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Energy Transfer in Ion–Molecule Association Reactions. Dependence of Collisional Stabilization Efficiency on the Collision Gas

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Abstract: The energized proton-bound dimer of $(CH_3)_3N$ is formed by reaction of $(CH_3)_3NH^+$ with $(CH_3)_3N$. Energy transfer from the energized dimer is accomplished by a variety of collision gases and relative per collision stabilization efficiencies, β, are obtained. There is a positive correlation of β with the dipole moment of the collision gas but no correlation with the reduced mass of the colliding pair (proportional to the "fly-by time" of the collision), to the polarizability of the neutral, or to the number of transitional modes of the collision pair. Comparisons are made with data of other workers on both ionic and neutral systems. A long-range rotational–rotational energy transfer mechanism is suggested.

Introduction

A great deal of both experimental and theoretical work has been devoted to the study of energy transfer in vibrationally excited molecules. Almost all this work has been done on neutral systems, and is generally discussed in terms of unimolecular reaction rate theory.[1] Tardy and Rabinovitch have given a very thorough review of this topic for neutral–neutral systems.[2]

Studies of energy transfer in thermal ion–molecule reactions are much less common. Harrison has reviewed the early work in this area.[3] Systematic studies using a variety of collision gases are rarer still. The first such study was reported by Anicich and Bowers,[4] where the effects of various third-body gases were measured in the stabilization of dimers of 1,1-difluoroethylene and benzene. Miasek and Harrison have done a similar study of the collisional deactivation of $(C_5H_9^+)^*$.[5] We now present a study of the effects of 22 inert gases in the dimerization of trimethylamine. This study was intended to test the validity of the assumption of unit stabilization efficiency for all stabilizers that has been used in all theoretical models of association reactions. We have attempted to determine which molecular parameters are important in determining this efficiency. Neilson et al. have presented a complete experimental study of the dimerization of pure trimethylamine[6] and Bass et al. have developed a theoretical model of the system based on statistical theory.[7]

Kinetic Analysis

The general mechanism is of the type

$$AH^+ + A \xrightarrow{k_2} A_2H^+ \tag{1}$$

$$d[A_2H^+]/dt = k_2[AH^+][A] \tag{2}$$

where k_2 is, in general, pressure dependent. A more detailed mechanism which has been applied to a number of ion–molecule systems is[4,7]

$$AH^+ + A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (A_2H^+)^* \tag{3}$$

$$(A_2H^+)^* + A \xrightarrow{k_s} A_2H^+ + A \tag{4}$$

$$(A_2H^+)^* + M \xrightarrow{k'_s} A_2H^+ + M \tag{5}$$

where the asterisk indicates that the molecule is in some rotationally and/or vibrationally excited state. This mechanism yields

$$d[A_2H^+]/dt = (k_s[A] + k'_s[M])[A_2H^+]^* \tag{6}$$

Making a steady-state approximation for $[A_2H^+]^*$ and substituting into eq 6 gives an expression for $d[A_2H^+]/dt$ that may be equated with eq 2 and solved for k_2. The resulting expression is

$$k_2 = \frac{k_f k_s[A] + k_f k'_s[M]}{k_b + k_s[A] + k'_s[M]} \tag{7}$$

From eq 7, it may easily be seen that, in the limit as both A and M approach zero

$$dk_2/d[M] = k_f k'_s/k_b \equiv k_{3,M} \tag{8}$$

$$dk_2/d[A] = k_f k_s/k_b \equiv k_{3,A} \tag{9}$$

Thus, assuming that k_f and k_b are constant, the ratio of $k_{3,M}$ to $k_{3,A}$ gives the desired result:

$$k_{3,M}/k_{3,A} = k'_s/k_s \tag{10}$$

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Table I. Relative Stabilization Efficiencies for the Reaction ($[(CH_3)_3N]_2H^+)^* + M \rightarrow [(CH_3)_3N]_2H^+ + M$ at 304 K (for $M = (CH_3)_3N$, $\beta = 1$)

M	$k_{3,M}/k_{3,A}$	β^a	$\alpha \times 10^{24}$ cm^3	μ_D, D	N^b
He	0.22	0.31	0.204		3
Ne	0.13	0.38	0.396		3
Ar	0.16	0.31	1.64		3
Kr	0.17	0.35	2.48		3
Xe	0.18	0.33	4.0		3
D_2	0.31	0.31	0.79		5
N_2	0.28	0.46	1.76		5
CO_2	0.32	0.51	2.65		5
COS	0.45	0.58	5.69	0.67	5
HCN	1.40	1.28	2.59	2.98	5
CH_4	0.38	0.40	2.60		6
CH_3F	1.46	0.62	2.67	1.79	6
CH_2F_2	1.61	0.64	2.64	1.97	6
CHF_3	1.15	0.53	2.69	1.65	6
CF_4	0.42	0.41	2.73		6
CCl_2F_2	0.45	0.49	6.34	0.51	6
CH_3Cl	1.15	0.76	5.22	1.87	6
$CClF_3$	0.63	0.63	4.50	0.50	6
$CHCl_3$	0.59	0.51	8.23	1.01	6
$CHClF_2$	0.91	0.57	4.44	1.41	6
C_2H_4	0.26	0.39	4.26		6
C_3H_8	0.36	0.39	6.29		6

[a] Estimated error ±10%. [b] Number of "transitional" modes. See text.

To convert this ratio of stabilization rate constants to a "per collision" stabilization efficiency, β, it is necessary to divide each k_3 by the appropriate collision rate constant. For nonpolar stabilizers the collision rate constants were calculated using LGS theory.[8] For polar neutrals the recently developed variational theory[9] was used to estimate k_{coll}. Variational theory, as the name implies, gives an upper limit to the actual collision rate constant, and comparison with experimental data and with the results of trajectory calculations has shown the variational rate constants to be within 10-15% of the true classical collision rate constants on the ion-dipole surface.[9] Hence,

$$\beta = \left(\frac{k_{3,M}}{k_{coll,M}}\right) \Big/ \left(\frac{k_{3,A}}{k_{coll,A}}\right) \tag{11}$$

Here k_{coll} is the collision rate constant for $[(CH_3)_3N]_2H^+$ with either A or M.

In this analysis the assumption was made that, while k_s may change from one stabilizer to another, both k_f and k_b remain constant. This is almost certainly true for k_f, but, since the value of k_b depends on the energy distribution of the excited complexes,[7,10] k_b should change both with increasing pressure and with the different stabilizers. Theoretical calculations done by Bass et al.[7] show that for the pure trimethylamine system k_b changes little in the pressure range used in these experiments even though $(CH_3)_3N$ is a rather efficient stabilizer. This leads us to conclude that any error made in assuming that k_b is constant is small enough to be neglected.

Experimental Section

All experiments were performed on a home-built drift cell ICR that has been described in detail elsewhere.[11] Gases used were the best grades available and, where possible, were purified by successive freeze-pump-thaw cycles. Pressures were measured on an MKS Baratron capacitance manometer and thermal transpiration corrected.

In practice, experiments were performed holding the pressure of A at some constant value and adding M in small increments. "Low concentration" of A was defined experimentally as the lowest pressure attainable where a reasonable dimer signal was observed. This was typically on the order of 1.5×10^{-4} Torr. The maximum partial pressure of M used was generally 3×10^{-4}. An iterative computer program was used to calculate k_2 as a function of the pressure of A and M. The slope of a plot of k_2 vs. pressure then gave the desired $k_{3,M}$. The rate constant $k_{3,A}$ was determined from the intercepts of these plots and from separate experiments where the pressure of A was varied without any added M. A typical plot of k_2 vs. M is shown in Figure 1. The linear portion at small values of [M] is expected from the general solution to the kinetic equations, eq 7.

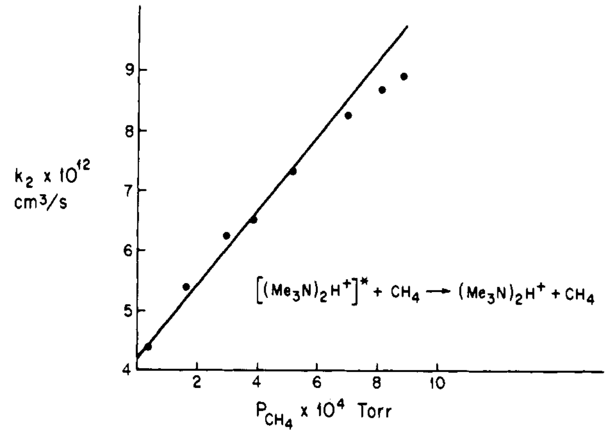

Figure 1. A plot of the apparent second-order rate constant for reaction 1 with $A = (CH_3)_3N$ as a function of CH_4 bath gas pressure.

Stabilization efficiencies were obtained for 22 different M atoms and molecules at room temperature, Table I. This should represent enough data to make meaningful observations about the effects of the physical properties of M on β. Some of these comparisons will be examined in detail.

Collision Duration Model

In a study of the stabilization of the dimer ions of 1,1-difluoroethylene, Anicich and Bowers[4] found a correlation between stabilization efficiency and the reduced mass of the colliding pair. This dependence was attributed to a matchup between the duration of the collision between the dimer ion and M and the "active" vibrational modes of the dimer. Clearly, no such effect is seen in the data presented in Table I; for instance, all the rare gases exhibit approximately the same efficiency, though their masses range from 4 to 131 amu. The data of Miasek and Harrison for the collisional stabilization of $(C_5H_9^+)^*$ are in general agreement with the data presented here.

Number of Transitional Modes

Lin and Rabinovitch[12] have suggested that β is dependent on the number of transitional modes in the collision complex, N. This is simply the number of translations and rotations of the separated species that become vibrations in the complex. In the systems that we report here there is no obvious dependence of β on N. The general trends observed here, however, are in accordance with what one would expect from the model proposed by Lin and Rabinovitch. Monatomic species have about the same efficiency. In general, for two stabilizers of similar mass, the more complex one will be more efficient. Among the polyatomics, going from five to six transitional modes does not ensure an increase in efficiency. Other effects are obviously important in these cases.

Effect of Neutral Polarizability

The ion-induced dipole term in the ion-molecule intermolecular potential is $-q^2\alpha/2r^4$, where α is the polarizability of the neutral, q is the charge on the ion, and r is the distance separating the ion and M. For molecules lacking a permanent dipole moment, this term determines the ion-molecule collision rate.

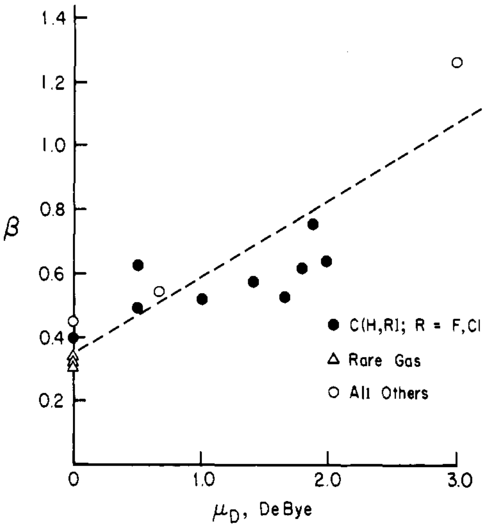

Figure 2. A plot of the relative stabilization efficiencies β vs. the dipole moment of the bath gas molecule.

In the thermal isomerization of neutral CH_3NC, Chan et al.[13] found that β tended to increase with increasing polarizability of M. Our data seem to show a slight increase in β with increasing α, though the rare gases are a notable exception. In fact, it may well be argued that, within experimental error, the efficiency of all nonpolar stabilizers studied is the same. This correlation seems to break down completely for stabilizers that possess a dipole moment. This fact is not surprising since the intermolecular potential for such systems has a strong dependence on the dipole moment.

Effect of Neutral Dipole Moment

The ion-permanent dipole term in the ion-molecule potential is $-(q\mu_D/r^2)\cos\theta$, where μ_D is the dipole moment of the neutral and θ is the angle that the dipole makes with r. This term becomes important at longer range than the ion-induced dipole term. As Figure 2 shows, there is a strong dependence of β on μ_D of the stabilizer. In fact, since the collisional rate constants calculated from variational theory are upper limits, these values of β are lower limits and the actual dependence on μ_D may be even more pronounced.

This dependence of β on dipole moment has been noted before. Volpe and Johnson[14] found such a correlation in their study of the decomposition of nitryl chloride; for a given molecular weight, the more polar molecule was the more efficient stabilizer. It has been suggested[2] that this correlation was merely fortuitous, due to the small number of stabilizers investigated. For this reason, we attempted to use a number of polar stabilizers over as large a range of dipole moments as possible.

In their study of CH_3NC isomerization Chan et al.[13] found that β did increase with μ_D, but that complex nonpolar molecules were still more efficient than simpler polar molecules. An important point to note here is that in neutral systems the dipole term in the intermolecular potential depends on $1/r^6$, and, therefore, results in a relatively short range force, while in ion-molecule systems the dipole term goes as $1/r^2$, resulting in a long-range force. It is not, therefore, so surprising that the dipole moment of the stabilizer seems to play a more important role in ion-molecule systems.

It is interesting to note that Miasek and Harrison reported no correlation between β and μ_D in the deactivation of $(C_5H_9{}^+)^*$. Their method of calculating β was, however, rather ambiguous. Using variational collisional rates to calculate β from their data reveals a dependence on μ_D similar to that shown in Figure 2, though some complex nonpolar stabilizers are still more efficient than simpler polar molecules.

Discussion

There appears to be a rather striking lack of agreement between the data presented here and data of other apparently similar studies. It should be noted, however, that the trimethylamine system differs substantially from systems studied by other authors. In most other cases there is an exothermic reaction channel competing with stabilization; in the trimethylamine dimerization, stabilization competes only with thermoneutral dissociation back to reactants, and hence only a relatively small amount of energy need be removed from the excited dimer to stabilize it.

Trimethylamine is itself a very efficient stabilizer, even though it is relatively nonpolar. Similarly, Anicich and Bowers found in their study[4] that benzene was extremely efficient in stabilizing the $(C_{12}H_{12}{}^+)^*$ dimer ion. This probably means that a ligand-exchange mechanism is operative in these cases, with the displaced monomer unit carrying off the excess energy. This also implies that the monomer units retain their chemical identity in the complex.

Another important point is that CH_4, CF_4, C_2H_4, and C_3H_8 are about equally efficient. This fact seems to rule out any extensive participation of the internal modes of these collider molecules in the stabilization event.

It is our belief that rotational energy is the easiest to remove from the dimer and that R-T or R-R transfer are probably the dominant energy-transfer processes in this system. The case for R-R transfer seems particularly strong when the enhanced efficiencies of polar stabilizers are considered. At long ranges, interaction of the dipole and the ion causes an oscillatory transfer of angular momentum between the colliding molecules.[15] As the positive end of the dipole rotates toward the ion, the rotor is decelerated; as the negative end of the dipole rotates toward the ion, the rotor accelerates. The net effect is that the rotor velocity oscillates in the plane of the collision. We believe that this may increase the coupling between rotational degrees of freedom in the complex and lead to enhanced transfer of energy between the dimer and the stabilizer. Both experimental[16] and theoretical[17] studies on ion-polar molecule momentum transfer indicate that this process occurs at impact parameters considerably larger than the capture radius, results in support of the interpretation given here. Further work on this topic, both experimental and theoretical, is currently in progress.

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