On the Activation Energy for Hydrogen Randomisation in the t-Butyl Cation

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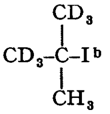
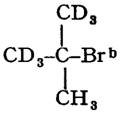
Summary The energy required for the loss of methane from the t-butyl cation in the mass spectrometer [1·9 ± 0·3ev; 44 ± 7 kcal mol^{-1}; (1·8 ± 0·3) × 10^2 kJ mol^{-1}] is also sufficient to randomise the hydrogens in the t-butyl cation; the difference in heats of formation of n-butyl and t-butyl cations, calculated on the basis that these ions lose methane by decomposition over the same potential energy surface is 33 ± 9 kcal mol^{-1} [(1·4 ± 0·4) × 10^2 kJ mol^{-1}].

RECENT n.m.r. studies of carbonium ions in strong acid solutions have resulted in the estimation of energies required for rearrangements of carbonium ions.[1] Saunders, *et al.*[2] have shown that the energy barrier for hydrogen and deuterium scrambling in the $[1,1,1,2,2,2\text{-}{}^2H_6]$-t-butyl cation generated in strong acid solution is greater than 28 kcal mol^{-1} (1·2 × 10^2 kJmol^{-1}).

In the mass spectrometer, the hydrogens and deuteriums in the $[{}^2H_6]$-t-butyl cation, generated from labelled t-butyl iodide and bromide are completely randomised prior to the loss of methane (Table). This behaviour parallels the scrambling observed in the n-butyl cation.[3]

The loss of deuteriated methanes from $C_4H_3D_6^+$ *generated from* t-$C_4H_3D_6$I *and* t-$C_4H_3D_6$Br [a]

Neutral species lost from $C_4H_3D_6^+$	 $CD_3\text{–}\overset{CD_3}{\underset{CH_3}{C}}\text{–}I$ [b]	 $CD_3\text{–}\overset{CD_3}{\underset{CH_3}{C}}\text{–}Br$ [b]	Calculated values for: Complete randomisation	No randomisation[c]
CD_4	15 ± 3%	13 ± 3%	12·0%	33·3%
CHD_3	40 ± 8	39 ± 8	47·6	33·3
CH_2D_2	36 ± 7	40 ± 8	35·7	0
CH_3D	9 ± 2	8 ± 2	4·7	33·3

[a] The data are taken from metastable transitions in the first field-free region of an AEI MS9 mass spectrometer, operating at 4 kv. The total loss of deuteriated methane for each compound is normalised to 100. [b] The comparatively large errors in the data arise from the interference of metastable transitions for the loss of deuteriated methyl radicals from *m/e* 62 (*M*$^+$ — HX). [c] Assuming 1,2-elimination and no isotope effect.

Appearance potential measurements on the metastable peak for methane loss show that the energy required for the loss of methane is 1·9 ± 0·3 ev [44 ± 7 kcal mol^{-1}; (1·8 ± 0·3) × 10^2 kJ mol^{-1}].† The value represents the upper limit for the activation energy for hydrogen randomisation in the t-butyl cation. Additional measurements show that the loss of methane from the n-butyl cation requires only 0·5 ± 0·3 ev [11·5 ± 7 kcal mol^{-1}; (0·48 ± 0·3) × 10^2 kJ mol^{-1}].

Prior to the loss of methane, n-butyl cations and t-butyl cations isomerise to a common structure (or a mixture of structures),[3] and the loss of methane occurs over a common potential energy surface (Figure), giving rise to metastable peaks of the same shape. The difference in energies required for the loss of methane from t-butyl and n-butyl cations therefore gives directly (without recourse to the heats of formation of other neutral species) the difference in heats of formation of the two ions. This is found to be 32·5 ± 9 kcal mol^{-1} [(1·4 ± 0·4) × 10^2 kJ mol^{-1}]. For ions in solution, it has been estimated[5] that the difference between tertiary and primary carbonium ions is about 30 kcal mol^{-1} (1·25 × 10^2 kJ mol^{-1}). Previous estimations[6] of the heats of formation in the gas phase of the t-butyl cation (176 kcal mol^{-1}; 7·4 × 10^2 kJ mol^{-1}) and the n-butyl cation (218 kcal mol^{-1}; 9·1 × 10^2 kJ mol^{-1}) give a difference of 42 kcal mol^{-1} (1·7 × 10^2 kJ mol^{-1}) for the two ions. These values are in broad agreement with our direct measurements.

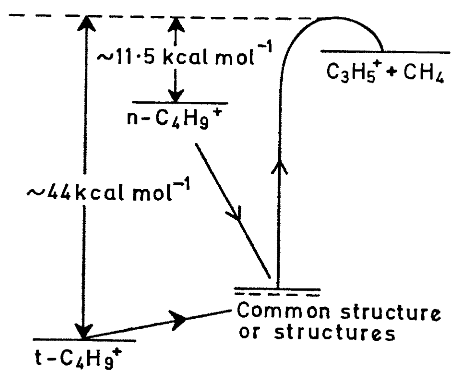


FIGURE. *Schematic representation of energy levels of n- and t-butyl cations and their decomposition.*

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† The error quoted is the estimated accuracy of the method used for appearance potential measurements (electron impact, semi-logarithmic plots) (ref. 4).

[1] See, *e.g.* M. Saunders in "Magnetic Resonance in Biological Systems " ed. A. Ehrenberg, Pergamon Press, Oxford, 1967, pp. 85—99.

[2] M. Saunders and J. Rosenfeld, *J. Amer. Chem. Soc.*, 1969, **91**, 7756.

[3] B. Davis, D. H. Williams, and A. N. H. Yeo, *J. Chem. Soc.* (*B*), 1970, 81.

[4] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionisation Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," National Bureau of Standards, U.S., 1969, p. 2.

[5] A. G. Evans, "The Reactions of Organic Halides in Solution," Manchester University Press, Manchester, 1946, p. 15,

[6] Ref. 4, p. 51.