Electrochemical studies were conducted in a previously described vacuum line and cell,[3] to which solvent was added by distillation. After a freeze–pump–thaw cycle, the solvent was melted and released to atmospheric pressure by means of dried nitrogen gas. For protonation studies, the acid dissolved in the appropriate solvent was added and nitrogen gas was bubbled through the solution for at least 15 min before making electrochemical measurements.

Potentials were measured against an aqueous saturated calomel electrode (sce), which was separated from the working electrode compartment by a sintered glass disk and agar gel. The relative difference in liquid junction potentials between DMF, AN, and DMSO can be related to $E_{1/2}$ for Rb(I) reduction vs. sce: -1.94 V in AN and DMF; -1.95 V in DMSO; -2.13 V in water.[34]

Ultraviolet spectra were recorded using 1-cm silica cells, a Beckman Model DB spectrophotometer, and a strip-chart recorder.

Sources and purification of other chemicals, apparatus, and electrochemical procedures have been described.[3] The background electrolyte was 0.1 M tetra-n-butylammonium perchlorate (Matheson, dried).

The following discussion of specific aspects of the behavior of some of the purines investigated is intended to amplify and supplement previous statements and the data presented in the figures and tables.

Purine. Since purine exhibits an adsorption prewave, which is strongly dependent on purine concentration, most measurements were made at low concentration (<0.6 mM) where adsorption effects are small. The polarographic diffusion current, i_{d}, for purine varies linearly with concentration in the region below 1.5 mM, where only one wave is observed. When the prewave appears, the sum of the two wave currents is in line with the current seen at low concentration.

Controlled potential electrolysis of 0.8 to 2.1 mM purine at -2.0 to -2.2 V in DMF gave faradaic n values of 0.94 to 1.10 and replacement of the purine absorption maximum at 266 nm by a broad maximum in the 300-nm region. The original purine absorption maximum returned after controlled potential oxidation of the reduced solution at 0.2 to 0.4 V.

Chromatographic examination of the solution before and after electrolysis gave R_f values of 0.76 for purine and 0.54 for its reduction product. The following procedure was used. Four or five drops of the solution is spotted on a 5.5 in. Whatman No. 1 sheet with base line about 0.75 in. from the bottom. The paper is slowly introduced into the cyclindrical developing jar containing developing solution and is allowed to remain for 3 to 4 hr at about 24°. The paper is then air dried and the spots are visually examined on illumination with ultraviolet light. Cut portions of the spots showed ultraviolet absorption maxima at nearly the same wavelengths as described for solutions. The developing solution was prepared by dissolving 77 g of ammonium acetate in 750 ml of H_2O, adjusting the pH to 7.5 with NH_3, and diluting to 1 l., and then mixing 300 ml of the latter solution with 700 ml of 95% ethanol.

Adenine. Adenine showed both polarographic prewave and normal wave over the concentration range of 0.8 to 2.0 mM in DMF; the sum of the two currents is proportional to concentration.

The cyclic voltammetric prepeak ($E_{\mathrm{p}} = -2.0$ V) showed a complementary reversible anodic peak in DMF at sweep rates as low as 0.041 V/sec. The normal peak showed a complementary reversible anodic peak at sweep rates of 10 to 25 V/sec. Due to the stirring effect,[19] the anodic peak is not a single smooth peak but consists of several peaks grouped around the reported E_{pa}. At lower concentration (0.2 mM), the magnitude of the stirring effect is smaller.

During controlled potential electrolysis at -2.60 V in DMF, the electrolysis current decayed smoothly with time and the solution remained colorless. The faradaic n value was 1.0. The adenine absorption maximum at 263 nm was replaced by one at 300 nm. Reversal oxidation at 0.20 V regenerated the original adenine absorption and cyclic voltammetric peaks.

Chromatographic examination of the solution before and after electrolysis, using the previously described procedure, gave R_f values of 0.80 and 0.56.

6-Methylpurine. Controlled potential electrolysis in DMF at -2.55 V consumed coulombs equivalent to an n of 1.02. The electrolysis current decayed smoothly to the background value. Cyclic voltammetry of the electrolyzed solution showed an anodic peak at 0.02 V with an associated sharp prepeak (presumably due to adsorption) at -0.20 V. The ultraviolet spectra of the solution before and after electrolysis showed maxima at 242 and 328 nm, respectively. Oxidation of the reduced solution at 0.20 V consumed 0.75 coulomb compared to 0.86 coulomb for the original electrolysis.

The other 6-substituted purines had behavior patterns similar to those described for 6-aminopurine (adenine) and 6-methylpurine.

(34) J. Broadhead and P. J. Elving, *J. Electrochem. Soc.*, **118**, 63 (1971).

Effect of Charge Redistribution on Ion–Molecule Reaction Rates

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Abstract: The application of the charge redistribution model to ion–molecule reaction systems of general interest is discussed. The effect of charge redistribution on the reaction rates of 25 exothermic ion–molecule reactions is evaluated. A strong correlation is shown to exist between reactions involving the central atoms of the reactants and the electronegativities of those atoms. It is observed that reactions in which a large charge redistribution would have to take place occur with much lower probability than reactions where the charge redistribution would be small.

Since 1950 the field of ion–molecule reactions has been one of the most extensively studied in all of chemistry. However, it is well recognized that experiment has generally outstripped theory in this field.[1] There have been several theories set forth which do explain various aspects of ion–molecule reactions. The Gioumousis–Stevenson (G–S) treatment[2] permits one to calculate the total interaction cross section using an ion-

(1) M. Henchman, "Ion Molecule Reactions," Vol. I, J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1971, Chapter 5.

(2) G. Gioumousis and P. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

induced dipole model. The locked dipole[3] extension of this treatment includes a dipole term and extends the G–S treatment to molecules with large permanent dipoles which become oriented during the course of reaction. Light's phase space theory[4] and extensions of quasi-equilibrium theory,[5] when adapted to ion–molecule reactions, explain certain aspects of these reactions. While all the above models are useful, and do explain various aspects of ion–molecule reactions, all except the first have the disadvantage of depending strongly on a prior detailed knowledge of the reaction mechanism or the structure of the reactant and the intermediates which may be formed. Unfortunately, it is difficult if not impossible to know with certainty the detailed structure of many reactant and product ions, much less that of an intermediate. Indeed, in many cases it is difficult to know whether an intermediate has been produced at all. As a result, there are inherent limitations to many of the commonly used models and theories which cannot be overcome. In spite of the great amount of work which has been done in the field, there is still a lack of general knowledge regarding the factors governing ion–molecule reactions and why, for example, some exothermic reactions proceed with large probabilities while others do not.

A model of ion–molecule reactions which deals with this last problem and which does not depend on either the detailed reaction mechanism or the detailed structure of reactants and products has also been set forth.[6,7] The model as originally proposed dealt only with reactions which could be written in the form

$$A^+ + BC \longrightarrow AB^+ + C \qquad (1)$$

and where A, B, and C were only carbon, oxygen, and nitrogen atoms. The model, in effect, extended a well known theory of charge exchange[8] to reaction chemistry in hypothesizing that the electronic structure of the initial and final states of the reacting system would have to be similar in order for the reaction probability to be large. As distinguished from other approaches, the model requires only a qualitative knowledge of charge distribution in the reactants and products. The model proposed that the requirement for a large rearrangement of charge density during the reaction (regardless of the detailed mechanism by which the reaction takes place) would act to limit the probability of the reaction. It was proposed that the electronegativity of A, B, and C could be used to qualitatively determine the amount of charge rearrangement required in the reaction. The model was shown to account for 11 reactions involving C, N, and O atoms, but as it was limited to only those atoms, its potential applicability to other systems of interest has never been demonstrated.

We now extend the original charge redistribution model to systems of more general chemical interest and also quantify the results so that the correlation between charge density rearrangement and reaction probability will be more easily seen. We have found that 25 reactions, many of which show anomalous behavior, may be accounted for by the extended model.

The original model was formulated such that no substituents were allowed on the atomic centers. Thus, for reactions of positive ions, only reactions A–H in Table I were considered. This was done because the model cannot treat the behavior of hydrogen atoms or in general other atoms with electronic structures which are grossly different from the reacting centers. This is still true, but in the extended model we propose that the properties of the central atoms will be determinant insofar as reaction between the central atoms is concerned. Many more reactions can be included in the extended model if we permit atoms such as hydrogen to be present in the reactants but simply make no attempt to predict how they will be distributed in the final products. For example, consider reaction 2, where A, B, and C are

$$AX_n^+ + BCX_m \longrightarrow ABX_p^+ + CX_q \qquad (2)$$

large central or core atoms and X represents the hydrogen substituents on each molecule and ion. The subscripts n, m, p, and q denote the distribution of hydrogen atoms on the reactant and product core atoms. It is always necessary that $n + m = p + q$. Reactions V–Z are of this type and have been discussed in some detail (except reaction Z) in ref 9. To use an extension of the electron density model for such reactions, one ignores the final disposition of the hydrogen atoms and considers only the central atoms as determinant in terms of the overall reaction probability. The hypothesis that such a simplification can be made certainly appears to be supported by the experimental evidence (Figures 1 and 2).

Another type of reaction which can be dealt with using such an extension of the original model is

$$AX_n^+ + BX_m \longrightarrow ABX_r^+ + sX_2 + tX \qquad (3a)$$

or

$$AX_n^+ + BXC_m \longrightarrow ABCX_r^+ + sX_2 + tX \qquad (3b)$$

Here it is necessary that $n + m = r + 2s + t$. Such reactions are quite common and involve bond formation between the central atoms accompanied by ejection of hydrogen atoms and molecules. As above, the number and distribution of H atoms on the AB$^+$ or ABC$^+$ core is not treated. Any or all of the exothermic combinations for a given system would be equivalent insofar as the model is concerned.

A specific example of such a reaction would be

$$NH_3^+ + CH_4 \longrightarrow CH_3NH_2^+ + H_2 \qquad (4a)$$
$$ \longrightarrow CH_3N^+ + 2H_2 \qquad (4b)$$

There is no intent to imply that the rearrangement of H atoms may not be important in reactions such as these, for indeed it may, and as a consequence one exothermic channel may be favored over another. However, the model does not distinguish such effects, and therefore it does not permit one to make any predictions regarding them.

Reaction Probability

To determine whether or not any correlation exists between reactivity and charge redistribution, one must have some measure of reaction probability which is

(3) T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39**, 1413 (1963).
(4) J. C. Light, *J. Chem. Phys.*, **40**, 3221 (1964).
(5) S. E. Butrill, *J. Chem. Phys.*, **52**, 6174 (1970).
(6) J. Schaefer and J. M. S. Henis, *J. Chem. Phys.*, **49**, 5377 (1968).
(7) J. Schaefer and J. M. S. Henis, *J. Chem. Phys.*, **51**, 4671 (1969).
(8) N. F. Mott and H. S. Massey, "The Theory of Atomic Collisions," 3rd ed, Oxford University Press, London, 1965, pp 346–387.

(9) J. M. S. Henis, M. Loberg, and M. J. Welch, *J. Amer. Chem. Soc.*, **96**, 1665 (1974).

Table I

Reaction no.	Reactants	Products	Δε A-R^a	P^b	$K_T^c \times 10^9$, cm^3 mol^{-1} sec^{-1}	$K_{e(c)} \times 10^9$, cm^3 mol^{-1} sec^{-1}	P_c
A	$O^+ + N_2{}^e$	$NO^+ + N$	+0.43	+0.40	0.98	0.003	0.003
B	$O^+ + N_2O^f$	$NO^+ + NO$	+0.43	+0.40	1.3	0.1	0.076
C	$O^+ + N_2O^g$	$O_2^+ + N_2$	0.0	0.0	1.3	0.02	0.015
D	$O^+ + CO_2{}^{e,g,h}$	$O_2^+ + CO$	0.0	0.0	1.2	1.2	1.0
E	$N^+ + O_2{}^g$	$NO^+ + O$	−0.43	−0.40	0.94	0.5	0.53
F	$N^+ + N_2O^g$	$NO^+ + N_2$	−0.43	−0.40	1.2	0.55	0.46
G	$C^+ + O_2{}^{g,h}$	$CO^+ + O$	−1.0	−0.89	0.99	1.1	1.1
H	$C^+ + CO_2{}^{g,h}$	$CO^+ + CO$	−1.0	−0.89	1.3	1.9	1.5
I	$NH_2^+ + CH_4{}^i$	(a) $CH_3NH_2^+ + H$; (b) $CH_2NH_2^+ + H_2$; (c) $CHNH^+ + 2H_2$	+0.57	+0.49	1.3	<0.01	<0.0076
J	$NH_3^+ + CH_4{}^i$	$CH_3NH_2^+ + H_2$	+0.57	+0.49	1.2	<0.01	<0.0083
K	$OH^+ + CH_4{}^i$	(a) $CH_2OH^+ + H_2$; (b) $CHO^+ + 2H_2$; (c) $CH_2O^+ + H_2 + H$; (d) $CH_3OH^+ + H$	+1.0	+0.89	1.1	<0.05	<0.045
L	$H_2O^+ + CD_4{}^i$	(a) $CD_3OH^+ + HD$; (b) $CD_3OD^+ + H_2$; (c) $CD_2HOH^+ + D_2$	+1.0	+0.89	1.2	<0.01	<0.0083
M	$S^+ + CH_4{}^i$	$CH_2SH^+ + H$	−0.06	+0.03	1.2	0.14	0.12
N	$HS^+ + CH_4{}^i$	$CH_2SH^+ + H_2$	−0.06	+0.03	1.1	0.1	0.09
P	$CH_2^+ + NH_3{}^i$	$CH_2NH_2^+ + H$	−0.57	−0.49	1.1	1.2	1.1
Q	$CH_2^+ + H_2S^i$	(a) $CH_2SH^+ + H$; (b) $CHS^+ + H_2 + H$	+0.06	−0.03	1.4	0.6	0.43
R	$CH_2^+ + H_2O^i$	$CH_2OH^+ + H$	−1.0	−0.89	1.3	0.52	0.40
S	$CH_3^+ + NH_3{}^i$	$CH_2NH^+ + H_2$	−0.57	−0.49	1.1	0.66	0.60
T	$CH_3^+ + H_2S^i$	$CH_2SH^+ + H_2$	+0.06	−0.03	1.3	0.50	0.38
U	$CH_3^+ + H_2O^i$	$CH_2OH^+ + H_2$	−1.0	−0.89	1.3	<0.01	<0.0076
V	$CD_3^+ + CH_3F^j$	(a) $CH_3^+ + CD_3F$; (b) $CD_3^+ + CH_3F$; (c) $CH_2F^+ + CD_3H$; (d) $CD_2F^+ + CH_3D$	−1.6	−1.43	1.41	1.86 ± 0.24	1.32
W	$CD_3^+ + CH_3Cl^j$	(a) $CH_3^+ + CD_3Cl$; (b) $CD_3^+ + CH_3Cl$; (c) $CH_2Cl^+ + CD_3H$; (d) $CD_3Cl^+ + CH_3D$	−0.33	−0.61	4.0^d	2.62 ± 0.22	0.66
X	$CD_3^+ + CH_3Br^j$	(a) $CH_3^+ + CD_3Br$; (b) $CD_3^+ + CH_3Br$; (c) $CH_2Br^+ + CD_3H$; (d) $CD_2Br^+ + CH_3D$	−0.24	−0.41	3.9^d	3.9 ± 0.42	1.0
Y	$CD_3^+ + CH_3I^j$	(a) $CH_2I^+ + CD_3H$; (b) $CD_2I^+ + CH_3D$; (c) $CD_3I^+ + CH_3$; (d) $CH_3I^+ + CD_3$	+0.29	−0.11	3.6^d	0.22 ± 0.10	0.061
Z	$CD_3^+ + CH_3OH^k$	(a) $CH_3^+ + CD_3OH$; (b) $CD_3^+ + CH_3OH$; (c) $CH_2OH^+ + CD_3H$; (d) $CD_2OD^+ + CH_4$; (e) $CH_3OH^+ + CD_3$; (f) $CD_3OH^+ + CH_3$	−1.0	−0.89	4.1^d	4.2 ± 0.3	1.02

^{a} Allred–Rochow electronegativity scale, A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958). ^{b} Pauling electronegativity scale, from A. L. Allred, *ibid.*, **17**, 215 (1961). ^{c} Theoretical rate constant based on Gioumousis and Stevenson model. ^{d} Theoretical rate constant based on locked dipole model. ^{e} F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, *J. Chem. Phys.*, **44**, 3022 (1966). ^{f} Jacob Schaefer and J. M. S. Henis, *ibid.*, **49**, 5377 (1968). ^{g} E. W. McDaniel, V. Cérmak, A. Dalgarno, E. E. Ferguson, and L. Friedman, Ed., "Ion–Molecule Reactions," Wiley-Interscience, New York, N. Y., 1969. ^{h} F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, *J. Chem. Phys.*, **45**, 23 (1966). ^{i} W. T. Huntress, Jr., R. F. Pinizzotto, Jr., and J. B. Laudenslager, *J. Amer. Chem. Soc.*, **95**, 4107 (1973). ^{j} J. M. S. Henis, M. D. Loberg, M. J. Welch, ref 9. ^{k} J. M. S. Henis and M. K. Tripodi, unpublished work.

consistent from system to system. For this purpose we define a probability P_c according to eq 5.

$$P_c = \frac{K_{e(c)}}{K_T} \qquad (5)$$

P_c is the reaction probability for the central or core atoms, $K_{e(c)}$ is the measured experimental rate constant for reaction involving the central atoms, and K_T is the total theoretical rate constant calculated either from the G–S model or the locked dipole model. If a reactant ion (*i.e.*, CH_4^+) reacts only by proton, hydride, or H atom transfer with a neutral substrate, and no evidence

is found for condensation of the CH_4^+ with the substrate during the reaction, P_c, insofar as the model is concerned, will be small even though the rate constant for CH_4^+ reaction is large. This is so because $K_{e(c)}$ will be small.

Charge Redistribution

It was originally suggested[5] that a valid measure of charge distribution in the reacting systems would be provided by the electronegativities of the central atoms.

For example, in reaction 1, if B is very much more electronegative than A, it is reasonable to expect that
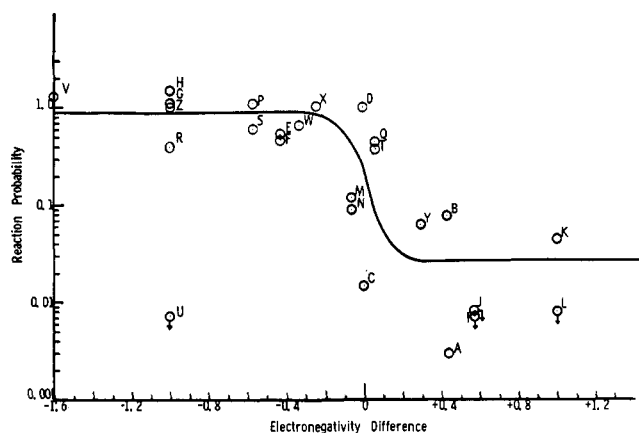
Figure 1. Reaction probability, P_c, plotted against the electronegativity difference, $\Delta\epsilon$, between the ionic and neutral centers using the Allred-Rochow electronegativity scale (footnote a, Table I).
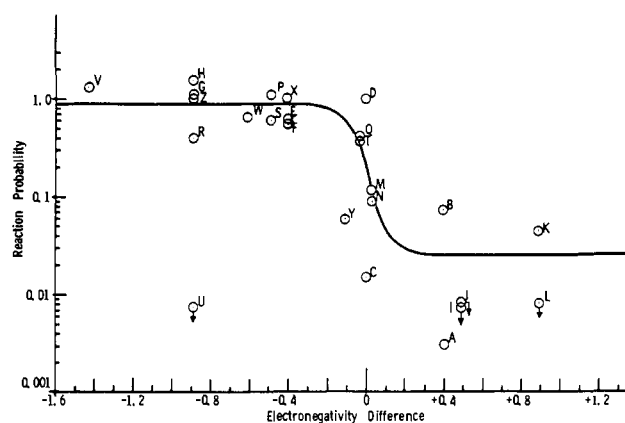

Figure 2. Reaction probability, P_c, plotted against the electronegativity difference, $\Delta\epsilon$, between the ionic and neutral centers using a Pauling-type electronegativity scale (footnote b, Table I).

the positive charge in the AB$^+$ product will still reside principally on the A atom after reaction. In that case, there would be very little charge redistribution during the reaction. By the original model such a reaction would be favorable.

As the model is extended, this assumption becomes more tenuous. Indeed, there are two points of concern. First, in many of the cases used in this work, we are dealing not with an atom in an ion but with a functional group in an ion. Hence, we are really concerned with the relative electronegativities of the functional groups in the reactants and products.

Secondly, the scale chosen to measure the electronegativity itself may be questioned, because we are really asking for the electronegativity of an atom (or a functional group) in a complex ion. This is somewhat different from the conventional definitions of electronegativity.

However, in Figures 1 and 2 we show the correlation between reactivity and the simple electronegativity of the central or core atoms in 25 ion–molecule reactions. The correlation is quite strong and shows that reactions in which charge redistribution is expected to be small proceed with essentially unit probability, while those in which charge redistribution is expected to be large are one to two orders of magnitude less probable.

If this, or indeed any, reaction model is to be useful, it must be generally applicable. We have made the assumption that, to a first approximation, we may disregard the presence of H atoms on the central atoms and use the electronegativities of only the central atoms. We have further assumed and shown in Figures 1 and 2 that the precise measure of electronegativity used is unimportant and that the observed correlation between reactivity and charge distribution is not particularly dependent upon the electronegativity scale chosen. We have used two of the better known electronegativity scales as measures of charge redistribution and found the same general results in both cases. Therefore, it is reasonable to conclude that the strong correlation observed for the reactions shown here justifies the simplifications made in the model. Nevertheless, it is recognized that where the electronegativities of the central atoms are close the choice of scales, and the inclusion of substituent effects, can be important.

Data Treatment

The three types of reactions discussed above are summarized in Table I. A total of 25 reactions are listed which fall into the class of reactions 1, 2, or 3. Included in Table I are the source of the rate constants for each reaction and the calculated reaction probability based on the reported experimental rate constant for reaction involving the central or core atoms. Also, included is the electronegativity difference between the ion and the neutral determined as in ref 6 by subtracting the electronegativity of the central atom in the ion from that in the neutral.

It should be noted that a wide variety of techniques and procedures were used to measure these rate constants and that there is undoubtedly a wider range of kinetic energies associated with the data than is desirable. We have tried to use the lowest kinetic energy values where a choice was available, as the model is derived for low or thermal energy reactions.

Where proton, H-atom, or hydride transfer or charge exchange accompanies other reactions, these rate constants are subtracted from the total reaction rate constant used to calculate the reaction probability. If only reactions involving hydrogen or charge transfer occur, a maximum value for other condensation type reactions, which would necessarily involve the core atoms, is given.

The reactions of CH$_4^+$ ions were not included because CH$_4^+$ undergoes mainly proton and H-atom transfer. Although there is evidence that some of the proton transfer reactions may involve complex formation,[9] it is not known whether this is true for the reactions reported here, and we have not anticipated the answer to that question.

Although Figures 1 and 2 use different measures of electronegativity, the correlation between the two figures is evident. Where the central atom in the reacting ion is significantly more electronegative than the central atom in the neutral (i.e., when $\Delta\epsilon$ is positive), the rate constant for condensation or forward reaction is always small. These reactions are prohibited by the model because the charge in the final product would have to be considerably redistributed from its original site. Where the central atom in the reacting ion is substantially less electronegative than that in the neutral (i.e., when $\Delta\epsilon$ is negative), the observed rate constants and probabilities

are all large (~ 1) with only a single exception. These reactions would be favorable according to the model because one would expect the charge to remain essentially on the same atom. Finally, in the intermediate region where the electronegativities are close, there are a range of observed probabilities, indicating that as stated above many effects may be important in determining overall reactivity in this region.

In determining the ratios of $K_{e(o)}/K_T$ used, three groupings were used. All of the points with $\Delta \epsilon < -0.2$ were averaged, yielding a value of 0.85 ± 0.30. The points with $\Delta \epsilon > +0.2$ averaged 0.025 ± 0.025, and the points in the intermediate region $-0.2 < \Delta \epsilon < +0.2$ averaged 0.2 ± 0.2. Because of the assumptions involved, and the qualitative nature of the model, it is probable that more detail would be necessary than is likely to be available for predicting the reactivity for systems in this region.

Significance of the Model

Simply stated, the model prohibits reaction involving the large central atoms if the electronegativity difference ($\epsilon_{ion} - \epsilon_{neutral}$) between the central atom in the ion and the central atom in the neutral is positive and places no restriction on reaction if the difference is negative. This means that, regardless of other factors, one should not observe a large reaction probability for a reaction falling significantly on the positive side of zero in Figures 1 or 2. However, since hydrogen ion or atom transfer can occur in reactions of types 2 and 3 by direct abstraction mechanisms and without involving the central atoms, one may observe such reactions which involve the same ions and neutrals as in reactions 2 and 3 without violating the model. The point to emphasize here is that a reaction in which the central atoms discussed above must bond either in an intermediate or in the final products would not be allowed.

If a reaction is allowed by the model, this does not mean that it must occur or that it cannot be obscured by some other factor specific to the reaction or to the structure of the complex produced in the reaction. The only reaction which appears at first glance to violate the model is reaction U. However, this reaction has been discussed before[10] and it has been suggested that the condensation products of CH_3^+ reacting with H_2O may not be observed because of restrictions regarding the rearrangement of the $CH_3OH_2^+$ intermediate. If it were possible to measure the production of such a complex (e.g., by measuring the angular distribution of CH_3^+ in a beam experiment), it would likely be found that the reaction to produce the complex had proceeded with high probability. Indeed, reaction U does not violate the model; it merely illustrates that all allowed reactions may not necessarily proceed.

(10) W. T. Huntress, R. F. Pinizzotto, and J. B. Lauchenslager, *J. Amer. Chem. Soc.*, **95**, 4107 (1973).

It is generally true that ion–molecule rate constants do not include the amount of back reaction of an intermediate to yield the initial reactants. If back reaction is inordinately large for any reason, this will certainly result in a misleadingly small measured rate constant. This is treated in detail in ref 9 and reactions V–Z in Table I do include this factor. Unfortunately, most of the other reactions reported here do not.

Finally, it must be recognized that if hydrogen ion or atom or charge transfer occurs with very large rate constants for a given pair of reactant ions, a small or intermediate rate constant will be observed for other reactions even if the reactions are allowed by the model. This is another example of a reaction which may be allowed by the model but is still limited by other factors. Therefore, an attempt to apply the model to mixed systems where extensive charge exchange, proton, hydride, or hydrogen atom transfer reactions are occurring may lead to misleading results since such reactions will tend to obscure and limit the observation of reactions between the central atoms.

Consequences of the Model

In summary, if the model prohibits a reaction, it should not be observed, but, if the model allows a reaction, it may or may not be observed. As may be seen from Figures 1 and 2 most of the allowed reactions do proceed, and none of the prohibited reactions are observed. The correlation is indeed very strong with the allowed reactions ($\Delta \epsilon$ negative) average probability value being 0.85 ± 0.30 and the prohibited reactions ($\Delta \epsilon$ positive) average being 0.025 ± 0.025. There is more than an order of magnitude difference between the two kinds of reaction. Indeed, this difference may be considerably greater since many of the rate constants reported for the disallowed reactions represent upper limits.

Using the model and the observed correlation, it is possible to explain the failure to observe many exothermic reactions in mixed systems and also to predict the results expected in other systems which have not yet been studied. Huntress, et al.,[10] have commented on the surprising lack of reactivity of NH_2^+ and OH^+ with methane. However, one can see that the lack of reactivity is expected on the basis of the charge redistribution model. Similarly,[9] we can account for the behavior of CH_3^+ in the methyl halides and the anomalously low reactivity of CH_3I. It should be pointed out that extension of the model to mixed systems involving molecules which are in different rows in the periodic table will be tenuous for the same reasons that hydrogen reactions cannot be treated. The electronic configuration of the reactive centers will be too different. However, on the basis of the results reported here, it is reasonable to reemphasize the importance of charge redistribution as a governing and important controlling factor in many ion–molecule reactions.