

Experimental Verification of the Intermediacy and Interconversion of Ion-Neutral Complexes as Radical Cations Dissociate

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Specific hydrogen exchange provides experimental verification of the intermediacy of ion-neutral complexes in the reactions of simple alcohol and ether radical cations; interconversion of ion-neutral pairs can occur when loss of alkyl radicals and loss of alkane molecules have similar energy requirements.

Unimolecular rearrangements of gas-phase radical cations have been thought of traditionally as transformations within the covalently bonded molecular ion. Recently, ion-neutral complexes have been invoked as intermediates in radical cation dissociation reactions to account for a variety of intramolecular hydrogen transfer reactions.¹⁻⁵ These intermediates are suggested to arise by simple bond cleavage, leading not to immediate separation of the incipient fragments, but, instead, to an ion-radical pair bonded by electrostatic forces (ion-dipole or ion-induced dipole interactions). The assumption that inter-species hydrogen transfer can occur within the complex provides a convenient means to rationalize reactions that are considered impossible or implausible for the initial molecular ion. However, the putative intermediacy of such complexes has not been verified experimentally, nor has the presumed presence of intermediate complexes provided testable predictions. We show here that simple thermochemical considerations can provide exacting predictions for the reactions of intermediate ion-neutral complexes. Experimental confirmation, in turn, lends direct support to the suggested intermediacy of complexes and shows that reversible interconversion of complexes can occur.

Hydrogen transfer is the simplest inter-species reaction possible in an ion-neutral complex formed by attempted dissociation of an aliphatic radical cation. If the hydrogen transfer is appreciably exothermic rapid dissociation will ensue, since the initial complex is only moderately stabilized relative to the separated fragments.⁵ This is the more commonly encountered situation; the intermediacy of the complex may have kinetic consequences,⁶ but it is otherwise difficult experimentally to distinguish the complex-mediated process [equation (1)] from a transformation within the covalently bonded molecular ion.

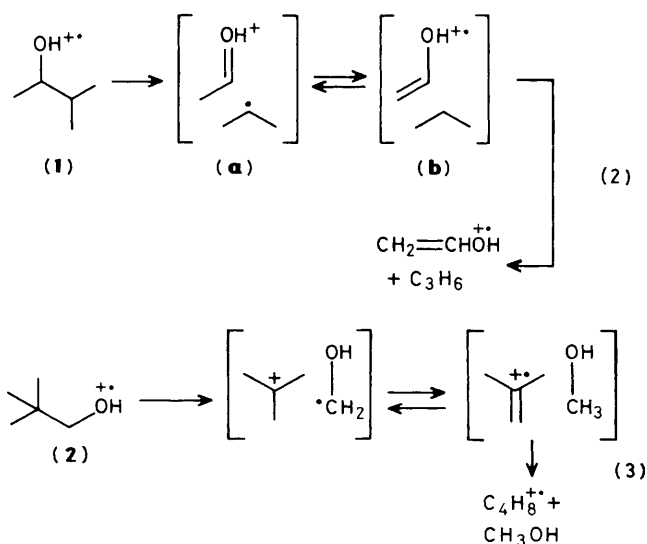
However, an approximately thermoneutral hydrogen transfer will not result in rapid dissociation but in formation of a second ion-neutral complex, in which the bonding electrostatic interactions should be of the same magnitude as in the initial complex. More importantly, thermoneutral hydrogen transfers could well be reversible if the complexes are sufficiently stabilized with respect to dissociation, which in suitable cases should allow interchange of hydrogen atoms.

The reactions of the 3-methylbutan-2-ol (1) and neopentyl alcohol (2) radical cations allow these predictions to be examined. Simple cleavage close to threshold in both cases may involve intermediate formation of stabilized ion-radical

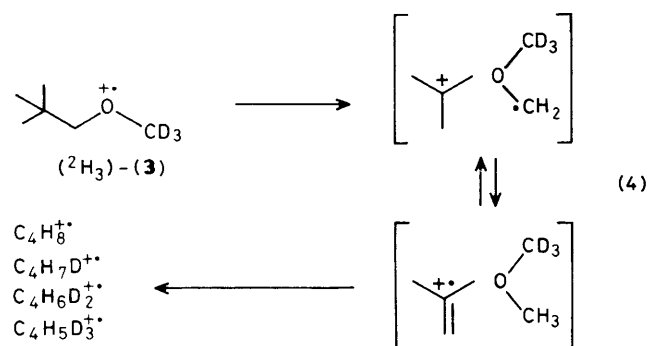
complexes,⁵ and the products formed by simple cleavage (radical loss) and by rearrangement [equations (2) and (3)] are very close in energy; that is, the hydrogen transfer is in both cases approximately thermoneutral.[†] The simple cleavage reactions predominate in the ion source, whereas propane loss from (1) and methanol loss from (2) are the major processes observed for the low-energy ions reacting in the second field-free region.⁹

If in the reaction of 3-methylbutan-2-ol (1) the interconversion of complexes (a) and (b) [equation (2)] were reversible, exchange of the C(1) and C(3) hydrogen atoms should occur, whereas the remaining hydrogen atoms should retain their positional identity. The spontaneous and collision-induced reactions of low-energy molecular ions demonstrate that this is the case. The predominant spontaneous reaction of (²H₃)-(1) is loss of C₃H₆D₂, which requires exchange as well as specific transfer; loss of propane is also a collision-induced process (suggesting the presence of species with a preformed C₃H₈ unit), in which (²H₃)-(1) loses C₃H₆D₂ as well as C₃H₇D (1:1). The major collision-induced simple cleavage reactions include loss of CHD₂[•] and C₃H₆D[•], both processes demonstrating exchange. Correspondingly, the collision-induced reactions of (²H₁)-(1) show considerable loss of C₃H₇[•]. Deuterium atoms introduced at other positions do not participate in the transfer and exchange processes.

The reactions of closely related radical cations such as those



[†] The exothermicity of hydrogen transfer calculated as the difference between the heats of formation of the products of simple cleavage (alkyl loss) and the heats of formation of the products of hydrogen rearrangement (alkane loss), by using data from refs. 7 and 8.



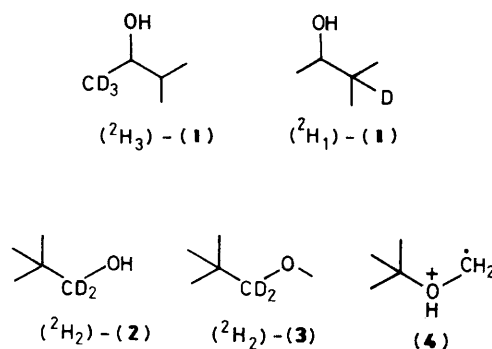
of propan-2-ol, butan-2-ol, pentan-3-ol, and 2-methylpentan-3-ol show isotopically specific loss of alkane molecules, without appreciable H/D exchange in the spontaneous or collision-induced reactions. In these cases, the hydrogen-transfer step is exothermic, causing immediate dissociation of the [alkane + enol]⁺ pair. Hydrogen exchange is not important prior to loss of ethane from labelled *s*-butyl methyl ether, even though the hydrogen transfer should be close to thermoneutral, presumably because the ethane–vinyl ether complex is not sufficiently stabilized.

The elimination of neutral CH₃OH from low-energy neopentyl alcohol radical cations (2) is accompanied by hydrogen exchange between the α-CH₂ and *t*-butyl groups. The fragmentation of (2H₂)-(2) shows incorporation of 0, 1, or 2 deuterium atoms in the C₄H₈⁺ product (ratio *ca.* 1:2:1). The labelled methyl neopentyl ethers, (2H₂)-(3) and (2H₃)-(3), react analogously; extensive deuterium incorporation into the C₄H₈⁺ product ion is observed in both cases [equation (4)]. Exchange is expected if (2) and (3) react *via* ion–neutral complexes, since the hydrogen transfer step is close to thermoneutral in both cases.[†] These complexes are particularly stabilized by virtue of the permanent dipole in the neutral species. In fact, the electrostatic interactions in a [t-C₄H₉⁺ · CH₂OH] complex at moderate inter-species distances will exceed the strength of the bond broken; that is, the neopentyl alcohol radical cation is higher in energy than the complex.[‡] A similar situation is encountered for the neopentyl bromide radical cation, but loss of CH₃Br is not accompanied by exchange, since the hydrogen transfer is exothermic.[§]

The orientation of the C–O bond in the molecular ions of (2) is almost the opposite of that of the C–O dipole in the complex; the latter in turn resembles a distonic isomer (4) of *t*-butyl methyl ether, for which similar exchange and fragmentation reactions are expected.¹¹ The H/D exchange for (2H₃)-(3) demonstrates that the inter-species separation in the ion–neutral complex can be large enough to allow the two species to rotate with respect to each other, rendering the two methyl groups in the dimethyl ether fragment equivalent [equation (4)].

† The heat of formation of the complex is calculated as the heats of formation of the products less the electrostatic stabilization. The Δ*H*_f value for the neopentyl alcohol radical cation is 155 kcal mol^{−1} (estimated⁷); Δ*H*_f(*t*-C₄H₉⁺) is 165 kcal mol^{−1}⁸ and Δ*H*_f(·CH₂OH) is −6 kcal mol^{−1}.⁸ The [t-C₄H₉⁺ · CH₂OH] complex is stabilized by about 9 kcal mol^{−1} (ref. 5) at an inter-species distance of 4 Å, making it some 5 kcal mol^{−1} lower in energy than the molecular ion. A similar calculation shows that the energy of the [CH₃CH=OH⁺ · C₃H₇] complex is close to that of (1)⁺⁺.

§ The value of Δ*H*_f for (CH₃)₃CCH₂Br⁺⁺ is 196 kcal mol^{−1}; Δ*H*_f(C₄H₉⁺ + ·CH₂Br) is 205 kcal mol^{−1}; Δ*H*_f(C₄H₈⁺ + CH₃Br) is 199 kcal mol^{−1}; stabilization at 4 Å, 12 kcal mol^{−1}; thermochemical data from refs. 7, 8, and 10. Loss of neutral CH₃Br is also observed from (CH₂Br)₂CHOH⁺⁺.



The metastable peaks for loss of alkane molecules from ether and alcohol molecular ions are exceedingly narrow when the hydrogen transfer step is close to thermoneutral [e.g. the kinetic energy released when (1) loses C₃H₈ is 1 meV; loss of CH₃OH from (2) also releases 1 meV]. The kinetic energy released when the alkanes arise by exothermic hydrogen transfer reactions is typically between 10 and 25 meV, reflecting the exothermicity of the final step. The metastable peak width is thus not necessarily a good indicator of whether or not a reaction is complex-mediated;¹² such reactions, however, should not give rise to dish-shaped metastable peaks.

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