Energy Transfer in Excited Ionic Species. Collisional Stabilization of the Dimer Ions $(C_4H_4F_4 \cdot {}^+)^*$ and $(C_{12}H_{12} \cdot {}^+)^*$ in 1,1-Difluoroethylene and Benzene[1]

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Abstract: Absolute third-order rate coefficients have been measured for reactions of the type $A \cdot {}^+ + A \rightleftarrows (A_2 \cdot {}^+)^*$ $(+M_i) \rightarrow A_2 \cdot {}^+$, where A is 1,1-difluoroethylene and benzene and M_i = He, Ne, Ar, Kr, Xe, N_2, CO, and the parent gases. Relative collisional stabilization efficiencies for the various M_i are also obtained. From these data it is determined that V–T transfer dominates all of the stabilization collisions except when M_i = C_6H_6 in the benzene system. In this one case an anomalously high stabilization efficiency is observed and either V–V transfer or a C_6H_6 switching reaction is inferred. From the data it is deduced that the structure of the $C_{12}H_{12} \cdot {}^+$ dimer ion in benzene is composed of two benzene like C_6H_6 moieties while the $C_4F_4H_4 \cdot {}^+$ dimer in 1,1-difluoroethylene is believed to be cyclic with a cyclobutane type structure. Ion cyclotron resonance spectroscopy is utilized.

The field of energy transfer in vibrationally excited molecules is currently one of considerable interest and activity. To date, virtually all of the reported work has been on neutral systems. These studies are of two general types. The first of these is collision induced energy transfer from a known distribution of vibrational states in the reactants to translational, rotational, and vibrational distributions of the products.[2-4] Often, the initial distribution of states of the reactants is simply a single vibrational state of a diatomic or triatomic molecule. If atomic species, such as rare gas atoms, are chosen as collision partners, the rate of transfer of the vibrational energy to either relative translational energy (V–T) or molecular rotational energy (V–R) can be studied. For molecular collision partners, vibrational–vibrational (V–V) processes can occur in addition to the V–T and V–R processes. It has been found that near resonant V–V transitions are very much faster than either V–T or V–R energy transfer.[5] It has been proposed that the maximum rate of energy transfer in V–T and V–R processes occurs when the vibrational frequency matches the "frequency" of the collision duration,[5-7] or the molecular rotational frequency.[5,8] Experimental data appear to be consistent with these suggestions. It thus appears that "frequency matching" is an important factor in determining the efficiency of energy transfer in gas phase neutral systems.

The second type of study encompasses chemical activation studies of unimolecular processes and the subsequent deactivation of the highly vibrationally excited species by collision. Much of the work in this field is attributable to the pioneering efforts of Rabinovitch and coworkers.[9] The studies are often coupled with statistical calculations using the Rice–Ramsburger–Kassel–Marcus (RRKM) theory of unimolecular reactions. Although a considerable amount of work has been accomplished in this area, the complexity of the systems studied has prevented a precise elucidation of the factors that govern energy transfer in these systems.

To our knowledge there has been only one previous paper on energy transfer in ionic systems, the work of Gill, Inel, and Meisels[10] on the collisional stabilization of the $(C_4H_8 \cdot {}^+)^*$ dimer in ethylene. Ionization was accomplished with an argon resonance lamp and the deactivation followed by measuring the ratio of neutralized C_4H_8 isomers as a function of pressure. A stepladder model was used to quantitatively analyze the data.

In this paper we present our first study of the factors that govern vibrational energy transfer in gas phase ion molecule collisions. We have chosen to create the excited ions by ion molecule reaction and subsequently deactivate them with chemically inert collision partners. The systems we have chosen are dimerization reactions of the sort

$$A \cdot {}^+ + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (A_2 \cdot {}^+)^* \overset{k_{2i}}{\underset{M_i}{\longrightarrow}} A_2 \cdot {}^+ \tag{1}$$
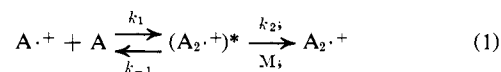
where A is either 1,1-difluoroethylene or benzene and M_i is He, Ne, Ar, Kr, Xe, N_2, CO, or the parent gases. These systems were chosen because the rate of dimerization is relatively fast and in each case the dimerization reaction is the only reaction occurring. In this paper the relative deactivation efficiencies of the various M_i species are determined, as well as the overall third-order rate constants. The data are discussed qualitatively in terms of several deactivation models. Ion cyclotron resonance (icr) spectroscopy is utilized.

(1) This research was supported by the National Science Foundation under Grant GP-15628.

(2) D. Rapp and T. Kassel, *Chem. Rev.*, **69**, 61 (1969), and references therein.

(3) H. Chen and C. B. Moore, *J. Chem. Phys.*, **54**, 4080 (1971), and references therein.

(4) E. Weitz and G. Flynn, *J. Chem. Phys.*, **58**, 2679 (1973), and references therein; J. T. Knudtson and G. Flynn, *ibid.*, **58**, 2684 (1973).

(5) See, for example, P. Borrell, *Advan. Mol. Relaxation Processes*, 1, 69 (1967).

(6) B. Stevens, *Mol. Phys.*, 3, 589 (1960).

(7) (a) R. L. Brown and W. Klemperer, *J. Chem. Phys.*, 41, 3072 (1964); (b) J. I. Steinfeld and W. Klemperer, *ibid.*, 42, 3475 (1965); J. I. Steinfeld, *ibid.*, 44, 2740 (1966).

(8) C. B. Moore, *J. Chem. Phys.*, 52, 1450 (1965), and references therein.

(9) (a) See, for example, L. D. Spicer and B. S. Rabinovitch, *Annu. Rev. Phys. Chem.*, 21, 349 (1970); (b) J. H. Current, B. S. Rabinovitch, C. A. Heller, and A. S. Gordon, *J. Chem. Phys.*, 39, 3535 (1963), and references therein; (c) J. H. Current and B. S. Rabinovitch, *ibid.*, 40, 274 (1964), and references therein; (d) Y. N. Lin and B. S. Rabinovitch, *J. Phys. Chem.*, 74, 3151 (1970), and references therein.

(10) P. S. Gill, Y. Inel, and G. G. Meisels, *J. Chem. Phys.*, 54, 2811 (1971).

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Experimental Section

The icr spectrometer has been previously described.[11,12] A "flat" four-section cell was utilized. The ions were formed *via* electron impact and modulated by the pulsed grid technique. Phenomenological ionization potentials were obtained by electronically scanning the electron energy.[12,13] All experiments were run at *ca.* 1 eV above the ionization potential of the parent gas (*ca.* 10.2 eV for benzene and *ca.* 11.3 eV for 1,1-difluoroethylene). These electron energies yielded sufficient ion intensity so that the experiments could be performed but minimized the amount of internal energy in the ion. The chosen electron energy values were well below the ionization potentials of the added collision gases, thus eliminating chemistry that might originate in those ions as well as eliminating possible space charge effects originating from the additive. Pressures were measured directly on an MKS Series 90 Baratron capacitance manometer. Reaction times were measured using the trapping plate modulation technique.[14] Reaction temperatures were *ca.* 300°K. Trapping voltages were kept at 0.3 V.

Results

Kinetic Analysis. In the drift cell icr spectrometer integrated ionic power absorption intensities are the primary data. A straightforward kinetic analysis relates these observed signals to ion intensities and ultimately to rate coefficients for ion–molecule reactions.[11,15–18] The approximate theory of Anicich and Bowers[11] is easily modified to include third-order processes. The appropriate expression for the third-order rate coefficient in a pure substance is

$$k = E/\tau[N]^2 \tag{2}$$

where E is the extent of reaction defined below, $\tau = \tau_p' + (\tau_p/3)$ is the reaction time, τ_p' and τ_p are the drift times for the primary (monomer) ions through the source and analyzer region of the spectrometer, respectively, and [N] is the concentration of the neutral monomer.

In the stabilization experiments a nonreactive neutral, M_i, is added. The appropriate third-order rate constant is given by eq 3. The extents of reaction E and

$$k_i = E'/\tau[M_i][N] \tag{3}$$

E' are defined by

$$E = \frac{A_s}{A_pC_{ps} + A_sB} \tag{4a}$$

$$E' = \frac{A_s'}{A_p'C_{sp} + A_s'B} \tag{4b}$$

and

$$E_T = E + E' \tag{4c}$$

where A_s is the integrated power absorption of the secondary ion (in this case the dimer ion), A_p is the integrated power absorption of the primary ion (mono-

(11) V. G. Anicich and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, 11, 329 (1973).
(12) V. G. Anicich, Ph.D. Thesis, Department of Chemistry, University of California, Santa Barbara, Calif. 93106.
(13) V. G. Anicich and M. T. Bowers, *Rev. Sci. Instrum.*, to be submitted for publication.
(14) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, 42, 1632 (1971).
(15) M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, 72, 3599 (1968).
(16) S. E. Buttrill, Jr., *J. Chem. Phys.*, 52, 2752 (1970); A. G. Marshall and S. E. Buttrill, Jr., *ibid.*, 52, 2752 (1970).
(17) M. B. Comisarow, *J. Chem. Phys.*, 55, 205 (1971).
(18) G. C. Goode, R. M. O'Malley, A. J. Ferrer-Correia, R. I. Massey, K. R. Jennings, J. H. Futrell, and P. M. Llewellyn, *Int. J. Mass Spectrom. Ion Phys.*, 5, 393 (1970).

mer ion), and B and C_{ps} are factors that are related to the ion masses and drift times.[19] From eq 2–4 it follows that

$$E_T = [N]\tau(k[N] + k_i[M_i]) \tag{5a}$$

$$dE_T/d[M_i] = dE'/d[M_i] = [N]k_i \tag{5b}$$

and

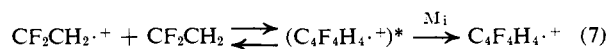$$\lim_{[M]\to 0} E_T = E = [N]^2 k\tau \tag{5c}$$

It is apparent from eq 5 that a plot of E_T *vs.* $[M_i]$ will have a slope $[N]k_i\tau$ and an intercept $[N]^2k\tau$. Since [N] and τ are measured quantities, k and k_i are determined. In practice, k is measured independently in the pure system and used as a check of the intercept measured in the mixed system. Occasional fluctuations in [N], the neutral monomer concentration, occur when the nonreactive collision partner is introduced to the ion cyclotron resonance cell. Such fluctuations are readily detectible by this technique and true values for [N] are readily obtained.

The lifetime of the excited species, $(A_2\cdot^+)^*$, is short enough that $A_2\cdot^+$ is not directly observed in the icr at low pressures. In this case it is permissible to perform a steady state analysis on $(A_2\cdot^+)^*$ in reaction 1 yielding

$$k_i = \frac{k_1 k_{2i}}{k_{-1} + k_{2i}[M_i]} \tag{6}$$

All of the results reported in this paper were obtained at very low conversion (0–5%). Therefore, $k_{-1} \gg k_{2i}[M_i]$ and $k_i/k_j \cong k_{2i}/k_{2j}$, where i and j represent two different nonreactive collision partners. This result is important because it implies that the relative rates of stabilization are given directly by a ratio of the measured third-order rate constants. In other words, the values of the experimental third-order rate constants give directly a measure of the relative efficiency of the various nonreactive species for removing (vibrational) energy from the $(A_2\cdot^+)^*$ complex. In order to make these relative efficiencies quantitative, the quantities k_i/ξ_i should be compared, where ξ_i is the total collision frequency for the dimer species $(A_2\cdot^+)^*$ with the nonreactive neutral M_i. Values for ξ_i are not yet available experimentally for the benzene dimer ion and 1,1-difluoroethylene dimer ion colliding with the M_i species used in this work. Reasonably accurate values can be obtained from the simple polarization theory[20] for the nonpolar substrates and from the average dipole orientation (ADO) theory[21] for the CF_2CH_2 substrate. These theoretical collision frequencies will be used to approximate the true ξ_i values.

1,1-Difluoroethylene. The pure 1,1-difluoroethylene system has been previously studied[22] and an overall rate constant obtained for reaction 7 of $k_7 = 1.2 \times$

$$CF_2CH_2\cdot^+ + CF_2CH_2 \underset{}{\overset{}{\rightleftarrows}} (C_4F_4H_4\cdot^+)^* \overset{M_i}{\longrightarrow} C_4F_4H_4\cdot^+ \tag{7}$$

10^{-24} cm^6 molecule^{-2} sec^{-1} for $M_i = CF_2CH_2$. Utilizing eq 3–5, plots of the extents of reaction E_T *vs.* the concentrations of the nonreactive neutral species, $[M_i]$,

(19) The quantities B and C in eq 4 are defined in ref 11.
(20) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, 29, 294 (1958).
(21) T. Su and M. T. Bowers, *J. Chem. Phys.*, 58, 3027 (1973); T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, 12, 347 (1973).
(22) R. M. O'Malley, K. R. Jennings, M. T. Bowers, and V. G. Anicich, *Int. J. Mass Spectrom. Ion Phys.*, 11, 89 (1973).
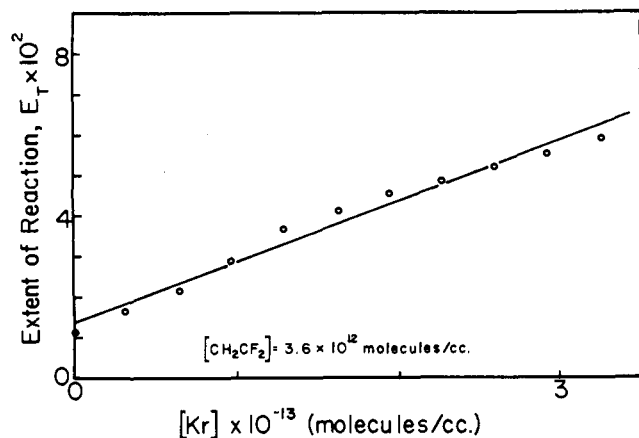
Figure 1. The extent of the dimerization reaction in 1,1-difluoro-ethylene as a function of krypton concentration. See the discussion following eq 5 in the text.
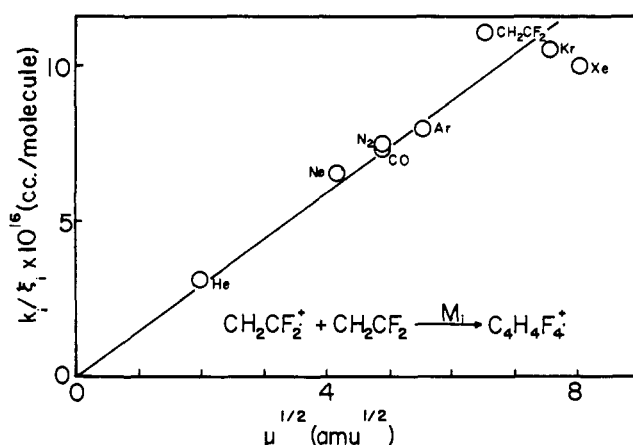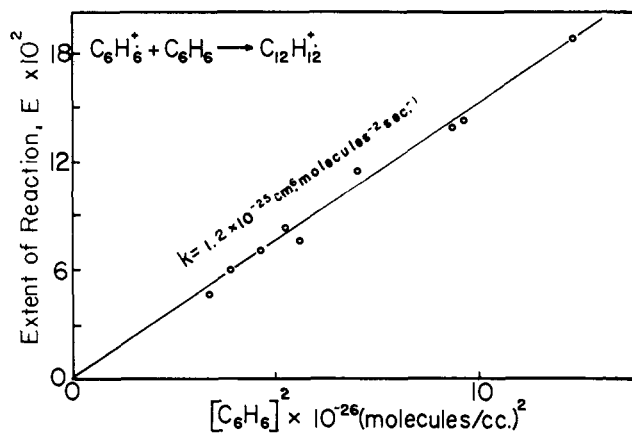

Figure 3. A plot of the extent of the benzene dimerization reaction as a function of the square of the benzene concentration.

Figure 2. A plot of the stabilization efficiency $vs.$ the square root of the reduced mass for a series of collision partners, M_i. See the discussion in the text following eq 6 and 7.
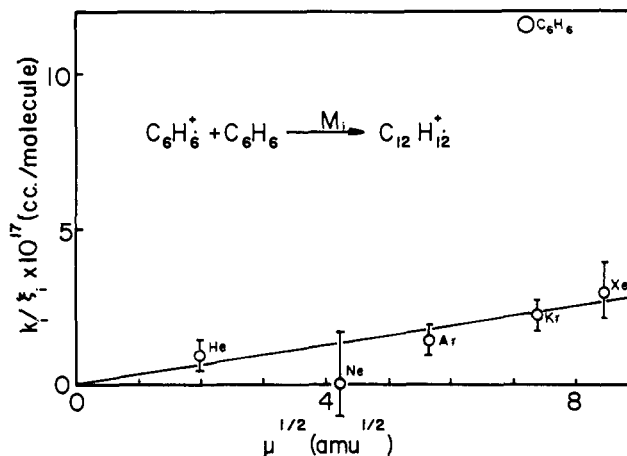

Figure 4. A plot of the stabilization efficiency $vs.$ the square root of the reduced mass for a series of collision partners, M_i. See the discussion in the text following eq 6 and 8.

were performed for the species M_i = He, Ne, Ar, Kr, Xe, N_2, and CO. A typical plot for M_i = Kr is given in Figure 1. The values of k_i so obtained are listed in Table I. The relative energy transfer efficiencies of the

Table I. Dimerization Rate Constants for
A·$^+$ + A $\rightleftharpoons$(A$_2$·$^+$)* $\longrightarrow$ A$_2$·$^+$.

M	$k_m \times 10^{26}$, cm^6 molecule^{-2} sec^{-1} CF$_2$CH$_2$·$^+$ + CF$_2$CH$_2$^{a}	C$_6$H$_6$·$^+$ + C$_6$H$_6$
He	17	0.4 ± 0.2
Ne	23	0.0 ± 0.6
Ar	43	0.7 ± 0.6
Kr	54	1.1 ± 0.3
Xe	58	1.6 ± 0.6
N$_2$	48	
CO	50	
CF$_2$CH$_2$	120	
C$_6$H$_6$		12 ± 2.5

^{a} The absolute uncertainty in these numbers is ±20%. The relative values are considerably more accurate, however.

various M_i, k_i/ξ_i, are obtained as discussed following eq 6 and are plotted in Figure 2 $vs.$ the square root of the reduced mass of the collision partners, $\mu^{1/2}$. The reason

for making such a plot and its possible significance will be given in the Discussion.

The absolute uncertainty of the rate coefficients in Table I is ca. ±20% but the relative values are considerably more accurate. Most of this uncertainty arises from the necessarily low signal-to-noise ratios of the power absorption signals obtained in this work. The remainder is primarily due to the usual difficulty in exactly measuring the pressure and drift times.

Benzene. The dimerization reaction 8 is the only reac-

$$C_6H_6·^+ + C_6H_6 \rightleftharpoons (C_{12}H_{12}·^+)* \xrightarrow{M_i} C_{12}H_{12}·^+ \qquad (8)$$
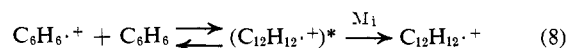
tion observed to occur in pure benzene. A plot of the extent of reaction E $vs.$ the square of the benzene concentration is given in Figure 3. The linearity of the plot establishes that reaction 8 is pure third order with a rate constant of k_8 = 1.2 × 10^{-25} cm^6 molecule^{-2} sec^{-1}.

Plots of E_T $vs.$ [M_i] were obtained for M_i = He, Ne, Ar, Kr, and Xe. The values of k_1 so obtained are listed in Table I. Energy transfer efficiencies, k_i/ξ_i, are plotted in Figure 4 $vs.$ the square root of the reduced mass, $\mu^{1/2}$, for the various neutral collision partners. The possible significance of this plot will be discussed in the following section.

Discussion

General Mechanism and Dimer Lifetimes. In principle, there are two different mechanisms that can give pure third-order kinetics. One is the collisional stabilization mechanism exemplified by reaction 1. A second is a conditioning charge exchange reaction followed by a second-order condensation reaction. From

$$(A \cdot ^+)^* + A \longrightarrow A \cdot ^+ + A^* \tag{9a}$$

$$A \cdot ^+ + A \longrightarrow A_2^+ \tag{9b}$$
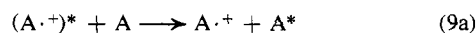
plots of extent of reaction *vs.* concentration squared in the neat systems it is not possible to distinguish between the two mechanisms. The fact that nonreactive third bodies, which cannot participate in charge exchange reactions, also give third-order kinetics establishes the stabilization mechanism of reaction 1. The charge exchange mechanism in the pure systems cannot be completely ruled out on this basis, but it certainly must play at best a minor part in the reaction mechanism. The very long lifetime of the excited dimer ions also serves to support the stabilization mechanism and to rule out a long range charge transfer reaction as the initial stage in the mechanism.

The lifetimes of the initially formed dimer ions of benzene and 1,1-difluoroethylene can be crudely estimated. At low conversion, $k \cong k_1 k_2 / k_{-1}$. k_1 can be estimated from collision theory[20,21] and k is measured experimentally. The stabilization rate can be approximated by $k_2 = \rho k_2'$ where ρ is the probability of stabilization of $(A_2 \cdot ^+)^*$ per collision and k_2' is the theoretical collision frequency. The values of the lifetimes are thus $(k_{-1})^{-1} \cong (1.0 \times 10^{-6})/\rho$ sec and $(1.0 \times 10^{-7})/\rho$ sec for $(C_4F_4H_4 \cdot ^+)^*$ and $(C_{12}H_{12} \cdot ^+)^*$, respectively At the observation frequencies utilized (153 kHz), ions of lifetimes greater than *ca.* 1×10^{-4} sec would have been observed directly without stabilization. It is not possible to put an accurate lower limit on the lifetime. At the pressures utilized in the icr (1×10^{-3} Torr maximum) it seems unlikely that the lifetime of the $(A_2 \cdot ^+)^*$ ions could be substantially less than 1×10^{-5} sec, however. Thus, crudely, 1×10^{-5} sec $< k_{-1} < 1 \times 10^{-4}$ sec. It follows then that $10^{-2} < \rho(CF_2CH_2) < 10^{-1}$ and $10^{-3} < \rho(C_6H_6) < 10^{-2}$ in the pure substances. The upper limit on k_{-1} is certainly valid to within a factor of about 2, but the lower limit may be in error by as much as an order of magnitude.

Mechanism of Energy Transfer. There are a number of conceptually different mechanisms for energy transfer in systems such as those reported here. The first of these suggests that energy transfer will be maximized when the collision frequency matches the vibrational frequency of the active mode(s) of the excited ion. This model has evolved from energy transfer studies on highly quantized systems. The second model treats the collision between the excited ion and the bath molecule in the statistical sense. A long-lived complex is assumed to be formed and energy transfer occurs when the departing particle is either translationally or vibrationally excited. In neutral systems this model is usually applied to highly excited chemically activated species (with internal energies in the 80–110 kcal range) and the analysis done using RRKM theory.[23] A third

type of energy transfer is possible in the neat systems. In these cases a switching reaction may occur in which the neutral bath molecule is "exchanged" for an identical moiety in the excited dimer. The departing molecule may carry off a significant amount of vibrational energy thus deactivating the dimer. This process is represented in reaction 10. A mechanism similar to

$$(A_1A_2 \cdot ^+)^* + A_3 \longrightarrow A_1A_3 \cdot ^+ + A_2^* \tag{10}$$

(10) has been proposed to account for the deactivation of vibrationally excited H_3^+ ions.[24]

$$(H_3 \cdot ^+)^* + H_2 \longrightarrow H_3^+ + H_2^* \tag{11}$$
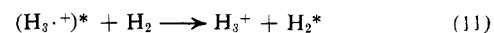
The statistical approach has merit in that the reactions studied here are formally similar in some respects to those that have been successfully analyzed using this approach in neutral systems. There are several important differences in the particular ionic systems reported here and the neutral systems, however. First, there are no competitive reaction channels in these ionic systems. The only allowed unimolecular reaction is dissociation to starting materials. In neutral chemical activation studies there is always a competition between various unimolecular reaction channels, usually an elimination reaction or isomerization reaction competing with dissociation to starting materials. These additional channels are usually very exothermic relative to dissociation of the neutral activated species into starting material. The variation of the observed unimolecular rate with pressure (usually reported experimentally as an S/D ratio, S = stabilization, D = decomposition) gives information about the efficiency of energy transfer per collision when analyzed using collision theory and RRKM theory.[23] Such an analysis is useful for the type of ionic reactions reported by Gill, Inel, and Meisels[10] but is not directly applicable to the studies reported in this work. Statistical calculations might still be useful in interpreting the data presented here, however. These calculations would entail a determination of the relative probability of the species M departing from a complex of the form $(A_2 \cdot ^+–M)^*$ with a sufficient amount of energy (translational or vibrational) to result in stabilization of the excited dimer. What is needed for successful calculations of this type is detailed information on the system energetics including well depths, activation energies, vibrational frequencies, etc. In addition, some idea of the structure of the dimer and of how the bath molecule M attaches itself is essential. None of these factors are available with any certainty. We have developed QET programs[24] that are suitable for application to this problem with some modifications. The icr spectrometer is being modified for temperature-dependence studies that will yield the well depths of the dimer ions. The structures of the dimers are not known although implications drawn from the data presented here and elsewhere yield qualitative information in this regard. The detailed mechanism of attachment and detachment of the third body to the dimer is totally unknown, however, and presents the largest barrier to any semiquantitative examination of the statistical model. Calculations on simplified models using QET will be

(23) Recent examples are given in K. Dees, D. W. Setser, and W. G. Clark, *J. Phys. Chem.*, 75, 2231 (1971); H. W. Chang, L. L. Craig, and D. W. Setser, *ibid.*, 76, 954 (1972).

(24) W. T. Huntress and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, 12, 1 (1973); M. T. Bowers, W. J. Chesnavich, and W. T. Huntress, *ibid.*, 12, 357 (1973).

pursued to indicate whether more realistic calculations are justified.

There are reasons why a collision duration model may be usefully applied to the data presented here. The well depths of the dimers are sufficiently shallow (10–30 kcal)[12] that only a few quanta of vibrational energy are involved. In addition there is no evidence that the two dimer ions form a long-lived complex with any of the neutral species used as third bodies. To the contrary, the data of Figures 2 and 4 are consistent with the notion that stabilization efficiency may be dependent on the relative velocity of the colliding species and hence the collision duration. For practical reasons such a model is appealing as well. There is no need to have any detailed structural or energetic information about the dimers. A simple collision duration model can be readily solved using classical mechanics and electrostatics. Within the framework of such a model suggestions can be made regarding qualitative ion structures and limits on the frequencies of the active modes obtained. The model follows.

The "duration" of an ion–molecule collision can be estimated from a classical model. The attractive charge induced dipole force, F, is given by

$$F = 2\alpha q^2/r^5 \tag{12}$$

where r is the separation between the ion and neutral, α is the polarizability of the neutral, and q is the charge on the ion. The resulting energy of the interaction can be obtained by an integration over the allowable values of r, the result equated with $1/2\mu v_r^2$, and this equation solved for the ion–neutral relative velocity, v_r

$$v_r = (\alpha q^2/\mu r^4)^{1/2} \tag{13}$$

If the initial relative velocity of the particles, v_0, is considered, the total relative velocity of the ion and neutral is

$$v = (v_0^2 + v_r^2)^{1/2} \tag{14}$$

The neutral particles have a Boltzmann distribution of velocities. Since the experiments are carried out under conditions where the ions undergo many collisions to a first-order approximation, the ions also have a Boltzmann distribution of velocities. In this case v_0 can be approximated by the average Boltzmann velocity $(8kT/\pi\mu)^{1/2}$.

In the above analysis the short range repulsive forces are ignored. The effect of including a short range repulsive force would be to decrease the velocity at small r and reduce the distance of travel by requiring that a minimum, finite distance exist between the collision partners at the distance of closest approach. These two effects of neglecting the repulsive term will cancel, to a degree, and for this simple model we have chosen to ignore effects due to the repulsive forces.

From eq 14 it is now possible to calculate the "collision duration" as a function of the separation at which the collision is assumed to start, r_c. Such a plot for a collision between $C_4F_4H_4 \cdot^+$ and Xe is given in Figure 5. A very similar plot holds for $C_{12}H_{12} \cdot^+$ and Xe. It is reasonable to assume the collision "starts" at r_c values between 2 and 4 Å. Such collisions have durations between 0.6×10^{-13} and 4.3×10^{-13} sec. Since the energy transfer efficiency is either still increasing or is maximized for Xe, this result indicates
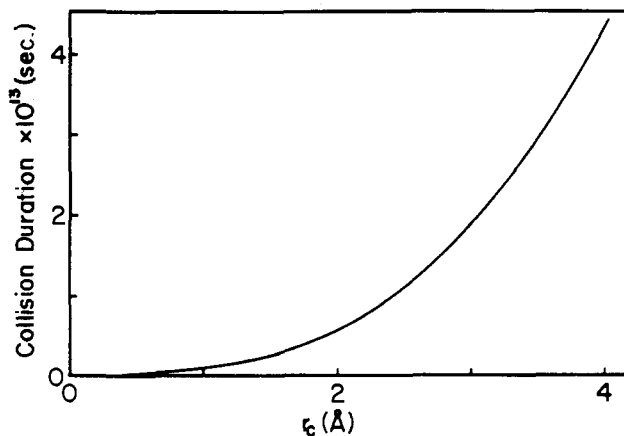

Figure 5. A plot of the collision duration $vs.$ the separation at which the collision starts, r_c, for a collision between $C_4F_4H \cdot^+$ and Xe. See the discussion in the text following eq 12.

that the "active" vibrational frequencies of the excited $(C_4F_4H_4 \cdot^+)^*$ and $(C_{12}H_{12} \cdot^+)^*$ dimers are less than or equal to $ca.$ 550 cm^{-1}.

The data of Figure 2 suggest that CF_2CH_2 is no more efficient at deactivating $(C_4F_4H_4 \cdot^+)^*$ than either the rare gas atoms or the CO and N_2 molecules. An exchange reaction as exemplified in reaction 10 appears thus to be ruled out. So also does V–V transfer arising from frequency matching in $(C_4F_4H_4 \cdot^+)^*$ and CF_2CH_2. It has been suggested that the $(C_4F_4H_4 \cdot^+)^*$ dimer in 1,1-difluoroethylene has a cyclobutane type structure.[22] Such cyclic structures are known to exist for certain C_4 ionic intermediate in selected fluoroethylene reactions.[12,25,26] Fluorinated cyclobutane neutrals have ring puckering vibrational modes[27] between 90 and 200 cm^{-1} while linear butenes most likely do not have frequencies this low. The 1,1-difluoroethylene molecule[28] has no observable vibrational modes below 430 cm^{-1}. It thus appears the data presented here are consistent with a cyclic $C_4F_4H_4 \cdot^+$ ion.

The data in Figure 4 for benzene are considerably different. Benzene neutral is $ca.$ 10 times more efficient at deactivating $(C_{12}H_{12} \cdot^+)^*$ than expected on a reduced mass basis alone. An exchange reaction is a possible explanation. In addition, benzene[29] has a number of low-frequency modes that may be undergoing V–V transfer with $(C_{12}H_{12} \cdot^+)^*$. In either case the structure of the dimer ion is suggested to be composed of two C_6H_6 moieties that retain local benzene character. This conclusion is in contrast to that drawn for the CF_2CH_2 case.

Finally, the possibility of V–R transfer is believed to be small in the collisions considered in this manuscript. Large V–R contributions result when the rotational velocity is greater than or equal to the translational

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velocity.[5,8] The ions of interest ($C_4F_4H_4\cdot^+$ and $C_{12}H_{12}\cdot^+$) have large moments of inertia and thus low rotational velocities. The atomic collision partners cannot be rotationally excited. The molecules CO and N_2 have relatively small moments of inertia and might contribute on this basis. However, the strong ion-molecule potential causes the relative translational energy of the ions to become much greater than thermal and thus the translational velocity is much greater than the rotational velocity even for small molecular collision gases. For these reasons V–R transfer was not considered in the energy transfer model.

Summary

The dimerization reactions of $CF_2CH_2\cdot^+$ in CF_2CH_2 and $C_6H_6\cdot^+$ in C_6H_6 are found to be third order at threshold electron impact energies and thermal kinetic energies. Nonreactive collision gases are also effective in stabilizing the dimers in these two systems. These experiments confirm that the collisional deactivation mechanism of reaction 1 dominates. Absolute third-order rate constants and relative stabilization efficiencies are determined for all collision gases.

Analysis of the energy exchange between the excited dimer ion and the nonreactive collision gases using a collision duration model suggests that the excess energy removed from the dimer is in the form of low-frequency vibrational energy. The linearity of the k_i/ξ_i vs. $\mu^{1/2}$ plots, Figures 3 and 4, imply V–T exchange dominates all systems except the benzene dimer ion stabilized by the benzene neutral. In this case it appears that either V–V energy transfer or energy transfer via an exchange reaction dominates. This latter result suggests the structure of the $C_{12}H_{12}\cdot^+$ dimer may be composed of two benzene type moieties. The fact that CF_2CH_2 deactivates $C_4F_4H_4\cdot^+$ only by V–T transfer suggests that the $C_4F_4H_4\cdot^+$ ion has a structure unlike the parent olefin. A cyclic cyclobutane type structure is suggested.

Addition of Trimethylsilyl Radical to Ethylene. A Flash Photolysis–Electron Spin Resonance Kinetic Study[1]

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Abstract: The rate of addition of trimethylsilyl radical to ethylene was measured over the temperature range $+20$ to $-74°$. At $20°$, $k = 1.7 \pm 1.0 \times 10^5\ M^{-1}\ \text{sec}^{-1}$. An activation energy 2.5 ± 0.2 kcal/mol and frequency factor $\log A = 7.0 \pm 0.2$ were determined. It is confirmed that ethylene is an efficient scavenger for silyl radicals. This is the first direct kinetic study of an addition reaction which may be considered the prototype for the chain-carrying steps in free radical polymerization of olefins.

Addition reactions of silicon-centered radicals and olefins or acetylenes are of great synthetic importance, constituting one of the major methods for the creation of silicon–carbon bonds.[2] The detection of silyl radicals as intermediates in photochemical[3a] and nuclear recoil[3b] reaction systems by the use of olefin scavengers depends on the rapidity of the addition reaction. Very little information is available, however, on the rates of silyl radical addition reactions.[4] Recently, Strausz and coworkers have estimated the rate constant for addition of disilanyl radicals to ethylene, employing quantum yield measurements in steady-state photolysis experiments.[5]

$$SiH_3SiH_2\cdot + CH_2{=}CH_2 \longrightarrow SiH_3SiH_2CH_2CH_2\cdot$$
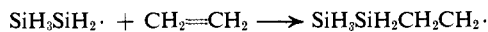
The recent detection of silyl radicals by electron spin resonance spectroscopy in the solid[6] and liquid phases[7,8] has led the way to kinetic studies of silyl radical reactions. Direct kinetic studies of self reactions (dimerization or disproportionation) of several silicon-centered radicals have been reported by Ingold and coworkers[9] and by ourselves.[10] Despite strenuous efforts over two decades, silyl radicals have not been directly detected in the gas phase.[11]

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