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P. S. Skell,* J. C. Day

Department of Chemistry, The Pennsylvania State University
 University Park, Pennsylvania 16802

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Entropy Changes for the Protonation of Alkenes

Sir:

We wish to report experimentally determined entropy and enthalpy changes for proton transfers to olefins, which clarify inconsistencies in the literature, and give the first experimental values for the absolute entropies of tertiary alkyl ions.

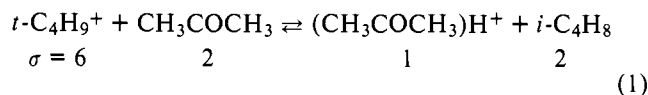
In recent studies of proton-transfer equilibria,¹ reaction enthalpies were derived from measured values for the free-energy change, ΔG° ,

$$-RT \ln K_{eq} = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (I)$$

making the assumption that the entropy change for the reaction can be predicted from changes in rotational symmetry numbers between products and reactants:

$$\Delta S^\circ (\text{proton transfer}) \approx \Delta S_{Rot} \approx R \ln (\sigma_{AH^+} \sigma_B / \sigma_{BH^+} \sigma_A) \quad (II)$$

However, a comparison of data from an ICR study^{1a} at 300 K with that from a high pressure mass spectrometric study^{1b} at 600 K reveals that there are reactant pairs for which "experimental" values of ΔS° show inconsistencies with eq II. In particular, the entropy change predicted for the equilibrium



was estimated to be +3.56 cal/(K mol) from eq II, assuming that the symmetry numbers are as shown above.^{1a,b} However, on this basis, the value for ΔG° measured at 600 K^{1b} should have been greater than the value determined at 300 K^{1a} by 1.1 kcal/mol (assuming, as usual, that ΔS° is approximately temperature independent). In fact the values determined^{1a,2} for ΔG° at 300 and at 600 K^{1b} differ by only 0.1 \pm 0.1 kcal/mol over this 300 K temperature range.

A determination of the entropy change associated with reaction 1 was carried out in the NBS pulsed ICR spectrometer.³ Equilibrium constants were determined in binary gas mixtures (pressure 10⁻⁶-10⁻⁵ Torr; observation time 0.2-0.3 s; temperature 300-400 K) in a pulsed ICR cell which can be ex-

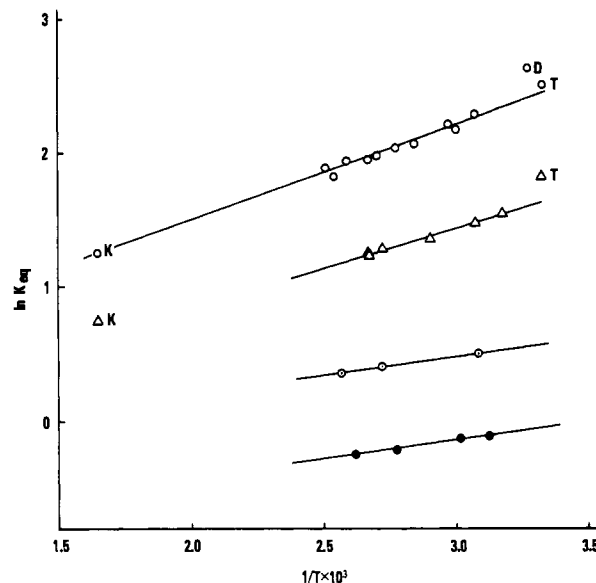
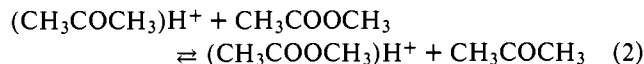


Figure 1. Plots of $\ln K_{eq}$ vs. $1/T$ for the equilibria: (1) (O); (2) (Δ); (3) (\odot); (4) (\bullet). Points labeled T are from ref 1a, K from ref 1b, and D from ref 2a.

ternally heated. Under these conditions, there was no evidence of ion loss due to the occurrence of competing reactions.^{2a} The resulting van't Hoff plot (Figure 1) indicates that, indeed, the entropy change for reaction 1 is 0.0 ± 0.3 cal/(K mol), rather than +3.56 cal/(K mol), assuming that ΔH_{Rn} is constant over the temperature range of the experiment.

In order to interpret this result it is important to note evidence that the entropy change associated with the protonation of acetone is 0. The value of ΔS° determined (Figure 1) for the process



is -0.45 ± 0.20 cal/(K mol). (This is in agreement with the value of -0.7 cal/(K mol) derived from values in the literature for K_{eq} at 300^{1a} and 600 K.^{1b}) As shown in Table I, this entropy change can be entirely attributed to the "intermolecular entropy change",⁴ $\Delta S_{Int} = R \ln Z_f/Z_r$, where Z_f and Z_r are, respectively, the ion-molecule collision rates in the forward and reverse directions.⁵ (This term approximates the configuration integral.) That is, for these reactants, ΔS_{Rot} (eq II) must be 0. The interpretation of this result is uncertain, but it implies either that the symmetry numbers for acetone and protonated acetone are the same (contrary to the assumption usually made), or that there is an additional contribution to ΔS° which cancels the contribution due to changes in external symmetry numbers. The same conclusion is indicated by the results presented in reference 1b, where an entropy change of $+0.16 \pm 0.4$ was determined for the equilibrium $(\text{CH}_3\text{COCH}_3)\text{H}^+ + \text{C}_2\text{H}_5\text{COOCH}_3 \rightleftharpoons (\text{C}_2\text{H}_5\text{COOCH}_3)\text{H}^+ + \text{CH}_3\text{COCH}_3$. For this equilibrium the entropy change

Table I. Entropy and Enthalpy Changes Determined for Proton-Transfer Reactions

Equilibrium	ΔH° , kcal/mol ^a	cal/(K mol)			
		Exptl $\Delta S^\circ =$	$\Delta S_{Rot}^b + \Delta S_{Int}^c + \Delta S_{other}^d$		
$t\text{-C}_4\text{H}_9^+ + \text{CH}_3\text{COCH}_3 \rightleftharpoons (\text{CH}_3\text{COCH}_3)\text{H}^+ + i\text{-C}_4\text{H}_8$	-1.47 ± 0.20	0.0 ± 0.3	$+2.19^e$	$+1.14$	-3.3
$t\text{-C}_5\text{H}_{11}^+ + \text{CH}_3\text{COCH}_3 \rightleftharpoons (\text{CH}_3\text{COCH}_3)\text{H}^+ + (\text{CH}_3)_2\text{C}=\text{CHCH}_2$	-0.55 ± 0.05	-0.64 ± 0.10	0^e	$+0.77$	-1.4
$t\text{-C}_6\text{H}_{13}^+ + \text{CH}_3\text{COOCH}_3 \rightleftharpoons (\text{CH}_3\text{COOCH}_3)\text{H}^+ + (\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_3$	-0.50 ± 0.10	-1.7 ± 0.3	0^e	$+0.09$	-1.8
$(\text{CH}_3\text{COCH}_3)\text{H}^+ + \text{CH}_3\text{COOCH}_3 \rightleftharpoons (\text{CH}_3\text{COOCH}_3)\text{H}^+ + \text{CH}_3\text{COCH}_3$	-1.20 ± 0.06	-0.45 ± 0.02	0^e	-0.50	

^a 1 kcal/mol = 4.18 kJ. ^b Calculated from eq II. ^c $\Delta S_{Int} = R \ln Z_f/Z_r$; see discussion. The collision rates were calculated using the formulations of ref 5a-d. ^d Attributed to loss of internal rotation; see discussion. ^e See discussion and note 6.

Table II. Relative Heats of Formation of Tertiary Alkyl Ions

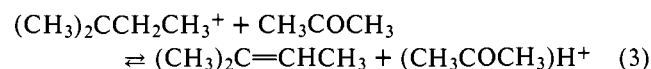
Ion	kcal/mol		
	This work	Ref 9a	Ref 9b
(CH ₃) ₃ C ⁺ ^a	0	0	0
(CH ₃) ₂ C ⁺ C ₂ H ₅ ^b	-6.8 ± 0.2	-7.6 ± 0.2	-8.0 ± 0.2
(CH ₃) ₂ C ⁺ CH ₂ CH ₂ CH ₃ ^b	-13.3 ± 0.4	-14.1 ± 0.4	-13.5 ± 0.4

^a On the basis of the appearance potential of *t*-C₄H₉⁺ from neopentane (B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961)), a value of 168.2 ± 0.55 kcal/mol can be derived for Δ*H*_f(*t*-C₄H₉⁺) (taking a value of 34.8 ± 0.2 kcal/mol for Δ*H*_f(CH₃) (K. E. McCulloh and V. H. Dibeler, *ibid.*, **64**, 4445 (1976)). The value for Δ*H*_f(*t*-C₄H₉⁺) is commonly based on the heat of formation and the ionization potential of the *t*-C₄H₉ radical. Taking the revised value for Δ*H*_f(*t*-C₄H₉) (12 ± 1 kcal/mol) (W. Tsang, *Int. J. Chem. Kinet.*, in press) and the ionization potential reported earlier (F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970)) (159.8 ± 1 kcal/mol), one obtains Δ*H*_f(*t*-C₄H₉⁺) = 172 ± 2 kcal/mol, rather than the unrevised number of 169.1 kcal/mol usually quoted. ^b Error limits are essentially those ascribed to the heats of formation of the relevant neutral species.

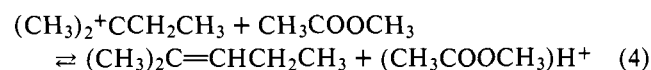
(Δ*S*_{Rot} + Δ*S*_{Int}) would be -1.8 cal/(K mol) if the symmetry numbers associated with acetone and protonated acetone were, respectively, 2 and 1.

Accepting that there is no Δ*S*_{Rot} associated with the protonation of acetone, a re-examination of the results for equilibrium 1 (Table I) reveals that since Δ*S*_{Rot} (eq II) is now be assumed to be *R* ln 6/2 or 2.19 cal/(K mol),⁶ and Δ*S*_{Int} is 1.14 cal/(K mol), the measured entropy change of 0 can only be accounted for if there is an additional unexplained component of the entropy change equal to -3.3 cal/(K mol). This entropy change can best be explained in terms of the loss of an internal rotation when a C-C bond in *t*-C₄H₉⁺ is replaced by a double bond in isobutene.⁷ An alternate view may be taken that the experimental result simply indicates that there is substantial rotational-vibrational coupling in the *tert*-butyl ion which invalidates the calculation of Δ*S*_{Rot} using such simplified concepts as symmetry numbers or losses of internal rotations. Taking a value of 70.17 cal/(K mol) for the absolute entropy of isobutene,⁸ these results indicate that the absolute entropy of the *tert*-butyl ion must be (70.17 + 1.14) cal/(K mol) or 71.3 cal/(K mol) (again taking the entropy change associated with the protonation of acetone to be 0).

Figure 1 also shows van't Hoff plots determined for the equilibria



and



The results are summarized in Table I. Since, in both cases, there should be no net change in external rotational symmetry numbers, it is only necessary to take into account Δ*S*_{Int} in order to calculate from the observed entropy changes the Δ*S* which may be associated with changes in internal rotation. These results lead to the conclusion that the loss of internal rotation in going from a C₅ or C₆ tertiary carbonium ion to the corresponding 2 olefin corresponds to an entropy change of -1.4 to -1.8 cal/(K mol).⁹ Taking a value of 80.92 cal/(K mol) for the absolute entropy of 2-methyl-2-butene, these results lead to a value of 82.3 cal/(K mol) for the absolute entropy of the *tert*-pentyl ion.

From these results, relative heats of formation of the (CH₃)₃C⁺, (CH₃)₂C⁺C₂H₅, and (CH₃)₂C⁺CH₂CH₂CH₃ ions were derived, and are compared in Table II with relative

heats of formation of these ions derived from equilibrium constants for hydride-transfer equilibria.¹⁰ The agreement is good within the error limits stated.

Acknowledgment. The authors express their appreciation to Dr. Michael Henschman for his thoughtful comments.

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- (6) If the symmetry of *t*-C₄H₉⁺ is taken as C_{3v} (W. J. Hehre in "Applications of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum Press, New York, N.Y., 1977, p 277), then Δ*S*_{Rot} is +0.81 cal/(K mol), and the measured entropy change of 0 can only be accounted for if the additional component is -1.9 cal/(K mol). This does not affect the value suggested from the experimental results for the absolute entropy of *t*-C₄H₉⁺, as the overall entropy change associated with the loss of a proton from *t*-C₄H₉⁺ is still -1.1 cal/(K mol).
- (7) The entropy change of -3.3 cal/(K mol) associated with the loss of the rotation of a -CH₃ group in going from *t*-C₄H₉⁺ to *t*-C₄H₈ is the same as the change of -3.4 cal/(K mol) associated with the loss of a methyl rotation in going from CH₃CHCH₂ to *c*-C₃H₆.⁸
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Pierre Ausloos,* Sharon G. Lias

Institute for Materials Research
National Bureau of Standards, Washington, D.C. 20234

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N-Cycloheptatrienyliidenemethylamine Oxide: Synthesis, Electronic Spectra, and Cycloadditions of a Fulvenoid Dipole

Sir:

The union of one terminus of a 1,3 dipole with both termini of a polyene gives a "fulvenoid dipole". Whether such a compound is stabilized or destabilized with respect to the fragments depends on the symmetries and relative energies of the π orbitals of the isolated moieties. Using the symbol X for the 1,3-dipole fragment,¹ the stabilities and reactivities of various fulvenoid dipoles can be predicted according to the simple model given in Figure 1.

Because of the polyene HOMO and LUMO symmetries, X will stabilize the diene if X is a good donor, while it will stabilize the triene only if X is a good acceptor. In such cases, strong HOMO-LUMO interactions between the fragments will stabilize the composite system and decrease its reactivity. However, union of a good donor, X, with the triene will lead not to stabilization, but to four-electron destabilization owing to closed-shell repulsion. Furthermore, the resulting increase in triene HOMO energy will lead to increased reactivity toward electrophiles. Union of a good acceptor X with a diene leads neither to stabilization nor to destabilization, but the diene