ventional titration methods at salt concentrations from 0.02 to 0.2 *M*. The observed rates are shown in Table III. All were lower than the corresponding k_2 values determined by the conductance method. The assumption that only the free anion is reactive can be tested by setting $\alpha_{A^-} = k_2'/k_2$ and calculating an association constant from this value. An additional assumption made in this treatment is that the rate of the displacement reaction is not affected significantly by a change in ionic strength. This assumption probably is valid for reactions of the type studied here.[14] These association constants are shown in Table III along with the calculated thermodynamic association constant K_A, where the activity coefficients were again calculated by the extended Debye–Hückel equation. The resulting K_A values agree closely with those previously determined by both the reaction conductance method described here and by normal conductance. These results are consistent with the premise that only the free ion is reactive. Also, K_A values thus determined support the validity of those determined by reaction conductance and conventional high-precision conductance methods.

Table III. Rates of Displacement Reactions with *n*-Butyl Iodide at Higher Nucleophile Concentrations in Acetonitrile at 24.9°

Nucleophile	Concn	k_2'	α_{A^-}[a]	K_A'[b]	K_A[c]
NEt_4Cl	0.2196	3.10×10^{-3}	0.777	1.7	9
	0.1015	3.30×10^{-3}	0.827	2.4	10
	0.0516	3.45×10^{-3}	0.865	3.5	11
	0.0208	3.66×10^{-3}	0.917	4.7	11
KSCN	0.1123	3.57×10^{-4}	0.623	8.6	32
	0.0313	4.53×10^{-4}	0.791	10.7	27
NaSCN	0.1100	2.42×10^{-4}	0.422	29	92
	0.0296	3.41×10^{-4}	0.595	39	86

[a] $\alpha = k_2'/k_2$, where k_2 (3.99×10^{-3} M^{-1} sec^{-1} for the chloride reaction and 5.73×10^{-4} M^{-1} sec^{-1} for the thiocyanate reaction) was determined by the conductance method. [b] Calculated from α by eq 9. [c] Calculated by eq 10, with activity coefficients calculated by eq 11.

Conclusions

Accurate rate constants corrected for ion-pairing effects can be obtained by high-precision conductance. To maximize the accuracy of the rate measurement, it may be advantageous to select nucleophile salts that are associated. For the reactions studied, uncertainties in rates on the order of ±1% were obtained through selection of cation and salt concentration. The limit of accuracy in each case is the presence of a small background reaction. Other systems, perhaps less likely to exhibit this complication, may have much smaller uncertainties in the k_2 values obtained.

Also, accurate association constants can be obtained from the conductance–rate data. This feature is particularly valuable for the determination of association constants of slightly soluble salts.

The method should be useful also for the study of systems where the reactivity of the ion pair is in question. The data allow simultaneous measurement of a reaction rate and the degree of association, the interrelation of which indicates the relative reactivity of free and associated anions.

Acknowledgment. Financial support by the National Research Council of Canada is gratefully acknowledged.

---

[14] K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1965, p 221.

Reversible Reactions of Gaseous Ions. VIII. The $t\text{-}C_4H_9^+$ ($i\text{-}C_5H_{12}$, $i\text{-}C_4H_{10}$) $t\text{-}C_5H_{11}^+$ System

J. J. Solomon and F. H. Field*

Contribution from The Rockefeller University,
New York, New York 10021.
Received March 3, 1973

Abstract: The equilibrium $t\text{-}C_4H_9^+ + i\text{-}C_5H_{12} \rightleftarrows t\text{-}C_5H_{11}^+ + i\text{-}C_4H_{10}$ has been investigated using the chemical ionization technique at source pressures up to 5 Torr. The existence of equilibrium in the mass spectrometer source was established by extensive pressure and repeller studies and by variation of the partial pressures of $i\text{-}C_4H_{10}$ and $i\text{-}C_5H_{12}$. Thermodynamic quantities have been determined from the temperature variation of the equilibrium constant over the temperature range 323–548°K. The following thermodynamic values were obtained: $\Delta G°_{300} = -2.9$ kcal/mol, $\Delta H° = -3.6$ kcal/mol, and $\Delta S° = -2.3$ eu. The heat of formation of the *tert*-pentyl ion was found to be 161 kcal/mol. This value is referred to $\Delta H_f°(t\text{-}C_4H_9^+) = 169$ kcal/mol.

Reversible association reactions of gaseous ions have been studied extensively using mass spectrometric techniques by Kebarle,[1] DePaz, Leventhal, and Friedman,[2] and Field and coworkers.[3] Other workers

---

[1] (a) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967); (b) A. Good, D. A. Durden, and P. Kebarle, *J. Chem. Phys.*, **52**, 212 (1970); (c) A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 7627 (1972).

[2] M. DePaz, J. J. Leventhal, and L. Friedman, *J. Chem. Phys.*, **51**, 3748 (1969).

[3] (a) F. H. Field, *J. Amer. Chem. Soc.*, **91**, 2827 (1969); (b) D. P. Beggs and F. H. Field, *ibid.*, **93**, 1567 (1971); (c) *ibid.*, **93**, 1576 (1971); (d) F. H. Field and D. P. Beggs, *ibid.*, **93**, 1585 (1971); (e) S. L. Bennett and F. H. Field, *ibid.*, **94**, 5186 (1972); (f) *ibid.*, **94**, 5188 (1972); (g) *ibid.*, **94**, 6305 (1972); (h) *ibid.*, **94**, 8669 (1972).

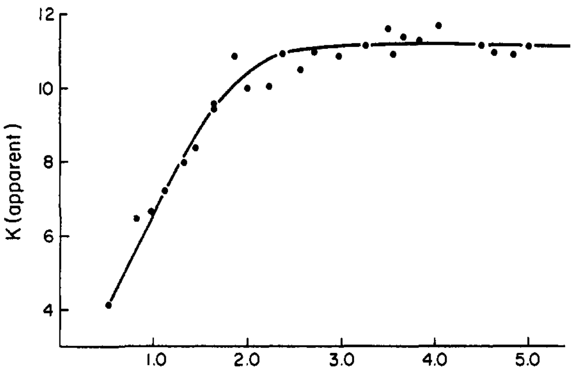

Figure 1. The apparent equilibrium constant *vs.* the source pressure for reaction 2: $T = 436 \pm 2$°K, $E/P = 5.0 \pm 0.2$ V/(cm Torr), 1.17 ± 0.02% i-C_5H_{12} in i-C_4H_{10}.

using mass spectrometric[4-6] and icr techniques[7-9] have determined equilibrium constants for proton- and halide-transfer reactions in order to obtain proton affinities and carbonium ion stabilities. In all save one of these experiments[4,5,7-9] the measurements were made at fixed temperatures, and thus the enthalpies of the reactions investigated could not be determined directly. They were obtained from the experimentally determined free energies (equilibrium constants) either by assuming that the entropy changes in the reactions were zero or by calculating the entropy changes from postulated structures. In the study which included measurements at different temperatures,[6] the entropy change was found to be small.

No successful investigations have been reported of equilibria between homologous carbonium ions and their corresponding homologous parent hydrocarbons, namely

$$R_1^+ + R_2H \rightleftharpoons R_2^+ + R_1H \qquad (1)$$

Making such measurements is very desirable because it offers the opportunity of establishing networks of equilibrium thermodynamic quantities for gaseous carbonium ions. These will supplement and perhaps eventually replace the current body of data, which comprises only energy values (ΔH values) derived from kinetic-type measurements such as mass spectrometric appearance potentials and from measurements of ionization potentials of radicals. Accurate equilibrium thermodynamic values of carbonium ions in the gas phase will enable one to examine the effects of both small and large structural variations in the ions upon thermodynamic properties without the complication of solvent effects.

We have undertaken to make such equilibrium studies on hydrocarbon systems, and we report here the results of our investigations of the t-$C_4H_9^+$ (i-C_5H_{12}, i-C_4H_{10}) t-$C_5H_{11}^+$ system, namely

$$t\text{-}C_4H_9^+ + i\text{-}C_5H_{12} \rightleftharpoons t\text{-}C_5H_{11}^+ + i\text{-}C_4H_{10} \qquad (2)$$

Because this reaction comprises our first investigation of what might be termed a metathetical equilibrium (as distinguished from the associative equilibria with which we have been concerned in the past[3]), we have devoted considerable attention to the problem of whether equilibrium was established in the ionization chamber of the mass spectrometer. In fact, for reasons which we now understand and which we will discuss later in the paper, it appears that equilibrium is established only with greater difficulty than that which we have encountered in previous studies.

Experimental Section

The Esso chemical physics mass spectrometer used in these experiments has been described previously.[3b,f] The mass spectrometer is equipped with an ion source (source III) which can be cooled to liquid-nitrogen temperature or heated to 550°K. The instrument was operated under so-called approximate field free conditions[3b] wherein the electric fields in and adjacent to the ionization chamber were maintained at the minimum values compatible with adequate sensitivity. The electron accelerating potential used was 600 V, and the repeller potential was adjusted to keep the ratio of E/P (E = repeller field strength, P = source pressure) constant at 5 V/(cm Torr).

The reagents used were Matheson Instrument grade (99.5%) isobutane and Matheson Coleman and Bell Spectroquality grade (99+ mol %) isopentane.

Results and Discussion

The equilibrium expression for reaction 2 is

$$K = \frac{(t\text{-}C_5H_{11}^+)(i\text{-}C_4H_{10})}{(t\text{-}C_4H_9^+)(i\text{-}C_5H_{12})} = \frac{I_{t\text{-}C_5H_{11}^+}P_{i\text{-}C_4H_{10}}}{I_{t\text{-}C_4H_9^+}P_{i\text{-}C_5H_{12}}} \qquad (3)$$

The initial ionization of the system is by electron impact, and, as in conventional chemical ionization experiments, the ions initially produced rapidly react with the substrate gases to produce t-$C_4H_9^+$ and t-$C_5H_{11}^+$ in the near vicinity of the electron beam. These ions then equilibrate during the remainder of their residence in the ionization chamber. A series of tests were made to check whether equilibrium was established in our ion source. The effects on K of varying the source pressure, the E/P ratio, and the $P_{i\text{-}C_4H_{10}}/P_{i\text{-}C_5H_{12}}$ ratio were investigated. Once the conditions producing equilibrium were established, values of the equilibrium constant K were determined at a series of temperatures utilizing these conditions.

The effect of source pressure on the equilibrium constant is shown in Figure 1. This experiment was done at a fixed temperature ($T = 436 \pm 2$°K) and at a constant E/P of 5.0 ± 0.2 V/(cm Torr). The value of the apparent equilibrium constant rises as the pressure is increased and then remains constant between 2.4 and 5 Torr. In our experience this behavior is characteristic of a reversible reaction which has attained equilibrium above some minimum pressure. However, it is of considerable interest that in all save one of the other systems studied in our mass spectrometer[3b-h] (all associative equilibria), the apparent equilibrium constants leveled off at pressures of 1 Torr or less. The one exception to this involved the equilibrium

$$H_3^+ + H_2 \rightleftharpoons H_5^+ \qquad (4)$$

for which it was found[3h] that equilibrium was not achieved at pressures below 4 Torr. This was ascribed to the low efficiency of hydrogen molecules as third bodies and the relatively short ion residence times to be anticipated with the very light ions involved in the hydrogen system.

---

[4] S.-L. Chong and J. L. Franklin, *J. Amer. Chem. Soc.*, **94**, 6347 (1972).

[5] S.-L. Chong and J. L. Franklin, *ibid.*, **94**, 6630 (1972).

[6] J. P. Briggs, R. Yamdagni, and P. Kebarle, *ibid.*, **94**, 5128 (1972).

[7] M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *ibid.*, **93**, 4314 (1971).

[8] D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972).

[9] T. B. McMahon, R. J. Blint, D. P. Ridge, and J. L. Beauchamp, *ibid.*, **94**, 8934 (1972).

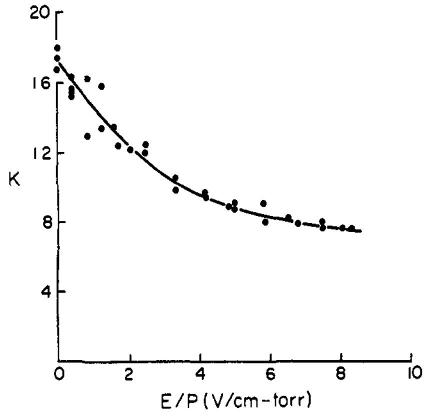

Figure 2. The effect of the repeller voltage on K: $T = 437 \pm 5$°K, $P = 3.00 \pm 0.05$ Torr, $10.96 \pm 0.08\%$ i-C_5H_{12} in i-C_4H_{10}.

Clearly such an explanation is not applicable to the bulky butane–pentane system here being considered, and we believe the behavior observed is to be attributed to the fact that the rate constant for the forward reaction producing t-$C_5H_{11}^+$ ions is significantly lower than those for the associative reactions studied in previous experiments. Ausloos and Lias[10] have shown that the rate constants for the hydride-transfer reactions of t-$C_4H_9^+$ with 22 alkanes (C_5–C_8) are on the order of 10^{-10}–10^{-11} cm^3/(molecule sec). These rate constants are significantly lower than the 10^{-9} cm^3/(molecule sec) which may be assigned to simple association reactions. One can demonstrate from a previously given[3c] analysis of equilibria in the mass spectrometer ionization chamber that the rate of approach to equilibrium is dependent upon the sum of the rates of the forward and reverse reactions involved in the equilibrium. Then one would expect that the slow forward rate constant involved in reaction 2 would cause the equilibrium to be achieved much more slowly than that which would be encountered in the faster associative equilibria. This in turn would require higher pressures (more collisions and longer residence times) for equilibrium to be attained. Similar findings have been made in icr experiments,[7,9] for it is found that 30–50 collisions are required to achieve equilibrium in a proton-transfer reaction between amines, but hydride-transfer reactions involving carbonium ions require several hundred collisions to reach equilibrium.

The ratio of the repeller field strength to the source pressure, E/P, is a measure of the mean energy acquired by the ions from the electric field. At sufficiently low E/P the ionic motion is characterized by slow drift in the field direction superimposed on the much faster random thermal motion.[11] In the "low field" region, $E/P \leq 10$ V/(cm Torr),[12] the ionic velocity distribution is approximately Maxwell–Boltzmann. The effect of E/P on the equilibrium constant is shown in Figure 2. In this experiment the pressure was kept at 3 Torr and the repeller was adjusted. The decrease in K as E/P increases may be due to the effect of the nonthermal component of ionic energy. Alternatively, the decrease in K may be attributed to the fact that as E increases the residence time of the ions decreases and results in a time limitation to the establishment of equilibrium.

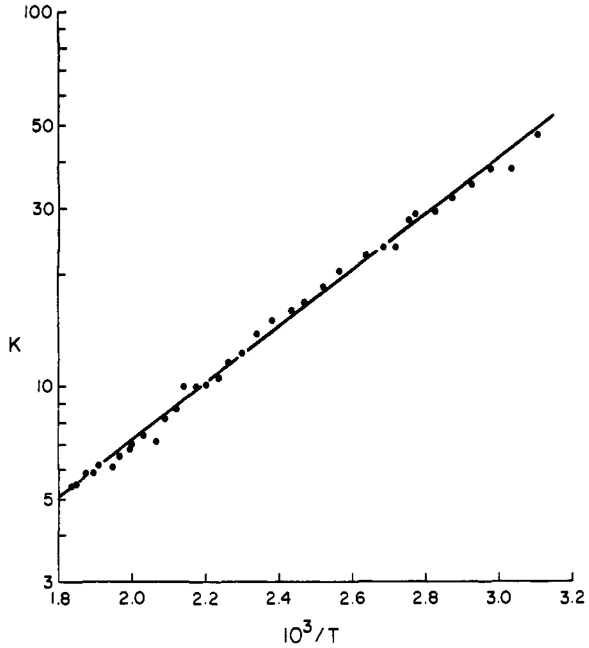

Figure 3. A van't Hoff plot for reaction 2: $P = 3$ Torr, $E/P = 5$ V/(cm Torr), i-C_4H_{10}/i-C_5H_{12} = 8.78.

Variation of the neutral gas ratios, $P_{i\text{-}C_4H_{10}}/P_{i\text{-}C_5H_{12}}$, was found to have little effect on K. The results of a study where $P_{i\text{-}C_4H_{10}}/P_{i\text{-}C_5H_{12}}$ was varied by a factor of 80 are given in Table I. The equilibrium constants determined ranged between 10.75 and 11.29.

Table I. Effect of Varying i-C_4H_{10}/i-C_5H_{12} Ratio on K^a

i-C_4H_{10}/ i-C_5H_{12}	K
84.76	11.17
8.78	11.24
3.70	11.29
1.04	10.75

[a] Pressure = 3 Torr, E/P = 5 V/(cm Torr), T = 436°K.

Reaction 2 was investigated as a function of temperature at 3 Torr of source pressure. The repeller was maintained at 6 V ($E/P = 5$ V/(cm Torr)) in order to obtain a usable instrumental sensitivity. Measurements were made on three neutral mixtures: 1.17 ± 0.02, 10.22 ± 0.08, and $49.02 \pm 0.13\%$ i-C_5H_{12} in i-C_4H_{10}. A van't Hoff plot for the second of these mixtures is given as an example in Figure 3. The plots obtained for the other two mixtures are analogous. Thermodynamic quantities obtained from least-squares regression analyses of the experimental points in the several plots are given in Table II. The average thermodynamic values obtained for the mixtures are $\Delta G°_{300} = -2.51 \pm 0.06$ kcal/mol, $\Delta H° = -3.57 \pm 0.10$ kcal/mol, and $\Delta S° = -3.5 \pm 0.3$ eu.

As is shown in Figure 2, the value of the equilibrium constant depends somewhat on E/P, but our past experience[3h] has been that ΔH is independent of E/P in the range with which we are here concerned. Thus, using Figure 2 we correct our value of $\Delta G°$ to that ap-

---

(10) P. Ausloos and S. G. Lias, *J. Amer. Chem. Soc.*, **92**, 5037 (1970).

(11) E. W. McDaniel, "Collision Phenomena in Ionized Gases," Wiley-Interscience, New York, N. Y., 1964, Chapter 9.

(12) E. W. McDaniel, V. Cermak, A. Dalgarno, E. F. Ferguson, and L. Friedman, "Ion-Molecule Reactions," Wiley-Interscience, New York, N. Y., 1970, p 65.

Table II. Experimental Thermodynamic Values[a] for $t\text{-}C_4H_9^+ + i\text{-}C_5H_{12} \rightleftharpoons t\text{-}C_5H_{11}^+ + i\text{-}C_4H_{10}$

$i\text{-}C_4H_{10}/i\text{-}C_5H_{12}$	$\Delta G°_{300}$, kcal/mol	ΔH, kcal/mol	ΔS, eu
84.76	−2.42	−3.57	−3.8
8.78	−2.56	−3.47	−3.0
1.04	−2.55	−3.67	−3.7
	Av −2.51 ± 0.06	−3.57 ± 0.10	−3.5 ± 0.3

[a] Pressure = 3 Torr, E/P = 5 V/(cm Torr).

propriate to zero field strength and in turn we calculate the corresponding value of $\Delta S°$ from the corrected $\Delta G°$ and the experimental $\Delta H°$. The values obtained are $\Delta G°_{300} = -2.9$ kcal/mol, $\Delta H° = -3.6$ kcal/mol, and $\Delta S° = -2.3$ eu. The experimental heat of reaction, $\Delta H° = -3.6$ kcal/mol, is equal to the difference between the hydride ion affinities of *tert*-butyl and *tert*-pentyl ions.

Lossing and Semeluk[13] have determined the ionization potential of *tert*-butyl ion to be 6.93 ± 0.05 eV (160 ± 1 kcal/mol). When this value is combined with a recent value for $\Delta H_f°(t\text{-}C_4H_9)$ of 9.3 kcal/mol,[14] we get the value $\Delta H_f°(t\text{-}C_4H_9^+) = 169$ kcal/mol. This is not an equilibrium value, but for present purposes it must serve as a starting point for our potential network of equilibrium energy values for gaseous carbonium ions. Combining this value with our value of ΔH from reaction 2 gives us a value for the heat of formation of *tert*-pentyl ions of $\Delta H_f°(t\text{-}C_5H_{11}^+) = 161$ kcal/mol. No reference point for free energies and entropies for gas-phase ions as yet exists, and it is probably wise to defer on a decision concerning choices for these quantities until more experimental $\Delta G°$ and $\Delta S°$ values are obtained. We are undertaking further measurements in this direction.

Our value for the enthalpy change for reaction 2 and the heat of formation of $t\text{-}C_5H_{11}^+$ may be compared with previously obtained energy values. The best value for $\Delta H_f°(t\text{-}C_5H_{11}^+)$ given by Franklin, *et al.*,[15] is 164 kcal/mol, which is taken from the photoionization measurements of Inghram and coworkers[16] on 2,2-dimethylbutane. The best value for $\Delta H_f°(t\text{-}C_4H_9^+)$ given by Franklin, *et al.*, has been superseded, and we consider the best value for this quantity to be the one we quoted above, namely, 169 kcal/mol. It is of interest that the value of $\Delta H_f°(t\text{-}C_4H_9^+)$ obtained by Inghram and coworkers[16] from photoionization measurements on *neo*-C_5H_{12} is 170 kcal/mol. The difference in the heats of formation of the *tert*-pentyl and *tert*-butyl ions obtained from the photoionization measurements is thus 6 kcal/mol. Our equilibrium experimental value for the enthalpy change in reaction 2 ($\Delta H = -3.6$ kcal/mol) may be combined with the difference in the heats of formation of isobutane and isopentane to yield a value of 8.4 kcal/mol for the difference in the heats of formation of *tert*-pentyl and *tert*-butyl ions. This agreement between the values obtained by two vastly different methods is as good as can be expected.

We think it of interest to point out that our value for the difference in the heats of formation of the two ions indicated that the introduction of a methylene group into *tert*-butyl ion involves a lowering of the heat of formation which is 3 kcal/mol greater than the lowering encountered when the methylene is inserted into isobutane to produce isopentane. Franklin[17] (see also Benson[18]) pointed out that the introduction of methylene groups into alkanes uniformly effects a lowering of the heat of formation of the molecule by 5 kcal/mol. The greater lowering observed between the *tert*-butyl and *tert*-pentyl ions is doubtless the effect of a polarization of the added methylene group by the charge on the pentyl ion.

Acknowledgments. This work was supported in part by a grant from the National Science Foundation. We wish to thank Esso Research and Engineering Co., Linden, N. J., for the gift of the Esso chemical physics mass spectrometer.

---

(13) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

(14) W. Tsang, *J. Phys. Chem.*, **76**, 143 (1972).

(15) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **26**, 45 (1969).

(16) B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961).

(17) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949); *J. Chem. Phys.*, **21**, 2029 (1953).

(18) S. W. Benson, "Thermochemical Kinetics," Wiley, New York N. Y., 1968.