Proton-Transfer Reactions Involving Alkyl Ions and Alkenes. Rate Constants, Isomerization Processes, and the Derivation of Thermochemical Data

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Abstract: Rate constants and mechanisms have been determined for proton-transfer reactions of the type $AH^+ + M \rightleftarrows MH^+ + A$, where A is propylene, isobutene, *trans*-2-butene, cyclopentene, and cyclohexene. In order to avoid competing side effects the AH^+ reactant ions are generated in alkanes and alkyl halides. It is observed that the rate constants for exothermic direct proton transfer reactions, from AH^+ to M or from MH^+ to A, are equal to the collision rate only when the total rotational, vibrational, and electronic entropy change associated with the reaction is positive, and when the exothermicity of the reaction exceeds 2–4 kcal/mol. On the basis of rate constants in the forward and reverse direction for multiple reaction pairs, internally consistent values are obtained for the proton affinities of propylene, isobutene, and cyclopentene. Protonation of *trans*-2-C_4H_8 by H_3O^+ ($\Delta H_{Rn} = -10$ kcal/mol, 41.84 kJ/mol) yields *sec*-$C_4H_9^+$ exclusively. However, carbon skeletal rearrangement to the *t*-$C_4H_9^+$ configuration becomes important when the ΔH of the proton transfer is <10 kcal/mol. The experimental evidence indicates that the isomerization occurs before departure of $C_4H_9^+$ from the reaction complex. The isomerization process which also occurs upon collision of *sec*-$C_4H_9^+$ with polar molecules is dependent on the dipole moment of M. For *sec*-$C_4H_9^+$/*trans*-2-C_4H_8 and c-$C_6H_{11}^+$/c-C_6H_{10}, where these isomerization processes are especially important, thermochemical information is derived from qualitative considerations of trends in reaction rates. Scales of relative proton affinities of the olefins and relative heats of formation of the alkyl ions are derived and compared with data on absolute heats of formation. Taking a value of $\Delta H_f(t\text{-}C_4H_9^+) = 162.1 \pm 0.8$ kcal/mol (678.2 kJ/mol), the values derived for the heats of formation in kcal/mol (1 kcal/mol = 4.184 kJ/mol) follow: *sec*-$C_3H_7^+$, 184.5 ± 2.1; c-$C_5H_9^+$, 183.8 ± 1.9; *sec*-$C_4H_9^+$, 176.7 ± 2.9; c-$C_6H_{11}^+$, 171 ± 3; c-$C_5H_8CH_3^+$, 164.2 ± 1.7; *t*-$C_5H_{11}^+$, 154.6 ± 2.0; c-$C_6H_{10}CH_3^+$, 152.7 ± 1.7; *t*-$C_6H_{13}^+$, 148.5 ± 1.8 (the last four from an analysis of data from the literature). Heats of formation of some of the corresponding radicals, in kcal/mol, calculated from ionic heats of formation and ionization potential data, follow: C_3H_7, 14.8 ± 2.6; c-C_5H_9, 17.5 ± 2.4; c-C_6H_{11}, ~6; *t*-C_4H_9, 7.6 ± 2.2.

Introduction

In recent years, a great deal of information about the thermochemistry of alkyl ions has been obtained from studies of ion-molecule equilibria.[1] That is, a determination of the equilibrium constant of the reaction

$$A^+ + B \rightleftarrows C^+ + D \qquad (1)$$

leads to a value of the free-energy change of the reaction, ΔG, at a particular temperature, and, if the equilibrium constant is determined as a function of temperature, the enthalpy change of the reaction is obtained:

$$-RT \ln K_{eq}(T) = \Delta G = \Delta H - T\Delta S \qquad (2)$$

Such studies of hydride transfer equilibria

$$A^+ + RH \rightleftarrows R^+ + AH \qquad (3)$$

(where A^+ and R^+ are alkyl ions) have generated information about the relative heats of formation of alkyl ions.[2] In other investigations, similar information has been derived from equilibrium constants of proton-transfer reactions involving olefins or cycloolefins:[3]

$$AH^+ + C_nH_{2n}(C_nH_{2n-2}) \underset{k'}{\overset{k}{\rightleftarrows}} C_nH_{2n+1}{}^+(C_nH_{2n-1}{}^+) + A \qquad (4)$$

An inherent limitation of the equilibrium technique for the determination of thermochemical information about alkyl ions is that it cannot be used in a straightforward way for ions which may undergo rearrangements to different structures during or after reaction. Furthermore, proton-transfer equilibria involving olefins are in some cases difficult to establish because of the occurrence of competing reactions such as condensation of the ions with the olefin.

In this article, we will describe experimental results aimed at establishing the relative heats of formation of the *sec*-propyl, *sec*-butyl, *tert*-butyl, cyclopentyl, and cyclohexyl ions through examinations of proton-transfer reactions involving these ions and various comparison bases, or involving the corresponding olefins with proton donors. (Extensive interlocking scales of relative gas-phase basicities of organic compounds are now available for comparison purposes.[3c,d,g]) Although direct equilibrium constant determinations are made wherever possible, the main thrust of this work is in deriving ways of circumventing the difficulties presented by the isomerization of alkyl ions, and the occurrence of competing reactions in systems containing olefins.

In the simplest cases, where isomerization does not have to be considered, an equilibrium constant can be estimated in spite of the occurrence of competing reactions, by measuring the rate constants k and k' (eq 4) under conditions such that the competing channel does not interfere. For example, k' can be measured in the absence of olefin by generating the alkyl ions in other compounds. (This approach will be used to derive the relative proton affinity of propylene.) In other cases (*trans*-2-C_4H_8, c-C_5H_8), where a fraction of the ions resulting from protonation of the olefin rearrange to a more stable structure, it will be shown that, if the two isomeric ions can be distinguished by their reactivity, or lack of reactivity, toward selected reactants, an estimate of the thermochemical properties of the system can be made both from considerations of rate constants k and k' and sometimes from examinations of the extent of isomerization. Finally, when all, or nearly all, of the ions formed by protonation of the olefin (i.e., cyclohexene) undergo rearrangement, certain qualitative considerations allow an estimate of the relative proton affinity of the olefin within wide error limits.

The relative heats of formation of the ions obtained in these experiments will be compared with information derived from recently reported determinations of the adiabatic ionization potentials of the corresponding alkyl radicals:[4]

$$R\cdot \xrightarrow{\mathrm{IP}} R^+ + e^- \qquad (5)$$

Since

$$\Delta H_f(R^+) = \mathrm{IP} + \Delta H_f(R\cdot) \qquad (6)$$

(taking $\Delta H_f(e^-)$ and the heat capacity of the electron to be zero at all temperatures), the relative values of $\Delta H_f(R^+)$ established by the experiments reported here, when combined with the values of the ionization potentials of the radicals, lead to information about the relative heats of formation of the radicals. At this writing the absolute heats of formation of many alkyl radicals (and hence the heats of formation of the corresponding alkyl ions) are still matters of controversy. The condition that both ion and radical heats of formation must conform to the limits set by the relative determinations reported here may aid in the establishment of the values for the absolute enthalpies of formation of these species.

Experimental Section

The experiments were performed using the NBS pulsed ion cyclotron resonance spectrometer which has been described before.[5] The experimental and computational procedures followed in deriving reaction rate constants and equilibrium constants have also been described previously,[5b] as has the procedure for determining the rate constant for reaction of an ion in the presence of an unreactive ion of the same mass,[5c] or for determining the relative abundances of two isomeric ions.[5c,d]

The pressures used in these experiments were in the range 10^{-7}–10^{-5} Torr. The ions were observed at times in the range 10^{-3}–0.5 s.

Discussion

The Scale of Gas-Phase Basicities and Proton Affinities. In the discussion which follows, the equilibrium constants and rate constants, k and k', of reaction 4 will be used to estimate Gibbs free energies of proton-transfer reactions, which in turn will be evaluated in terms of the relative gas basicities of the comparison compounds, M, in order to derive information about the relative proton affinities of the various olefins. In the Appendix are given the experimentally determined[3b-d,f] scales of values of ΔG for the proton-transfer reaction:

$$MH^+ + CH_3COCH_3 \rightleftarrows (CH_3COCH_3)H^+ + M \qquad (7)$$

at 320 and 600 K for many of the reference compounds used in this study. Acetone is chosen as the reference compound for the scale, rather than the more commonly used standard of comparison, ammonia, because (1) there is no rotational entropy change associated with the protonation of acetone[3b] which simplifies the treatment of the data, and (2) the position of acetone in the scale is well established, whereas there is some disagreement about the position of ammonia. This scale may be considered to be a ladder of relative gas basicities (GB), where the gas basicity is defined as the negative of the Gibbs free energy change (ΔG) of the protonation process:

$$M + H^+ \rightarrow MH^+ \qquad (8)$$

The negative of the enthalpy change of this process is the proton affinity.

Proton Transfer Involving i-C_4H_8/t-$C_4H_9^+$. On the basis of a recent study[3b] in which the equilibrium constant of the reaction

$$t\text{-}C_4H_9^+ + CH_3COCH_3 \rightleftarrows (CH_3COCH_3)H^+ + i\text{-}C_4H_8 \qquad (9)$$

was determined as a function of temperature, the position of isobutene in the gas basicity scale (Appendix) has been established. Because the thermodynamic relationships for proton transfer involving i-C_4H_8/t-$C_4H_9^+$ are known, we shall use this case to demonstrate some of the reasoning which will be used to derive thermodynamic information from rate constants for exothermic and endothermic reactions for the protonation of the other olefins. The individually determined rate constants for the proton-transfer reactions

$$t\text{-}C_4H_9^+ + M \rightarrow MH^+ + i\text{-}C_4H_8 \qquad (10)$$

and

$$MH^+ + i\text{-}C_4H_8 \rightarrow t\text{-}C_4H_9^+ + M \qquad (11)$$

are listed in Table I along with the corresponding values of $\Delta H_{\text{reaction}}$ (Table I) where these have been experimentally determined from van't Hoff plots,[3b] or can be estimated from the data given in the Appendix. The reactant t-$C_4H_9^+$ ions were generated in *neo*-C_5H_{12}, so that the occurrence of the reverse reaction 11 did not have to be considered. Rate constants for reaction 11 were measured in mixtures containing low concentrations of i-C_4H_8, continuously ejecting $C_4H_9^+$ to prevent the occurrence of reaction 10.

There are several features of the data in Table I worth noting. First, in the cases for which k_{10} and k_{11} have both been experimentally determined, the ratios k_{10}/k_{11} are in good agreement with the equilibrium constants corresponding to the values of ΔG at this temperature. Second (Table I), the probability that a collision will result in reaction, k/Z (hereafter called the reaction efficiency), is clearly lower for reactions which are close to thermoneutral than for reactions which are more exothermic. It is seen that as reaction 10 or 11 becomes more exothermic the efficiency increases and reaches ~1 for reaction 11 when M = CH_3SH or CH_3CHO (i.e., $\Delta H = \sim -7$ or -8 kcal/mol). (Similar trends of reaction efficiency with ΔH have been seen on many occasions.)[5a,b,8,9] The efficiency of reaction 10, however, does not reach unity for the compounds listed but levels off at values of ~0.7 when the reaction is exothermic by 5 kcal/mol or more. It has been shown[3b] that $\Delta S(t\text{-}C_4H_9^+ \rightarrow i\text{-}C_4H_8) = -1 \pm 0.5$ cal/deg·mol. This value includes changes in external rotational symmetry numbers, the loss of an internal rotation upon deprotonation, and the change in the moments of inertia (−0.3 cal/deg·mol). Thus, for reactions for which the only contribution to ΔS_{rot} will be that associated with the loss of a proton from t-$C_4H_9^+$, $e^{\Delta S(\text{internal})/R} = 0.5$–$0.8$, which suggests that this factor may be directly equated to the reaction efficiency[11,12] when reaction is sufficiently exothermic:

$$k_{10}/Z_{10} \approx e^{\Delta S(\text{internal})/R} \qquad (12)$$

This is not an unreasonable surmisal. The ideal internal entropy change associated with changes in distributions of internal energies ($\Delta S_{\text{internal}} = \Delta S_{\text{rot}} + \Delta S_{\text{vib}} + \Delta S_{\text{elec}}$) for proton-transfer reactions consists mainly of a contribution from the change in rotational symmetry numbers between products and reactants[1,3]

$$\Delta S_{\text{internal}} \approx \Delta S_{\text{rot}} \approx R \ln \frac{(\sigma_{AH^+})(\sigma_B)}{(\sigma_{BH^+})(\sigma_A)} \qquad (13)$$

(where σ_x is the rotational symmetry number associated with a reactant in the proton-transfer reactions $AH^+ + B \rightleftarrows BH^+ + A$) plus any contributions from gain or loss of internal rotations in the reaction. Thus the term $e^{\Delta S(\text{internal})/R}$ is the same as the usual statistical factor invoked in chemical kinetics[10] except for the small contribution from the change in moment of inertia.

It should be emphasized (as shown in the tables) that near-thermoneutral reactions usually show reaction efficiencies lower than those which would be predicted by eq 12.[8,9]

Proton Transfer Involving CH_3CHCH_2/*sec*-$C_3H_7^+$. In Table II are listed the rate constants and reaction efficiencies

Table I. Rate Constants at 315 K and Thermodynamic Parameters for the Reaction

$$t\text{-}C_4H_9^+ + M \underset{k_{11}}{\overset{k_{10}}{\rightleftarrows}} MH^+ + i\text{-}C_4H_8$$

M	$k_{10} \times 10^{10}$, cm^3/molecule·s[f]	k_{10}/Z_{10}[d,e]	$k_{11} \times 10^{10}$, cm^3/molecule·s	k_{11}/Z_{11}[d,e]	K_{eq}: k_{10}/k_{11}	K_{eq}: $e^{\Delta G/RT}$	ΔH_{10} ($-\Delta H_{11}$), kcal/mol	ΔG_{10} ($-\Delta G_{11}$), kcal/mol
i-$C_3H_7)_2O$	12.2	0.76						−10.3
NH_3	11.3[a,b]	0.63						−7.8
$(n$-$C_3H_7)_2O$	11.0	0.67						−7.0
$(C_2H_5)_2CO$	14.3	0.67						−5.6
$CH_3COOC_2H_5$	11.8	0.72						−5.0
$(C_2H_5)_2O$	10.6	0.72						−4.6
$C_2H_5COOCH_3$	11.0	0.68						−4.3
$CH_3COC_2H_5$	12.6	0.58						−4.1
c-C_4H_8O	9.9	0.61						−3.8
CH_3COOCH_3	10.0	0.63	0.15	0.013	67.	53.	−2.7	−2.5
CH_3COCH_3	10.2,[c] 8.7	0.38	0.87	0.069	10.0	10.0	−1.5	−1.5
i-C_4H_8								
$HCOOC_4H_9$	2.6	0.15	5.1	0.45	0.51	0.53	+0.3	+0.4
$HCOOC_3H_7$	1.9	0.11	5.3	0.46	0.36	0.39	+0.5	+0.6
$C_2H_4OC_2H_4O$	0.24	0.021						+1.2
n-C_3H_7CN	1.2	0.044						+1.6
$HCOOC_2H_5$	0.19	0.011	7.9	0.66	0.024	0.029	+1.9	+1.9
CH_3SH			12.6	0.95				+7.4
CH_3CHO			13.0	0.96				+8.3

[a] The concentration of NH_3 was kept low (≤10%) in all experimental measurements to ensure that the reacting t-$C_4H_9^+$ ions were deactivated by collisions with the precursor compound (neopentane) before undergoing reaction with ammonia. [b] Values reported in ref 6a: 9.1, 11.6, 9.7 14.0 × 10^{-10} cm^3/molecule·s. Value reported in ref 6b: 9.0 ± 0.8 × 10^{-10} cm^3/molecule·s. [c] Value taken from ref 6c. [d] Calculated from formulations derived in ref 7. [e] See footnote 12. [f] ±15%.

Table II. Rate Constants at 350 K and Thermodynamic Parameters for the Reaction

$$sec\text{-}C_3H_7^+ + M \underset{k_{15}}{\overset{k_{14}}{\rightleftarrows}} MH^+ + CH_3CHCH_2$$

M	rel gas basicity,[a] kcal/mol	$k_{14} \times 10^{10}$, cm^3/molecule·s[j]	k_{14}/Z_{14}[b,c]	$k_{15} \times 10^{10}$, cm^3/molecule·s	k_{15}/Z_{15}[b,c]	ΔG_{350}[i] (14), kcal/mol	CH_3CHCH_2 rel gas basicity, kcal/mol
$(i$-$C_3H_7)_2O$	+8.8	17.7 ± 1.3	1.0				
$(C_2H_5)_2CO$	+4.1	21.9 ± 1.0	0.94				
$(C_2H_5)_2O$	+3.1	14.3 ± 0.8	0.90				
$C_2H_5COOCH_3$	+2.8	16.7 ± 0.4	0.95				
c-C_4H_8O	+2.3	16.7 ± 0.6	0.95				
CH_3COCH_3	0	19.7 ± 0.6	0.83				
i-C_3H_7CHO	−3.9	23.4 ± 0.8	1.0				
C_2H_5CHO	−6.8	20.7 ± 1.0	0.91				
$HCOOCH_3$	−7.2	15.8 ± 1.0	0.94				
PH_3	−8.5	5.2 ± 0.5	0.43				
CH_3SH	−8.9	11.4 ± 0.9	0.73				
CH_3CHO	−9.8	16.0 ± 0.4	0.72				
CH_3OH	−13.6	7.1 ± 0.4	0.42	1.6 ± 0.5	0.11	−1.0[f]	−14.6
CH_3CHCH_2							
CH_3NO_2	−14.8	3.4 ± 0.3[d]	0.14	4.8 ± 0.3	0.41	+0.25[e,g]	−14.6
AsH_3	−15.7	0.97 ± 0.2	0.097	3.5 ± 0.2	0.31	+0.87[h]	−14.8
HCOOH	−16.1	1.1 ± 0.3	0.077	8.5 ± 0.5	0.68	+1.4	−14.7
						selected value	−14.7

[a] $\Delta G(MH^+ + CH_3COCH_3 \rightleftarrows (CH_3COCH_3)H^+ + M)$ from Table VII (Appendix). [b] Calculated from the formulations derived in ref 7. [c] See footnote 12. [d] Value reported in ref 3e: 23 ± 3 × 10^{-10} cm^3/molecule·s. (This value, which is close to the collision rate, is inconsistent with the fact, reported both in this paper and in ref 3e, that this is an endothermic reaction.) [e] Mackay and Bohme (ref 3e) report ΔG(300 K) = +0.6 kcal/mol. [f] ΔG(600 K) (ref 3d) = −1.2 ± 0.2 kcal/mol. [g] ΔG(347 K) from direct observation of K_{cq} = +0.15 kcal/mol. [h] ΔG(390 K) from observation of K_{cq} = +1.2 kcal/mol; ΔG from k_{14}/k_{15} at 380 K = 1.1 kcal/mol. [i] $\Delta G = -RT \ln k_{14}/k_{15}$. [j] Cited error limits = standard deviation of measurements. Error: ±15%.

for a number of proton-transfer reactions from the sec-$C_3H_7^+$ ion to various proton acceptors:

$$sec\text{-}C_3H_7^+ + M \rightarrow MH^+ + CH_3CHCH_2 \quad (14)$$

as well as for proton-transfer reactions from proton donors to propylene:

$$MH^+ + CH_3CHCH_2 \rightarrow sec\text{-}C_3H_7^+ + M \quad (15)$$

Also given are the values of ΔG derived from the ratios of the rate constants, k_f/k_r, for M = CH_3OH, CH_3NO_2, AsH_3, and HCOOH, as well as (in the footnote) three estimates of ΔG obtained from directly measured equilibrium constants. It should be noted that the equilibrium constants for proton-transfer reactions involving propylene can be measured directly only with difficulty because of a competing reaction of $C_3H_7^+$ with propylene. In order to prevent complications from the

Table III. Rate Constants at 350 K and Thermodynamic Parameters for the Reaction

$$c\text{-}C_5H_9^+ + M \underset{k_{18}}{\overset{k_{17}}{\rightleftarrows}} MH^+ + c\text{-}C_5H_8$$

M	rel gas basicity,[a] kcal/mol	$k_{17} \times 10^{10}$, cm^3/molecule·s[e]	k_{17}/Z_{17}[b,c]	$k_{18} \times 10^{10}$, cm^3/molecule·s	k_{18}/Z_{18}[b,c]	ΔG_{350},[d] kcal/mol	c-C_5H_8 rel gas basicity, kcal/mol
CH_3COCH_3	0	16.6 ± 2.0	0.79				
$HCOOC_2H_5$	−3.4	12.9 ± 1.0	0.81				
C_2H_5CHO	−6.8	14.1 ± 1.0	0.70				
CH_3CN	−8.0			0.28 ± 0.2	0.018		
CH_3SH	−8.9			0.23 ± 0.2	0.016		
CH_3CHO	−9.8	11.3 ± 1.5	0.56	3.1 ± 0.7	0.19	−0.91	−10.7
c-C_5H_8							
$C_2H_5NO_2$	−11.2	5.0 ± 1.0	0.22	8.9 ± 1.0	0.65	+0.40	−10.8
CH_3OH	−13.6			6.2 ± 0.5	0.38		
CH_3NO_2	−14.8			11.6 ± 0.5	0.80		
						selected value	−10.75

[a] $\Delta G(MH^+ + CH_3COCH_3 \rightleftarrows (CH_3COCH_3)H^+ + M)$ from Table VII (Appendix). [b] Calculated from the formulations derived in ref 7. [c] See footnote 12. [d] $\Delta G = -RT \ln k_{17}/k_{18}$. [e] Cited error limits = standard deviation of measurements. Error: ±15%.

occurrence of reaction 15 or the reaction of $C_3H_7^+$ with propylene, the rate constants of reaction 14 were determined in mixtures in which *sec*-$C_3H_7^+$ was generated in propane. In determinations of k_{15} the product $C_3H_7^+$ ions were continuously ejected from the cell to prevent the occurrence of these reactions.

Estimates of the equilibrium constant for proton-transfer equilibria involving CH_3OH, CH_3NO_2, AsH_3, and HCOOH are obtained from the ratios of the rate constants, k_{14}/k_{15}. A comparison of the relative values of ΔG cited in the table for reactions 14/15 with the relative free energy scale for the various reactant compounds given in Table VII shows that there is good agreement within ±0.2 kcal/mol. Within these error limits, there is also good agreement between the thermochemical information estimated from ratios of rate constants and that obtained from direct equilibrium constant determinations.

From the relative values of ΔG listed in the table, it is possible to obtain estimates of ΔH for the protonation of propylene, and thereby to determine the position of propylene in the relative proton affinity scale.

For many reactant pairs in Table II, $k_{14}/Z_{14} \approx 1$. Accepting the arguments advanced above (eq 12), this would indicate that $\Delta S(sec\text{-}C_3H_7^+ \rightarrow CH_3CHCH_2) \geq 0$. The results given in the table for reaction involving CH_3OH at 350 K and the ΔG measured at 600 K are not in disagreement with an entropy change of zero if one considers the error limits associated with the 600 K determination. Thus, the enthalpy change of the reaction

$$sec\text{-}C_3H_7^+ + CH_3COCH_3 \rightleftarrows (CH_3COCH_3)H^+ + CH_3CHCH_2 \quad (16)$$

would be assumed to be approximately equal to the free-energy change for the reaction, −14.7 ± 0.1 kcal/mol.

It should be noted that, as predicted by eq 12, the efficiency of proton transfer from $C_3H_7^+$ to PH_3 is much lower than the efficiencies of analogous reactions of lower exothermicity. However, the efficiency of reaction is greater than would be predicted from a consideration of the statistical factor alone (0.25). If it is assumed that indeed the maximum probability of a reactive collision is determined by the overall internal entropy change, then one would predict an efficiency of 0.4 for this reaction, in good agreement with the experimental result.

Proton Transfer Involving c-C_5H_8/c-$C_5H_9^+$. Table III gives the rate constants and reaction efficiencies measured at 347 K for proton transfer from $C_5H_9^+$ ions generated in c-C_5H_9Br:

$$c\text{-}C_5H_9^+ + M \rightarrow c\text{-}C_5H_8 + MH^+ \quad (17)$$

and the same information for proton transfer from various proton donors to cyclopentene:

$$MH^+ + c\text{-}C_5H_8 \rightarrow c\text{-}C_5H_9^+ + M \quad (18)$$

In the determinations of k_{18}, reaction 17 was prevented from occurring by the continuous ejection of $C_5H_9^+$ ions from the cell.

It was seen that a portion (~30–40%) of the $C_5H_9^+$ ions generated in c-C_5H_9Br were unreactive with all the additives, indicating that an isomerization, probably ring opening, occurs. (The rate constants listed apply to the reactive isomer only.) Previous electron-induced fragmentation studies of deuterium- and ^{13}C-labeled methylcyclopentanes have indicated that about 50% of the parent ions may undergo ring opening prior to loss of a methyl group.[16] It is of interest that the $C_5H_9^+$ component, which is unreactive toward the polar compounds listed in Table III, does transfer a proton to molecules with a basicity which is approximately 3 kcal/mol below that of NH_3. This observation is consistent with the thermodynamic data reported by Aue and Bowers[1b] for the $C_5H_9^+$ ion having the structure of protonated 1,3-pentadiene.

From the cases for which rate constants have been measured for reaction in both directions, the estimated values for ΔG (350 K) shown in the table are obtained. Comparison with the scale of relative gas-phase basicities (ΔG) in the Appendix shows that these estimated free-energy changes accurately reproduce the interval between CH_3CHO and $C_2H_5NO_2$.

The results show that the maximum efficiency of reaction, when reaction 17 is moderately exothermic, is ~0.8. Accepting eq 12, this leads to an estimate that the overall internal entropy change associated with the change (c-$C_5H_9^+ \rightarrow$ c-C_5H_8) is ~−0.4. On this basis, the enthalpy change for proton transfer from c-$C_5H_9^+$ to acetone is −10.65 kcal/mol.

Proton Transfer Involving *trans*-2-C_4H_8/*sec*-$C_4H_9^+$. Table IV gives the rate constants for proton transfer from *sec*-$C_4H_9^+$ ions generated in *n*-C_4H_{10} to various proton acceptors:

$$sec\text{-}C_4H_9^+ + M \rightarrow MH^+ + trans\text{-}2\text{-}C_4H_8 \quad (19)$$

(where it is assumed that the thermodynamically most stable linear C_4H_8 isomer, *trans*-2-C_4H_8, will predominate as the neutral product of reaction 19). (It has been demonstrated[5d] that 80–90% of the $C_4H_9^+$ ions generated in *n*-butane have and retain the *sec*-$C_4H_9^+$ structure under the conditions of these experiments.) Table IV also shows the rate constants for proton

Table IV. Rate Constants and Reaction Efficiencies at 390 K for Proton Transfer and Isomerization Reactions Involving *sec*-$C_4H_9^+$ and *trans*-2-C_4H_8

	cm^3/molecule·s^c				cm^3/molecule·s^c			
M	$k_{total} \times 10^{10}$ *sec*-$C_4H_9^+$ + M →	$k_{19} \times 10^{10}$	$k_{19}/Z^{a,b}$	$k_{isom}/Z^{a,b}$	$k_{total} \times 10^{10}$ MH^+ + *trans*-2-C_4H_8 →	$k_{20} \times 10^{10}$	$k_{20}/Z^{a,b}$	$k_{isom}/Z^{a,b}$
CH_3CN	21.7 ± 0.7	21.7 ± 0.7	0.84	0.0	1.8 ± 0.2	~0	~0	0.13
CH_3SH	11.4 ± 0.3	11.4 ± 0.3	0.81	0.0	0.56 ± 0.1	~0	~0	0.04
CH_3CHO	17.6 ± 0.3	17.6 ± 0.3	0.87	0.0	1.7 ± 0.2	~0	~0	0.13
$C_2H_5NO_2$	13.7 ± 0.3	9.0 ± 2.	0.4	0.2	6.8 ± 0.6			
C_6H_5F	2.0 ± 0.5	1.4 ± 0.9	0.09	0.04				
CH_3OH	2.4 ± 0.5	1.5 ± 0.9	0.09	0.06	1.8 ± 0.2	~0	~0	0.14
CH_3NO_2	<0.2				10.4 ± 0.9	~0	~0	0.86
AsH_3					6.5 ± 0.2	3.1 ± 0.5	0.27	0.29
H_2S					12.1 ± 1.4	9.2 ± 2.	0.65	0.20
H_2O					17.7 ± 1.0	17.7 ± 1.0	1.0	0.0

[a] Calculated from the formulations derived in ref 7. [b] See footnote 12. [c] Cited error limits = standard deviation of measurements. Error: ±15%.

Table V. Rate Constants for Reaction of Proton Donors with Cyclohexene at 360 K: $MH^+ + c\text{-}C_6H_{10} \rightarrow C_6H_{11}^+ + M$

M	$k \times 10^{10}$, cm^3/molecule·s^c	$k/Z_{ADO}{}^{a,b}$	μ_D	rel ΔG_{320} $MH^+ + CH_3COCH_3 \rightarrow (CH_3COCH_3)H^+ + M$
$HCOOC_2H_5$	no reaction	0.0	1.9	−3.4
i-C_3H_7CHO	3.1 ± 0.4	0.25	2.7	−3.9
$(CH_3)_2O$	no reaction	0.0	1.3	−4.5
C_2H_5CN	10.7 ± 0.7	0.79	4.0	−4.7
C_2H_5SH	3.0 ± 0.3	0.22	1.6	−5.3
$HCOOCH_3$	5.3 ± 0.2	0.36	1.8	−7.2
CH_3CN	10.7 ± 0.6	0.71	3.8	−8.0
PH_3	2.0 ± 0.3	0.12	0.55	−8.5
CH_3SH	4.3 ± 0.2	0.30	1.3	−8.9
CH_3CHO	13.7 ± 0.6	0.94	2.7	−9.8

[a] Calculated from the formulations derived in ref 7. [b] See footnote 12. [c] Cited error limits = standard deviation of measurements. Error: ±15%.

transfer to *trans*-2-C_4H_8 from corresponding proton donors:

$$MH^+ + trans\text{-}2\text{-}C_4H_8 \rightarrow sec\text{-}C_4H_9^+ + M \quad (20)$$

It was seen that in many systems some or all of the $C_4H_9^+$ ions resulting from proton transfer to *trans*-C_4H_8 originate with the *t*-$C_4H_9^+$ structure rather than the *sec*-$C_4H_9^+$ structure. This was shown by examining the product $C_4H_9^+$ species in the absence and in the presence of added CH_3OCH_3. The *sec*-$C_4H_9^+$ ion transfers a proton to this compound:

$$sec\text{-}C_4H_9^+ + CH_3OCH_3 \rightarrow (CH_3OCH_3)H^+ + trans\text{-}2\text{-}C_4H_8 \quad (21)$$

but the *t*-$C_4H_9^+$ ion does not:

$$t\text{-}C_4H_9^+ + CH_3OCH_3 \rightarrow \text{no reaction} \quad (22)$$

Furthermore, when *sec*-$C_4H_9^+$ ions react with some of the proton acceptors listed in the table, a certain fraction of the collisions result in isomerization of the ion to the *t*-$C_4H_9^+$ structure rather than in proton transfer. That is, reactions 19 and 20 should be written more completely:

$$\begin{tikzcd} sec\text{-}C_4H_9^+ + M \arrow[r, shift left] & (C_4H_9M)^+ \arrow[l, shift left] \arrow[r, shift left] \arrow[d] & MH^+ + trans\text{-}2\text{-}C_4H_8 \arrow[l, shift left] & (23) \\ & t\text{-}C_4H_9^+ + M & & \end{tikzcd}$$

The table gives not only the rate constants of reactions 19 and 20 as written, but also the total rate constants for loss of *sec*-$C_4H_9^+$ and MH^+ and the estimates obtained for the fraction of collisions resulting in isomerization. In Figure 1, these reaction efficiencies are plotted as a function of the scale of relative gas-phase basicities (data given in the Appendix, corrected to 390 K).

It is evident from an examination of Table IV and Figure 1 that in this case a straightforward estimation of equilibrium constants from the ratios of proton-transfer rate constants is not possible because of the occurrence of the isomerization which sometimes precludes proton transfer for reaction in both directions (reaction 23). An approximate estimate of the relative gas-phase basicity of *trans*-2-C_4H_8 can be obtained by bracketing. That is, reaction 19 occurs for M = CH_3OH but not for M = CH_3NO_2, and reaction 20 occurs for M = AsH_3 but not for M = CH_3NO_2 or CH_3OH; therefore $\Delta G(AsH_3) < \Delta G(trans\text{-}2\text{-}C_4H_8) < \Delta G(CH_3OH)$, or $\Delta G(trans\text{-}2\text{-}C_4H_8) \approx \Delta G(CH_3NO_2) \pm 1.1$ kcal/mol (where the error limits indicate only the bracket width).

In the reaction of MH^+ with *trans*-2-C_4H_8, it is seen that, in cases for which reaction 20 is apparently inaccessible for energetic reasons (Figure 1), the formation of *t*-$C_4H_9^+$ may be an efficient channel. It is also evident from an examination of Figure 1 that the probability that a collision between MH^+ and *trans*-2-C_4H_8 will result in the formation of a *t*-$C_4H_9^+$ ion seems to be greatest in the region where the ΔG of the competing proton-transfer reaction to form *sec*-$C_4H_9^+$ is approximately zero; this probability shows a general overall diminution as reaction 20 becomes increasingly endothermic or exothermic. No isomerization at all is observed when the reaction is ~9–10 kcal/mol exothermic (M = H_2O). Since the reaction to form *t*-$C_4H_9^+$ is approximately 14 kcal/mol more exothermic than reaction 20, *t*-$C_4H_9^+$ formation is exothermic for all the proton donors listed in the table and the figure. Apparently, the formation of *t*-$C_4H_9^+$ involves a proton transfer to *trans*-2-C_4H_8 to give a (M·*sec*-$C_4H_9^+$) complex followed by a rearrangement in the complex to give (M·*t*-$C_4H_9^+$):

$$MH^+ + trans\text{-}2\text{-}C_4H_8 \rightleftharpoons (MH^+ \cdot 2\text{-}C_4H_8)$$

$$\begin{tikzcd} \arrow[r] & (M \cdot sec\text{-}C_4H_9^+) \arrow[r] \arrow[d] & (M \cdot t\text{-}C_4H_9^+) \arrow[r] & M + t\text{-}C_4H_9^+ & (24a) \\ & M + sec\text{-}C_4H_9^+ & & & (24b) \end{tikzcd}$$

On the basis of this mechanism it is obvious that (24a/24b) will depend on the energy content of (M·*sec*-$C_4H_9^+$). The figure also shows that the decreasing efficiency of *t*-$C_4H_9^+$ formation from MH^+ is not simply proportional to the ΔH of reaction 20, but shows striking variations depending on the identity of MH^+. Since the most efficient intracomplex proton transfer-isomerization processes occur when M has a high dipole moment (peaks in the curve shown in Figure 1 are for M = CH_3NO_2, $C_2H_5NO_2$, and CH_3CN, of μ_D = 3.4, 3.5, and 3.8 D, respectively), it seems that the dipole moment of M in the ($M{\cdot}sec\text{-}C_4H_9^+$) complex facilitates $t\text{-}C_4H_9^+$ formation, presumably because a strong ion-dipole interaction permits the activation energy for the rearrangement ($sec\text{-}C_4H_9^+ \rightarrow t\text{-}C_4H_9^+$) to be overcome. A similar observation about the enhancement of isomerization by the dipole moment of a departing molecule has been reported for the unimolecular decomposition of ions.[17] Further evidence for the mechanism (24) is given by the observation that, although the total rate constant of reaction of CH_3CNH^+ with $trans\text{-}2\text{-}C_4H_8$ (resulting in 100% $t\text{-}C_4H_9^+$ formation) is 1.8×10^{-10} cm^3/molecule·s, the rate of disappearance of CD_3CND^+ in reaction with the same molecule is 7.2×10^{-10} cm^3/molecule·s, with CD_3CNH^+ appearing as a second ionic reaction product:

$$\begin{tikzcd}
CD_3CND^+ + trans\text{-}2\text{-}C_4H_8 \arrow[r, shift left, "1.0"] & (CD_3CND^+ \cdot 2\text{-}C_4H_8) \arrow[l, shift left, "0.54"] \\
\rightleftarrows (CD_3CN \cdot sec\text{-}C_4H_8D^+) \arrow[r, "0.14"] \arrow[d, "0.32"] & (CD_3CN \cdot t\text{-}C_4H_8D^+) \arrow[d] \\
CD_3CNH^+ + 2\text{-}C_4H_7D & CD_3CN + t\text{-}C_4H_8D^+ \quad (25)
\end{tikzcd}$$

(where the fraction of collisions resulting in a given exit channel at 390 K are indicated). The observation of CD_3CNH^+ as a product proves the existence of a long-lived ($M{\cdot}sec\text{-}C_4H_9^+$) complex, since, if the H–D exchange involved a prior or simultaneous rearrangement of the linear C_4 carbon skeleton, the deuteron would be carried off by the hydrocarbon and only $t\text{-}C_4H_8D^+$ formation would be observed.

Because the maximum efficiency of reaction 19 is high (0.84 ± 0.03), it is assumed that the internal entropy change associated with deprotonation of $sec\text{-}C_4H_9^+$ is small (~−0.3 cal/deg·mol). Thus, based on the estimate derived above that the relative gas basicity of $trans\text{-}2\text{-}C_4H_8$ is approximately the same as that of CH_3NO_2 (−14.8 ± 1.1 kcal/mol), and ΔH for the process

$$sec\text{-}C_4H_9^+ + CH_3COCH_3 \rightleftarrows (CH_3COCH_3)H^+ + trans\text{-}2\text{-}C_4H_8 \quad (26)$$

can be estimated to be −14.8 ± 1.1 kcal/mol.

Proton Transfer to $c\text{-}C_6H_{10}$. Table V lists the rate constants measured at 360 K for proton transfer to cyclohexene from a number of proton donors. The product $C_6H_{11}^+$ ions were, insofar as it is possible to determine, indistinguishable from methylcyclopentyl ions. The rate constants observed for these ions, as well as for $C_6H_{11}^+$ ions generated in cyclohexane and cyclohexyl bromide, are the same as the rate constants for reactions of $C_6H_{11}^+$ ions generated in methylcyclopentane or through protonation of methylcyclopentene. Therefore, it must be concluded that the isomerization of cyclohexyl ion to the methylcyclopentyl ion occurs without a significant energy barrier. It cannot be ruled out that some of the isomerization may be collisionally induced.

Although no quantitative thermochemical data about the cyclohexyl ion can be obtained from these experiments, it is possible to proceed by analogy with the preceding discussion of protonation of $trans\text{-}2\text{-}C_4H_8$ (where isomerization of the ion was also important) to develop information about the heat of formation of the cyclohexyl ion. That is, it is assumed by analogy that the isomerization in the complex of $C_6H_{11}^+$ is preceded by a proton transfer forming a ($M{\cdot}c\text{-}C_6H_{11}^+$) complex. Further, as above, it will be assumed that the proton transfer–isomerization reaction

$$MH^+ + c\text{-}C_6H_{10} \rightarrow (M{\cdot}c\text{-}C_6H_{11}^+) \rightarrow c\text{-}C_5H_8CH_3^+ + M \quad (27)$$

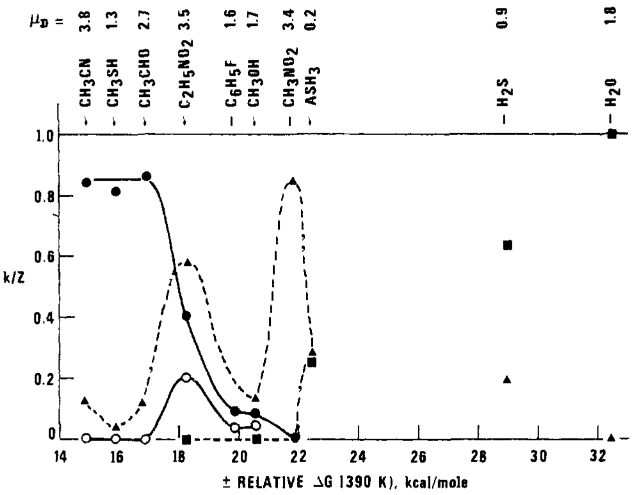

Figure 1. The reaction efficiencies, k/Z, at 390 K for the reactions $sec\text{-}C_4H_9^+ + M \rightarrow MH^+ + C_4H_8$ (●) and $sec\text{-}C_4H_9^+ + M \rightarrow t\text{-}C_4H_9^+ + M$ (○), as well as $MH^+ + trans\text{-}2\text{-}C_4H_8 \rightarrow sec\text{-}C_4H_9^+ + M$ (■) and $MH^+ + trans\text{-}2\text{-}C_4H_8 \rightarrow t\text{-}C_4H_9^+ + M$ (▲), given as a function of the relative gas-phase basicities of M (ΔG values relative to NH_3 from Table VII, corrected to 390 K). For $sec\text{-}C_4H_9^+$ reactants (● and ○), the proton-transfer reaction is increasingly exothermic for smaller $|\Delta G|$; for MH^+ reactants, proton transfer is increasingly exothermic for larger $|\Delta G|$.

will proceed even when the proton transfer to form $c\text{-}C_6H_{11}^+$ would be endothermic, and that the relative efficiency of the isomerization will vary directly with the dipole moment of M and indirectly with the endothermicity of the initial proton-transfer step. Thus, on the basis of a comparison of the efficiency of reaction with chemically similar molecules having approximately the same dipole moment (i.e., compare k/Z for M = $HCOOC_2H_5$ and M = $HCOOCH_3$, or compare results for M = $i\text{-}C_3H_7CHO$ with M = CH_3CHO), in Table V, one can conclude that −4.5 kcal/mol ≤ GB($c\text{-}C_6H_{10}$) ~ −9.8 kcal/mol or ΔG($c\text{-}C_6H_{11}^+ + CH_3COCH_3 \rightarrow (CH_3COCH_3)H^+ + c\text{-}C_6H_{10}$) ~ −7 ± 3 kcal/mol. The lower limit is unambiguously established by the fact that protonated ethyl formate and dimethyl ether do not react with cyclohexene even though reaction 27, proton transfer to form the rearranged product ion, is exothermic. It has been noted[18] that the hydrogen affinities of ions

$$HA = -\Delta H(A^+ + H \rightarrow AH^+) \quad (28)$$

remain approximately constant for a homologous series.[19] Assuming then that the hydrogen affinities of $c\text{-}C_5H_8^+$ and $c\text{-}C_6H_{10}^+$ are the same:

$$\Delta H_f(c\text{-}C_5H_9^+) - \Delta H_f(c\text{-}C_5H_8^+) = \Delta H_f(c\text{-}C_6H_{11}^+) - \Delta H_f(c\text{-}C_6H_{10}^+) \quad (29)$$

From the heats of formation of the two parent olefin ions, $\Delta H_f(c\text{-}C_5H_9^+) - \Delta H_f(c\text{-}C_6H_{11}^+)$ = 11 kcal/mol. This leads to an estimate that the proton affinity of cyclohexene is approximately 2 kcal/mol above the proton affinity of cyclopentane (or about 8 kcal/mol below that of acetone), which is within the error limits of the values estimated above, assuming that there is no entropy change.

Comparison of Relative Proton Affinities of Olefins with Thermochemical Data on Absolute Enthalpies of Formation of Ions and Radicals. The relative proton affinities of the various olefins derived in this paper are summarized in Table VI. Taking into account the heats of formation of the alkenes and cycloalkenes, the relative proton affinity scale can be converted to a scale of relative heats of formation of the corresponding alkyl ions, also given in Table VI. Results from equilibrium or rate constant determinations in the literature are also

Table VI. Relative Proton Affinities of Alkenes and Heats of Formations (kcal/mol) of Alkyl Ions. Comparison with Data on Ionization Potentials and Heats of Formation of Radicals

R^+	rel proton affinity[a] (R–H)	rel $\Delta H_f(R^+)$[c]	$\Delta H_f(R^+)$[c]	adiabatic IP(R·)	derived $\Delta H_f(R\cdot)$ $[\Delta H_f(R^+) - IP]$	$\Delta H_f(R\cdot)$ lit.
sec-$C_3H_7^+$	−14.7 ± 0.4	+22.4 ± 0.6[e]	184.5 ± 2.1	169.7 ± 0.5[h]	14.8 ± 2.6	17.6 ± 1.[k] 18.2 ± 1.5[l] 20.2 ± 0.8[m]
c-$C_5H_9^+$	−10.65 ± 0.2	+21.7 ± 0.4[d]	183.8 ± 1.9	166.3 ± 0.5[i]	17.5 ± 2.4	22.5[k] 24.3 ± 1.[l]
sec-$C_4H_9^+$	−14.8 ± 1.2	+14.6 ± 1.4	176.7 ± 2.9			
c-$C_6H_{11}^+$	−7 ± 3	+8.7 ± 3	171 ± 3	164.9 ± 0.9[i]	6 ± 4	12.4[k] 13.0 ± 1[n] 13.9 ± 1[p]
c-$C_5H_8CH_3^+$	+0.1 ± 0.2[b]	+2.1 ± 0.2[b]	164.2 ± 1.7			
t-$C_4H_9^+$	−1.5 ± 0.1	0.0	162.1 ± 0.8[g]	154.5 ± 0.7[h] 151.7 ± 0.2[j]	7.6 ± 2.2	8.4 ± 1.0[o] 11 ± 1.5[m]
t-$C_5H_{11}^+$	+0.2 ± 0.5[p]	−6.8 ± 0.2[p] −7.6 ± 0.2[e] −8.0 ± 0.2[f]	154.6 ± 2			
c-$C_6H_{10}CH_3^+$	+1.9 ± 0.2[b]	−9.4 ± 0.2[b]	152.7 ± 1.7			
t-$C_6H_{13}^+$	+0.4 ± 0.6[p]	−13.3 ± 0.4[p] −14.1 ± 0.4[e] −13.5 ± 0.4[f]	148.5 ± 1.8			

[a] $\Delta H(R^+ + CH_3COCH_3 \rightleftarrows (CH_3COCH_3)H^+ + (R\text{–}H))$. Results from discussion except where otherwise noted. $PA(CH_3COCH_3)$ = 200.8 ± 1.5 accepting values for $\Delta H_f(R^+)$ derived here (see Discussion). [b] Derived from results of ref 3a. [c] Error limits include the estimate of the error limits associated with the position of a particular olefin in the relative proton affinity scale plus the error limits cited for the heats of formation of relevant neutral species (ref 23). [d] Hydride transfer equilibrium results from ref 2e indicate $\Delta H_f(c\text{-}C_5H_9^+) - \Delta H_f(C_3H_7^+)$ = 0.5 ± 0.5 kcal/mol. [e] From hydride transfer equilibrium measurements, ref 2d. [f] From hydride transfer equilibrium measurements, ref 2c. [g] Primary standard; see Discussion. [h] Reference 4b. [i] Reference 4c. [j] Reference 4d; authors of ref 4b analyze these data and suggest the presence of hot bands. [k] Reference 24a. [l] Reference 24b. [m] References 20a and 20c. [n] Reference 24c. [o] Reference 20b. [p] Reference 3b.

given for c-$C_5H_8CH_3^+$, *t*-$C_5H_{11}^+$, c-$C_6H_{10}CH_3^+$, and *t*-$C_6H_{13}^+$.[2c,d,3a]

In order to compare this scale with absolute values for the heats of formation of these ions, it is necessary to choose as a standard of comparison an ion for which the heat of formation is well established. The *t*-$C_4H_9^+$ ion has often been selected for this purpose, but recent conflicting redeterminations of the heat of formation of the *tert*-butyl radical[20] as well as of its ionization potential[4b,d] have left the value for the heat of formation of this ion uncertain. However, a maximum value for $\Delta H_f(t\text{-}C_4H_9^+)$ of ≤164.2 ± 0.8 kcal/mol can be derived from the appearance potential of *t*-$C_4H_9^+$ in both neopentane[14] and *tert*-butyl iodide.[21] The most recent determination[4b] of the adiabatic ionization potential[22] of the *tert*-butyl radical (154.5 ± 0.7 kcal/mol) when combined with the two recently published[20] values for $\Delta H_f(t\text{-}C_4H_9\cdot)$ leads to a heat of formation of the *tert*-butyl ion of either 162.9 ± 1.7 or 165.5 ± 2.2 kcal/mol.[20a,c] These values are, within the cited error limits, in agreement with one another and with the maximum limit. The appearance potential of *t*-$C_4H_9^+$ in isobutane[23] leads to a maximum value for $\Delta H_f(t\text{-}C_4H_9^+)$ of 162.1 ± 0.8 kcal/mol, in good agreement with the lower of the two absolute values cited above (162.9 ± 1.7 kcal/mol).

Taking a value of 162.1 ± 0.8 kcal/mol for the heat of formation of *t*-$C_4H_9^+$, the relative scale of heats of formation of ions is assigned the absolute values reported in the fourth column of Table VI. Combining these values with recently determined adiabatic ionization potentials of the corresponding radicals[4] where available (eq 6), an internally consistent set of heats of formation of radicals is obtained, as listed in the sixth column of the table. Although the error limits which must be assigned to these absolute enthalpies of formation of radicals are wide, it is evident from a comparison of the derived heats of formation with the experimentally determined values for the propyl, cyclopentyl, and cyclohexyl radicals that the derived heats of formation are much lower. Even if one were to base such estimates on the maximum value of 164.2 kcal/mol for the heat of formation of *t*-$C_4H_9^+$, the derived heats of formation of the radicals would still be lower than the literature values by 2–4 kcal/mol. The source of the discrepancy could lie in the adiabatic ionization potential determinations and/or in the heats of formation of the radicals.

On the basis of the values for the ion heats of formation assigned here, the proton affinity of *i*-C_4H_8 is calculated to be 199.3 ± 1.5 kcal/mol, that of acetone is 200.8 ± 1.5 kcal/mol, and that of NH_3 is 207.1 ± 1.7 (results reported in the Appendix) or 208.5 ± 1.5 kcal/mol (expanded scale of Taft et al.,[3c] see Appendix), assuming the integrated heat capacity of the electron to be zero so that the value of $\Delta H_f(H^+)$ in the defining eq 8 is 365.7 kcal/mol.

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Appendix. The Scale of Gas Basicities

The authors of the extensive published scale of relative gas-phase basicities at 300 K[3c] have found that the actual temperature at which their measurements were carried out was somewhat higher than 300 K, and therefore that the scale needs to be expanded by about 6.7%.[3f] In the course of this, and other studies in this laboratory, a number of the equilibrium constants for individual steps in the ladder have been measured at 320 K, so that it is possible to construct the ladder of gas basicities at this temperature from NH_3 to AsH_3 independently. The expanded version of the published scale and the scale determined in this laboratory are given in Table VII. In addition several relative gas basicities for certain of these compounds quoted in a recent review[1b] by Aue and Bowers from their own unpublished work are given. In the region of the scale between acetone and arsine, the agreement between the results obtained in this laboratory and the expanded scale of Taft et al.[3c] is generally quite good, although there are certain discrepancies for individual compounds (e.g., CH_3OCH_3, C_2H_5SH, CH_3OH, and AsH_3). In the region of the scale from acetone to ammonia, the results obtained in this

Table VII. Values of $\Delta G(MH^+ + CH_3COCH_3 \rightarrow (CH_3COCH_3)H^+ + M)$ (kcal/mol)

M	Taft et al.[3c] 320 K	Aue and Bowers[1b] 300 K	this work 320 K	Lau,[3g] Yamdagni, and Kebarle[3d] 600 K	values used in Discussion 320 K
$(i\text{-}C_3H_7)_2O$	+9.7	+9.2	+8.8		+8.8
NH_3	+7.7	+6.5	+6.3	+6.5	+6.3
$(n\text{-}C_3H_7)_2O$	+5.8	+5.7	+5.5		+5.5
$(C_2H_5)_2CO$	+4.9		+4.1		+4.1
$CH_3COOC_2H_5$	+4.1	+3.6	+3.5	+3.4	+3.5
$(C_2H_5)_2O$	+3.8	+3.2	+3.1	+3.7	+3.1
$C_2H_5COOCH_3$	+3.5				+2.8
$CH_3COC_2H_5$	+2.9		+2.6		+2.6
$c\text{-}C_4H_8O$	+2.7	+2.4	+2.3		+2.3
CH_3COOCH_3	+1.3	+0.6	+1.0	+0.8	+1.0
CH_3COCH_3	0	0	0	0	0
$i\text{-}C_4H_8$	−1.5	−1.6	−1.5	−1.6	−1.5
$HCOOC_4H_9$	−1.9	−1.9			−1.9
$HCOOC_3H_7$	−2.1		−2.1	−3.0	−2.1
$\overline{C_2H_4OC_2H_4O}$	−2.7				−2.7
$n\text{-}C_3H_7CN$	−3.1	−3.9			−3.1
$HCOOC_2H_5$	−3.3	−3.5	−3.4	−3.5	−3.4
$i\text{-}C_3H_7CHO$	−3.9				−3.9
CH_3OCH_3	−4.0		−4.5		−4.5
C_2H_5CN	−4.4		−4.7		−4.7
$n\text{-}C_3H_7CHO$	−4.9		−5.0		−5.0
C_2H_5SH	−6.1		−5.25		−5.3
C_2H_5CHO	−6.7		−6.8	−6.7	−6.8
$HCOOCH_3$	−7.0		−7.2	−7.0	−7.2
CH_3CN	−7.8		−8.0	−8.0	−8.0
PH_3	−8.2		−8.5		−8.5
CH_3SH	−8.9		−8.9		−8.9
CH_3CHO	−9.9		−9.8	−9.6	−9.8
$C_2H_5NO_2$			−11.2		−11.2
C_6H_6	−12.6		−12.9	−11.9	−12.9
CH_3OH	−12.9		−13.6	−13.2	−13.6
CH_3NO_2			−14.8		−14.8
AsH_3	−15.1		−15.7		−15.7
HCOOH	−15.6			−17.1	−16.1
H_2S	−22.0			−25.3	−22.5
H_2O	−25.8			−28.2	−26.4

laboratory are in generally better agreement with those quoted by Aue and Bowers[1b] than with the expanded scale of Taft et al.

Further, although two recent studies[3e,26] carried out at pressures in the range of 1 Torr have reported that ΔG(300 K) for the proton-transfer equilibrium involving CH_3NO_2 and CH_3OH is 0.2-0.3 kcal/mol, our value obtained at low pressures (where competitive clustering of the ions with the polar neutral species is less important) is 1.2 ± 0.2 kcal/mol. This value was confirmed in experiments in which the ΔG of proton transfer was examined individually for reaction with propylene, which lies between CH_3OH and CH_3NO_2 on the relative basicity scale. As shown in Table II, the sum of the two steps equals 1.2 kcal/mol.

The ΔH of the process

$$H_3O^+ + NH_3 \rightleftarrows NH_4^+ + H_2O \qquad (1)$$

is −33.5 kcal/mol according to the expanded scale of Taft et al.,[3b] or −32.7 kcal/mol using the results obtained in this laboratory (accepting the interval reported by those authors[3c] for the interval from AsH_3 to H_2O). These results can be compared with the values obtained for ΔG of reaction I of −34.7 kcal/mol at 600 K.[3g] Thus, although one would predict that the entropy change for this reaction should be ∼−0.5 to −0.7 cal/deg·mol, the results lead to estimated entropy changes of +4 or +7 cal/deg·mol, respectively. This suggests that the 320 K scales actually need to be expanded somewhat more. (A 4% expansion, corresponding to an operating temperature of 333 K, would bring the entropy change to the predicted value.) At any rate, it must be concluded that the accuracies with which the temperatures are known are apparently such that comparisons between the high-temperature and low-temperature scales can only be made over relatively small intervals (<∼3 kcal/mol) if entropy changes are to be estimated.

In the earlier publications of relative scales of gas-phase proton affinities,[3c,d,f] the assumption was usually made that the entropy change for a particular proton-transfer equilibrium could be approximated by considering the change in external rotational symmetry numbers of the various reactants. It has also been pointed out[1c,12] that these reactions should exhibit an additional entropy change due to the operation of intermolecular forces among the reactants; this "intermolecular" entropy change should equal $R \ln Z_f/Z_r$ (where Z_f and Z_r are respectively the ion-molecule collision rates in the forward and reverse direction). Because it is not generally accepted at the present time that such a contribution should be included, we have calculated values of ΔH (proton transfer) in the accompanying discussion ignoring this contribution. If one takes this into account, the enthalpy changes estimated for reaction 7 would be diminished by 0.4, 0.25, and 0.5 kcal/mol, respectively, for M = CH_3CHCH_2, $c\text{-}C_5H_8$, and *trans*-2-C_4H_8.

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(19) This observation is borne out by the hydrogen affinities of olefin ions which can be calculated from the results obtained or cited here. For instance, based on the heats of formation of the alkyl ions derived in the concluding sections of this paper and cited in the third column of Table VI, the hydrogen affinities of olefin ions with internal double bonds are (kcal/mol) 2-$C_4H_8^+$, 83.4; c-$C_5H_8^+$, 84.3; c-$C_5H_7CH_3^+$, 83.9. For olefin ions with terminal double bonds one obtains $CH_3CHCH_2^+$, 96.6; 1-$C_4H_8^+$, 94.4; *i*-$C_4H_8^+$, 98.0.

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A Vibrational Study of Zirconium Tetraborohydride Supported on Aluminum Oxide. 1. Interactions with Deuterium, Deuterium Oxide, and Water Vapor

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Abstract: Supported complexes, formed by grafting known homogeneous catalytic compounds onto support materials, are currently of significant interest and have great potential value in industrial applications. Progress in this field, however, has been hampered by a lack of information about the structure of the supported complexes. In the current study, inelastic electron tunneling spectroscopy (IETS) has been used to probe the vibrational structure of $Zr(BH_4)_4$ supported on Al_2O_3 as a function of temperature between 300 and 475 K. A number of surface species have been identified. Interactions of the supported zirconium complex with H_2O, D_2O, and D_2 have been observed also over the same temperature range. Vibrational transitions throughout the entire spectral range from 240 to 4000 cm^{-1} are clearly observed, and peak assignments are presented based on vibrational results available for a number of related compounds and systems. This study demonstrates the utility of IETS and at the same time provides significant new insight on a system of considerable interest and importance.

Introduction

Since 1970, there has been increasing interest in attempts to form new types of catalysts combining the desirable features of both homogeneous and heterogeneous catalytic systems.[1] Traditionally, heterogeneous systems have provided for easy separation of catalyst from products, good catalyst stability, and high activity. Homogeneous catalysts, while being often expensive, fragile compounds easily lost due to separation problems, can typically provide greater selectivity, and can be tailored and adapted to fit a specific process in a more logical and easy fashion than their heterogeneous counterparts. Efforts to combine the advantages from both areas into a new class of catalysts have centered on attempts to graft or anchor homogeneous catalytic compounds onto high surface area supports

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