Deuterium Isotope Effects in a Triply Degenerate Cyclopropylethyl Cation†

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The equilibrium isotope effect on the degenerate rearrangement of the 1-(2,3-dimethylcyclopropyl)ethyl cation is compared with theoretical and other experimental data and the implications for the interpretation of kinetic isotope effects and for the investigation of hyperco-ordinated carbocations are discussed.

The fast rate of solvolysis and the rapid interconversion of cyclopropylmethyl and cyclobutyl derivatives have been extensively investigated.[1] The 'primary cyclopropylmethyl cation' $C_4H_7^+$, and its methyl analogue, $C_4H_6Me^+$, are, with the 2-norbornyl cation,[2] carbocations whose structures have led to much controversial discussion. The size and direction of the deuterium equilibrium isotope effect (E.I.E.) in the two C_4-cation systems can be explained consistently only if hyperco-ordinated triply degenerate bicyclobutonium ions are the minimum energy species.[3—5]

To support this conclusion and to show the scope and further applications of the deuterium perturbation method[6] we have investigated the E.I.E. in the 1-(2,3-dimethylcyclopropyl)ethyl cation, (1), a closely related species for which the structure and dynamic behaviour are not in dispute.

The fast triply degenerate rearrangement[7] of cation (1) (−70 °C; [13]C n.m.r. δ 136.64, averaged C^+/C-2/C-3; 89.23, C-1; 19.34, averaged Me-groups) has been frozen out in the 100 MHz [13]C n.m.r. spectrum.‡ At −70 °C the averaged C^+/C-2/C-3 methine signals already show large kinetic line broadening and separate at −154 °C into two broad lines (δ 232, C^+; 88, 2,3-CH).§ The averaged methyl groups are split into two signals (−154 °C; 29.8, C^+-Me; 13.6, 2,3-Me [Figure 1(a)]. The low temperature spectrum is as expected for the 1-(2,3-dimethylcyclopropyl)ethyl cation with a tri-co-ordinated cationic carbon centre. This is direct experimental proof for the same earlier assumption,[7] which was deduced from applying the additivity of chemical shift analysis to cation (1).[8]

The [13]C n.m.r. spectrum of a mixture of (1) and [2]H-(1) at −70 °C shows typical isotope splittings of those peaks which are averaged in the unlabelled ion, whereas the signal for the 1-cyclopropyl carbon atom which is not averaged shows no effect. The splittings are caused by the loss of degeneracy of the rearrangements in the deuteriated ion and as expected the E.I.E. and thus the isotope splittings disappear in the spectrum of the frozen out cation at −154 °C.

Three peaks for the averaged C^+/CH-carbon atoms and for the Me groups are observed in the ion mixture (1)–[2]H-(1). The methyl signals [Figure 1(c)] show less kinetic line broadening and are thus easier to recognize than the broad methine signals. The middle peak in Figure 1(c) (δ 19.34) results from the non-labelled cation (1) [Figure 1(b)]. The two outer lines are from the deuteriated ion [2]H-(1). Intensity ratios and relative size of the isotope splittings are not symmetric with respect to the peak of the protio ion (1). The intensity ratio of

2 : 1 for the downfield and the upfield signals of [2]H-(1) results from the fact that only one of the three methine positions is deuteriated.

The ratio of the isotope shifts is 1 : 2 for the downfield and the upfield peaks of [2]H-(1) relative to (1), when an intrinsic shift for the highfield signal is taken into account.¶ The two site fast exchange taking place between the singly populated lowfield site (the C^+-Me position) and the doubly populated highfield site (the two equivalent cyclopropyl Me positions) is perturbed by deuterium. The direction of the E.I.E. can be derived from the intensity ratios. A peak with relative intensity 1 is shifted upfield indicating that the Me group which is bound to the deuteriated methine is preferentially on the cyclopropyl ring.

An analogous interpretation is possible for the isotope splittings of the perturbed methine carbon atoms. The direction of the E.I.E. is not only evident from the intensity ratio (2:1) of the two signals from the deuteriated ion, but also because the upfield peak (intensity 1) shows extra broadening due to unresolved deuterium couplings. The relative size of the splittings, corrected for a one bond intrinsic isotope shift¶ is 1 : 2, downfield *vs.* upfield with respect to the signal for the unlabelled ion.

The splitting patterns for both averaged positions are as expected and show that the ring deuteriated cations (1b) and (1c) are preferred over (1a) in the equilibrium (1a) ⇌ (1b) ⇌ (1c).

The observed isotope splittings are a direct measure of the perturbation of the equilibrium by the deuterium atom. The equilibrium constant K is calculated from the isotope splittings¶ δ_{iso} in the deuteriated cation using the equation $K = \Delta + \delta_{iso}/\Delta - 2\delta_{iso}$ where Δ is the shift difference of exchanging sites in the static cation. K Varies from 1.299 to 1.205 between −110 °C and −65 °C. Thermodynamic parameters for the equilibrium are determined from $\ln K = -\Delta H^0/(RT) +$

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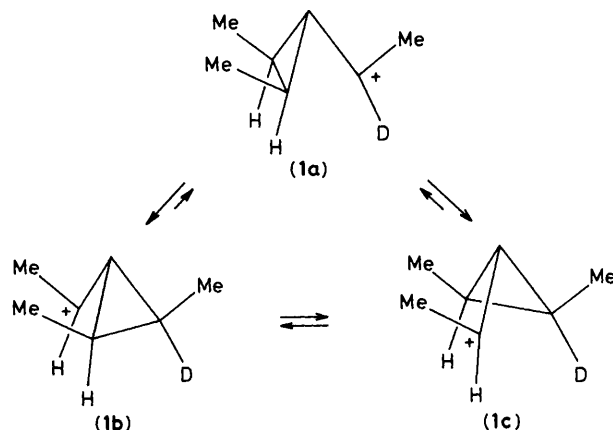
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‡ Previous attempts to freeze out the process were not successful (ref. 7).

§ Low temperatures were extrapolated from calibrated temperatures down to −125 °C. Viscosity and kinetic line broadening may contribute to the line width and lead to accidental overlap of C-1 and C-2,3 peaks.

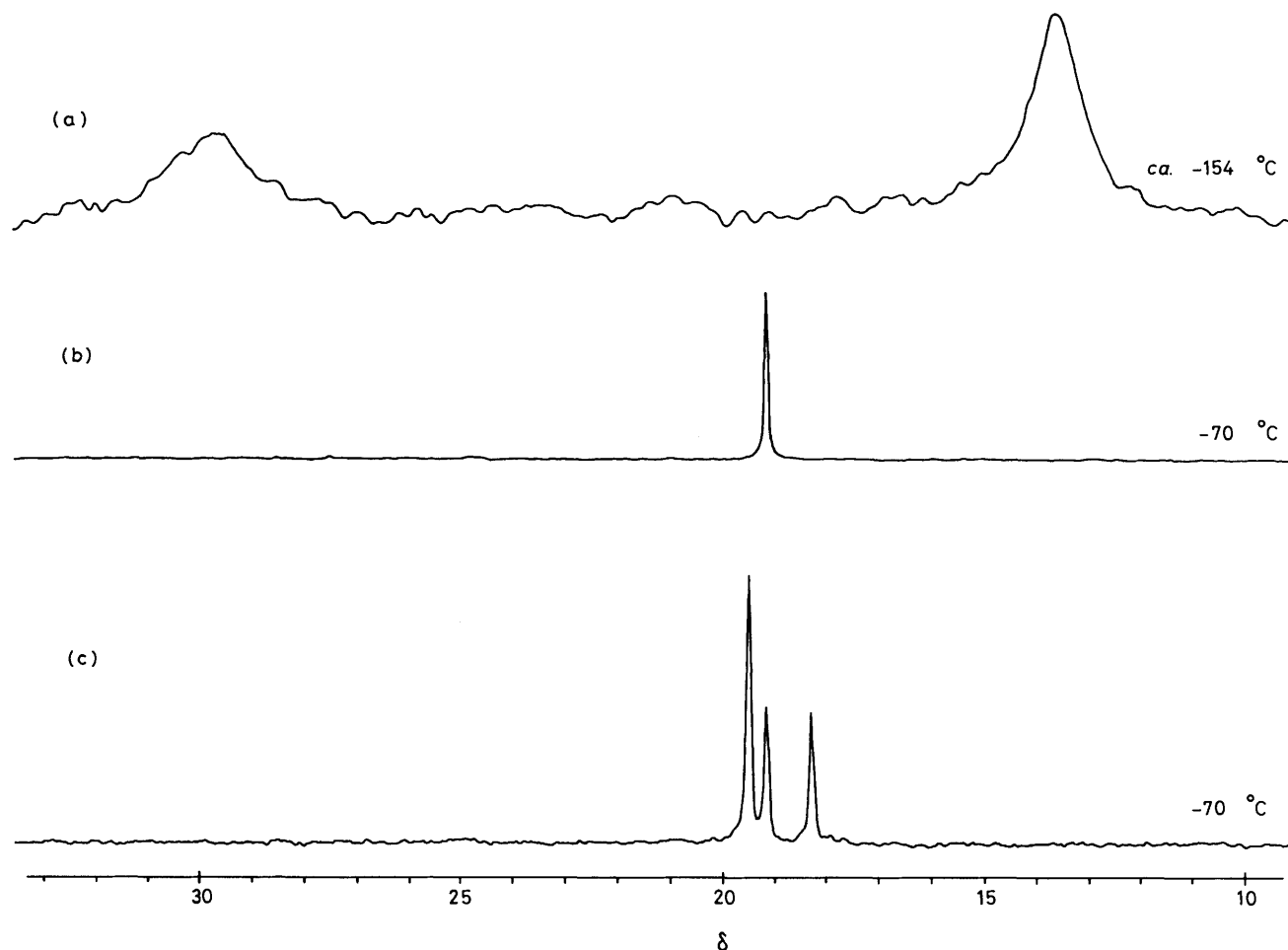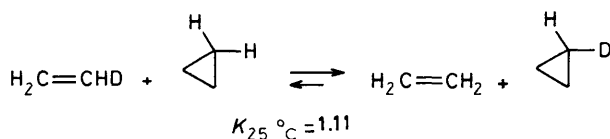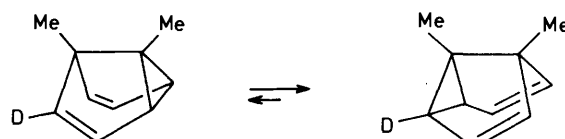¶ Intrinsic upfield shift: δ 0.48 (C^+) and 0.17 (C^+-Me).

Figure 1. Methyl region of 100.62 MHz ^{13}C n.m.r. spectra in $SO_2ClF-SO_2F_2$ (2:1). (a) (1), -154 °C; (b) (1), -70 °C; (c) ^2H-(1) and (1) (3:1), -70 °C.

Scheme 1

Scheme 2

$(\Delta S^0/R)$ via regression analysis as $\Delta H^0 = -115.5 \pm 2.5$ cal mol^{-1} and $\Delta S^0 = -0.18 \pm 0.01$ cal mol^{-1} K^{-1}. ‖

The E.I.E. in cation ^2H-(1) which, strictly speaking, is a differential α- vs. γ-effect** may be compared with H/D fractionation factors of simple molecules which can be calculated from vibrational spectral data via the Bigeleisen equation or via force field calculations.[10] The fractionation factor, K_f, for [^2H]cyclopropane relative to [^2H]ethene is 1.11 at 25 °C.[11] This is a model value for the maximum expected size of an α-deuterium isotope effect for a hypothetical reaction in which a C–D bond at a sp^2 hybridized carbon in an alkene is exchanged with a C–D bond at a cyclopropane

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‖ 1 cal = 4.184 J. Thermodynamic parameters are given with the favoured sign in the direction of the E.I.E.

** γ-Deuterium isotope effects in cyclopropylmethyl cations are small (ref. 9).

(Scheme 1). This value of K_f, being greater than unity, indicates that the deuterium binding is tighter and its vibrations are stiffer in a cyclopropane position than at the sp^2 hybridized carbon position. The zero point energy (Z.P.E.) for C–H and C–D bond vibrations is therefore higher for bonds at the cyclopropyl position. Protons which have a higher Z.P.E. for a given bond force constant prefer, in an isotopic exchange equilibrium, the position with the lower force constant which is at the sp^2 carbon atom.

The experimental results on cation ^2H-(1) are in good agreement with the calculated value; extrapolation of the measured K for ^2H-(1) to 25 °C gives $K = 1.11$. The quantitative coincidence may be rather accidential considering the simplifications inherent in this model.

In the Cope rearrangement of 1,5-dimethyl-2-deuterio-

semibullvalene[12] a comparable exchange situation exists for the deuterium bonded either to a sp^2 hybridized carbon or to a cyclopropane ring (Scheme 2). The experimentally observed α- vs. γ-E.I.E. in this system ($K_{25\,°C} = 1.11$; $\Delta H^0 = -116$ cal mol^{-1}; $\Delta S^0 = -0.18$ cal mol^{-1} K^{-1}) shows very good agreement with the observed values for the equilibrium constant and the thermodynamic parameters in the cation, as well as with the fractionation factor.

This confirms the postulate derived from kinetic isotope effect measurements in nucleophilic substitution reactions that the tightness of binding of deuterium is the same at an sp^2 hybridized carbon atom in a carbonium ion and an alkene.[10] We have demonstrated that the perturbation method can be applied successfully to this kind of cation system. Detailed information on the relative strength of bond force constants is obtained which cannot be obtained easily by other methods. These results support the current interpretation of the E.I.E. as observed in hyperco-ordinated bicyclobutonium ions which are different in sign and magnitude and depend on the different bonding strengths for the two protons at the pentaco-ordinated carbon atom.[3,4]

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