respectively. From the emissive phase pattern obtained by means of CIDEP of the anions at 77 and 4.2 K, the germyl and stannyl radicals are tentatively considered to be produced through the triplet state of the germyl and stannyl anions.

Experimental Section

^1H NMR spectra were recorded on a Varian FT 80A, with tetramethylsilane as internal standard. GC–mass spectra were obtained with a JEOL JMS-DX 303 mass spectrometer. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. UV and visible spectra were recorded on a Shimazu UV-180 and a Hitachi U-3400 spectrometers. Gas chromatography was performed on a Shimazu GC-6A and -8A with 2-m 20% SE-30 and 2-m 30% Apiezon L columns. Liquid chromatograph was performed on a JASCO TWINCLE with Finepak SIL C_{18} column.

Materials. Ph_3SnCl was commercially available. $PhMe_2SiCl$, bp 112–115 °C (36 mmHg),[30] $Ph_2MeSiCl$, bp 105–108 °C (0.9 mmHg),[31] Ph_3SiCl, mp 95 °C,[32] $PhMe_2GeCl$, bp 115–124 °C (24 mmHg),[33] $Ph_2MeGeCl$, bp 135–140 °C (1 mmHg),[28] and Ph_3GeCl, mp 114 °C,[34] were prepared as described in the cited references.

Solvent. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen.

Absorption Spectra of the Anions. The phenyl-substituted group 4B element-centered anions are extremely sensitive to oxygen and moisture. A closed absorption cell was used to observe the absorption spectra of these anions.[35] The absorption cell apparatus used in these studies consists of a 1-cm quartz absorption cell sealed to a side arm of a round-bottom flask. The apparatus was connected to a high-vacuum system for alternate degassing and flushing with argon. Access to the flask was through a second side arm closed by a rubber syringe cap. The anions were prepared by contact with lithium metal with the corresponding chlorides in highly degassed THF solvent in the round-bottom flask. The concentrations of the anions were determined as follows. The anions were taken out via a Hamilton syringe, protected by an argon atmosphere. A slight positive argon pressure was maintained when piercing the rubber cap. The anion was hydrolyzed with water to produce the corresponding hydrides. The concentrations of hydrides produced were estimated as those of the anion.

Photochemical Reactions of the Anions. The THF solution containing the anion ($0.5–1.0 \times 10^{-3}$ M) was sealed in vacuum in a quartz tube connected to a Pyrex tube as the upper part. The irradiation of the sample was carried out using a Xe lamp (1 kW) of USHIO Electric Co., Type UXL-1000 D-0, Pyrex cylinder lens, and a 10-cm water cell filter. After irradiation, the reaction mixture was hydrolyzed with water. The organic layer was dried over anhydrous sodium sulfate. The products were analyzed by gas chromatography, liquid chromatography, and GC–mass spectrometry.

Time-Resolved Optical Absorption. The samples contained in quartz cells with an optical length of 5 mm were degassed by four freeze–pump–thaw cycles. The concentration of the anion was ca. $1.0–2.0 \times 10^{-4}$ M. Laser-photolysis experiments were performed at room temperature by using the fourth harmonic (266 nm) of a Quanta-Ray DCR-1 Nd:YAG laser as an exciting light source. The laser pulse width was ~5 ns. The details of the laser-photolysis apparatus were published elsewhere.[20] The signals were monitored by a Tektronix 485 oscilloscope (350 MHz) and recorded by an Iwatsu DM-901 digital memory (10 ns/point, 8 bit) controlled by an NEC PC 8801 microcomputer.

ESR Measurement at Room Temperature. ESR spectra were taken on a Varian E-109 spectrometer at room temperature. About $2.0\text{-}3.0 \times 10^{-3}$ mol of the anion in THF was sealed in vacuo, in a Pyrex tube (ϕ 10 mm), carrying a quartz side arm (ϕ 4 mm). The irradiation was carried out by using a Xe lamp (1 kW) of USHIO Electric Co., Type UXL-1000D-0, and a Pyrex lens or a Molectron UV 14 nitrogen laser.

ESR Measurements at 77 K. ESR spectra were taken on a Varian E-109 spectrometer with minor modification. Two cavities were employed: a multipurpose E-231 cavity and a bimodal E-236 cavity, the latter having been used to set up the condition in which the microwave magnetic field was parallel to the external field. A Molectron UV 24 nitrogen laser was used for the excitation of the degassed samples with a repetition rate of 20 Hz. An NF BX-531 boxcar integrator was used in a fixed gate mode to record the time-resolved ESR spectra. The details of the apparatus were published elsewhere.[36]

ESR Measurement at 4.2 K. Transient ESR spectra were taken on a JEOL-FE3X ESR spectrometer. The ESR spectra were taken by feeding the output of the preamplifier of the microwave unit to a PAR 160 boxcar integrator whose gate was open at 1.5 μs after the laser excitation. A Lumonics TE 861 M excimer laser with XeCl fill was used as the exciting light source. The details of the apparatus were published elsewhere.[37]

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Hyperconjugation: Equilibrium Secondary Isotope Effect on the Stability of the *tert*-Butyl Cation. Kinetics of Thermoneutral Hydride Transfer

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Abstract: The thermochemistry of the hydride transfer equilibrium $(CD_3)_3C^+ + (CH_3)_3CH \rightleftarrows (CH_3)_3C^+ + (CD_3)_3CH$ was measured by pulsed high-pressure mass spectrometry. Measurements over a wide temperature range, 145–600 K, allowed an accurate determination of the values: $\Delta H° = -0.57 \pm 0.02$ kcal/mol; $\Delta S° = -0.57 \pm 0.08$ cal/(mol·K); $\Delta G°_{298} = -0.40 \pm 0.07$ kcal·mol; and $K_{298} = 1.97 \pm 0.20$. The direction of the observed isotope effect is consistent with C–H bond weakening in the ion due to hyperconjugation. The kinetics of the reaction show a slow rate and a large negative temperature coefficient, with $k_{300} = 0.36$ and $k_{600} = 0.00625 \times 10^{-10}$ cm^3 s^{-1}, i.e., reaction efficiencies of about 0.03 to 0.0005. The observed negative temperature coefficient, $k = AT^{-5.8}$, is larger than those observed for more exothermic hydride transfer reactions. The approach to collision rate is abrupt.

Hyperconjugation interactions between charged centers and alkyl substituents are assumed to occur in alkylated ions. For example, hyperconjugation in the carbonium ions $C_2H_5^+$, $i\text{-}C_3H_7^+$, and $t\text{-}C_4H_9^+$ arises as a filled π symmetry orbital on methyl groups

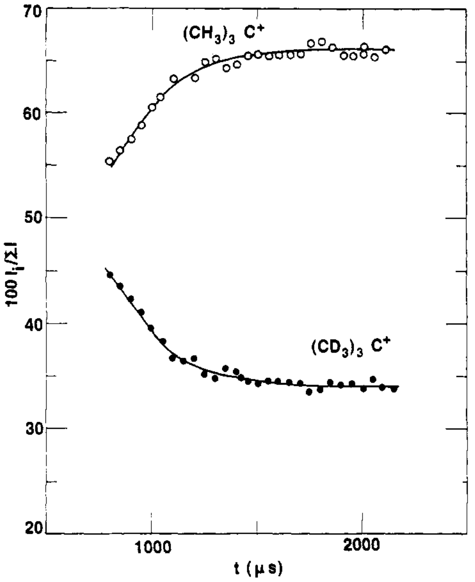

Figure 1. Approach to equilibrium in the exothermic direction. A mixture of 0.018% $(CH_3)_3$ and 0.018% $(CD_3)_3CH$ in CH_4 at 1.84 Torr, 311 K.

interacts with the empty p orbital on the carbonium center, resulting in electron withdrawal from the methyl group.[1] This weakens the methyl C–H bonds in the ions versus the corresponding neutrals and decreases their vibrational frequencies and zero-point energies, resulting in the stabilization of the ions. A similar effect occurs with C–D bonds in the deuteriated methyl groups; however, these have lower zero-point energies in the neutrals and the reduction of their zero-point energies in going to the ions is also smaller than that of C–H bonds. Therefore, the stabilizing effect of hyperconjugation is smaller in the deuteriated ion, and reaction 1 should be exothermic.

$$(CD_3)_3C^+ + (CH_3)_3CH \rightleftarrows (CH_3)_3C^+ + (CD_3)_3CH \quad (1)$$

This secondary isotope effect is a direct test of hyperconjugation, and the *tert*-butyl cation is considered a prototype example. However, equilibrium 1 has not been measured directly. The measurement is difficult because isotope effects on the energies of the ions are small, less than 1 kcal/mol. Such small effects can be complicated by solvation effects and also by possible entropy contributions to the equilibrium. To measure unequivocally the solvent-free isotope effect on ion energies, we carried out measurements on equilibrium 1 in the gas phase over a wide temperature range, which allows an accurate measurement of ΔH°_1 in the absence of solvent effects.

Approach to equilibrium in reaction 1 yielded also the kinetics of this hydride transfer reaction over a wide temperature range. This is of interest because we have previously observed large negative temperature coefficients in hydride transfer reactions, and we found correlations between the exothermicities and rate constants in these slow reactions.[2] The extension of these correlations to near-thermoneutral reactions is of interest because in some cases, such as proton and electron transfer reactions, a drop in the rate constants is observed as thermoneutrality is approached.[3] The present reaction makes it possible to observe a slow hydride transfer reaction near the thermoneutral limit.

Experimental Section

The measurements were performed on the NBS pulsed high-pressure mass spectrometer, using standard methods.[4]

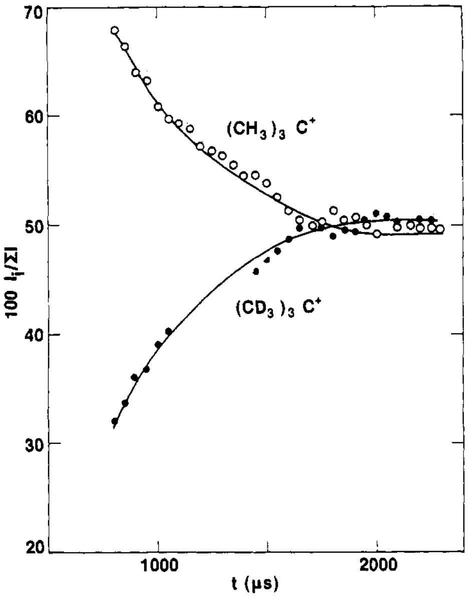

Figure 2. Approach to equilibrium in the endothermic direction. A mixture of 0.0131% $(CH_3)_3CH$, 0.0253% $(CD_3)_3CH$, and 2% $(CH_3)_4C$ in CH_4 at 0.88 Torr, 299 K.

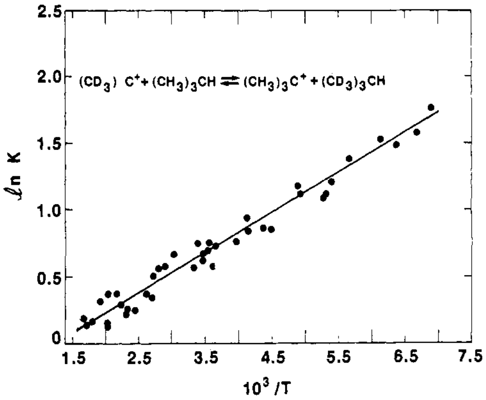

Figure 3. van't Hoff plot for the isotope exchange reaction 1. Note that the thermochemical values are not derived directly from the plot, the ΔH° is derived from the slope and ΔS° from the replicate values for $\Delta S^\circ(298)$ as explained in the text.

Reaction mixtures of $(CH_3)_3CH$ and $(CD_3)_3CH$, neat or in carrier gases, were allowed to flow to the ion source. The gas mixtures were ionized by 1-ms pulses of 500-eV electrons. The ions diffusing out of the source were observed for 2–4 ms after the ionizing event.

In one set of experiments, a mixture of 1:1 of the light and deuterated components was employed. Equilibrium was observed in the neat mixture, and also in a mixture diluted to 2.7% of each component in CH_4 as carrier gas. A test by the diluted system is important since chemical ionization in this system minimizes the possible presence of $(M - 2H)^+$ type olefin ions that may form by direct ionization. In this reaction system, $(CH_3)_3C^+$ and $(CD_3)_3C^+$ are generated at about equal concentrations by initial chemical ionization processes, and the equilibrium in reaction 1 is approached in the forward, exothermic direction as written (Figure 1).

In a second set of experiments, a mixture of 1:2 $(CH_3)_3CH$ and $(CD_3)_3CH$ was prepared. Equilibrium was measured in the neat mixture and also in a mixture diluted to 1%, 0.3%, and 0.1% in the carrier gas. In these experiment, 4–10% neopentane, $(CH_3)_4C$, was also added. In this case, the initial ion produced from neopentane was $(CH_3)_3C^+$, and equilibrium 1 was approached from the reverse, endothermic side (Figure 2) (a nonreactive $C_5H_{11}^+$ ion was also observed). Rate constants were measured mainly in this mixture. To further confirm the results, we also studied D^- transfer equilibrium in a reaction mixture of 0.2% $(CH_3)_3CD$ and 0.5% $(CD_3)_3CD$, with 2% $(CD_4)_4C$ in CH_4 as the carrier gas.

The equilibrium constants at 298 ± 10 K were measured in all the mixtures and gave values of $K(298) = 1.8$ to 2.1, corresponding to $\Delta G^\circ_{298} = -0.48$ to -0.34 kcal/mol. The consistency of K with varying source conditions was also confirmed by varying the total source pressure in the range 0.4–2.0 Torr.

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Results and Discussion

1. Equilibrium Hyperconjugation Isotope Effects. van't Hoff plots for equilibrium 1 were obtained over a temperature range of 145–600 K (Figure 3). Over this wide temperature range K_1 varies from 1.1 to 5.5, and this allows an accurate determination of the slope of the van't Hoff plot and therefore $\Delta H°$. From the two series of measurements (see Experimental Section) we obtain $\Delta H°_1 = -0.55 \pm 0.04$ and -0.59 ± 0.03 kcal/mol (error based on standard deviation of slope). Measurements of the equilibrium constant at 298 K in five reaction mixtures of different compositions gave $\Delta G°_{298} = -0.40 \pm 0.07$ kcal/mol. From these results we obtain, in summary

$$(CD_3)_3C^+ + (CH_3)_3CH \rightleftarrows (CH_3)_3C^+ + (CD_3)CH \quad (1)$$

$$\Delta H° = -0.57 \pm 0.02 \text{ kcal/mol}$$

$$\Delta S° = -0.57 \pm 0.08 \text{ cal/(mol·K)}$$

$$\Delta G°_{298} = -0.40 \pm 0.07 \text{ kcal/mol}$$

$$K_{298} = 1.96 \pm 0.22$$

$\Delta H°$ was also measured for the D^- transfer reaction 2. The result was $\Delta H° = -0.46 \pm 0.06$ kcal/mol, in reasonable agreement with results from reaction 1.

$$(CD_3)C^+ + (CH_3)_3CD \rightleftarrows (CH_3)_3C^+ + (CD_3)_3CD \quad (2)$$

On the average, deuterium substitution increases the energy of the ion by 0.19 kcal/mol per methyl group. In other words, the effect on zero-point energy difference between the a C–D versus C–H bond in the neutral molecule versus the carbonium ion is on the average 0.06 kcal/mol. However, in terms of $\Delta G°$, the effect is only 0.13 kcal/mol per methyl group. This is comparable in absolute magnitude to the effect in $CH_3NH_3^+$, for which $\Delta G°_{298} = 0.13$, and $(CH_3)_3NH^+$, for which $\Delta G°_{298} = 0.10$ per methyl group, was reported.[5] However, unlike the present case, in the amines the equilibrium is exothermic in the direction of the deuteriated ion. This is explained by DeFrees et al.[5] on the basis that in the amines the C–H bond stretching force constants and zero-point energies increase upon ionization (protonation). This happens because electron donation from the nitrogen lone pair into C–H antibonding orbitals weakens the bond in the neutral, and this effect becomes smaller, i.e., less bond-weakening, when the lone pair is protonated. Therefore, the zero-point energies of C–H bonds increase upon ionization. The effect is larger in the light versus heavy compounds, resulting in an increased *destabilization* of the light versus heavy ion. In contrast, in the present carbonium ion, the hyperconjugation effect results mainly from electron withdrawal from C–H bonding orbitals by the charged carbonium ion center. This causes a decrease in the zero-point energies of C–H bonds upon ionization. Again, the effect is larger in the light versus heavy compounds, but now it is a stabilizing effect. Therefore, the result here is the increased *stabilization* of the light versus heavy ion. The observed direction of the effect in the *tert*-butyl ion, which is confirmed in the present measurements, and its opposite direction to that in ammonium ions are therefore consistent with the theoretical predictions about hyperconjugation.[1,5]

The free energy change of reaction 1 was calculated by ab initio methods to be between −0.04 and 0.02 kcal/mol per methyl group.[1] The present experimental results show a significantly larger effect. However, the present results are consistent with solvolysis kinetic results, which showed that $(CD_3)_3Cl$ solvolyzes 2.4 times more slowly than the hydrogenated compound, which suggests that the activation energy needed to reach the carbonium ion intermediate is smaller in the light compound.[6] Further, the existence of an isotope effect in this direction is also supported by results on X^- (X = halogen) transfer equilibria analogous to reaction 1, which show $\Delta G°_{300}$ values between 0.23 and 0.58 kcal/mol.[7]

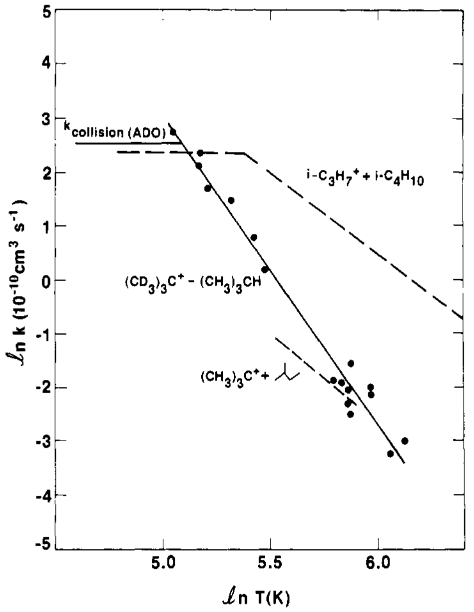

Figure 4. Temperature dependences of slow ion–molecule reactions. Note the sharp approach to collisionally limited kinetics.

Experimentally, the *tert*-butyl cation is uniquely suitable for the present type of measurements for several reasons. First, clustering in this system is negligible above about 150 °C, which allowed measurements over a wide temperature range. Second, in this system only one hydrogen can be exchanged, and this avoids complications with more exchangeable hydrogens such as in ethyl at propyl ions, as will be discussed presently.

It must be noted that the system must contain the correct mixture of deuteriated species for true equilibrium. For example, reaction 1 cannot be studied in a mixture of $(CH_3)_3CH$ and $(CD_3)_3CD$, because hydride exchange will produce also a different neutral, $(CD_3)_3CH$.

$$(CD_3)_3C^+ + (CH_3)_3CH \rightarrow (CH_3)_3C^+ + (CD_3)_3CH \quad (3)$$

If this neutral is only produced by ionic reactions, it will be a negligible component in the mixture, and the reverse reaction will not occur. Therefore, a mixture of $(CH_3)_3CH$ and $(CD_3)_3CD$ would not allow true equilibrium.

In reactions containing more than one acidic hydrogen, this problem can be overwhelming. For example, consider reaction 4

$$(CH_3)_2CH^+ + (CD_3)_2CD_2 \rightleftarrows (CD_3)_2CD^+ + (CH_3)_2CHD \quad (4)$$

In this case, reverse reaction between the products can yield not only the reactant neutral but also $(CD_3)_2CHD$. For similar reasons, a correct equilibrium system would have to contain known amounts of all of $(CH_3)_2CH_2$, $(CH_3)_2CHD$, $(CH_3)_2D_2$, $(CD_3)_2CH_2$, $(CD_3)_2CHD$, and $(CD_3)_2CD_2$. In the analogous system in ethane, seven differently deuteriated neutrals must be present. These problems make hydride transfer equilibrium isotope studies difficult in any but tertiary hydrocarbons.

2. Kinetics of Near-Thermoneutral Hydride Transfer. Kinetics were obtained from approach to equilibrium 1, using standard reversible kinetics methods. Most rate constants were obtained from systems where the $(CH_3)_3C^+$ ion was generated from chemical ionization of $(CH_3)_4C$. In most cases $(CH_3)_4C$ was present in excess of the isobutane reactants. In these systems, $(CH_3)_3C^+$ is produced first, and equilibrium 1 is approached in the reverse, endothermic direction (Figure 2).

As other slow exothermic hydride transfer reaction rate constants, k_1 exhibits a large negative temperature coefficient. The

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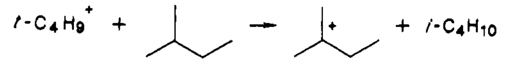
temperature dependence of the rate constant is plotted as ln *k* versus ln *T* in Figure 4. Least-squares fitting to the plot gives $k_{300} = 0.36$ and $k_{600} = 0.0062 \times 10^{-10}$ cm^3 s^{-1}. The temperature dependence of the reaction can be expressed as $k = AT^{-5.8}$.

Figure 4 compares the kinetics of reaction 1 with several other hydride transfer reactions. The most closely similar reactants are of reaction 5. As Figure 4 shows, this reaction has a similar rate constant to reaction 1 at high temperatures, but a smaller negative temperature coefficient ($T^{-3.2}$). Since $\Delta H^\circ_5 = -3.4$ kcal/mol, the relation between the temperature coefficients agrees with a trend noted before, of increasingly negative temperature coefficients with decreasing exothermicity.[2] In fact, the negative temperature coefficient of reaction 1 is one of the largest observed, and similar to those of other near-thermoneutral reactions, such as 6 and 7, whose $\Delta H^\circ = -1.3$ and -1.5 kcal/mol, and whose temperature coefficients are $T^{-5.4}$ and $T^{-6.0}$, respectively.



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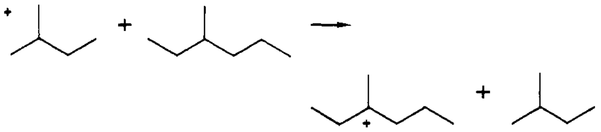

(7)

Another interesting feature of reaction 1 is the approach to collision rate with decreasing temperature. We observe that ln *k* remains linear versus ln *T* as the collision limit is approached, and the limit is reached abruptly. Similar behavior was observed in several other hydride transfer reactions (see an example in Figure 2).[2] Furthermore, similar behavior was observed in such diverse reactions as CH_3^+ transfer from $(CH_3)_2Cl^+$ to $(CH_3)_2O$ and $(C_2H_5)_2O$[8] and, recently, in F^- transfer from SF_6^- to SOF_4.[9] In contrast to the observed behavior, all plausible mechanisms predict a gradual approach from collision-limited fast kinetics to tight-complex limited slow kinetics.

It is also remarkable that the rate constant does reach unit collision efficiency in the present near-thermoneutral reaction involving fairly hindered reactants. So far, collision rate was reached at accessibly low temperatures only in reactions of the primary carbonium ion $C_2H_5^+$ and the secondary carbonium ion i-$C_3H_7^+$, in reactions that were exothermic by tens of kcal/mol. For reactions with a small exothermicity, $-\Delta H^\circ < 2$ kcal/mol, even proton transfer and charge transfer reactions are usually slower than collision rate at 300 K.

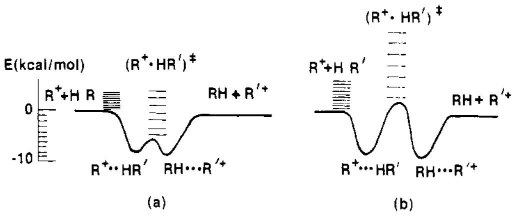

Figure 5. Potential energy surfaces for slow hydride transfer reactions. The negative temperature coefficient shows that the barrier is (a) below or (b) only slightly above the energy of the reactants. The well depth is drawn to scale.

The present results clarify some details about the potential energy surface for hydride transfer reactions, as follows. The slow kinetics of ion–molecule reactions is usually related to a low-entropy transition state according to the transition state theory (at the high-pressure limit),[2] or a transition state with a low density of states according to the double-well model[10] (Figure 5). Both also predict a negative temperature coefficient. A negative temperature coefficient is easily understood if the barrier between the two wells is below the energy of the reactants (Figure 5a). However, a negative temperature coefficient due to large entropy effects could mask a small positive temperature coefficient if the barrier is slightly above the energy of the reactants (Figure 5b). In this case, however, at low temperatures the energy barrier would slow down the reaction, and it could not reach the collision limit. Therefore, the present results show that the energy barrier, if present, is smaller than the depth of the energy well, i.e., smaller than the association energy in $R^+{\cdot\cdot}HR'$ (Figure 5).

To quantify this finding, we measured the depth of the energy well, by examining the equilibrium

$$(CD_3)_3C^+ + (CD_3)_3CH \rightleftarrows (CD_3)_3C^+{\cdot}(CD_3)CH \qquad (8)$$

We find that $\Delta G^\circ_8(148) = -4.1$ kcal/mol. For such weak clustering reactions, the entropy is usually between the limits $-25 < \Delta S^\circ < -15$ cal/(mol·K).[11] Therefore, from $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$ we obtain $\Delta H^\circ_8 = -7 \pm 0.7$ kcal/mol. (Note that at low temperatures the $T\Delta S^\circ$ term is small, and ΔH° can be estimated quite accurately from ΔG° with only a rough estimate of ΔS°.) Using this result, we can conclude that the intrinsic barrier (i.e., the barrier for symmetry reactions) for hydride transfer between carbonium ions and hydrocarbons is smaller than 7 kcal/mol.

The present observations suggest that, possibly, most exothermic reactions that are slow because of entropy effects in the reaction complex can reach unit efficiency at sufficiently low temperatures.

Acknowledgment. I thank Dr. D. J. McLennan for suggesting these measurements and Dr. W. Hehre for helpful discussions.

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