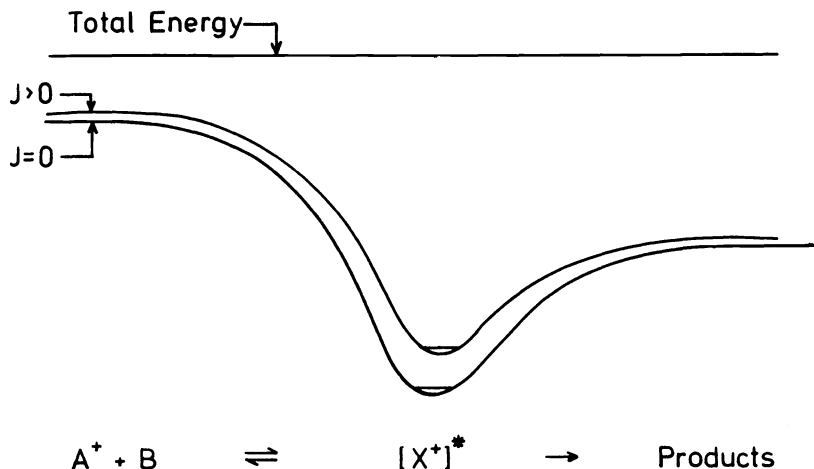

Fig. 1. Gas phase ion-molecule potential energy surface.

Given the existence of at least one minimum in such potential surfaces, one must then provide a rationalization of how reactions can proceed to give products which are less stable than the intermediate species, and why efficiencies can be less than unity. First, it should be noted that these reactions are carried out at quite low pressure (10^{-7} to 1 torr) and intermediate complexes are relatively unlikely to be stabilized by collision prior to decomposing, unless they are unusually long lived. Second, assuming that the reaction process is indeed governed by statistical theory, we expect that single well potential surfaces (Fig. 1) will result in highly efficient reactions. Consequently, we need a more complex surface to account for the dynamics.

We have suggested (ref. 5-7) that a double minimum surface (Fig. 2) can account for reactions with low efficiencies. Entropy bottlenecks might also be expected to play some

role as well, but we have shown that such effects are not important in determining the macroscopic dynamics (ref. 8). In brief, for surfaces such as that in Fig. 2, the reaction

$$A^- + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- \cdots B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C^- \cdots D \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C^- + D$$
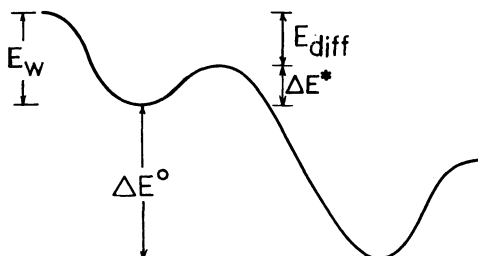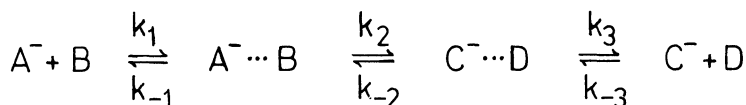

Fig. 2. Double minimum potential energy surface.

is slow because passage over the central barrier is entropically unfavorable relative to dissociation back to reactants. This arises because the association-dissociation transition state is very loose, with the two essentially freely rotating reactants orbiting about each other, whereas the transition state at the central barrier involves a species with formation of chemical bonds and in which rotations have been converted to vibrations with a consequent decrease in the available number of quantum states. Naturally, the surface may be even more complex depending on the specific chemistry involved, so that multiple minima may well be common (ref. 9). It is the relative heights of the entrance channel and the central potential E_{diff} which alone determine the efficiency. A deeper well will cause the complex to be longer lived, but the efficiency depends only on the relative rates of reaction of the intermediate and is thus insensitive to the well depth. The model also predicts that slow reactions following this surface will become even slower if the energy or temperature is raised (ref. 3 & 5).

If the central barrier is sufficiently low (5-10 kcal/mole below the entrance channel) the efficiency will approach unity. Similarly, if the central barrier is very high (for large molecules it need be only a few kcal/mole above the entrance channel) the efficiency will become too low to measure--less than ca. 10^{-4} to 10^{-5}. Thus, in contrast to neutral chemistry, the range over which experimental information can be obtained is rather limited.

This analysis can be put on a quantitative basis by the use of unimolecular reaction rate (RRKM) theory. Since the reaction efficiency, eff, depends on the partitioning between the dissociation and reaction transition states [eff = $k_2/(k_{-1} + k_2)$ for $k_{-2} \ll k_3$], one can calculate the values of $k_2(E)$ and $k_{-1}(E)$ at each energy, then integrate over the energy distribution function which characterizes the complex. We have previously shown that the absolute value for reaction through k_{-1} can be calculated accurately, this being the significant quantity required to characterize three-body stabilized association reactions (ref. 10 & 11).

In order to calculate the values of $k_{-1}(E)$ and $k_2(E)$ it is necessary to know the critical energies of the respective transition states as well as their vibrational frequencies, moments of inertia, and symmetries. In fact, we estimate the frequencies and moments of inertia (frequently using quantum calculations), then calculate what the efficiency would be for given values of the energy difference, E_{diff} (Fig. 2). Thus we choose the energies to fit the experimentally observed efficiency.

We are also interested in knowing the activation energy ΔE^*. This cannot be obtained directly from the experimental rate data, since the efficiency does not depend on the well depth, E_w. The well depth can, however, be evaluated from other experimental data on complexes (ref. 12 & 13), or from estimates based on electrostatic arguments. In many cases this can be done with sufficient accuracy to allow us to be reasonably confident of the numbers. The overall thermochemistry can also be measured independently, leading to values for ΔE^o. Thus, we are able to evaluate all of the necessary quantities required to characterize completely the surface shown in Fig. 2.

DYNAMICS OF METHYL TRANSFER REACTIONS

A great deal of information on the nature of the methyl transfer (S_N2) reaction surface has been obtained in recent years through the study of the rates of this process in the gas phase (ref. 14 & 15). The S_N2 displacement is an attractive reaction for study, since it exhibits a range of structural features, including a large variation in thermodynamics. Moreover, it is a mechanistically "clean" reaction, especially in the case of methyl transfer in which elimination is not possible. The S_N2 reaction quickly proved interesting because it was observed to be significantly less than unit efficient, even for strongly exothermic processes. Prior to these studies it had been observed that, in general, even slight exothermicity was sufficient to make gas phase ion-molecule reactions unit efficient.

Based in part on the slow kinetics of the reaction of chloride ion with methyl chloride, and also on the observation of nonequivalent chlorines in $[Cl \cdots CH_3Cl]^-$, a double-minimum potential energy surface was proposed (Fig. 2) (ref. 6). This form of the potential is analogous to the double-well potential introduced for slow proton transfer reactions (ref. 5). As explained in the introduction, a central barrier lower in energy than that of the reactants can slow a reaction because the back reaction (from the first complex to regenerate the reactants) is greatly favored by entropy. The transition state between the wells has a trigonal bipyramid structure; it is much "tighter" than the orbiting transition state separating the reactants from the first complex, which allows free rotation of the incoming fragments in all dimensions.

The RRKM analysis requires the frequencies and moments of inertia of the relevant chemical species as input data. These data for the two "competing" transition states (orbiting and S_N2) are all that are needed in order to evaluate the branching fraction $k_2/(k_{-1} + k_2)$. (For absolute rate constants, data on the complex are also required.) Most of the uncertainty in this calculation arises from the frequencies and structure of the S_N2 transition state, since the free rotations of the fragments in the complex become in the S_N2 transition state low frequency vibrations whose magnitudes are difficult to estimate. When these frequencies can be estimated, one then adjusts the energy difference E_{diff} between the two transition states in order to match the experimentally observed efficiency. Along with information on the well depth E_w (which, if not known, can usually be accurately estimated), this value allows a determination of the activation energy ΔE^*. In general, for measurably fast processes the energy of the S_N2 transition state lies below that of the reactants; due to this characteristic and also to the greater entropy of the orbiting transition state, these reactions are predicted to exhibit negative temperature dependence (ref. 3, 5 & 16).

Many of the results to come out of the initial kinetics studies on displacement reactions, while valuable, might have been expected. For instance, the rates were observed to be much faster than in solution, since in solution the reactants (with localized charge) are better stabilized with respect to transition state (with delocalized charge). In addition, these reactions exhibited steric inhibition and lack of reactivity at bridgehead carbons. Overall, however, attempts to understand more precisely the rates of S_N2 reactions as a function of structure were not very successful. Although the efficiencies of S_N2 reactions were generally observed to increase with increasing exothermicity, reactions of similar exothermicity often proceeded with very different efficiencies. Indeed, neither the efficiencies nor the activation energies correlate very well with exothermicity.

In more recent work (see references below), the interpretation of S_N2 kinetics results has been clarified through better understanding of the quantitative contributions of "intrinsic reactivity" and thermodynamic driving force on the energy and structure of the transition state. A Hammond postulate analysis predicts a lower energy, more reactant-like transition state as the exothermicity of the reaction is increased. Accordingly, a more objective measure of the surface of these reactions might include characterization of the central barrier in the absence of a thermodynamic driving force, that is, when $\Delta E^\circ = 0$. Several formalisms (ref. 17) allow the calculation of the magnitudes of such "intrinsic barriers". The most widely used formalism, and one of the simplest, is that first advanced by Marcus for electron transfer (ref. 18). The Marcus equation is given in (1), where ΔE° is the energy of reaction, ΔE^* is the activation energy, and ΔE_0^* is the intrinsic activation energy. Figure 3 illustrates how the Marcus equation formally accommodates the effect of

$$\Delta E^* = \frac{(\Delta E^\circ)^2}{16\Delta E_0^*} + \Delta E_0^* + \frac{1}{2}\Delta E^\circ \tag{1}$$

exothermicity; an observed activation energy is the sum of the intrinsic activation energy plus a term dependent on ΔE°. The Marcus equation has since been rederived using numerous
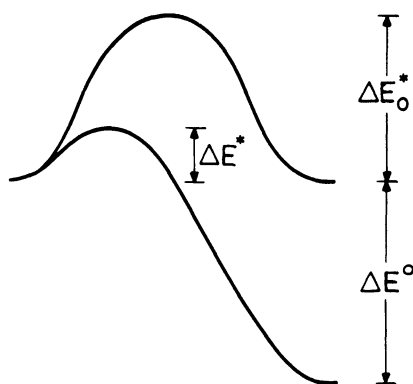
Fig. 3. Relation between the quantities ΔE°, ΔE^*, and ΔE_0^* used in the Marcus equation.

approaches, often making only very general assumptions about reactivity patterns (ref. 19); thus it is not surprising that the theory has found viable application (ref. 20) to both electron and larger group transfer. Formalisms such as Marcus theory are especially attractive in the interpretation of gas phase results because they are designed to treat single-step, unimolecular transformations, exemplified by passage over the central barrier, converting one complex to the other. Complications such as "work terms" introduced by the presence of solvent are obviated in gas phase studies.

We have applied Marcus theory to a number of methyl transfer reactions in the gas phase (ref. 21), and compiled a set of intrinsic activation energies ΔE_0^* for nucleophile-leaving group pairs (X,Y in the equation $X^- + CH_3Y = XCH_3 + Y^-$). A useful feature of the Marcus treatment is that nucleophilicity and leaving group ability become equivalent; the intrinsic barrier for the general cross reaction $X^- + CH_3Y$ is the same in either the forward or reverse directions. The intrinsic barriers for the identity reaction $X^- + CH_3X$ were obtained either by studying the actual reaction (in which case $\Delta E_0^* = \Delta E^*$), or by making the usual assumption that ΔE_0^* for the cross reaction $X^- + CH_3Y = XCH_3 + Y^-$ is the mean of the ΔE_0^* for the two identity reactions. Intrinsic barriers obtained from different reactions were consistent with one another. Values of $\Delta E_0^*(X,X)$ for various groups X are listed in Table 1.

TABLE 1. Intrinsic nucleophilicities of selected anions.

X^-	ΔE_0^* $(X^- + CH_3X)$ (Kcal/mole)
Cl^-	10.2
Br^-	11.2
F^-	26.2
CH_3O^-	26.6
$t-BuO^-$	28.8

The most important feature of Table 1 is how poor (i.e. large ΔE_0^*) most of the nucleophiles are, especially those involving first row atoms. The better nucleophiles, such as Cl^- and Br^-, react rapidly in identity reactions both in the gas phase and in solution; others, such as F^- and RO^-, are unreactive in both phases. Most of the activation energy for the Cl^- identity reaction in solution is a consequence of solvation effects; F^- and RO^- are intrinsically poorer nucleophiles and their reactions have additional significant activation barriers. Consequently, reactions such as the Williamson ether synthesis occur because they are very exothermic, with some of the exothermicity manifested in the stability of the activated complex.

Theoretical support for the applicability of the Marcus equation to gas phase methyl transfer has been provided by Wolfe et al., (ref. 22) from the results of ab initio calculations. In addition, Albery, Kreevoy, Lewis et al. (ref. 23) in work concurrent with that of Pellerite and Brauman, found reasonable and consistent intrinsic barriers for methyl transfer in solution. Other workers (ref. 24) have discussed theoretical aspects of S_N2 reactions, including solvent effects.

Recently, we have been able to justify the application of Marcus theory to methyl transfer in the gas phase by studying the rates of a series of substituted benzyl anions reacting with methyl bromide (ref. 25). The Brønsted coefficient $\alpha = d\Delta E*/d\Delta E^o$ can be considered to be a measure of the position of the transition state along the reaction coordinate ($\alpha = 0$ and 1 for very exothermic and endothermic reactions, respectively), and can be measured directly for a group of closely related reactions through a Brønsted-type plot or calculated by using the Marcus equation. Differentiating (1) (assuming constant ΔE_0*) yields (2) (ref. 18), and thus the "local" Brønsted curvature can be calculated for any given member of the reaction series from a knowledge of ΔE^o and $\Delta E*$. Good agreement was found between the values of α calculated from each of the above methods.

$$\alpha = \frac{d\Delta E^*}{d\Delta E^o} = \frac{1}{2} + \frac{\Delta E^o}{8\Delta E_o^*} \qquad (2)$$

Finally, in studies designed to interpolate between the extremes of naked (gas phase) and solvated ion-molecule chemistry, Bohme has investigated the rates and mechanisms of displacement reactions utilizing nucleophiles solvated by one or more neutral molecules (ref. 26). The rates of reaction were found to decrease monotonically as neutral molecules were added stepwise to the anionic nucleophiles. For instance, the rate of reaction of OH^- with CH_3Br is decreased by about four orders of magnitude upon solvation of OH^- with three water molecules. Equilibrium studies of anionic clusters corroborate the notion that stepwise addition of solvent molecules should lower the energy (and thus the reactivity) of the nucleophilic species (ref. 27).

BIMOLECULAR PROTON TRANSFER REACTIONS

The kinetics of proton transfers in the gas phase have been extensively studied to probe the potential energy surface for this ubiquitous reaction (ref. 1). The dynamics of these gas phase ion-molecule reactions have also been probed by hydrogen-deuterium exchange (ref. 28). Many proton transfers involving localized ions proceed with unit efficiency, that is, at the collision rate (ref. 29). However, proton transfer rates between delocalized ions, which were known to be slow in solution, were also found to be slow in the gas phase, even when appreciably exothermic (ref. 5).

The dynamics of the slow gas phase proton transfers of delocalized ions such as enolates, phenoxides, and benzyl anion can be modeled by a double-minimum potential energy surface with a central barrier, as discussed above (ref. 5). These reactions may be slow because poor hydrogen bonding in the ion-molecule complexes may decrease the well depth, or the central barrier may be higher than in other proton transfers because of the charge localization and/or structural reorganization required in these delocalized ions. (Steric effects (ref. 11) can also slow gas phase proton transfers as in the case of pyridine bases.)

Central barrier heights for proton-transfer reactions have been estimated for these various delocalized systems and are found to be in the range of 3-5 kcal/mole. This leads to estimates of intrinsic barrier heights for these gas phase reactions which are in close agreement with the calculated intrinsic barrier heights for the solution phase reactions (ref. 11 & 30). This substantiates the conclusion that the slowness of the solution phase reactions is not due only to differential solvation effects.

UNIMOLECULAR ION DECOMPOSITIONS

As we have seen, kinetic studies do provide information concerning the details of ion-molecule reaction dynamics, particularly the general features of potential energy surfaces and how they manifest themselves. More recently, we have also been employing other probes of potential energy surfaces. In the double minimum potential model, Fig. 2, ion-molecule reactions proceed through long-lived complexes as intermediates (especially at moderate energies) and the efficiency of the bimolecular reaction depends only on unimolecular reactions of this chemically-activated intermediate; a unimolecular transformation (k_2) and a unimolecular dissociation (k_{-1}). The efficiency of an ion-molecule reaction in that scheme ($k_2/(k_{-1} + k_2)$) is therefore identical to the branching fraction for the chemically activated intermediate. The unimolecular transformation, k_2, can be modeled by RRKM theory (ref. 11) and the unimolecular dissociation, k_{-1}, has been modeled in three-body association reactions (ref. 9 & 10).

Gas phase ion-molecule reactions have intermediates that are lower in energy than the separated products or reactants, and thus offer the possibility of separately generating the intermediates directly by alternate means. Recently our efforts have been directed

towards generating such putative intermediates and studying their unimolecular decomposition to gain information about the dynamics of the corresponding bimolecular reaction. In this work, we have been using CO_2 laser IR radiation (ref. 31) to activate ions above reaction thresholds (ref. 32); collisional activation would be a complementary technique (ref. 33). We have carried out several studies on infrared multiple photon (IRMP) induced unimolecular decompositions of gaseous ions with particular emphasis on the mechanistic details (ref. 32). We will discuss here only those studies that are relevant to bimolecular reaction dynamics in that the ion is either an intermediate in a bimolecular ion-molecule reaction, or decomposes via a multistep pathway through a species which is such an intermediate.

Those intermediates which can be activated rapidly above both rearrangement and dissociation thresholds and result in product formation from both pathways will yield the most information. For this type of study to be meaningful, the mechanism of the unimolecular decomposition must be elucidated to verify whether the purported intermediate actually lies on the reaction coordinate of a bimolecular reaction.

Our work in this area has focused on proton transfer reactions due to the fundamental importance of this class of reaction and the relative ease of generating stable complexes, i.e. possible intermediates. In some cases, IRMP activation (ref. 31) of possible intermediates including both hydrogen bonded complex ions and covalently bound moieties, has resulted in formation of multiple products which are related by a proton transfer reaction. We have been able to address the following aspects of bimolecular reactions:
1. Mechanisms of proton transfer reactions can be elucidated by characterization of the intermediates on the reaction coordinate.
2. Features and energetics of potential energy surfaces can be probed.
3. Effects of internal energy can be studied by controlling laser parameters, because the extent of excitation is set by the pumping rate.

Stable complexes, $ROHF^-$, can be prepared by the reaction of F^- with alkyl formates, HCO_2R (ref. 34). Since these proton bound complexes have been characterized and proposed to be hydrogen bonded structures, they are obvious candidates for intermediates in the proton transfer reaction between F^- and ROH. In general, infrared photolysis of these complexes results in exclusive formation of only the lower energy product, RO^- or F^- depending on which is the weaker base. For instance, fluoride ion is the only ionic photoproduct from CH_3OHF^- (ref. 35). This is consistent with the observed rapidity of the corresponding bimolecular reactions and the large dissociation rates for these complexes even at threshold. Production of both products (RO^- and F^-) has been observed only when the two products are of very similar basicity. The proton bound complex $\underline{1}$ yields both neopentoxide anion and fluoride ion upon pulsed CO_2 laser irradiation (ref. 36). That the branching
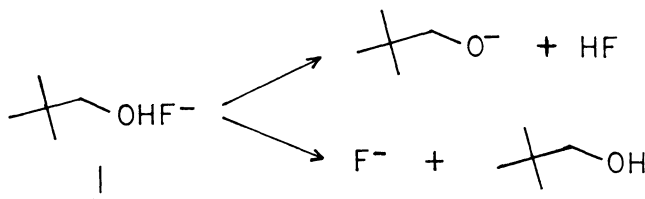

ratio in these systems is controlled only by thermodynamics further corroborates the notion that there is only a small barrier (if any at all) on the proton transfer reaction coordinate for most $F^- + ROH$ reactions, i.e. a single minimum potential or a double minimum potential with a small central barrier. Beauchamp has investigated cationic proton bound dimers of alcohols using low power infrared laser radiation (ref. 37). Cooks has recently studied the collisional induced decomposition of both positive and negative proton bound dimers (ref. 38).

We have been probing potential energy surfaces for carbon acid proton transfers in an analogous manner by IR photochemical studies on alkoxide anions, which are adducts of nucleophiles and ketones and therefore are on the hypersurface for the proton transfer reaction between carbon acids (RH) and ketones. Pulsed CO_2 laser irradiation of alkoxide anions, $\underline{2}$, produces alkanes and enolate ions. Detailed mechanistic studies (ref. 39)
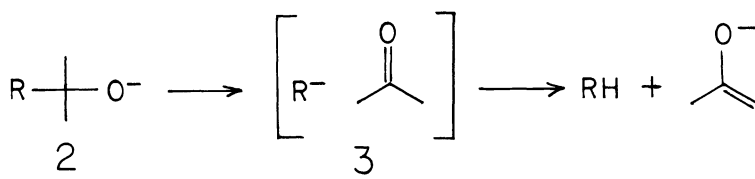
including measurements of competitive kinetic isotope effects (ref. 40) have elucidated a general stepwise mechanism involving initial heterolytic cleavage to an intermediate ion-molecule complex, <u>3</u>, followed by a subsequent proton transfer reaction. Although stable covalent adducts have been reported in the bimolecular reaction of carbanions with carbonyl compounds (ref. 41) and the possibility exists that proton transfer reactions between these species proceed directly through these adducts <u>via</u> a concerted four-centered elimination, our mechanistic work reveals that such pathways are not operative and that the alkoxide ions do not lie directly on the proton transfer reaction coordinate. Rather, the proton transfer proceeds in a normal fashion by direct transfer within ion-molecule complexes such as <u>3</u>. Nevertheless alkoxides are useful probes because their unimolecular decomposition yields productive proton transfer intermediates.

Products resulting from both dissociation of intermediate <u>3</u> (CF_3^-) and proton transfer ($C_3H_5O^-$) were observed upon infrared photochemical activation of 1,1,1-trifluoro-2-methyl-propoxide anion (<u>2</u>: R = CF_3). The formation of both of these products whose thresholds
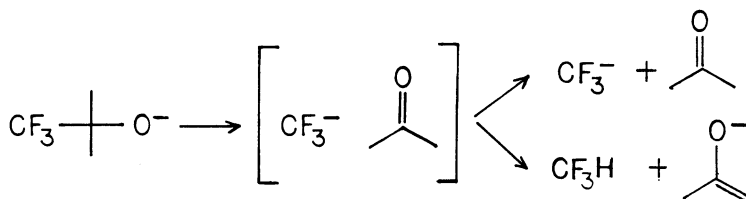
are 7 kcal/mole apart requires that the lower energy proton transfer channel (k_2) must be slower than further activation (pumping rate constant). This suggests a significant barrier to proton transfer between CF_3^- and acetone. In a similar set of experiments (ref. 36) on a related enolate ion, multiple products have been found in the IR photolysis of 1,1,1-trifluoroacetone enolate anion which corresponds to the proton transfer reaction between CF_3^- and ketene, where the difference in acidities is even larger (10 kcal/mole). The existence of a barrier in the corresponding bimolecular reaction has also been inferred from its relative inefficiency (ref. 36).

For the trifluoroalkoxide <u>2</u>, R = CF_3, the branching ratio (which is defined as acetone enolate/total photoproduct) decreases with fluence (ref. 32) (Fig. 4). Trifluoroacetone enolate exhibits similar behavior. In most IR photochemical experiments, the mean internal energy of reacting species increases monotonically with the up pumping rate which, in turn, is directly proportional to the laser intensity and thus fluence in these studies. As predicted by the double minimum potential model, the branching ratio decreases with increasing internal energy of the intermediate, analogous to the efficiency of the corresponding
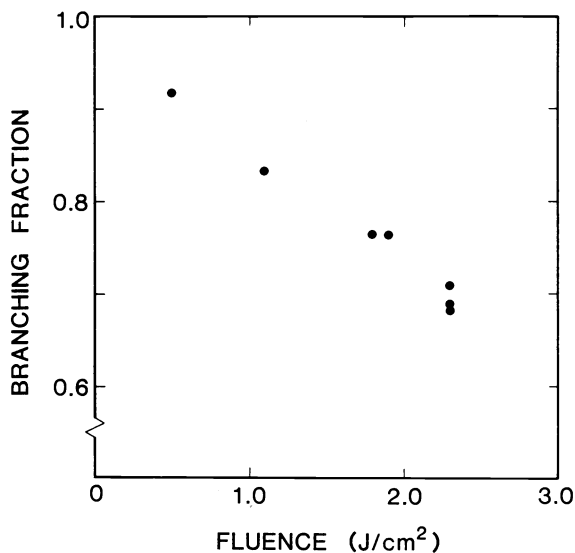

Fig. 4. Branching fraction [acetone enolate/(acetone enolate + CF_3^-)] from the decomposition of 1,1,1-trifluoro-2-methylpropoxide.

bimolecular reaction decreasing with temperature. Thus, intensity/fluence dependence of the unimolecular decompositions of putative intermediates provide information on internal energy effects of bimolecular ion-molecule reactions (ref. 42), which has proven difficult to ascertain for large species by other means.

Kinetic hydrogen isotope effect studies have provided considerable insight into many of the details of proton transfer reactions in solution, including transition state structures and overall dynamics. Surprisingly, there have been very few such studies on gas phase ionic systems (ref. 11, 43 & 44). In principle, the kinetic isotope effect for the bimolecular proton transfer reaction between R^- and acetone-d_3 could be measured indirectly as the competitive branching of $\underline{5}$ generated by IR photolysis of trideuteroalkoxides $\underline{4}$. This effect could be calculated from the ratio of d_3/d_2 enolates. A large isotope effect ($k^H/k^D = 6.0$) was found in the pulsed laser photolysis of $\underline{4}$ (R = CF_3) (ref. 39). This effect is much larger than those reported for the bimolecular reaction of alkoxide bases with acetone $\underline{d}_3$ (ref. 44).
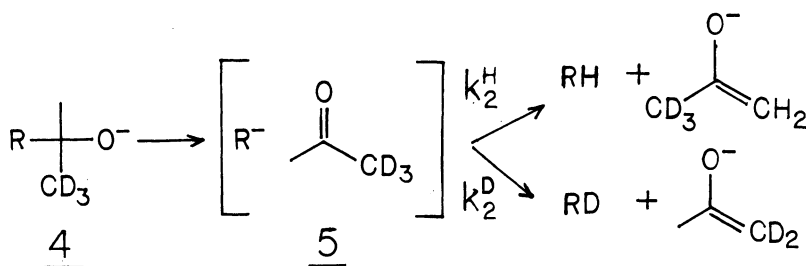
Since photolysis of all other alkoxides $\underline{2}$ studied to date yields only acetone enolate (proton transfer product), information regarding the bimolecular process can be extracted only from competitive kinetic isotope measurements (photolysis of $\underline{4}$). Initial results (ref. 39) from a systematic investigation reveal that k^H/k^D decreases as the exothermicity of the proton transfer reaction (ΔH^0_{PT}) increases (R: k^H/k^D: ΔH^0_{PT} (kcal/mole); CF_3: 6.0:-7; Ph: 2.5:-22; CH_3: 1.6:-40).

CONCLUSION

In the past few years, great progress has been made in the interpretation of rates and mechanisms of ionic reactions in the gas phase. The S_N2 reaction has been characterized extensively, and a plausible definition and measure of nucleophilicity has been developed.

Multiple photon infrared photochemical activation has been used to energize possible intermediates in bimolecular reactions. The results provide insight into proton transfer mechanisms.

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