Kinetics and Thermodynamics of Carbon–Carbon Bond Formation and Cleavage through Reactions of Carbocations and Carbanions

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The basic theme of this Account and the 20 years of research which lie behind it is the interplay between thermodynamics and kinetics of heterolysis reactions in solution. As Ingold pointed out many years ago,[1] heterolysis is the preferred mode of bond cleavage in solution (in contrast to the gas phase) because of the enormous solvation energies resulting from ion–solvent interaction. Carbocations and carbanions that are produced by heterolysis are therefore important intermediates in condensed-phase organic chemistry. This implies a close relationship between acid–base chemistry and heterolysis since these intermediates are produced respectively under acidic and basic conditions.

Related in structure and energy to carbocations and carbanions are the transition states for their formation or reaction. The transition-state theory is the principal intellectual tool for the study of reaction mechanisms and hence allows the discussion of rate processes in thermodynamic language and of the structures of the highest energy states along a reaction coordinate in terms of nearby high-energy minima.[2] Such is the case for the less stable carbocations and carbanions or their ion pairs.

Over the past two decades experimental results have become available from many sources which permit a complete analysis in thermodynamic, kinetic, and structural terms for many simple heterolysis reactions involving carbocations and carbanions. Although the present Account emphasizes the contributions to these developments from the author's laboratories, our work is heavily dependent on inspiration and collaboration from many other researchers in the field of whom we can refer, regretfully for reasons of space, to only a few principal sources.

Classical Sources of Carbocation and Carbanion Stabilities. Until the late 1960s rigorous analyses of heterolytic reaction mechanisms in terms of rates and thermodynamics were hampered severely by the fact that only the most stable carbocations or carbanions could be studied directly in acid or basic solution, whereas the highly reactive cations and anions which were most directly relevant to the kinetics of heterolysis

were too unstable for direct examination. The simplest and often most reactive ions had to be studied by mass spectrometry in the gas phase where their structures could not be confirmed directly. More often stabilities in solution were inferred indirectly from reaction rates using the approach of Hammond's postulate.[2] A direct proportionality was assumed between the activation energy for S_N1 solvolysis reactions and the thermodynamic stabilities of the carbocations, or their ion pairs, which were presumably formed from the heterolysis.

During the 1960s and 1970s, primarily in the laboratory of G. A. Olah,[3] it was shown that even very unstable carbocations (i.e., isopropyl or cyclopentyl) could be generated and maintained for prolonged periods at low temperatures in very nonbasic solvents by means of very strong Lewis acids. Under such superacidic conditions, hundreds of important carbocations were generated and their structures elucidated at leisure by means of a battery of spectroscopic techniques— primarily heteronuclear NMR.

Meanwhile, a comparable effort was being mounted, primarily in the laboratories of F. G. Bordwell[4] and A. Streitwieser[5] to generate a wide range of carbanions from many types of carbon acid precursors. The key to these studies was the development of superbase systems using the alkali-metal salts of dimethyl sulfoxide and cyclohexylamine in an excess of these nonhydroxylic solvents. Subsequently the pK_a's for ionization of over a thousand Brønsted acids covering a range of 35 pK_a units have become available from the work of Professor Bordwell's research group alone.

Thermochemical Studies of Ion Formation. Once the conditions for generating a wide range of carbocations and carbanions had been worked out in superacid and superbase base systems, the way was clear to apply the techniques of batch calorimetry for the direct measurement of heats of formation of these ions in solution from appropriate precursors. Solution calorimeters were developed to operate under superacidic conditions and the enthalpies of formation for nearly

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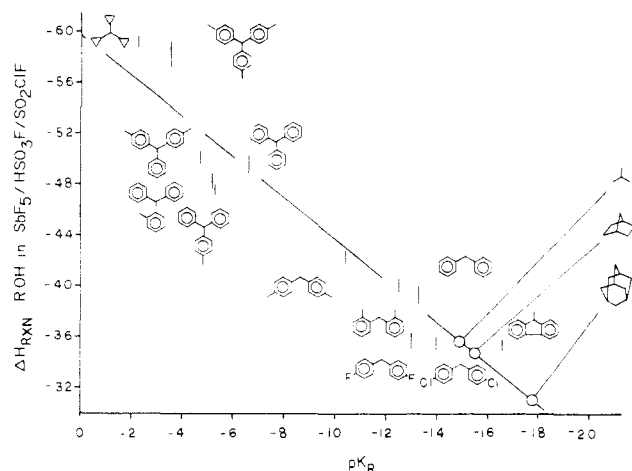
Figure 1. Extended correlation of heats of formation of resonance stabilized carbocations from their carbinols in superacid at low temperature vs. their pK_{R^+} values in aqueous H_2SO_4. Open circles provide interpolated pK_{R^+} values for some aliphatic cations not accessible by indicator studies. (Reprinted with permission from ref 6i. Copyright 1983 American Chemical Society.)
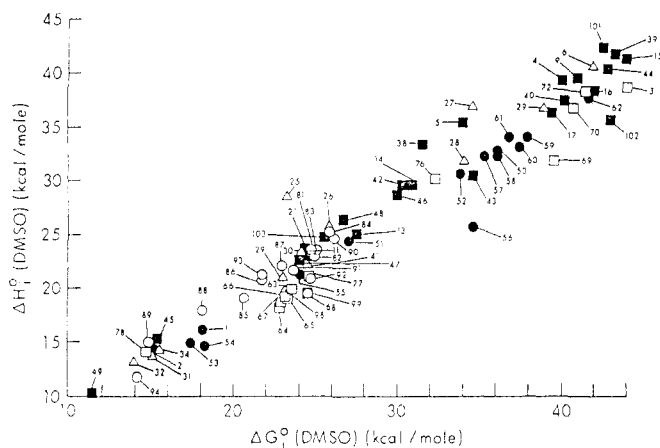

Figure 2. Plot of standard free energies vs. enthalpies of ionization for phenols (O), alcohols (□), benzoic acids (●), amines (■), thiophenols (△), and mercaptans (▲) in Me_2SO at 25 °C. (Reprinted with permission from ref 7c. Copyright 1983 American Chemical Society.)

a hundred carbocations were measured (Figure 1) ranging from thermodynamically unstable secondary ions to some of the most stable triarylmethyl systems.[6] Soon a similar series of studies was launched to determine heats of formation of weak acids in superbase systems[7] (Figure 2).

Solution calorimetry offers an enormous advantage over classical free energy determinations since a wide range of ionization processes can be compared in the same medium under the same conditions regardless of how far they are from equilibrium. In contrast, free
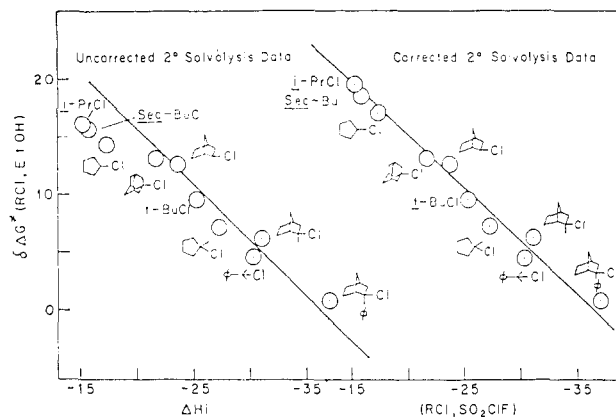
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Figure 3. Correlation of free energies of activation for ethanolysis of alkylchlorides vs. heats of formation of the respective alkyl carbocations in superacid at –60 °C. (Reprinted with permission from ref 8. Copyright 1979 American Chemical Society.)

energy measurements require the development of an extensive series of indicators whose ionization ranges must overlap in order to provide a consistent linear free energy scale.

With reliable heats of formation for carbocations and carbanions in hand it was possible at last to test the assumed relationship between kinetics and thermodynamics of ion formation. Correlation of free energies of activation and enthalpies of carbocation formation (Figure 3) gave strong support for the long held assumption that ion stabilities could be inferred from solvolysis rate constants.[6,8]

The direct proportionality, or often equivalence, between free energies and enthalpies of ionization was demonstrated abundantly by extrathermodynamic correlations between heats of deprotonation in potassium DMSYL–Me_2SO and Bordwell's free energies of ionization.[9] Subsequently, excellent correlations have been found between pK_a's in this superbase system and free energies of activation for displacement reactions and the free energies of electron transfer as determined from oxidation potentials.[10] Again, heats of ionization of triaryl carbinols to form carbocations in superacidic media correlate well with corresponding free energies of ionization obtained in aqueous sulfuric acid solutions.[6c]

Solvation. While the above thermodynamic determinations of ion stabilities in solution were being made, a breakthrough in gas-phase chemistry was taking place which would permit the rigorous determination of solvation energies for organic carbanions and anions. Three new techniques—ion cyclotron resonance, high-pressure mass spectrometry, and the flowing afterglow technique—provided for the first time thermodynamic measurements for ion–molecule reactions which could provide gas-phase acidities and basicities directly comparable to the corresponding measurements in solution.[11] For systems where both sets of data could be

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compared through a simple first law energy cycle, the difference between the gas-phase acidities (or basicities) and the corresponding values in solution must be attributable to the solvation energies of the neutral precursors and those of the corresponding ions.[12] Solvation energies of the neutrals in turn can be determined readily from Henry's law constants and/or heats of solution.

It had been recognized for nearly a century that rates and thermodynamics for processes in solution were the sum of an "inherent" contribution and contributions from interactions with the solvent. However, until the new gas-phase techniques were developed, the actual magnitude of solvation factors was left to calculation or inference. As the new results came in it was soon clear that the basic principles for understanding solvation energies were simple and intuitively reasonable.

Large delocalized carbocations and carbanions not only showed gas-phase acid–base properties which correlated well with those in solution, but quite frequently the slope of the correlation line was virtually unity.[13] Thus, although the absolute magnitude of ion solvation energies are in the neighborhood of 100 kcal/mol, the effect of structural change on the inherent ionization properties in the gas phase were reproduced faithfully in solution.

In contrast, ions with highly localized charge such as ammonium or alkoxide ions showed widely differentiated behavior between gas-phase and condensed-phase behavior.[14] Since the localized charge cannot be distributed internally by resonance delocalization, such ions stabilize themselves in solution primarily by hydrogen bonding with the solvent or by pairing with the counterion. Consistent with this interpretation is the fact that heats of formation for many charge-localized carbocations in non-hydrogen bonding superacid media correlate closely with the corresponding heats of formation in the gas phase.

Direct Study of the Coordination of Carbocations with Carbanions. With the techniques for generating long-lived carbocations and carbanions in hand and for measuring their relative stabilities through calorimetry or free energy measurements, one may consider study of the direct reaction between carbocations and carbanions in solution. Following Ingold's terminology,[1] we call this *coordination*—the reverse of *heterolysis*. The direct coordination of carbocations and carbanions has considerable appeal as the simplest polar reaction for carbon–carbon bond formation. It may also be regarded as the attack of a solvated electrophile on a solvated nucleophile with no involvement of a leaving group. Measurements of the heats of such coordination reactions by calorimetry should provide heterolytic bond energies directly merely by changing the sign ($\Delta H_{het} = -\Delta H_{coor}$). Furthermore, if conditions could be found for bringing such reactions to equilibrium and measuring their kinetics, it would be possible to obtain valuable information for comparing thermodynamics and kinetics for a primary bond-forming reaction in solution. We will describe the results of such a study below.

At first glance, the likelihood of finding conditions under which carbocations and carbanions could be prepared in a common solvent might seem unlikely in view of their usual requirement of strongly acidic or basic media for preparation. However, it is well-known that highly stabilized carbocations and carbanions can exist within the aqueous pH range and there is clear precedent for the study of cation-anion reactions in the extensive work of C. D. Ritchie,[15] Kessler,[16] and others.[17]

Takahashi and her students[18] observed the cleavage of oligomers of 1-cycloheptatrienylidene-4-(dicyanomethylidene)-2,5-cyclohexadiene to a zwitterionic species whose alternative resonance structure carries a π bond between the two rings. The dependence of the electronic spectrum of this system on solvent polarity strongly supports the contributions of these forms to variable structures of the hybrid (Figure 4).

An initial experimental search soon demonstrated that an enormous range of observable rates could be found for the reactions of carbocations and carbanions from diffusion control to systems where both parties coexisted with no sign of reaction at all after 6 months standing.[19] Further exploration finally produced several systems for which the coordination and heterolysis processes were so finely balanced that they could be observed at equilibrium.[20] Furthermore, because of

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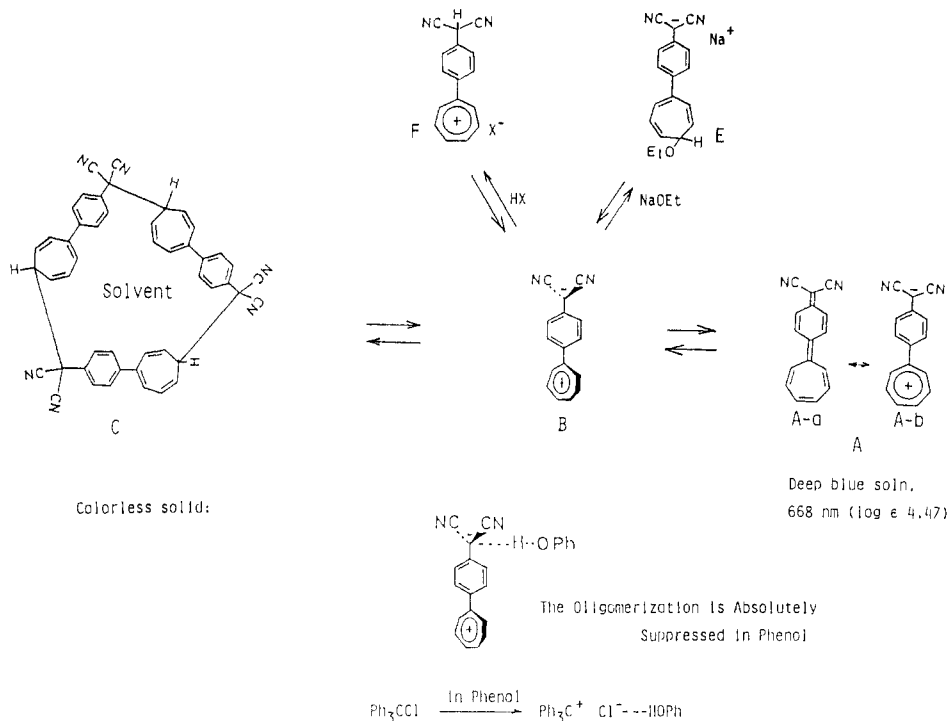
Figure 4. Equilibria between neutral oligomeric and zwitterionic form of Takahashi's compound. (Reprinted with permission from ref 18a. Copyright 1970 Pergamon Press.)

dielectric stabilization of the ions produced by heterolysis, it was possible to make compounds which were completely covalent in low dielectric solvents, such as ethers or hydrocarbons, but which were completely ionized in more polar media such as acetonitrile. Thus, the carbon–carbon bonds in such compounds may be broken merely by changing from a less polar to a more polar solvent.
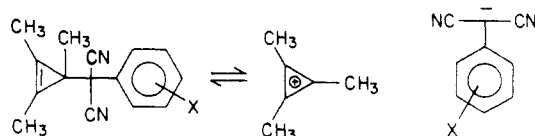
Some Extrathermodynamic Relationships. With thermodynamic data in hand for free energies, enthalpies, and entropies of coordination and proton transfer, the relations between these different properties should be tested for correlation.[20] In fact, the free energies of heterolysis give a linear correlation with the corresponding enthalpies and, of course, with the corresponding properties for coordination which simply involve a sign change. Of more importance, good correlation was found between the standard free energies for coordination of the carbocations with carbanions and the standard free energies for proton transfer to the same carbanions.

Finally, the redox potentials were obtained for both types of ions and again these showed good linear correlation with all of the other properties listed above. The conclusion from this combined set of correlations is that there is a good proportionality between the energetics for transferring two electrons from a delocalized carbanion either to a proton or to a delocalized carbo-

cation in solution and furthermore that the energetics of the two electron processes correlate well with those for single electron transfer as represented by redox potentials. Not surprisingly, some of the carbocation/carbanion pairs gave clear evidence by the formation of dimeric products from the carbanions that single electron transfer was an alternative channel to direct coordination of the carbanion to the carbocation.

Heterolytic Bond Energies and Bond Lengths. Is the Bond Really Weak? The carbon–carbon bonds whose formation and rupture may be studied at equilibrium are so weak relative to the resonance-stabilized carbocations and carbanions formed as products that they may actually be cleaved merely by solution in a high dielectric solvent.[18,20] Since the bonds are thermodynamically of unusual weakness relative to these products, it is natural to question whether the very low heterolytic bond dissociation energy is reflected in an unusually long carbon-to-carbon bond length—does the carbon-to-carbon bond in the covalent molecule reflect the fact that it could be converted into two very stable ions?

Only a full X-ray crystal study can answer this question and our first examination[20a] of trimethylcyclopropenium (*p*-nitrophenyl)malononitrile showed an unusually long bond (1.588 Å) between the malononitrile and cyclopropene carbon atoms. More importantly, this structure proved without a doubt that a covalent product was being formed from reaction of the carbocations and carbanions. Since charge-transfer complexes[21] or salts[18] have been isolated from electrophile–nucleophile reactions this matter needed to be settled.

Recently the relationship between ion stability and bond length has been tested by obtaining a second X-ray structure, this time of trimethylcyclopropenium

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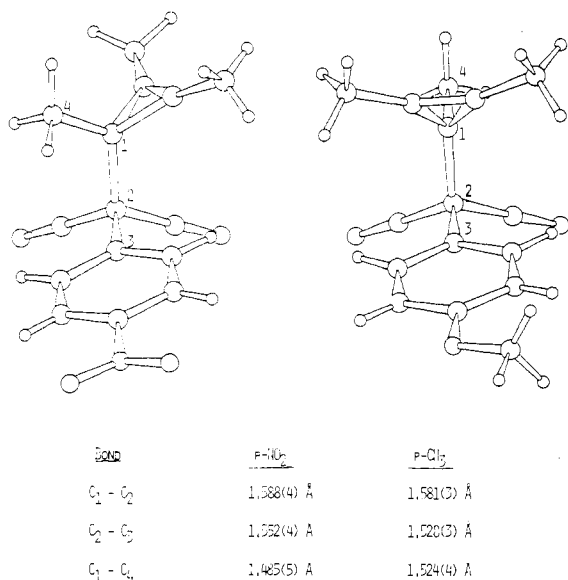(21) LeGoff, E.; LaCount, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1354.

Figure 5. Comparison of bond lengths in (trimethylcyclopropenyl) p-nitrophenylmalononitrile (left) and corresponding p-methoxy compound (right) (structure determinations by Professor A. McPhail).

Figure 6. Comparison of heats of heterolysis (ΔH_{het}) in benzonitrile at 25 °C for 19 compounds derived from carbocation-carbanion reactions vs. the pK_a's of the carbanion precursors. Heats of heterolysis are derived from heats of coordination by changing the sign (from data in ref 22).

(p-methoxyphenyl)malononitrile (by Professor Andrew McPhail) with the amusing result that by comparison with the p-nitro compound (Figure 5) virtually every other bond except the one in question had undergone some change in length. Clearly the stability of the heterolysis product is not reflected in the bond length of the neutral reactants! At this point we have no information on the inherent heterolytic energy of the carbon–carbon bond in the gas phase.

A Master Equation for Heterolytic Bond Energies? The results cited above show that heats of ionization are correlated closely with the corresponding free energies and hence to the pK_a's of carbon acids or to the pK_{R^+}'s of the carbocation precursors. Also ΔG_{het} correlates closely with pK_a's (Figure 6). This suggests the possibility of a master equation which could be used for predicting heats of heterolysis of carbon–carbon bonds to produce resonance-stabilized carbocations and carbanions in solution from the stabilities of the ions as determined by pK_{R^+}'s and pK_a's. This may be expressed formally through the equation

$$\Delta H_{het} = ApK_a + BpK_{R^+} + C \qquad (1)$$

which may be recast in the form of

$$\Delta H_{het} = D(pK_a + pK_{R^+}) + E \qquad (2)$$

if $A = B$. Figure 7 tests eq 2 using three sets of data for a variety of carbocation–carbanion systems.[22] It is truly extraordinary to see the success of such a simple treatment applied to such a variety of structures over a range of energies covering nearly 40 kcal/mol.

If such a simple expression continues to hold as the structure of the cation and anion is varied more widely, it could be of considerable value as a guide to the depolymerization of complex aromatic macromolecules such as are found in the fossil fuel industry. Acid-catalyzed depolymerization of various ranks of coal is already showing promise as an alternative to the tra-
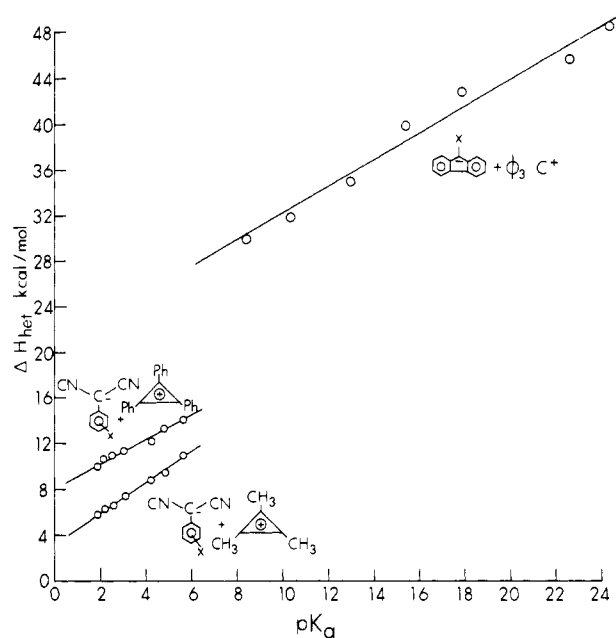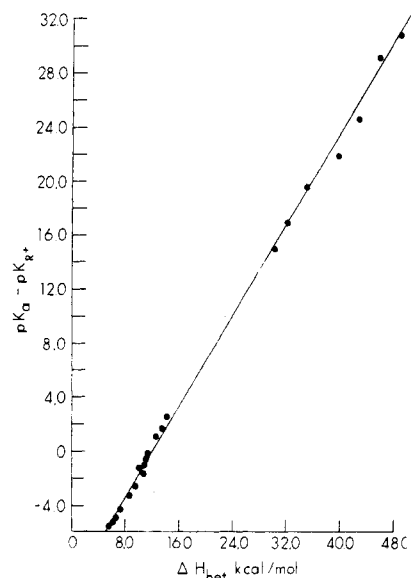

Figure 7. Fit of the systems shown in Figure 6 to eq 2. (Reprinted with permission from ref 22. Copyright 1985 American Chemical Society.)

ditional wasteful high-temperature pyrolytic techniques.[23] A simple guide to heterolytic bond energies in solution could be of considerable value in suggesting the most likely products of low-temperature base- or acid-catalyzed depolymerization processes.

Kinetics of Coordination and Heterolysis. A major reason for initiating this study was the possibility

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Table I.
Kinetics of Coordination and Heterolysis by Temperature Jump and NMR Line Broadening at 25 °C in Acetonitrile with and without Supporting Electrolyte[24]

X	k_{coor},[a] $M^{-1} S^{-1}$	k_{het},[a] S^{-1}	k_{het}[b] S^{-1}
		$R = CH_3$	
p-NO_2			560 ± 80
p-CN	$(7.21 \pm 0.77) \times 10^4$	$(5.23 \pm 0.56) \times 10^2$	190 ± 20
m-NO_2	$(1.71 \pm 0.20) \times 10^5$	$(3.36 \pm 0.39) \times 10^2$	
m-CN	$(2.72 \pm 0.34) \times 10^5$	$(2.28 \pm 0.28) \times 10^2$	
m-CF_3	$(6.18 \pm 0.37) \times 10^5$	$(1.67 \pm 0.10) \times 10^2$	$33 + 4$
m-Cl	$(7.86 \pm 1.20) \times 10^5$	$(9.43 \pm 1.44) \times 10^1$	27 ± 4
p-Cl	$(1.77 \pm 0.14) \times 10^6$	$(6.11 \pm 0.49) \times 10^1$	14 ± 2
H	$(6.07 \pm 1.14) \times 10^6$	$(2.97 \pm 0.56) \times 10^1$	3.8 ± 0.5
p-CH_3	$(1.27 \pm 0.18) \times 10^7$	$(1.65 \pm 0.24) \times 10^1$	2.2 ± 0.2
		$R = Phenyl$	
p-NO_2	$(1.63 \pm 0.08) \times 10^6$	$(2.04 \pm 0.10) \times 10^3$	
p-CN	$(1.33 \pm 0.08) \times 10^7$	$(9.95 \pm 0.60) \times 10^2$	
m-NO_2	$(7.80 \pm 0.91) \times 10^7$	$(7.74 \pm 0.90) \times 10^2$	
m-CN	$(1.14 \pm 0.14) \times 10^8$	$(6.51 \pm 0.81) \times 10^2$	

[a] Results from temperature jump kinetics; experiments performed under conditions of high ionic strength (0.48 M $Bu_4N^+BF_4^-$ in acetonitrile at 25 °C. [b] Results from NMR line broadening in acetonitrile-d_3 at 25 °C.

of obtaining both thermodynamic and kinetic data for an important bond-forming reaction. With a full set of thermodynamic properties in hand, the measurement of reaction kinetics reached a high level of priority. Test tube experiments demonstrated very quickly that both the heterolysis and coordination processes for the substituted cyclopropenium phenylmalononitrile systems were very fast and were even outside the stopped-flow range. However, proton magnetic resonance spectra suggested that the rates could be obtained by observing the line broadening as a function of temperature. Table I shows a number of rate constants obtained in this manner using a program developed by Professor Donald Chesnut. However, since both coordination and heterolysis are involved, it is reasonable to ask which process or combination of them is observed in the NMR experiment. An independent source of rate constants is needed.

The temperature jump technique is particularly attractive for determining the rates of reactions with highly colored species by perturbation–relaxation. Table I shows the results of such experiments in acetonitrile using tetrabutylammonium tetrafluoroborate as the inert conducting salt.[24] The coordination rates are much faster than the rates for heterolysis which in turn are much closer in magnitude to the rate constants obtained from the NMR experiment. Furthermore, both the rates and equilibria in the salt solution are shifted by the salt solution in just the way one would expect in response to an ionic strength effect.

We are now in a position to compare directly the free energies of activation and of reaction for coordination and heterolysis. Figure 8 shows such a comparison for reactions of the trimethyl- and triphenylcyclopropenium ions with a series of substituted phenylmalononitrile anions. Good linearity is found, and the
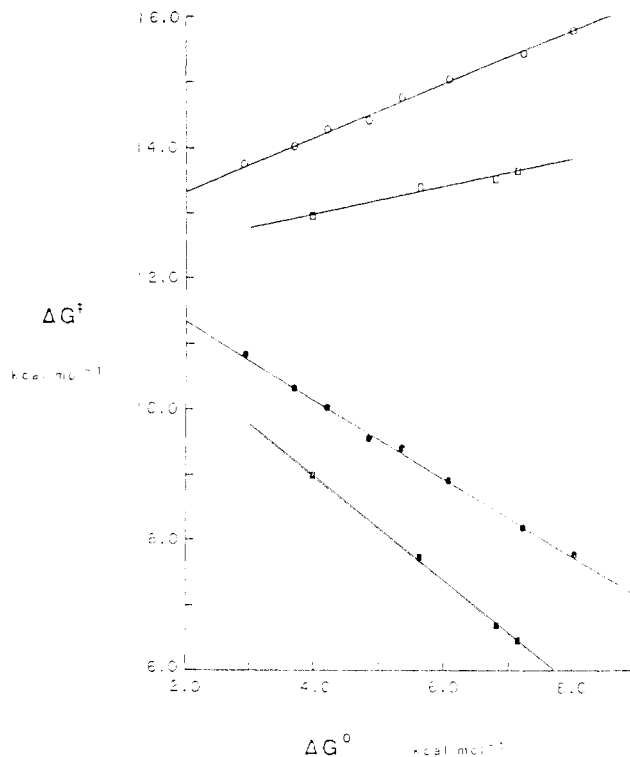
(24) Arnett, E. M.; Molter, K. E. *J. Phys. Chem.*, in press.

Figure 8. Correlations of free energies of activation and reaction for coordination of cyclopropenium cations with arylmalononitrile carbanions and the reverse heterolysis (eq 1). Data determined in 0.48 M NBu_4BF_4 in acetonitrile at 25 °C. (Reprinted with permission from ref 24. Copyright American Chemical Society.) ●, trimethylcyclopropenium, coordination; ○, trimethylcyclopropenium, heterolysis; ■, triphenylcyclopropenium, coordination; □, triphenylcyclopropenium, heterolysis.

corresponding slopes, $\delta\Delta G^{\ddagger}/\delta\Delta G°$, are as follows: (1) −0.796 for triphenylcyclopropenium coordination with arylmalononitrile anions; (2) −0.596 for trimethyl-cyclopropenium coordination; (3) 0.204 for (triphenyl-cyclopropenyl)arylmalononitrile heterolysis; (4) 0.404 for (trimethylcyclopropenyl)arylmalononitrile heterolysis.

By this criterion about a third to a half of charge development has occurred at the transition state for heterolysis. This is in the same range as is found from the ionic strength effect by comparing rates and equilibria for heterolysis in pure acetonitrile with those in a 0.48 M $Bu_4N^+BF_4^-$ solution.

It is important that these facts not be converted into pictures of a transition state in which the central C–C bond is half broken or other such notions concerning the "position of the transition state along the reaction coordinate". Whatever value there may be in such ideas when referred to simple reactions in the gas phase, they are quite out of place for cation–anion reactions in solution. All of the evidence in hand indicates that the heterolysis/coordination reactions are determined by ion solvation/desolvation: (a) the length of the central C–C bond is unrelated to the heterolysis energy; (b) several of the systems we have studied are covalent in low dielectric media but dissociate to ions in polar solvents; (c) the free energies of heterolysis are proportional to the reciprocal of the solvent dielectric constants in accordance with the Born electrostatic equation; (d) the entropies of heterolysis are small, although two ions are being made from one molecule, suggesting that the gain in translational entropy is

cancelled by the entropy of solvent electrostriction.

These systems are far removed from the highly exothermic or endothermic reactions to which Hammond's postulate applies[1] and, as Ritchie has argued,[15b] the Marcus equation does not apply to cation–anion reactions. We share[26c] Ritchie's strong skepticism[15d] concerning discussion of the transition states for such ostensibly "simple" reactions in terms of equilibrated solvated ions.

It may seem to be disappointing that in the process of simplifying the reactions of electrophiles and nucleophiles to the level of cation–anion reactions we have complicated the picture by drawing attention to solvent reorganization. However, highly stabilized ions are required in order to find systems whose equilibrium constants and rates for heterolysis/coordination can be studied in solution. Resonance delocalization provides much of this stabilization but obviously the difference between covalent or ionic bonding is finally settled by solvation. Since ion solvation provides the driving force for heterolysis, it follows that solvent displacement is required for coordination. Thus, the apparent simplification of the nucleophilic displacement reaction through using cation–anion reactions was achieved by replacing the familiar covalently bound leaving groups of S_N1, S_N2 systems with a number of electrostatically bound solvent molecules which must be shed in order to consummate the coordination reaction. Some measure of the solvation energies involved can be inferred from the gas-phase heterolytic bond energy of 148.7 kcal/mol for *tert*-butyl bromide, determined by Staley, Wieting, and Beauchamp.[25]

Another Violation of the Reactivity Selectivity Principle. A number of studies in Ritchie's laboratory[15f] and ours[26] have failed to follow the reactivity selectivity principle since a series of nucleophiles reacted at the same relative rates with a series of electrophiles regardless of the reactivities of the latter. The results in Figure 8 go a step further in actually reversing the RSP. Thus rates of reaction for the less stable triphenylcyclopropenium ion with the series of phenylmalononitrile anions are faster (lower $\Delta G^{\ddagger}$) than are the rates for the trimethylcyclopropenium ion, but the more reactive ion is more selective (slope is steeper). The credibility of the RSP has undergone steady erosion over the past decade.[27] It is time that it was dropped from textbooks as a tool for prediction or interpretation of reactions in solution in spite of its theoretical appeal.

Relation of Coordination Rates to Anion Basicities. It has been a common practice in physical organic chemistry to compare the logarithms of rate constants for the reactions of nucleophiles against the corresponding pK_a's of their conjugate acids. Figure 9 shows such an extended Brønsted plot. This is reasonably linear through its relationship to Figures 7 and 8. Moreover, its slope (0.461) is quite close to that (0.449) of the more correct correlation of $\delta\Delta G^{\ddagger}_{het}$ vs. ΔG°_{het} for
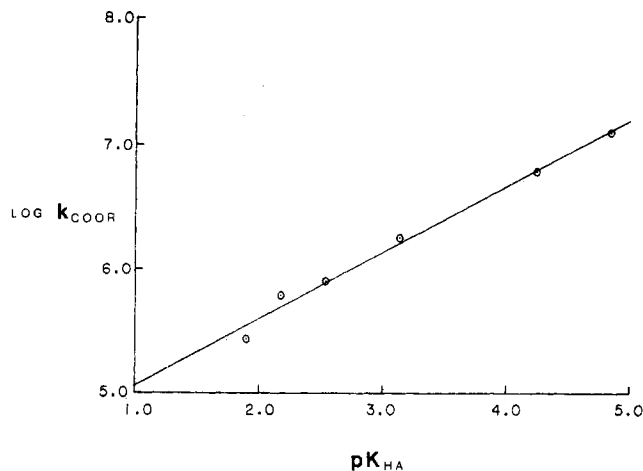

Figure 9. Extended Brønsted plot of coordination rates for reaction of trimethylcyclopropenium cation with arylmalononitrile anions vs. the pK_{HA}'s of the corresponding arylmalononitriles. (Reprinted with permission from ref 24. Copyright American Chemical Society.)

the heterolysis reaction itself.

In this case, which is the first where the question could be tested, the effect of structure variation on the equilibrium constant for transfer of a proton from the nucleophile to a basic solvent (Me_2SO) agrees surprisingly well with that for transfer of a proton from a resonance-stabilized carbocation to nonbasic acetonitrile. Since the solvents are of comparable dielectric constant, the agreement is probably not completely fortuitous and gives tentative support to the commonly used correlation of pK_a's with log k_{nuc}'s. The agreement between these two correlations is hard to understand in terms of hard–soft acid–base generalizations.

Conclusion

During the past 2 decades the use of superacidic and superbasic media has advanced the study of unstable carbocations and carbanions from reasonable mechanistic inference to established reality based on direct spectroscopic observation. In parallel with these developments, several new techniques for the investigation of ion–molecule reactions in the gas phase have been applied to rates and equilibria of simple organic chemical processes in the absence of solvent. Studies of free energies of formation of carbocations and carbanions in superacids, superbases, and the gas phase have been complemented by calorimetric determination of the heats of formation in our laboratory. When all of these data are combined with each other and with activation parameters for various types of ionization and displacement reactions, many of the basic notions of theoretical organic chemistry can be put to the test.

Recently, we have built on this background by investigating the direct reaction of carbocations with carbanions to form covalent carbon–carbon bonds. These data permit, in some cases, a unique and extensive catalogue of thermodynamic and activation parameters for the heterolysis and coordination reactions and can be compared to equivalent thermodynamic data for proton and electron transfer.

The results give strong support to the common practice of extending the Brønsted equation by correlating log k's for displacement reactions with pK_a's for proton transfer. Correlation of rates and equilibria for heterolysis and formation of C–C bonds from our most

(25) Staley, R. H.; Wieting, R. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5964.

(26) (a) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1976**, *98*, 1468. (b) Arnett, E. M.; Reich, R. *Ibid.* **1978**, *100*, 2930. (c) Arnett, E. M.; Reich, R. *Ibid.* **1980**, *102*, 5892.

(27) (a) Johnson, C. D. *Tetrahedron* **1980**, *36*, 3461. (b) Jencks, W. P.; Young, P. R. *J. Am. Chem. Soc.* **1979**, *101*, 3288. (c) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1980**, *45*, 3314.

complete study reverse the order expected from the reactivity selectivity principle and thus provide yet another argument for abandoning it as a general rule.

Heterolysis of carbon–carbon bonds to produce resonance-stabilized carbocations and carbanions in polar solvents appears to be dominated by solvation energies and resonance energies. This leads to a very simple and promising equation for predicting heterolysis energies in terms of the readily available pK_{R^+} of the cation and the pK_a of the carbanion. Correspondingly, the heat of formation of the C–C bond by coordination of the cation and carbanion probably says little about the relative strength of the bond being formed and mostly reflects variations in the energies of delocalization and electrostatic solvation of the ions.