Hydride Ion Transfer Reactions in the Gas Phase. Pressure Dependence of Reaction Efficiency as a Criterion for the Recognition of Anchimeric Assistance

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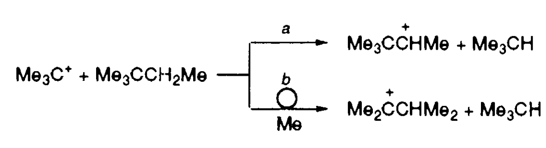
The efficiency (k_{obs}/k_{coll}) of the gas phase hydride ion transfer from 2,2-dimethylbutane to *tert*-butyl cation displays a pronounced positive pressure dependence, which suggests significant anchimeric assistance of the methyl groups of 2,2-dimethylbutane adjacent to the departing CH_2 hydride in the transition state.

In the isolated state, ion–molecule reactions occur at rates (k_{obs}) well below the collision rates (k_{coll}) because they are (*i*) moderately endothermic, (*ii*) exothermic, but involve an electrostatically-bonded encounter complex (EC) whose evolution to form the products requires crossing over an energy barrier $E^{\ddagger}$ protruding above the energy level E of the reactants ($\Delta E = E^{\ddagger} - E > 0$), or (*iii*) exothermic, but with $\Delta E = E^{\ddagger} - E$ small and negative.[1] Monitoring the temperature dependence of k_{obs} [positive for (*i*) and (*ii*), negative for (*iii*)] allows one to differentiate between these three cases. For case (*iii*) reactions, the negative temperature dependence of k_{obs} reflects the difference in the density of states of the transition structures which lead to reactants ('loose' transition state, high density, positive activation entropy) and products ('tight' transition state, low density, negative activation entropy).[2] Accordingly, a temperature decrease lowers the back-dissociation rate more than the rate of product formation, or, in other words, the lifetime of the EC increases together with the probability of crossing over the internal energy barrier to product formation.



$$Me_3C^+ + Me_3CCH_2Me \xrightarrow{a} Me_3C\overset{+}{C}HMe + Me_3CH$$
$$Me_3C^+ + Me_3CCH_2Me \xrightarrow[\text{Me}]{b} Me_2\overset{+}{C}CHMe_2 + Me_3CH$$

Scheme 1

The same condition can be attained by allowing the EC, excited by the interaction energy E developed in the ion–molecule association, to cool down *via* collisions with a buffer gas. In this case, a dependence upon the pressure of the buffer gas is expected for the reaction efficiency at constant temperature. In fact, increasing the buffer gas pressure favours collisional disposal of the excess internal energy of the EC and, therefore, its evolution through the lowest activation energy pathway [back-dissociation for (*i*) and (*ii*), conversion to products for (*iii*)].[3]

We aim here to verify whether the pressure dependence of the efficiency (k_{obs}/k_{coll}) of a given gas phase ion–molecule reaction

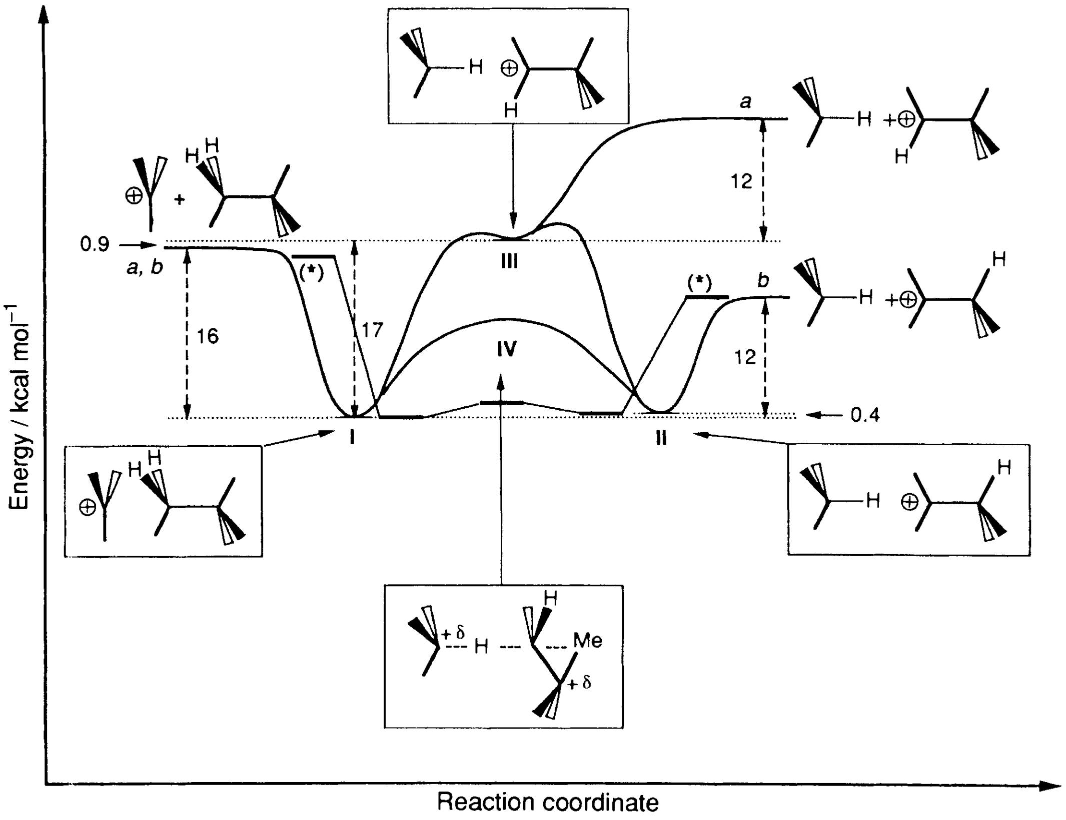


Fig. 1 Potential energy profiles of the gas phase hydride ion transfer from 2,2-dimethylbutane (curves *a*, *b*) or 2-methylbutane (*) to *tert*-butyl cation. Boxes depict electrostatically-bonded ion–molecule complexes. Thermochemical values taken from ref. 4. The depths of the potential wells corresponding to the electrostatically-bonded adducts **I**, **II** and **III** were obtained from classical ion–molecule interaction theory,[7a] taking 3.3 Å as the average distance between the ion and the neutral molecule. This distance is determined by coincidence of the calculated potential well depth of **II** with the experimental one (12.1 kcal mol^{-1}), measured for strictly related systems.[7b] The activation barrier connecting **III** to **I** is *ca.* 1 kcal mol^{-1},[7c] whilst that connecting **III** to **II** exceeds 3 kcal mol^{-1}.[7d] The internal activation barrier of profile (*) was estimated not to exceed 2 kcal mol^{-1}.[6] No quantitative significance is attached to the height of the activation barrier through **IV** which, however, must be comparable to that of curve (*).

can be used as a tool for the elucidation of some mechanistic details about the reaction. A reaction which lends itself to such an inference is the hydride ion transfer from 2,2-dimethylbutane to the *tert*-butyl cation (Scheme 1).

The relevant energy profiles are shown in Fig. 1.[4] Accordingly, occurrence of the remarkably endothermic reaction *a* [$\Delta H°(a)$ = +13 kcal mol^{-1}; 1 cal = 4.184 J] is expected to be prevented under all conditions, whereas process *b* might be observable [$\Delta H°(b)$ = −4 kcal mol^{-1}], depending upon the height of the energy barrier, and therefore upon the nature of the transition state, connecting complexes **I** and **II**.

Occurrence of hydride ion transfers *a* and *b* has been investigated at very different buffer gas pressures, using both FT-ICR† and radiolytic techniques.‡

In the FT-ICR experiments, no detectable formation of $C_6H_{13}^+$ products was observed after 30 s reaction time, namely after *ca.* 50 collisions with the neutral species.[5] In the radiolytic experiments, exclusive occurrence of reaction *b* was demonstrated by the formation of a single product, namely 2,3-dimethyl-2-butyl methyl ether, in appreciable yields (3–10%). In agreement with the endothermicity of reaction *a* and with FT-ICR results, 3,3-dimethyl-2-butyl methyl ether was never detected in all irradiated systems, in spite of a specific search.

The experimental evidence is summarized in Table 1, together with additional radiolytic data by Ausloos and Lias obtained at 143 Torr total pressure.[6]

The very poor efficiency of reactions *a* and *b* in the isolated state approached in the FT-ICR experiments (Table 1) conforms to the energy profile of Fig. 1, where complex **I** is separated from the high energy intermediate **III** by an energy barrier slightly protruding (ΔE = *ca.* 1–2 kcal mol^{-1}) over that of back-dissociation of **I** to reactants. At pressures ⩾ 160 Torr the reaction occurs readily,§ its efficiency being only 2.7 times lower than that of the 3 kcal mol^{-1} exothermic hydride ion transfer from 2-methylbutane to *tert*-butyl cation (denoted by * in Fig. 1), whose activation energy does not exceed 1.8 kcal mol^{-1}.[6] This necessarily implies that, at these pressures, a lower energy transition state becomes accessible along the reaction coordinate of reaction *b* (**IV** in Fig. 1). At pressures ⩾ 160 Torr, crossing over **IV** is allowed by efficient collisional quenching of complex **I**, which prevents its back-dissociation. In terms of timing, this means that, above 160 Torr, the high frequency of buffer gas stabilizing collisions ($\geqslant 5 \times 10^9$ s^{-1}) enhances the lifetime of **I** such that a methyl group adjacent to the cleaving C–H bond can anchimerically assist the departure of the hydride ion. At 4×10^{-8} Torr, back-dissociation of **I** by far prevails over its collisional quenching (collision frequency = *ca.* 2 s^{-1}) and, thus, anchimeric assistance to the hydride ion transfer has insufficient time to occur.

In conclusion, the non-occurrence of reaction *a* under all conditions and the positive pressure dependence of reaction *b* suggest, in compliance with previous indications,[8] that the efficiency of exothermic hydride ion transfers in the gas phase can be heavily influenced by the lifetime of the EC. Above a certain pressure limit, the EC lifetime becomes long enough to allow hydride ion transfer to proceed through a low energy, low entropy transition state, unaccessible at shorter EC lifetimes, which involves anchimeric assistance to the hydride ion transfer.

Table 1 Reaction efficiency (k_{obs}/k_{coll}) as a function of pressure

Pressure/Torr	k_{obs}/k_{coll}	$k_{obs}/k_{ref}{}^a$	Source
4.0×10^{-8}	$<4.0 \times 10^{-4b}$	—	This work^c
143	$<1.5 \times 10^{-4}$	$<5 \times 10^{-3}$	Ref. 6^d
160	*ca.* 0.1	—	This work^d
643	*ca.* 0.04	0.37	This work^d
702	*ca.* 0.03	—	This work^d

^{a} Competition experiments using 2-methylbutane as the reference substrate. ^{b} Calculated by considering the extent of the reaction *a* in Scheme 1 as below 2% after 30 s reaction time. ^{c} FT-ICR experiments. ^{d} Radiolytic experiments. Radiation dose: 1.5×10^4 Gy (dose rate: 10^4 Gy h^{-1}).

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Footnotes

† In the FT-ICR experiments, *tert*-butyl cations were generated by 70 eV electron bombardment of isobutane in the external chemical ionization source of an APEX 47e FT-ICR mass spectrometer (Bruker Spectrospin) at 25 °C and at 3×10^{-5} Torr.[9] The ions were transferred into the FT-ICR 'infinity cell'[10] containing 4×10^{-8} Torr of 2,2-dimethylbutane and quenched by collision with propane (*ca.* 10^{-6} Torr peak pressure) introduced into the cell by a pulsed magnetic valve.[11] After their sequential isolation by 'single shots',[12] *tert*-butyl cations were allowed to collide with 2,2-dimethylbutane.

‡ In the radiolytic runs, *tert*-butyl cations were readily generated at atmospheric pressure by γ-irradiation of isobutane or neopentane (150–680 Torr) ^{60}Co source, room temp.[9] and allowed to react with 2,2-dimethylbutane (10 Torr), in the presence of trace amounts of MeOH (1 Torr) as the nucleophile, and of O_2 (10 Torr) as a thermal radical scavenger.

§ The evident discrepancy between the reaction efficiency from the present experiments and Ausloos' ones is likely to be due to the completely different composition of the corresponding irradiated mixtures. In Ausloos' runs, in fact, the bulk component (*ca.* 70%) of the gaseous mixture is 2,2-dimethylbutane, instead of neopentane, and, therefore, formation of *tert*-butyl cations is severely hampered by absorption by 2,2-dimethylbutane of most of the radiation energy.

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