reasonably reliable calculations may be made by selectively excluding noncrucial degenerate modes. Furthermore, the kinetic isotope effect temperature dependence appears to be more reliable than the KIE measured at any one value, as a diagnostic tool for transition state models. Similarly, it should provide a more reliable experimental probe, since relative and reproducible errors tend to cancel in the slope determination.

A study of the force field variations also indicates certain assumptions which may be used for transition state calculations. (1) If ν_L is of the same symmetry as any other transition state vibration, and if the ground state interaction with that vibration is strong, the transition state interaction remains strong until the bond is broken. (2) Similarly, until the departing fragment actually ceases to be bound, there is little indication that the associated bending mode must be changed. Inordinately large 10–60 differences were observed whenever ν_6 decreased appreciably, whether from force constant adjustment (force field 5) or changes in geometry (models 27–30). (3) Slight changes in the other off-diagonal and degenerate force constants are not crucial. This is especially true of interaction constants which link modes of similar ground state but dissimilar transition state symmetry. It is also true of degenerate modes, which usually have higher energies and appreciably smaller isotopic shifts than their corresponding nondegenerate modes. In either case, the ground state constants may generally be used.

Although these conclusions have been drawn specifically for tert-butyl chloride, they should hold for other molecules with C_{3v} symmetry, or pseudo-C_{3v} symmetry. Thus, the conclusion should be applicable to methyl chloride, triphenylmethyl chloride, and similar molecules, as well as for analogous bromides. The (nominal) C–Cl stretch mode interactions with other modes are expected to be less in molecules of lower symmetry such as ethyl and isopropyl chloride, and more geometric parameters are required to describe the transition state configuration; thus the conclusions reported here are not immediately applicable to molecules of lower symmetry. However, it is expected that other work will extend these conclusions to models of lower symmetry. In such an extension, it is expected that the temperature dependence will continue to be dependent on the transition state C–Cl distance, the temperature-independent factor will be dependent on a combination of other geometrical parameters, and the use of these additional pieces of kinetic isotope effect information may help to unravel the complexity of transition state model choices.

Kinetics, Equilibrium, and Negative Temperature Dependence in the Bimolecular Reaction $t\text{-}C_4H_9^+$ ($i\text{-}C_5H_{12}$, $i\text{-}C_4H_{10}$) $t\text{-}C_5H_{11}^+$ between 190 and 570°K

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Abstract: The approach to equilibrium and the values of the equilibrium constant were investigated in the reaction system (k_f) $t\text{-}C_4H_9^+ + i\text{-}C_5H_{12} \rightleftharpoons t\text{-}C_5H_{11}^+ + i\text{-}C_4H_{10}$ (k_r) by pulsed high-pressure mass spectrometry. The equilibrium constants measured and the resultant thermodynamic values, $\Delta H = -3.3$ kcal/mol, $\Delta G_{300} = -2.5$ kcal/mol, $\Delta S_{300} = -2.7$ eu, showed good agreement with values obtained previously using a continuous ion source technique. The value of k_f was measured as 1.6×10^{-11} cm³/(mol sec) at 328°K. The rate constant for this slow exothermic bimolecular reaction exhibits a temperature dependence between 190 and 570°K best expressed as $k_f \approx CT^{-8}$. The meaning of this temperature dependence in the present reaction system, involving a highly complex reaction intermediate with $3N - 6 = 84$ internal degrees of freedom, is discussed in the context of transition state theory concepts.

The thermodynamics of the hydride-transfer equilibria occurring in the $t\text{-}C_4H_9^+$ ($i\text{-}C_5H_{12}$, $i\text{-}C_4H_{10}$) $t\text{-}C_5H_{11}^+$ system between 323 and 548°K was previously investigated in this laboratory[1] by high-pressure mass spectrometry applied in the continuous mode of ion production and extraction. The kinetics of the hydride-transfer reactions of tert-butyl ion with 22 C_5–C_8 alkanes at 298°K was studied by Ausloos and Lias[2]

using the techniques of radiation chemistry. They found the rates of these reactions to be uncharacteristically slow for exothermic ion–molecule reactions, with rate constants generally between 10^{-10} and 10^{-11} cm³/(mol sec), although hydride abstraction is the only reaction channel. An activation energy ($\leq$3.5 kcal/mol) inversely related to the exothermicity of the reaction was postulated.

In the present study, the temperature dependence of

(1) J. J. Solomon and F. H. Field, *J. Amer. Chem. Soc.*, **95**, 4483 (1973).

(2) P. Ausloos and S. G. Lias, *J. Amer. Chem. Soc.*, **92**, 5037 (1970).
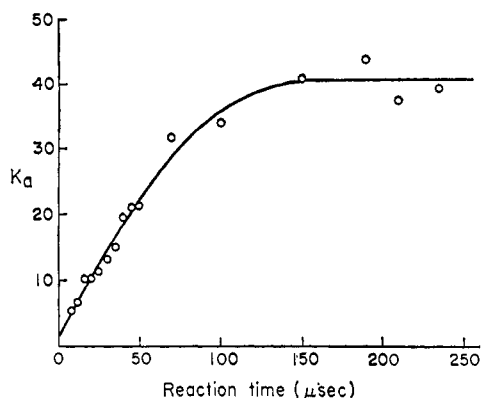
Figure 1. The apparent equilibrium constant $vs.$ reaction time for reaction 1: $T = 328°K$, $P = 0.6$ Torr, $P_{i\text{-}C_4H_{10}}/P_{i\text{-}C_5H_{12}} = 10.02$.

the equilibrium constant and the kinetics of the approach to equilibrium for the reversible reaction

$$t\text{-}C_4H_9^+ + i\text{-}C_5H_{12} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} t\text{-}C_5H_{11}^+ + i\text{-}C_4H_{10} \qquad (1)$$
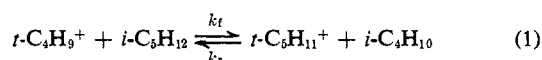
was investigated by means of pulsed high-pressure mass spectrometry. This was undertaken in order to gain further insight into the kinetics of these slow ion–molecule reactions. In addition, we wanted to verify our previous continuous equilibrium measurements and to check if there were any discrepancies between the continuous and pulsed equilibrium techniques.

Experimental Section

The Rockefeller Chemical Physics mass spectrometer used in these experiments and described elsewhere[3,4] has recently been modified to operate in the pulsed electron beam mode. A detailed account of the pulsed technique, which is similar to the method described by Kebarle,[5] will be forthcoming from this laboratory. The following is a brief description of the pulsed procedure used in this study.

The instrument was operated under field-free[3] conditions with the repeller maintained at ion chamber potential. The 600-eV electron beam was initially blocked by supplying a 40 V negative bias with respect to the filament to the electron beam control electrode. This potential was found to be sufficient to stop the electron current completely. The electron beam was then pulsed by supplying a +40-V pulse to the electron beam control electrode. The duration of the electron beam pulse, Δt_e, was typically several microseconds and generally occurred at a rate of 4 kHz. The ion focus electrode was permanently biased to defocus the ion beam, preventing ion transmission. At a variable delay time after the electron beam "on" pulse, the ion gate was opened by applying an ion-focusing pulse for a short period of time, Δt_f. The electron beam pulse, delay time, and ion-focusing pulse were obtained by a network of three General Radio Model 1217-C unit pulse generators. The ions collected during Δt_f have spent t_r μsec in the ion source and t_{fl} μsec in flight between the source and the ion-focus electrode. Since the source was operated at high pressures, $t_r \gg t_{fl}$, for sufficiently narrow pulse widths the reaction time is simply the time between the leading edge of the electron beam pulse and the leading edge of the ion-focusing pulse. The finite pulse widths lead to an uncertainty in the estimation of the reaction time, and consequently, the pulse widths were maintained at the minimum value compatible with adequate instrumental sensitivity. Typically, the pulse widths used were $\Delta t_e = \Delta t_f = 4$ μsec for reaction times <30 μsec and gradually increasing to 10 μsec at 100-μsec reaction time in order to compensate for the decrease in the total ion intensity with increasing delay time. The ion signal was detected

(3) D. P. Beggs and F. H. Field, *J. Amer. Chem. Soc.*, **93**, 1567 (1971).

(4) S. L. Bennett and F. H. Field, *J. Amer. Chem. Soc.*, **94**, 5188 (1972).

(5) D. A. Durden, P. Kebarle, and A. Good, *J. Chem. Phys.*, **50**, 805 (1969).
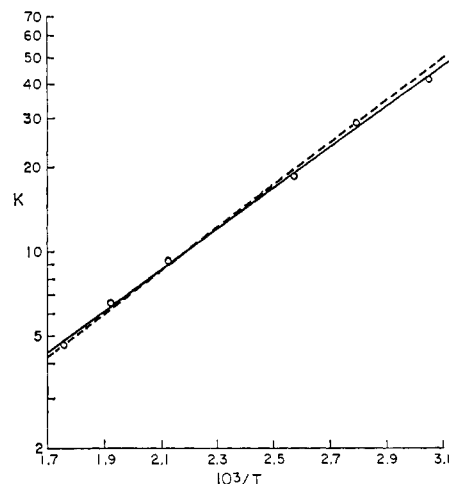
Figure 2. Comparison of van't Hoff plots: (—) pulse technique; (- - -) continuous technique.

continuously with a Bendix Model 4700 electron multiplier and a Keithley Model 427 current amplifier. In the pulsed mode of operation the dynamic range of ion current detection was limited to 30:1 by the low signal to noise ratio. The pulse widths and delay times were measured by a Telequipment Model D66 oscilloscope.

Matheson instrument grade (99.5%) isobutane and Matheson Coleman and Bell spectroquality grade (99 + mol %) isopentane were used. Gas mixtures of known composition of $i\text{-}C_4H_{10}/i\text{-}C_5H_{12}$ were prepared in 5-l. storage bulbs and were flowed directly into the ion source. Intensities of the *tert*-butyl (m/e 57) and *tert*-pentyl (m/e 71) ions were monitored at variable delay times at constant temperatures and pressures. The total source pressure was varied between 0.4 and 1.5 Torr and for most experiments was adjusted to keep the total number density at about 1.7×10^{16} mol/cm^3.

Results

A. Thermodynamics. The equilibrium constant for reaction 1 is given by the expression

$$K = \frac{(t\text{-}C_5H_{11}^+)(i\text{-}C_4H_{10})}{(t\text{-}C_4H_9^+)(i\text{-}C_5H_{12})} = \left(\frac{I_{71}}{I_{57}}\right)_{eq} \times \frac{P_{i\text{-}C_4H_{10}}}{P_{i\text{-}C_5H_{12}}} \qquad (2)$$

The approach to equilibrium was examined by measuring the ion intensity ratio I_{71}/I_{57} as a function of reaction time. A sample plot of the apparent equilibrium constant, $K_a = (I_{71}/I_{57})(P_{i\text{-}C_4H_{10}}/P_{i\text{-}C_5H_{12}})$, $vs.$ reaction time at constant temperature and pressure is shown in Figure 1. The achievement of equilibrium is observed above 100 μsec where K_a becomes time independent. In Figure 1 we see that K_a does not go through the origin. If we make the reasonable assumption that the cross sections for the initial formation of the $(M - 1)^+$ ion in isobutane and isopentane are equal, then at $t = 0$ we should expect an apparent equilibrium constant of unity ($I_{71}^0/I_{57}^0 \propto (P_{i\text{-}C_5H_{12}}/P_{i\text{-}C_4H_{10}})$ and therefore $K_a^0 = (I_{71}^0/I_{57}^0)(P_{i\text{-}C_4H_{10}}/P_{i\text{-}C_5H_{12}}) = 1$). Plots analogous to Figure 1 were obtained for several temperatures between 328 and 570°K. The temperature dependence of the equilibrium constant is given in Figure 2. The solid line is obtained from a least-squares analysis of the pulsed experimental points. The dotted line was obtained from our previous[6] continuous high-pressure equilibrium measurements on this system. The agreement between the van't Hoff plots obtained by the continuous and pulse techniques is excellent. The thermodynamic quan-

(6) Reference 1, Figure 3.

tities obtained from the pulse experiments are $\Delta G_{300} = -2.5$ kcal/mol, $\Delta H = -3.3$ kcal/mol, and $\Delta S_{300} = -2.7$ eu.

B. Kinetics. A general bimolecular ion–molecule transfer reaction can be written as

$$A^+ + BX \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B^+ + AX \tag{3}$$
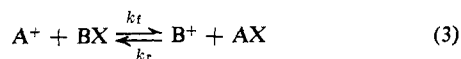
where k_f and k_r are the forward and reverse reaction rate constants. The equilibrium expression for reaction 3 is given by

$$K = k_f/k_r = [B^+/A^+][AX/BX] \tag{4}$$

Under typical high-pressure mass spectrometric conditions the neutral concentrations are much larger than the ionic concentrations; therefore reaction 3 can be treated as a system of opposing (pseudo) first-order reactions. Reaction 3 can now be rewritten as

$$A^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B^+ \tag{5}$$

where

$$k_1 = k_f[BX] \text{ and } k_{-1} = k_r[AX] \tag{6}$$

are the pseudo-first-order forward and reverse rate constants, respectively. Following Benson's[7] treatment for opposing first-order reactions we obtain the integrated rate expression

$$\ln (A^+ \cdot K' - B^+) = \ln (A_0^+ \cdot K' - B_0^+) -$$
$$(k_1 + k_{-1})t \tag{7}$$

where A^+ and B^+ are the instantaneous concentrations of A^+ and B^+, A_0^+ and B_0^+ are the initial concentrations (at $t = 0$) of A^+ and B^+, and

$$K' = k_1/k_{-1} = (B^+/A^+)_{eq} \tag{8}$$

is the equilibrium ion ratio.

When $k_1 \gg k_{-1}$ or $k_{-1} \gg k_1$ we can neglect the slower reaction and eq 7 reduces to the rate expression for a simple first-order reaction. When this simplification cannot be made we must first measure K' and then apply eq 7. A plot of $\ln (A^+ \cdot K' - B^+)$ vs. time yields a straight line whose slope is $-(k_1 + k_{-1})$. Combining this result with eq 8 permits the calculation of k_1 and k_{-1} and subsequently using eq 6 we can obtain k_f and k_r, the true bimolecular reaction rate constants.

A plot of $\ln [(I_{57}/(I_{57} + I_{71}))(I_{71}/I_{57})_{eq} - (I_{71}/(I_{57} + I_{71}))]$ vs. reaction time is shown in Figure 3, where $I_{57}/(I_{57} + I_{71})$ and $I_{71}/(I_{57} + I_{71})$ are the normalized time-dependent intensities of t-C$_4$H$_9^+$ and t-C$_5$H$_{11}^+$ ions, respectively, and $(I_{71}/I_{57})_{eq}$ is the equilibrium ion intensity ratio (K') obtained from the time-independent regime of K_a in plots such as Figure 1. We calculate k_1 and k_{-1} from the slope $(-(k_1 + k_{-1}))$ of the straight line in Figure 3 and from K' (k_1/k_{-1}). In these experiments, the source temperature and pressure were kept constant, and therefore from the known neutral mixture ratio (i-C$_4$H$_{10}/i$-C$_5$H$_{12}$) we calculate the number densities of isopentane (N_P) and isobutane (N_B). Using eq 6 with BX $= N_P$ and AX $= N_B$, we calculate the forward and reverse bimolecular rate constants for reaction 1.

The temperature dependence of k_f and k_r was determined by following the kinetics of the approach to
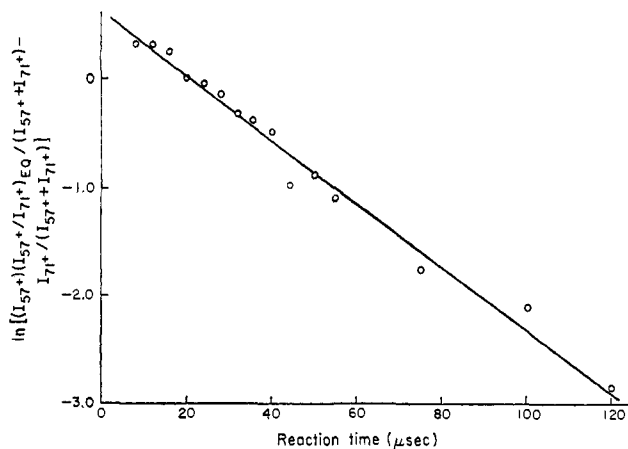
Figure 3. Determination of the (pseudo) first-order rate constants for reaction 1: slope $= -(k_1 + k_{-1})$, $T = 358°$K, $P = 0.7$ Torr, $P_{i\text{-}C_4H_{10}}/P_{i\text{-}C_5H_{12}} = 10.02$.

equilibrium as described above for several temperatures. The results are presented in Table I. Included

Table I. Experimental Temperature Dependence of Bimolecular Reaction Rate Constants

T, °K	P_{total}, Torr	$N_B \times 10^{-16}$, mol/cm^3	$N_P \times 10^{-16}$, mol/cm^3	K	$k_f \times 10^{12}$, cm^3/(mol sec)	$k_r \times 10^{12}$, cm^3/(mol sec)
190	0.41	1.48	0.61	1763	52.1	0.03
262	0.47	1.23	0.51	155	27.5	0.18
298					25.0[a]	
328	0.59	1.58	0.16	41.5	15.6	0.38
358	0.70	1.72	0.17	28.7	12.7	0.44
385	0.54	0.88	0.48	18.6	8.5	0.46
388	1.49	2.63	1.09	19.1	7.8	0.41
389	1.18	1.91	1.03	18.6	7.3	0.39
470	0.82	1.19	0.49	9.2	3.6	0.39
520	0.91	1.20	0.50	6.5	4.0	0.61
570	1.04	1.25	0.52	4.7	2.3	0.50

[a] Reference 8.

is the forward rate constant determined by Ausloos and Lias[8] at $T = 298°$K using $tert$-butyl ions generated in the γ irradiation of neopentane. They measured this rate constant using the technique of end-product analysis in deuterium-labeled mixtures. Good agreement is found in the absolute reaction rate constant although very different experimental techniques were used.

At the two lowest temperatures in the kinetic study the equilibrium constant K and hence K' were determined by extrapolating the least-squares line of the van't Hoff plot to the desired temperature. This was done to overcome the experimental difficulty of measuring very large equilibrium constants. Uncertainty in the extrapolated value for K at low temperatures should not seriously affect the determination of k_1 and k_f, because, as indicated in the general kinetic analysis, the values obtained for these quantities become largely independent of K' when it is large (i.e., $k_1 \gg k_{-1}$). However, the accuracy of k_{-1} and k_r are affected through the equilibrium constant relationship, eq 8.

As mentioned earlier, the finite pulse widths introduce an uncertainty in the assignment of the reaction time. This error is small when $\Delta t_e/t_r \ll 1$, i.e., when the

(7) S. W. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960.

(8) P. Ausloos and S. G. Lias, "Ion-Molecule Reactions," Vol. 2, J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1972, p 729.
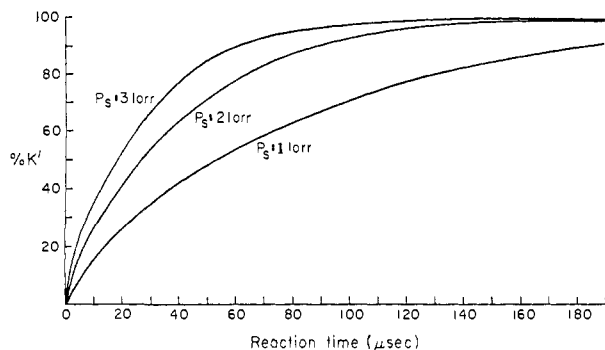
Figure 4. Time dependence of the ion intensity ratio expressed as per cent K', where K' is the equilibrium ion intensity ratio for a 1.17% mixture of i-C_5H_{12} in isobutane at $T = 436°K$.

pulse widths are negligible compared to the delay time. The error becomes potentially more significant when the kinetic study is restricted to a short reaction time, and t_r is comparable to Δt_e and Δt_f. This was the case in our experiments at low temperature, when the rate of the forward reaction is fast and the ion ratio, I_{71}/I_{57}, exceeds the dynamic range of the mass spectrometer after a short reaction time. The kinetic studies were also limited to a short reaction time when equilibrium is reached quickly because of the high total number density of the reactants. In our studies at the highest total number densities the equilibrium was achieved at ≈ 50 μsec.

We estimate the uncertainty in the tabulated rate constants given in Table I to be 10–20% due to the inaccuracy in assigned reaction times. It is worth noting that since the ion intensity ratio is time invariant after the attainment of equilibrium, the accuracy of measured equilibrium constants is unaffected by any uncertainty in the estimated reaction time.

Another conceivable source of error in the rate constant determination is the possibility of alternate reaction channels. This was investigated, specifically the possibility of dimer formation. Stabilized addition complexes $(C_5H_{11} \cdot C_4H_{10})^+$, $(C_4H_9 \cdot C_4H_{10})^+$, etc., were found to contribute less than 1% of the total ionization even at the lowest temperatures employed in this study.

A large negative temperature coefficient for the forward reaction rate constant k_f is clearly evident in the data of Table I. Because of the prevalence of negative temperature coefficients in three-body reactions,[5,9-14] the kinetic order of reaction 1 was investigated. This was done by changing the total pressure by a factor of 3 at constant temperature ($\sim$387°K). The bimolecular rate constants k_f and k_r obtained in these experiments were independent of pressure (see Table I).

Discussion

In our previous paper,[1] the conclusion that equilibrium was achieved in the continuous mode was based on two criteria: the equilibrium constant remained the

same while the neutral ratio, i-C_4H_{10}/i-C_5H_{12}, was varied by a factor of 85; and a plot[15] of the apparent equilibrium constant (K_a) vs. source pressure for a mixture of 1.17% i-C_5H_{12} in i-C_4H_{10} at $T = 436°K$ and $E/P = 5$ V/(cm Torr) remained constant above 2.4 Torr of source pressure. Thermodynamic quantities in the continuous study were obtained from van't Hoff plots made at 3.0 Torr of source pressure.

The thermodynamic and kinetic quantities determined with the pulse technique can be used to show why equilibrium was achieved in the continuous mode at 3 Torr of source pressure. From the thermodynamic and kinetic results, we can calculate that at $T = 436°K$ $K = 11.8$, $k_f = 5.7 \times 10^{-12}$ cm^3/(mol sec), $k_r = 0.5 \times 10^{-12}$ cm^3/(mol sec), and $K' = 0.14$ for the 1.17% isopentane mixture. We can now calculate the time dependence of the ion ratio, B^+/A^+, expressed as a percentage of the equilibrium ion ratio, K', by the use of eq 7. In this calculation we assume that A_0^+ and B_0^+, the initial normalized ion intensities, are equal to the fraction of the corresponding neutral in the reaction mixture. In Figure 4 we have plotted per cent K' vs. reaction time at 1.0, 2.0, and 3.0 Torr of source pressure. The calculated residence time using the complete Langevin treatment[16] for the $tert$-butyl ion in isobutane at $T = 436°K$ and $E/P = 5$ V/(cm Torr) (which applies to our previous continuous study[1]) is 32.4 μsec. Meisels[17,18] has shown that experimentally determined residence times are significantly longer than those calculated using Langevin drift theory. If we correct the calculated residence time similarly[19] by assigning the $tert$-butyl and $tert$-pentyl ions a residence time of 50 μsec, then from Figure 4 at 3 Torr of source pressure the reaction has proceeded to 0.85 K'. Given the uncertainty in our estimate of the average residence time, we believe it reasonable to conclude that equilibrium was attained for practical purposes at 3 Torr and that reliable thermodynamic values were obtained.

A particularly interesting aspect of our results is our finding (see Table I) of a negative temperature coefficient for the rate of the forward component of reaction 1. The temperature dependence of bimolecular ion-molecule reactions involving the transfer of massive particles in reactions with very small or zero activation energies has not been investigated or observed previously, especially for reactions involving species of the degree of complexity of the reactants investigated in this study. However, a small number of bimolecular ion–molecule electron transfer reactions exhibiting a negative temperature dependence have been reported previously.[20-24] In all of the reported cases reactions

(9) A. Good, D. A. Durden, and P. Kebarle, *J. Chem. Phys.*, **52**, 212 (1970).
(10) A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 7627 (1972).
(11) M. A. French, L. P. Hills, and P. Kebarle, *Can. J. Chem.*, **51**, 4561 (1973).
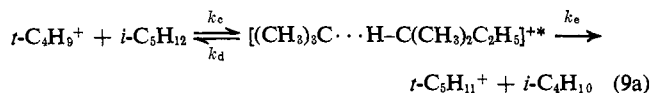(12) A. Good, *Trans. Faraday Soc.*, **67**, 3495 (1971).
(13) D. K. Bohme, D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, *J. Chem. Phys.*, **51**, 863 (1969).
(14) G. Porter, *Discuss. Faraday Soc.*, No. **33**, 198 (1962).

(15) Reference 1, Figure 1.
(16) E. W. McDaniel, "Collison Phenomena in Ionized Gases," Wiley-Interscience. New York, N. Y., 1964, Chapter 9.
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(18) C. Chang, G. J. Sroka, and G. G. Meisels, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 367 (1973).
(19) Meisels in ref 17 determines that $t_{exptl} = 1.7 t_{calcd}$ for CH$_5^-$ in CH$_4$.
(20) N. G. Adams, D. K. Bohme, D. B. Dunkin, and F. C. Fehsenfeld, *J. Chem. Phys.*, **52**, 1951 (1970).
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(23) E. E. Ferguson, D. K. Bohme, F. C. Fehsenfeld, and D. B. Dunkin, *J. Chem. Phys.*, **50**, 5039 (1969).
(24) D. B. Dunkin, F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, *J. Chem. Phys.*, **49**, 1365 (1968).

between a monatomic and diatomic or between two diatomic species were involved, and the negative temperature dependence was relatively small[20,22] (approximately $T^{-1/2}$).

The detailed mechanism of the forward processes in reaction 1 may be written as

$$t\text{-}C_4H_9^+ + i\text{-}C_5H_{12} \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [(CH_3)_3C\cdots H\text{-}C(CH_3)_2C_2H_5]^{+*} \overset{k_e}{\longrightarrow}$$

$$t\text{-}C_5H_{11}^+ + i\text{-}C_4H_{10} \quad (9a)$$

In generalized notation the reaction is

$$A^+ + BH \underset{k_d}{\overset{k_c}{\rightleftharpoons}} (BHA^+)^* \overset{k_e}{\longrightarrow} products \quad (9b)$$
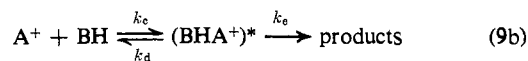
Here $(BHA^+)^*$ is the energized collision complex formed in the ion–molecule collision of A^+ and BH, and k_e is the rate constant for the decomposition of $(BHA^+)^*$ to the products via an activated transition complex in which the proper amount of energy is concentrated in the reaction coordinates.

It has been suggested[25,26] that such reactions may be treated in an approximate way using an expression for the rate of reaction of a complex consisting of S coupled oscillators. This type of treatment appears to be the only one given in the literature to date for gaseous ionic reactions with negative temperature coefficients, and thus we have investigated its applicability to our results. Applying this treatment to our system gives the expression

$$k_f = k_c k_e t_0 (D/akT)^{S-1} \quad (10)$$

for the rate constant for our over-all forward process. Here D represents the dissociation energy of the complex, t_0^{-1} is a characteristic frequency, a is a constant, and S is the number of effective degrees of freedom.

Equation 10 permits a determination of $S - 1$ from a plot of ln k_f vs. ln T. A plot of these quantities for our data is given in Figure 5, and it may be seen that the plot is nicely linear over the temperature range studied. The slope is -2.89, which to our knowledge is the largest negative temperature dependence which has been observed in bimolecular ion–molecule reactions. This slope corresponds to ≈ 4 active oscillators as derived from eq 10, which is very much smaller than the number of internal degrees of freedom in the reaction complex (84).

This difference may be the result of the possibility that only the low-frequency librations of the complex are of significance in the decomposition of the complex. Alternatively, it may be that back reaction of the complex is also temperature dependent and should be represented by an equation of the form of eq 10. If this is so, the experimentally determined number of degrees of active oscillators would be the difference between the number of oscillators coupled to the forward and reverse modes of reaction of the intermediate complex. Beyond these considerations, we are not clear as to what extent the basic assumptions about the decomposition of the complex may be applicable to our system. Since the treatment of our data by eq 10 yields equivocal results, we shall also apply the Eyring transition state theory to the forward process in reaction 1.

In most gas phase reactions the effect of preexpo-

(25) E. E. Ferguson, ref 8, Chapter 8.
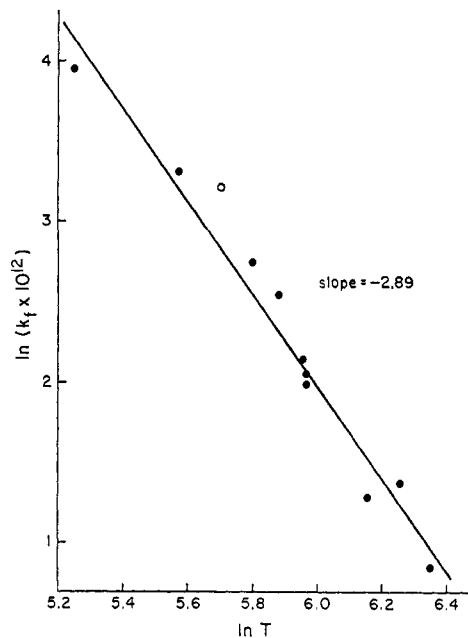(26) R. Wolfgang, *Accounts Chem. Res.*, **3**, 48 (1970).

Figure 5. Temperature dependence of k_f. Solid circles present data from pulse experiments; open circle taken from ref 8.

nential terms on the temperature coefficient is masked by the much stronger influence of the activation energy. As was shown by Gershinowitz and Eyring[27] in their treatment of termolecular reactions, however, in the absence of an activation energy the temperature dependence of the partition functions can result in a substantial negative temperature dependence of the reaction rate.

Using transition state theory, the rate constant for the forward component of reaction 1 may be written as

$$k_f = C \times$$

$$\frac{Q_{tr}^{\ddagger} Q_{rot}^{\ddagger} Q_{vib}^{\ddagger} Q_{el}^{\ddagger}}{(Q_{tr}Q_{rot}Q_{vib}Q_{el})_{t\text{-}C_4H_9^+}(Q_{tr}Q_{rot}Q_{vib}Q_{el})_{i\text{-}C_5H_{12}}} \frac{kT}{h} e^{-E_0/RT}$$

$$(11)$$

Here C is the transmission coefficient and Q's are the appropriate partition functions for the activated complex and reactants. The temperature dependence of the vibrational and electronic partition functions may be assumed to be sufficiently small to be neglected. The partition functions of the internal rotations that remain unchanged upon the formation of the transition complex cancel out in eq 11. Separating all the temperature-independent terms in eq 11 and labeling the origins of the temperature-dependent terms, eq 11 may be written as

$$k_f = \alpha C \frac{kT}{h} e^{-E_0/RT} \times$$

$$\frac{(T^{3/2})_{tr}(T^{3/2})_{rot}}{(T^{3/2})_{tr}^{t\text{-}C_4H_9^+}(T^{3/2})_{tr}^{i\text{-}C_5H_{12}} \times (T^{3/2})_{rot}^{t\text{-}C_4H_9^+}(T^{3/2})_{rot}^{i\text{-}C_5H_{12}}(T^{r/2})_{int\ rot}} \quad (12a)$$

$$k_f = \frac{\alpha Ck}{h} (T^{-(2+(r/2))}) e^{-E_0/RT} \quad (12b)$$

where r is the number of internal rotations that are con-

(27) H. Gershinowitz and H. Eyring, *J. Amer. Chem. Soc.*, **57**, 985 (1935).
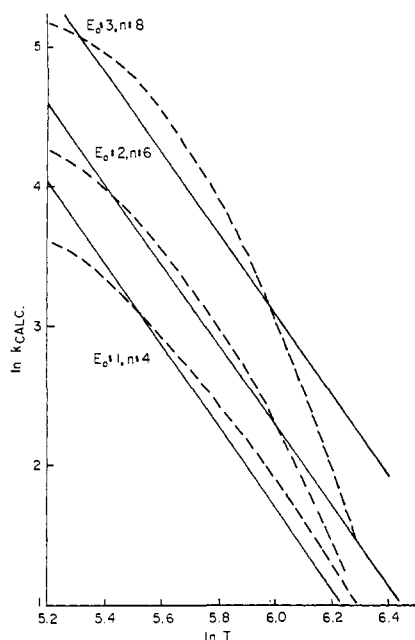
Figure 6. Several plots of $\ln k_{\text{calcd}} = \ln (A'T^{-n}e^{-E_a/RT}) = C' - n \ln T - E_a/RT$ $vs.$ $\ln T$, for the temperature range $200 \leq T \leq 600°K$, for $E_a = 1, 2,$ and 3 kcal/mol. For a given value of E_a, n is selected such that the hypothetical plot (- - -) will best approximate the experimental plot (—). The several pairs of lines (- - - and —) are arbitrarily separated on the drawing for the sake of clarity. The results illustrate that for hypothetical activation energies >2 kcal/mol no combination of E_a and n can yield a curve that acceptably approximates both the slope and the linearity of the experimental plot.

verted to torsional oscillations in the transition complex. For simplicity it is assumed here that these torsional oscillations are of high enough frequency that they will not contribute a significant temperature dependence to the transition complex, and thus no terms corresponding to these oscillators appeal explicitly in eq 12a and 12b. If this assumption about the torsional oscillators frequencies is not valid, temperature terms approaching a linear T dependence will appear in eq 12a for each low-frequency oscillator.

The linearity exhibited by the plot of $\ln k_f$ $vs.$ $\ln T$ in Figure 5 constitutes evidence that the exponential term in eq 12b is not operative, presumably because $E_0 = 0.$[28] Then the negative temperature dependence of the forward rate constant results from the transformation of rotational and translational degrees of freedom in the reactants to vibrational degrees of freedom in the transition complex. Examination of space filling models of the transition complex $(CH_3)_3C\cdots H\cdots C(CH_3)_2C_2H_5^+$ shows that up to six internal rotational modes may become hindered upon the formation of a tightly bound

(28) We wish to note that E_0 in eq 11 and 12 includes the additional zero-point energy of the vibrations created upon the formation of the transition complex. In principle, this term could introduce a positive activation energy for the formation of the complex and, consequently, for the rate constant of the transfer process. However, it is likely that any such term is more than counterbalanced by the energy released upon the formation of the ion–molecule association complex so that experimentally one finds $E_0 = 0.$ This point was originally made by one of the referees for this paper.

complex. Our result of $d \ln k_f/d \ln T \approx -3$ taken in conjunction with eq 12b suggests that only two internal rotations are lost upon the formation of the actual activated complex in the present reaction.

Although the linearity of the plot of $\ln k_f$ $vs.$ $\ln T$ (Figure 5) does not suggest the presence of an activation energy, it is worthwhile to determine the extent to which an activation energy may be ruled out on the basis of the experimental data. For this purpose we used the hypothetical equations

$$k = A'T^{-n}e^{-E_a/RT} \tag{13a}$$

$$\ln k = \ln A' - n \ln T - E_a/RT \tag{13b}$$

to calculate $\ln k$ as a function of T. We arbitrarily assumed the values of activation energy to be 1, 2, 3, ... kcal/mol, and for each activation energy we found the value of n which gave the plot of eq 13b most closely approximating the experimental plot of $\ln k$ $vs.$ $\ln T$. The results are illustrated in Figure 6, which shows that for activation energies larger than 2 kcal/mol no combination of activation energies and preexponential factors can yield an acceptable curve that approximates both the slope and the linearity of the experimental plot in Figure 5. Consequently, the observed temperature dependence cannot result from a compensatory combination of a strongly temperature-dependent term in the preexponential factor and a significant activation energy. Thus, as a conservative estimate, the presence of an activation energy larger than 2 kcal/mol may be ruled out by the experimental findings, although we think that the most reasonable interpretation of Figure 5 leads to a much smaller activation energy, namely, zero or very small. If an activation energy of 2 kcal/mol applied, the data would indicate the presence of a T^{-6} term in the preexponential factor and the loss of eight internal rotations on the formation of the association complex (from eq 12b). Thus the range of values of E_0 which is compatible with our experimental data ($0 \leq E_0 \leq 2$ kcal/mol) corresponds to the loss of two to eight internal rotations. The maximum loss estimated from models is six, and thus the guessed and calculated losses agree. This is encouraging, but the state of knowledge about the structures of the transition complex does not justify a more detailed speculation about it at the present time.

In conclusion, we think that the investigation of the temperature dependence of ion–molecule reactions involving small or zero activation energies constitutes a method for studying the bonding and energy distribution in a reaction complex. The investigation of reactions of this type may provide both an incentive for the further development of kinetic theories relating to the values of preexponential factors and their temperature dependence and a facile testing ground for such theories.