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Dynamics of Proton Transfer Involving Delocalized Negative Ions in the Gas Phase

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Abstract: Using pulsed ion cyclotron resonance spectroscopy, we have measured the proton-transfer rates of a number of delocalized anions (enolates, phenoxides, benzyl anion, etc.) with a variety of neutrals (ketones, phenols, toluene, etc.). Many of these reactions, although exothermic, are quite slow. The results can be interpreted in terms of a three-step process. Small barriers are required to explain the results.

Although rates ranging over several orders of magnitude have now been reported for gas-phase ion-molecule reactions, the long-standing generalization that such reactions proceed at the collision rate still seems to be widely held for the particular case of proton-transfer reactions.[1] In fact, Bohme reports that greater than 95% of all exothermic proton transfers measured occur with nearly unit efficiency.[2] In contrast to the general case, however, we have previously reported that some proton-transfer reactions involving delocalized ions as reactants or products proceed at substantially diminished rates.[3] In this paper, we report the results of a more comprehensive investigation of this phenomenon by pulsed ion cyclotron resonance spectroscopy[4] and suggest a general model that can account for the slowness of these reactions as a group and rationalize the relative rates.

One of the most important applications of previous gas-phase proton-transfer studies has been the elucidation of solvation effects in solution phase acid-base chemistry. The determination of the gas-phase basicity order among methyl-substituted amines, for example, demonstrated that the solution phase order, long a puzzle, resulted from opposing substituent and solvation effects.[5] One might hope that kinetic studies could be similarly informative. However, any comparison of kinetic rather than equilibrium properties in the two phases is considerably more complicated, since unambiguous interpretation of the relative rates in either phase is still impossible. Nonetheless, the gross correlation between the solution-phase results, which are characterized by diffusion-controlled rates for many simple proton-transfer processes, but much slower rates for proton transfers involving delocalized acids and bases,[6] and the gas-phase results, leads one to explore the common features of the two processes for an explanation. As subsequent discussion will show, the gas-phase results may be well rationalized in terms of general mechanistic properties first advanced to describe solution-phase proton-transfer behavior.

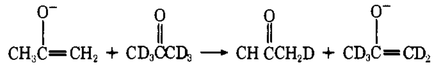
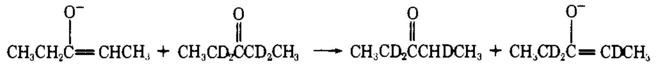
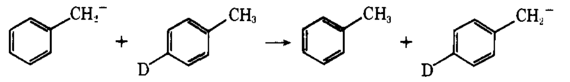
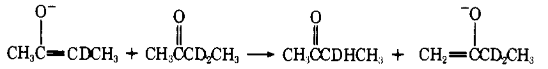
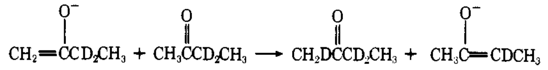
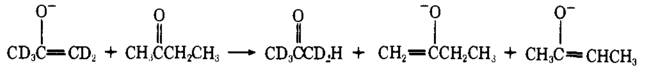
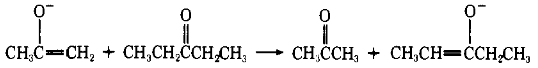
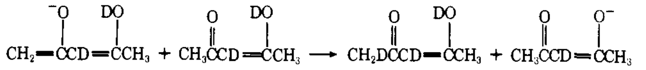
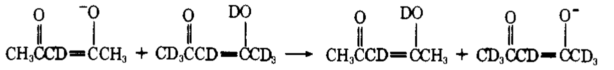
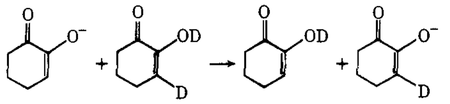
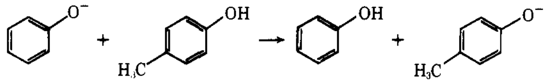
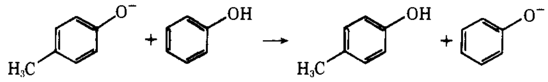
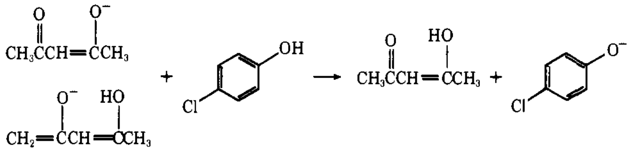
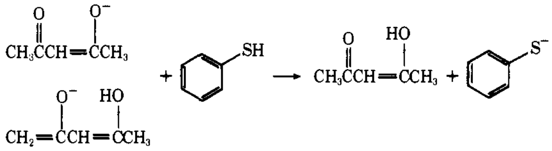
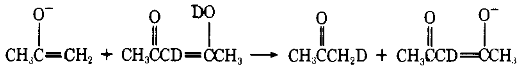
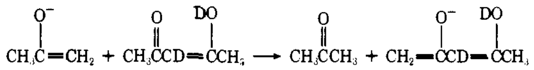
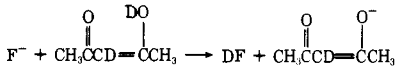
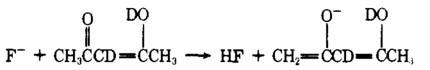
Experimental Section

Materials, General. The majority of chemicals used in this work were obtained from commercial sources and used without further purification. This includes acetone, acetone-d_6, 2-butanone, 3-pentanone, and acetylacetone. Nitrogen trifluoride was obtained from Dr. S. K. Brauman (SRI) and used without further purification. For those chemicals that were least volatile and where purity was therefore most critical, distillation or sublimation followed by extensive pumping on a vacuum line was employed prior to use. Chemicals in this category include phenol, *p*-cresol, *p*-chlorophenol, and 1,2-cyclohexanedione. Finally, several chemicals were synthesized.

Deuterated Ketones. Acetylacetone-d_8, 3-pentanone-d_4, and 1,2-cyclohexanedione-d_2 were prepared by refluxing approximately 2 ml of the perhydro compound and catalytic amounts of sodium carbonate in D_2O for intervals of about 6 h. Addition of NaCl and extraction with ether followed by solvent evaporation yielded reasonable recoveries of ketone. This procedure was repeated as many times as necessary to produce the isotopic purity required or until attrition of the ketone became too large. For example, 3-pentanone-*2,2,4,4*-d_4 (95% d_4 by mass spectrometry, 40 eV) was prepared by this method. Acetylacetone-d_2 and -d_6 were prepared by stirring acetylacetone-h_8 or -d_8 in D_2O or H_2O at room temperature for about 2 h, yielding at least 90% doubly exchanged product. Deuterated ketones with high enol contents were used within a day or so of preparation. The extent of deuteration was determined by positive ion mass spectra taken on the pulsed ICR. The position of deuteration was determined by ^1H NMR and in the case of acetylacetone-d_2 by ^2H NMR. For acetylacetone-*3,3*-d_2 ^2H NMR showed no deuterium incorporation in the methyl groups.[7] ^1H NMR showed >97% deuterium incorporation in the interior methylene and enolic positions. Acetylacetone-d_8 was contaminated by about 33% d_7 as shown by mass spectral analysis. The positions of deuteration in 1,2-cyclohexanedione were not well characterized, although NMR showed clearly that the enolic proton exchanged most rapidly on shaking with D_2O.

2-Butanone-*3,3*-d_2. Specifically deuterated 2-butanone was prepared by the method of Gemmer and Stephenson, which uses a zinc-copper couple to effect replacement of halogen atoms by deuterium.[8,9] The zinc-copper couple was prepared using 6.5 g (100 mmol) of zinc and 25 ml of 0.1 M $CuCl_2$ in 5% HCl. Tetraglyme was used as solvent

Table I. Rate Constants[a]

	Reaction	k, cm³/, molecule-s × 10¹¹	ΔH°, kcal/mol
1.	 $\mathrm{CH_3\overset{O^-}{\overset{\vert}{C}}{=}CH_2 + CD_3\overset{O}{\overset{\Vert}{C}}CD_3 \longrightarrow CH\,\overset{O}{\overset{\Vert}{C}}CH_2D + CD_3\overset{O^-}{\overset{\vert}{C}}{=}CD_2}$	0.32 ± 0.19	~0
2.	 $\mathrm{CH_3CH_2\overset{O^-}{\overset{\vert}{C}}{=}CHCH_3 + CH_3CD_2\overset{O}{\overset{\Vert}{C}}CD_2CH_3 \longrightarrow CH_3CD_2\overset{O}{\overset{\Vert}{C}}CHDCH_3 + CH_3CD_2\overset{O^-}{\overset{\vert}{C}}{=}CDCH_3}$	0.38 ± 0.30	~0
3.		0.30 ± 0.20	~0
4.	 $\mathrm{CH_3\overset{O^-}{\overset{\vert}{C}}{=}CDCH_3 + CH_3\overset{O}{\overset{\Vert}{C}}CD_2CH_3 \longrightarrow CH_3\overset{O}{\overset{\Vert}{C}}CDHCH_3 + CH_2{=}\overset{^-O}{\overset{\vert}{C}}CD_2CH_3}$	0.18 ± 0.15	~0[b]
5.	 $\mathrm{CH_2{=}\overset{O^-}{\overset{\vert}{C}}CD_2CH_3 + CH_3\overset{O}{\overset{\Vert}{C}}CD_2CH_3 \longrightarrow CH_2D\overset{O}{\overset{\Vert}{C}}CD_2CH_3 + CH_3\overset{O^-}{\overset{\vert}{C}}{=}CDCH_3}$	0.27 ± 0.22	~0[b]
6.	 $\mathrm{CD_3\overset{O^-}{\overset{\vert}{C}}{=}CD_2 + CH_3\overset{O}{\overset{\Vert}{C}}CH_2CH_3 \longrightarrow CD_3\overset{O}{\overset{\Vert}{C}}CD_2H + CH_2{=}\overset{^-O}{\overset{\vert}{C}}CH_2CH_3 + CH_3\overset{O^-}{\overset{\vert}{C}}{=}CHCH_3}$	0.64 ± 0.40	<0[c]
7.	 $\mathrm{CH_3\overset{O^-}{\overset{\vert}{C}}{=}CH_2 + CH_3CH_2\overset{O}{\overset{\Vert}{C}}CH_2CH_3 \longrightarrow CH_3\overset{O}{\overset{\Vert}{C}}CH_3 + CH_3CH{=}\overset{O^-}{\overset{\vert}{C}}CH_2CH_3}$	0.80 ± 0.40	<0[c]
8.	 $\mathrm{CH_2{=}\overset{^-O}{\overset{\vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CH_3 + CH_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CH_3 \longrightarrow CH_2D\overset{O}{\overset{\Vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CH_3 + CH_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{O^-}{\overset{\vert}{C}}CH_3}$	3.0 ± 0.5	<−2[d]
9.	 $\mathrm{CH_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{^-O}{\overset{\vert}{C}}CH_3 + CD_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CD_3 \longrightarrow CH_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CH_3 + CD_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{O^-}{\overset{\vert}{C}}CD_3}$	1.2 ± 0.3	~0
10.		9.7 ± 1.0	~0
11.		6.2 ± 2.0	1.2[e]
12.		18.0 ± 3.0	−1.2[e]
13.		15.0 ± 4.0	f
14.		30.0 ± 3.0	f
15.	 $\mathrm{CH_3\overset{O^-}{\overset{\vert}{C}}{=}CH_2 + CH_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CH_3 \longrightarrow CH_3\overset{O}{\overset{\Vert}{C}}CH_2D + CH_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{O^-}{\overset{\vert}{C}}CH_3}$	16.0 ± 2.0	−22[g]
16.	 $\mathrm{CH_3\overset{O^-}{\overset{\vert}{C}}{=}CH_2 + CH_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CH_3 \longrightarrow CH_3\overset{O}{\overset{\Vert}{C}}CH_3 + CH_2{=}\overset{O^-}{\overset{\vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CH_3}$	20.0 ± 3.0	f
17.	 $\mathrm{F^- + CH_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CH_3 \longrightarrow DF + CH_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{O^-}{\overset{\vert}{C}}CH_3}$	22.0 ± 3.0	−29[g]
18.	 $\mathrm{F^- + CH_3\overset{O}{\overset{\Vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CH_3 \longrightarrow HF + CH_2{=}\overset{O^-}{\overset{\vert}{C}}CD{=}\overset{DO}{\overset{\vert}{C}}CH_3}$	60.0 ± 6.0	f

[a] Ion loss corrections: reaction 8, method 1; reactions 4 and 5, methods 1 and 2; reactions 1, 2, 3, and 9, method 2; reactions 6 and 7, method 3. [b] The similar rate constants for reactions 4 and 5 suggest $\Delta H° \simeq 0$. [c] These reactions are slightly exothermic (1–5 kcal/mol) based on preliminary photodetachment data. No direct measurements are currently available. [d] Back reaction has $k \leq 10^{-12}$ cm³ molecule⁻¹ s⁻¹. [e] R. T. McIver, Jr., and J. H. Silvers, *J. Am. Chem. Soc.*, 95, 8462 (1973). [f] Reliable data not available. [g] T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, 96, 5940 (1974).

and 3,3-dibromo-2-butanone (5.8 g, 25 mmol) was the substrate. The brominated ketone had been previously prepared from 2-butanone by the method of Cox and Warkentin[10] (yield, ~75%, >90% of the desired isomer by VPC, NMR (CCl_4) δ 2.5 (s), 2.7 (s)). A freeze-pump workup yielded 1.1 g (14 mmol) of deuterated material consisting of predominantly (>75%) 2-butanone-*3,3-d*$_2$ by mass spectrometry. The relative amounts of deuterium at the methyl and methylene positions were determined by observation of the fragment peaks corresponding to α cleavage of the ketone in each of the two directions. These values plus total incorporation from the parent peak allowed determination of relative amounts of 2-butanone-*3,3*-d_2 (76%), 2-butanone-*3*-d_1 (20%), and 2-butanone-*1,3*-d_2 (4%). Therefore, *m/e* 73^- derived from this material must be >95% abstraction from position 1 and *m/e* $72^- >$ 80% abstraction from position 3, assuming no kinetic positional or isotope effect, a reasonable expectation in view of the exothermicity.

Instrumentation. The basic instrument used in this work was a pulsed ion cyclotron resonance spectrometer fitted with a trapped ion cell of the McIver design.[4] The marginal oscillator frequency was generally 240 KHz, but occasionally other frequencies were used. When double resonance ejection was employed, complete ion ejection was observed.

Pressures of the neutral reactants were measured in the operating range of 10^{-6}–10^{-5} Torr using a Varian model 971-0014 ionization gauge. These pressures were then corrected by calibrating the ionization gauge against an MKS Baratron capacitance manometer in the range of 10^{-5}–10^{-4} Torr for each neutral gas. The two instruments gave a constant ratio of pressures over this range for all gases.[11] The estimated error in absolute pressure measurement by the Baratron in this range is ±10%. This method has been shown in our laboratory to give the generally accepted rate constant for the reaction $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ of 1.1×10^{-9} cm^3 molecule^{-1} s^{-1}.

Generation of Ions. Ions of interest were generated by proton transfer to F^-. This was a convenient method for several reasons. (1) Electron impact methods for direct preparation of the ions employed were very ineffective. (2) F^- is easily obtained from NF_3 by dissociative electron attachment at thermal electron energies. (3) F^- is sufficiently basic in the gas phase to deprotonate all the acids employed in this study. (4) Most of the proton transfer reactions of F^-, even those that produce delocalized ions, seem to be relatively fast. Benzyl anion was generated by proton transfer to CH_3O^-.

Results

In Table I are listed all of the rate constants determined for this study. Nonreactive ion loss, which is an inherent problem in kinetic applications of pulsed ICR, was the major factor limiting the accuracy of these determinations leading to the large error limits for the slow reactions shown in the table. To illustrate, we may consider the simplest possible system (Figure 1) of an ion in the presence of a neutral with which it can react. The rate of reactive decay of that ion, $-d(A^-)/dt$, if no reactive impurities are present, is $k(A^-)(M)$, or, since the neutral is present in large excess, $k'(A^-)$. As long as k' is large relative to the rate constant for nonreactive decay, k_{ILA}, this analysis is accurate. It became apparent during the course of this work that nonreactive ion loss from the cell was competitive with, and in some cases faster than, reactive ion decay for proton transfers to delocalized ions.

Rather than attempting to make empirical corrections for ion loss, we have found that choosing systems so that the rate of ion loss may be directly measured or the effect of ion loss eliminated by a suitable data treatment is usually a more satisfactory procedure. For example, in Figure 1, if $k_{ILA} = k_{ILB}$, then the total number of ions $A^- + B^-$ will decay exponentially and the ratio $A^-/(A^- + B^-) = \exp[k(M)t]$. Thus, the rate constant k can be extracted directly from a plot of this ratio vs. time (method 1). On the other hand, if k_{ILA} can be measured, as for a reversible system at equilibrium, then it may be subtracted from the rate constant for total decay of A^- to yield a value of k (method 2). Even under such favorable circumstances, ion loss still leads to rather imprecise rate constants, since the reactive decay is often only a fraction of the nonreactive decay. In these cases, the assigned error limits represent the reproducibility of the rate constants over a large number (10–20) of determinations. When neither of these two exact methods of ion loss correction applied and ion loss was significant (i.e., $k_{\text{reaction}} < 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), approximate methods of eliminating it from the experimental data were employed. Two such methods are (1) numerical integration of product intensity using a measured value of k_{ILB} and comparison of the corrected growth of B^- with total decay of A^- over the same time interval, or (2) determination of approximate values of k_{ILA} from k_{ILB} or total decay of A^- under other conditions (method 3). In these cases, errors in both precision and accuracy may occur. The reported error limits reflect both the precision, via the reproducibility, and the accuracy through approximation of maximum and minimum values of k_{ILA}. For faster reactions, ion loss is not a significant impediment (e.g., $k_{IL} \simeq 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 12 kG) and the precision is much improved. In these cases uncertainty in the determination of the neutral pressures is the main factor limiting the accuracy. For each reaction, the method of ion loss correction employed is indicated in Table I.

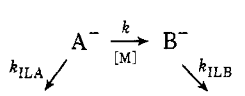


Figure 1. Reaction scheme for irreversible reactions. Ion loss rate constants for A^- and B^- are given by k_{ILA} and k_{ILB}, respectively.

All of the kinetic schemes from which these rate constants were derived are more complicated than that shown in Figure 1 and they may be divided into two main groups, the irreversible reactions (6–8, 14–18), and the reversible reactions (1–3, (4 + 5), 9, 10, (11 + 12), 13). The irreversible processes 6–8 and 14 are more complicated than Figure 1 only because the reactant ions are generated by proton transfer to F^-, so the overall sequence is the two-step process: $F^- + HA \rightarrow A^- + HF$; $A^- + BH \rightarrow B^- + HA$. However, since the first reaction is fast, it never constitutes a serious obstacle, and by using data after all F^- has reacted, these systems could be reduced to the form of Figure 1. The irreversible reactions 17 and 18 do not suffer this complication, since the reactant is a primary ion. They cannot be reduced to the simple form of Figure 1, however, because not only do they compete with each other, but also the products of the two paths interconvert. In this case, the sum of the rate constants k_{17} and k_{18} is obtained from the total decay of the primary ion, F^-, and the ratio may be obtained either from the ratio of products at short times or using the decay data in conjunction with the independently measured value for the rate constant for product interconversion by a nonlinear least-squares fitting procedure.[12] Both methods were employed yielding essentially identical results for k_{17} and k_{18}. The same approach was used to acquire k_{15} and k_{16} using, in this case, data after all F^- had decayed away (Figure 2).

The reversible reactions are more complicated than the scheme of Figure 1 because of the presence of F^- and because the anionic products of these reactions were also produced directly by proton transfer to F^-. Thus the total system from which the rate of reaction 1 was obtained is shown in Figure 3. This system can be reduced to one of the forms of Figure 1 by analyzing the data only after all F^- is gone and by applying a double resonance frequency that continuously ejects the product ion (i.e., $^-CD_2COCD_3$ for determination of k_1) from the cell. This is in essence the procedure used for all reversible systems. Reaction 9 was somewhat more complex because of the presence of several different ions in equilibrium, but it was analyzed in fundamentally the same way. This analysis applied to the system for reaction 10 may lead to rate constants that are somewhat too low (see later).

Discussion

With the reasonable assumption that gas-phase ion-molecule reactions proceed through long lived intermediate complexes,[13] one can describe the mechanism of such reactions as

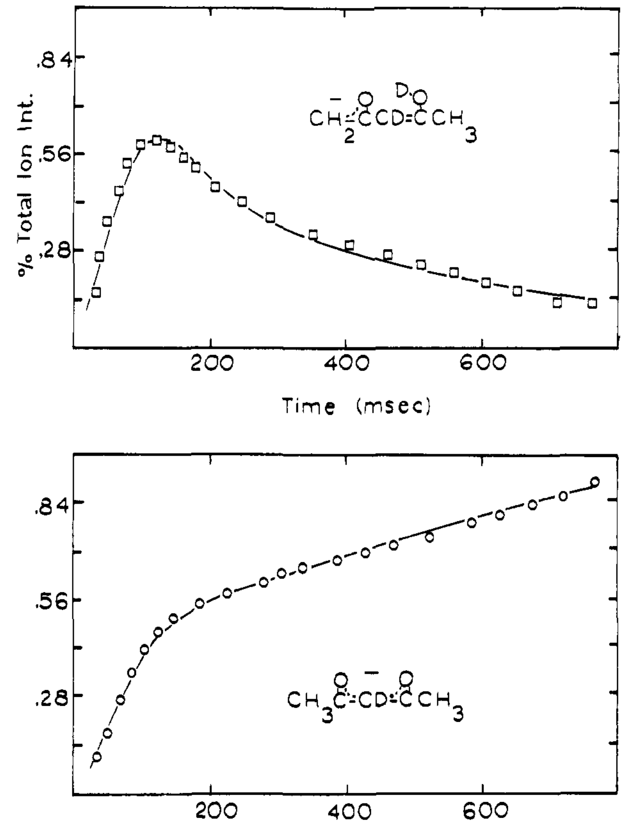


Figure 2. Experimental (□, ○) and calculated (—) percent of total ion intensity vs. time for products of the reaction of $CH_3COCH_2^-$ + acetylacetone-d_2.

consisting of at least two kinetically distinct steps

$$A^- + BH \underset{k_b}{\overset{k_c}{\rightleftarrows}} {}^{\delta-}A\cdots H\cdots B^{\delta-} \underset{k_c'}{\overset{k_b'}{\rightleftarrows}} AH + B^- \qquad (I)$$

Suppose $k_b' \gg k_b$. In the case of exothermic reactions, k_c will be rate determining and one will have regenerated the traditional picture of ion-molecule reactions occurring at every collision. Although the Langevin formalism,[14] $k = 2\pi q(\alpha/\mu)^{1/2}$ (α = polarizability of the neutral, μ = reduced mass), and its counterparts for polar molecules[15a] predict only modest changes in rates with structural variations of the type we have considered, it is possible that the theory, derived with a point-charge approximation, overestimates the rates of delocalized ions as a class.[15b] If charge delocalization led to smaller ion-induced dipole interaction energies at intermediate separations, fewer collisions might occur. This is not the case, as we have been able to demonstrate by using the previously described phase coherence pulsed ICR technique[16] to measure collision frequencies in several delocalized ion-neutral systems. The measured collision rate constants are of the order 1.3–1.9 × 10^{-9} cm^3 molecule^{-1} s^{-1}, similar to those measured in systems where fast proton transfers occur

$$^-OCH_3 + HOCD_3 \rightarrow {}^-OCD_3 + HOCD_3 \qquad (19)$$

or from collision rate constants calculated from Langevin or ADO[15a] theories. Therefore, rate distinctions must occur in subsequent unimolecular processes involving structural changes within the complex or decomposition of the complex to products. In order to understand the rates in terms of these elementary steps, information about the structures and energies of reactants, intermediates, and products will be required. The data in Table I will be used to elaborate this description.

Before considering the more speculative issue of intermediate structure and energy, the proton transfers among the simple aliphatic ketones (reactions 1, 2, 4–7) illustrate that in some cases even the structure and energy of the reactants and products is not easily determined. Since in ICR only ion intensities are measured and neutral reactants and products usually remain undetected, reaction 1 could, in the absence of other information, just as well be 20, 21, or 22. If the reactant neutrals in reactions 1, 2, 4–7 are the enol tautomers instead of the ketones as indicated in Table I, then these slow reactions may indeed be proceeding at the collision rate, but because the partial pressure of the enol is so low, collisions with enols are rare. Likewise, if the neutral product is the enol, then these reactions may be slow simply because they are endothermic. Clearly the important consideration is the keto-enol equilibrium constant. For reaction 20 or 22 to be significant requires that keto/enol ≤ 10^3 in the gas phase. If less enol is present, the rates cannot match the observed rates even if 20 or 22 were collision controlled. For reaction 21 to be important also requires an equilibrium constant ≤10^3, otherwise the reaction would be too endothermic to exhibit the observed rate.

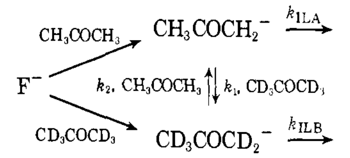
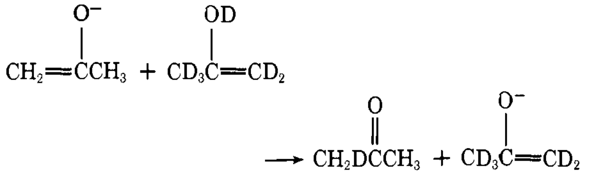
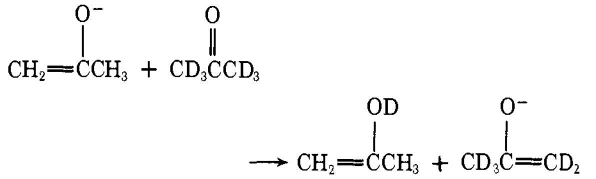


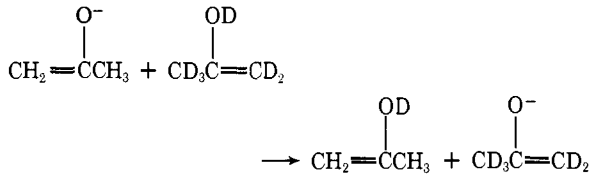
Figure 3. Reaction scheme for a typical set of reversible reactions.



$$CH_2{=}C(O^-)CH_3 + CD_3C(OD){=}CD_2 \rightarrow CH_2DC(=O)CH_3 + CD_3C(O^-){=}CD_2 \qquad (20)$$



$$CH_2{=}C(O^-)CH_3 + CD_3C(=O)CD_3 \rightarrow CH_2{=}C(OD)CH_3 + CD_3C(O^-){=}CD_2 \qquad (21)$$



$$CH_2{=}C(O^-)CH_3 + CD_3C(OD){=}CD_2 \rightarrow CH_2{=}C(OD)CH_3 + CD_3C(O^-){=}CD_2 \qquad (22)$$

There is good evidence that the gas-phase keto-enol equilibrium constant must be substantially above 10^3. Measured keto/enol equilibrium contents of aliphatic ketones in water are typically[17] of the order 10^5–10^7 and it would be expected that gas-phase enol contents would be even lower. Furthermore, thermochemical estimates of the equilibrium constants are in general agreement with this value, yielding enthalpy differences of 10–16 kcal for aliphatic ketones and enols in the gas phase.[18,19] Consequently, we believe that reactions 20–22 are not important.

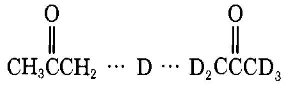
On the other hand, the two diones acetylacetone and 1,2-cyclohexanedione were chosen for this work precisely because they were expected to be highly enolic in the gas phase. The vinylic proton of the enol forms of these compounds has an NMR chemical shift that is quite distinct from any of the other absorptions of either the keto or enol forms. Hence enol contents in various solvents are easily determined. In both cases, we observe increasing amounts of ketone as the solvent polarity increases.[20] One would therefore expect that in the gas phase the enol content would at least be as high as that in the less polar solvents hexane or benzene, i.e., $K_{\mathrm{enol/keto}} \geq 10$. Available gas-phase data for acetylacetone confirms this expectation, the work of Conant and Thompson[21] yielding a value of 19 at 273 K. Other reported values are similar.[22]

In solution, the enolic protons of both 1,2-cyclohexanedione and acetylacetone can be exchanged by shaking with D_2O. That both of the compounds also undergo D-H exchange in the inlet system of the ICR, while aliphatic ketones fail to do so, is further evidence that they are largely enolic in the gas phase.

Specific deuteration experiments on acetylacetone demonstrate that both methyl and enolic protons are fairly acidic in the gas phase; the reactions of the two types of ions have been differentiated and analyzed separately. Experiments on 1,2-cyclohexanedione-d_1 (deuterium largely in the enolic position by NMR) indicate that F^- can abstract protons from both the enolic and α-keto positions in this compound as well. However, in this case enol abstraction predominated by greater than 3:1. These ions do not interconvert appreciably (no double resonance), but the relatively fast rate observed for reaction 10 requires that complications from the α-keto anion are not significant.[23] In summary, the ion and neutral structures of the reactants and products for the reactions listed in Table I are amply justified by available experimental evidence.

Experimental gas-phase acidities for some of the compounds employed in this work are available. We shall subsequently use this information for correlation of rate and equilibrium data for several of the reactions shown in Table I. Reactions 5-7 are all predicted to be exothermic in the direction observed in the present work and in order of increasing exothermicity $4 < 1,2 < 5 < 6 < 7$.[24] The equilibrium constant for reactions 4 and 5 determined from the rate constants and the fact that the reverse of 6 could not be observed are also both consistent with this order. Likewise, gas-phase acidities from other sources[25,26] predict the observed direction of proton transfer in the near thermoneutral cases 11-12, and a comparison of equilibrium constants for 11 and 12 determined from electron affinities and bond strengths[25] with that from the rate constants shows good agreement. Of the remaining reactions, 14-18 are quite exothermic, 1, 2, 9, and 10 are thermoneutral, and 8 is undetermined, although from the failure to observe any back reaction, the acidity difference must be at least 2 kcal/mol.

We can present no direct evidence on the structure of the intermediate collision complexes in these reactions. Based on the slow rates, however, it is possible to rule out a single symmetrical intermediate (as in eq I). The decomposition of such



$$\mathrm{CH_3\overset{\underset{\|}{O}}{C}CH_2 \cdots D \cdots D_2C\overset{\underset{\|}{O}}{C}CD_3}$$

an intermediate should proceed equally in the forward, k_b', and reverse, k_b, directions, since these decay routes would be structurally and energetically identical and thus k_{obsd} would be $k_c/2$. The observed rate constants are much smaller than this. Without further speculation at this point on the actual intermediate structures involved in reactions 1-18, we assert that the rates can be accommodated by the next simplest proposal, a three-step mechanism in which, for the symmetrical reactions, the symmetrical structure is the transition state for proton transfer,

$$\mathrm{AH + B^- \underset{k_b}{\overset{k_c}{\rightleftarrows}} [AH \cdots B]^-}$$

$$\mathrm{\underset{(A \cdots H \cdots B)^{\ddagger}}{\overset{k_p}{\rightleftarrows}} [A \cdots\ HB]^- \underset{k_c'}{\overset{k_b'}{\rightleftarrows}} A^- + HB} \qquad \text{(II)}$$

There is ample precedent for this mechanism in solution proton transfers where it has been widely used both in experimental and theoretical contexts,[27] and it has the added virtue of being the simplest combination of elementary steps that will explain the acetone rate (reaction 1). Beauchamp has recently proposed the classification of the energies of ion-molecule reaction intermediates into three groups based on the strength of the ion-molecule interaction:[28] (1) weak interactions (0-10 kcal) in which binding in the complex is dominated by the ion-induced dipole or ion-dipole attraction; (2) intermediate interactions (10-40 kcal) in which strong hydrogen bonds are formed; (3) strong interactions (>40 kcal) involving chemical bond formation. Reactions 1-18 may be expected to fall mainly into the second group with the possible exception of the aliphatic ketones, where a relatively weak CH···O or CH···C hydrogen bond might be expected to form. It is important to recognize, however, that even in cases where bonding of the ion and neutral is nonspecific, some complex, as a result of the ion-induced dipole attraction at worst, is more stable than separated reactants. Therefore, unless the excess energy is lost by radiative or collisional decay, the subsequent decomposition of the complex must be treated as a chemical activation problem.

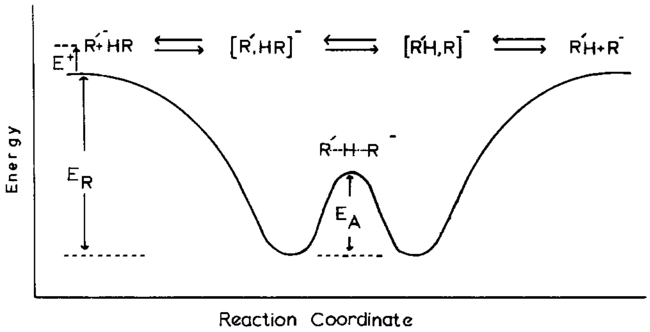


Figure 4. Potential surface for proton transfer. E^*, the total energy (see text) is the sum of $E_R + E^+$.

Figure 4 represents the general form of the potential surface for proton transfer between acetone enolate anions that emerges from this discussion. The rate of the reaction may be regarded as being determined by the competitive unimolecular decomposition of the chemically activated intermediate $[\mathrm{HR, R'}]^-$ back toward reactants or over a central barrier to products. As several authors have recently pointed out,[29] RRK theory[30] should provide a reasonable model for the *qualitative* features of the decomposition of an ion-molecule collision complex. For quantitative purposes, it would preferable to use RRKM theory, but the qualitative features should emerge from RRK. Within the framework of RRK theory, the rate constant is estimated as a product of the high pressure A factor times the fraction of states which have the critical energy in the reaction coordinate. For quantitative purposes it is more accurate to evaluate this fraction by quantum RRK theory;[30] for qualitative discussion we use the easily visualized approximation:[31]

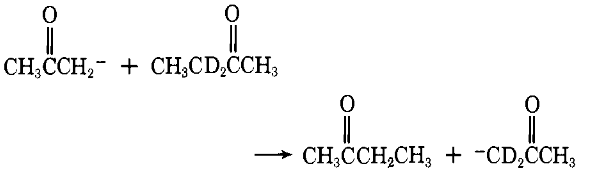
$$k(E^*) = A[(E^* - E_0)/E^*]^{s-1} \qquad \text{(III)}$$

Thus, the rate constant for reaction of an activated molecule of energy E^* depends on the critical energy required for reaction (E_0), the high-pressure Arrhenius preexponential factor (A), and the number of oscillators.[31] Since A increases with increasing entropy of the transition state, the relative sizes of k_b and k_p will be affected not only by E^* and the values of E_0 for each transition state, but also by the relative entropies of the two transition states. We expect that the entropy of the reverse reaction, k_b, will always exceed that of the forward reaction, k_p, since k_b involves a loose bond breaking step, while k_p is essentially an internal rearrangement. Therefore, ion-molecule processes involving complexes separated by large barriers should proceed at substantially less than the collision rate. This picture provides a satisfying explanation for the disarming characteristic of certain ion–molecule reactions of decreasing rate constant with increasing internal or translational energy.[32] Equation III discloses that increasing E^* makes the energy contributions to k_b and k_p more similar, and consequently the entropic terms become more important at high energy. The decrease in the absolute rate is expected. At low energy, the lower barrier process, k_p, becomes progressively more important. When more than one product can be formed from a given intermediate, as in the competitive decay of the intermediate obtained from $C_2H_4^+$ and C_2H_2, reported by Buttrill,[33] the change in product ratio with energy may be interpreted in these terms, decomposition proceeding more often through the energetically less favorable, entropically more favorable transition state at higher energies.

In this model what counterbalances, and in most cases dominates, the unfavorable entropy are large values of $E^* - E_0$, resulting from either strongly stabilized complexes or small rearrangement barriers or both (E_R and E_A are E_0 for reverse and forward reactions, respectively). The energy parameter which determines the partitioning is the difference between the two E_0's ($E_R - E_A$). For example, in the thermoneutral reaction 19, $k = 9.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, formation of a strongly hydrogen-bonded intermediate (large E_R) may mask any barrier and be largely responsible for the fast rate. In the proton transfers involving delocalized anions, both a small E_R and a large E_A may intervene to produce the unusually slow reactions. These characteristics correspond roughly to the explanations that have been offered for the abnormal behavior of delocalized systems in solution; poor hydrogen bonding (small E_R) or substantial barriers resulting from charge localization and structural reorganization[34] (large E_A).

The increasing rates of proton abstraction by acetone enolate anion in the series acetone (1), 2-butanone (1 + 3 positions) (6), and 3-pentanone (7) correlate with increasing exothermicity. In spite of the large error limits, we are confident that the relative rates are fairly accurate, and on a per proton basis, the trend is even clearer. Since k_c (eq II) cannot be rate determining, this trend is qualitatively consistent with enthalpy barriers whose heights are sensitive to the overall exothermicity occurring in these reactions. Alternative explanations consistent with the model, such as the entropy of the reaction increasing in the same order, or the exothermicity being reflected in the (reactant-like) intermediate stability (E_R) seem less likely, although a small increase in E_R probably contributes to the rate increase.[35]

Other trends in the data provide further evidence that relative barrier heights E_R and E_A are the significant factors in determining the overall rates of these ion–molecule reactions. For example, the increasing selectivity of abstraction of the methylene (or enolic) protons relative to the methyl protons in acetylacetone exhibited by decreasing the base strength in the series fluoride, acetone enolate, and acetylacetone enolate correlates with decreases in the total overall rate. Thus, as the base strength increases, so does the exothermicity, leading to lower E_A's for formation of both products, a greater overall rate, and simultaneously less selectivity. The decrease in the barrier E_A with increasing exothermicity follows the Hammond–Polanyi behavior commonly observed in many reactions. There is evidence from other sources[36] that in some cases E_A can exceed E_R. This situation would result in a rate that increases with increasing energy. With the added proviso that barriers must be constructed on a foundation of ion-induced dipole or more stabilizing forces, one expects reactions that proceed through conventionally unstable transition states to be relatively slow under these circumstances as well. For example, the displacement reaction 23, which is thermoneutral and not in competition with any fast processes in the gas phase,



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}CH_2^- + CH_3CD_2\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3 + {}^-CD_2\overset{\overset{O}{\|}}{C}CH_3} \qquad (23)$$

is not observed, presumably because of a large barrier. These trends are not surprising, but contribute to a growing body of evidence[29] that gas-phase reactivity of large ion–molecule systems may be described by unimolecular decay theory.

Why are proton transfers to delocalized ions slow? The data for the 1,2-cyclohexanedione reaction, 10, and the phenols, reactions 11 and 12, suggest that when the enol contents are high, the rates of the thermoneutral symmetrical proton transfers involving delocalized ions are considerably faster than when only keto forms are present. Reaction 11 is endothermic and k_b' is therefore probably influencing the overall rate. Reaction 12, or an average of 11 and 12, provides a more valid comparison with the thermoneutral cases 1, 2, 9, and 10. Acetylacetone (reaction 9) on the other hand, while not as slow as the aliphatic ketones, is nevertheless not as fast as the other high enol content cases. These rates may be rationalized in the following way.

As suggested by solution results, there may be a substantial "intrinsic" barrier to proton transfers involving delocalized ions, which results from loss of resonance energy in the transition state due to a requirement for charge localization. This barrier can be circumvented if proton transfer can occur without disruption to the delocalized π system, as for example to oxygen lone pairs. This picture is consistent with solution-phase observations of fast proton transfers to oxygen, but slow transfers to carbon in enolate anions, even though the thermochemistry favors carbon protonation.[37] On this basis the benzyl anion, toluene reaction (reaction 3) represents the high barrier case, since only the delocalized electrons are available for proton acceptance at the benzylic position. Symmetric reactions of enolate anions with ketones or enols, on the other hand, are potentially low barrier reactions, since protons may be transferred to oxygen. When such a reaction is allowed by the overall thermochemistry, a relatively fast reaction is observed (1,2-cyclohexanedione or phenol). For ordinary ketones, proton transfer to the oxygen of the anion leads to thermodynamically unfavorable enol products. Thus, the reaction is forced to proceed via the high barrier, carbon-to-carbon route. Acetylacetone is a special case. Eigen[38] has demonstrated that because of the internal hydrogen bond in this compound its proton-transfer reactions exhibit abnormally large barriers. The gas-phase results showing increased abstraction of the internally bound hydrogen with the considerably bulkier acetone enolate relative to F$^-$ indicate that the barrier is indeed not steric, but electronic in the gas phase as well. The internal hydrogen bond must be cleaved to achieve proton transfer. If the enolate anions derived from acetylacetone are allowed to react with a normal proton donor, even if the reaction is thermoneutral, a much smaller barrier is observed (reaction 13, compare to 9 and 8). And as expected from previous discussion, more exothermic processes are even faster (reaction 14). It is noteworthy that even the low barrier cases are still <25% efficient. That is, the rates are only 25% of the expected collision rates.

In spite of the qualitative appeal of this explanation, it is an oversimplification because it ignores the effects of structural variations in the reactants on the structure and energy of the intermediate; that is, the possibility that the rate distinctions between what we have called the high and low barrier cases are not related to a differential barrier height at all, but rather to differences in the stabilities of the complexes (E_R). Nevertheless, some barrier is required to explain the experimental results already presented, and order of magnitude calculations of the relative rates of the forward and reverse decompositions of the complex can be made to estimate the size of the barrier. For these calculations we have employed quantum RRK theory[30] with the assumptions that the characteristic frequencies of both transition states are all 1000 cm^{-1}, and the ratio of A factors is 10^5. This is approximately the ratio of A factors for the decomposition of an ionic complex[39] vs. a unimolecular isomerization with a very tight transition state. Since we do not know the correct frequencies for the proton-transfer transition state, we can only estimate the A factor. With these assumptions we calculate[39] that a complex more stable than reactants by 10 kcal/mol requires a barrier (E_A) of ca. 2 kcal/mol to produce a rate as slow as 2×10^{-12} cm^3 molecule^{-1} s^{-1}. More stable complexes will require larger barriers for comparable rates; a smaller entropy difference will also require a larger barrier.

Let us presume, then, that the barrier heights (E_A) of all the proton transfers are identical, and that the rate differences, therefore, reflect differences in E_R. It is possible to correlate rates with expected stabilities of the complexes? If electrostatic factors dominate E_R, one might argue that delocalized ions generally should exhibit slow reactions, since a full negative charge may not be operative in the ion–dipole or induced dipole attraction. Under those circumstances, we would expect a gross correlation between rates and degree of charge delocalization in the reactant ion. The data show no such correlation. Reaction 8, the symmetrical proton transfer of the acetylacetone enolate anion, with two equivalent resonance structures is faster than reaction 1, acetone enolate, acetone, where charge should be more highly localized. Similarly, comparison of reaction 9, 1,2-cyclohexanedione enolate symmetric proton transfer, and 1, where charge delocalization should be roughly similar, shows rates different by two orders of magnitude. If, on the other hand, the complex stability results primarily from hydrogen bonding between the anion and neutral, as Beauchamp has pointed out for several cases,[28] then a correlation between hydrogen bond strength and rate would be expected. To the extent that one can estimate the relative stabilities, the expected trend is observed. For example, it would be expected that no strong hydrogen bond can be formed between the reactants, benzyl anion and toluene, in reaction 3 ($E_R \leq 10$). That in itself may be sufficient to account for the slowness of the rate relative to methoxide, methanol (reaction 19), where the value of E_R is approximately 24 kcal/mol.[40] The aliphatic ketones as a group may, in fact, form less stable CH···O hydrogen bonds than the high enol content cases, where OH···O complexes are possible. Of course, the more stable the complexes in the slow reactions, the larger the barriers required to account for the slow rates—a somewhat paradoxical requirement. Ultimate resolution of the interplay between these two factors awaits improved descriptions of the structures and energies of the intermediates and the application of more sophisticated theories of unimolecular decay to ion–molecule reactions.

In their most primitive interpretation, these results demonstrate that the rates of slow proton-transfer reactions are not solely a result of solvent effects; that the isolated behavior of acids and bases is in many respects similar to their behavior in solution. On the other hand, the demonstration that many of the features of proton transfers that have been elucidated in solution are applicable to gas-phase results as well is an important step toward a general unification of the proton-transfer picture. In particular, the demonstration of a gross congruence in the factors leading to slow rates of proton transfers involving delocalized ions in both the gas and solution phases is significant. A major problem remaining for proton transfer studies in solution is identical with that faced by the gas-phase work; the quantitative analysis of the relative contributions of each step to the overall rate of the reaction. Recent reports of applications of Marcus theory[41] claim that the slow solution-phase proton transfers may be characterized by barriers both in the first, or "encounter," step, with additional "intrinsic" barriers in the second step. One would expect barriers to k_p, where solvent effects should be secondary, to be similar to the barrier heights E_A that would appear in the gas-phase processes. In fact, this may be a good example of a situation in which gas-phase and solution results can cross-fertilize toward the goal of the detailed description of potential surfaces for proton-transfer reactions.

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Relative Gas-Phase Acidities and Basicities from a Proton Potential Model

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Abstract: A proton potential model (PPM) calculation of gas-phase proton affinities was used to calculate relative PA values for various molecules and anions. The model, which uses CNDO/2 wave functions, provides separate values of inductive and polarization energies accompanying the gain or loss of a proton. Agreement with experiment ranges from excellent for acidities of substituted aliphatic acids to poor for certain unsaturated molecules. An approximate method for empirical separation of inductive and polarization effects is presented.

I. Introduction

The Bronsted acidity and basicity of a molecule, which measure that molecule's tendency to lose or gain a proton, are of considerable chemical interest. The increasing availability of accurate experimental values of gas-phase acidities and basicities has stimulated interest in estimating these quantities theoretically. Ab initio calculations with sufficiently large basis sets can predict absolute values of the proton affinities to within a few percent in the Hartree-Fock approximation.[1] These proton affinities (PA) are the energy E_b of the reaction

$$B + H^+ \rightarrow BH^+;\ E_b = -PA_m \qquad (1a)$$

or (minus) the energy E_a of the reaction

$$AH \rightarrow A^- + H^+;\ E_a = PA_a \qquad (1b)$$

Here the subscripts "a" and "m" denote proton affinities of the anions and neutral molecules, respectively. More accurate predictions of the absolute values of E_a and E_b would require very careful ab initio calculations, including electron correlations. Such calculations rapidly become impractical as the molecular size increases.

Relative acidities and basicities can be calculated to satisfactory accuracy using less sophisticated theoretical models. In this approach one tries to calculate the energy of the proton-transfer reaction

$$B + B'H^+ \rightleftarrows B' + BH^+ \qquad (2a)$$

for comparing two bases, or

$$AH + A'^- \rightleftarrows A'H + A^- \qquad (2b)$$

for comparing two acids. If the molecules to be compared lie in a group of molecules with enough similarities, some of the errors in E_b or E_a that arise from theoretical approximations will tend to cancel. Thus, Radom found good agreement with experiment for energies of several proton-transfer reactions involving acidities, using ab initio theory with minimal STO-3G basis sets.[2]

It would be highly desirable to use an intermediate level molecular-orbital theory such as CNDO/2 to estimate energies of proton-transfer reactions. Most of the applications of CNDO/2 for this purpose have been based on difference in total energy, with varying success.[3-6] This approach usually gives the correct order of acidity or basicity, but quantitative agreement with experiment is marginal.

An alternative potential-model approach was derived by Davis and Rabalais.[7] Based on differences in the electrostatic potentials at proton sites, calculated employing CNDO/2 wave functions, this approach is related to the "relaxation potential model" (RPM) used to estimate ESCA shifts. We shall term it the "proton potential model", or PPM. Davis and Rabalais calculated proton affinities of several molecules using the PPM approach. In this paper we report further results based on an improved PPM model. Proton-transfer energies were calculated for several series of molecules and anions, yielding relative acidities or basicities within each series. Our objective was to evaluate the PPM in its applications to a wide range of molecules.

Section II sketches the theory briefly. Results are given in section III. These are discussed in comparison with experiment in section IV. An empirical model of acidities and basicities is discussed in section V. Conclusions are briefly summarized in section VI.