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THE CHARACTERIZATION OF AND THE EVOLUTION OF MOLECULAR HYDROGEN BY THE μ-HYDRIDO-BRIDGED CYCLODECYL CATION. RELEVANCE TO THE QUESTION OF HYDROCARBON PROTONATION BY SUPERACIDS

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Abstract The observable cyclodecyl cation is established as having a 1,5-μ-hydrido-bridged structure and most probably exists as a mixture of conformational isomers. This solution carbocation is unique in organic chemistry in that it evolves molecular H_2 at temperatures below -100°C to give the 9-decalyl cation. The mechanism of this reaction is postulated to involve a pentacoordinated carbocation intermediate or transition state with a structure identical to what one would get by protonating the bridgehead C-H bond of decalin. Since conversion of decalin to the decalyl cation in superacids is not accompanied by significant H_2 production, the mechanism of these two reactions must be different, and in the latter case could not involve a protonated pentacoordinate carbocation intermediate, as has been postulated.

In this paper, we would like to report the full details of the characterization of the cyclodecyl carbocation system[1], including work on the subsequent rearrangement of this cation to the decalyl cation and dihydrogen. Since the decalyl cation can also be prepared by the addition of decalin to superacids, one has a unique opportunity to examine the mechanism of the latter reaction, which is a still controversial subject.

Results and Discussion

The addition of 1-chlorocyclodecane to a solution of either 1:1 SbF_5-FSO_3H or pure SbF_5 in a mixture of SO_2ClF-SO_2F_2 at ca. -140°C or the addition of either cis or trans-cyclodecene to the 1:1 SbF_5-FSO_3H mixture results in a light yellow carbocation solution. Both the ^1H and ^{13}C NMR spectra (Figs. 1 and 2) are characteristic of a μ-hydrido-bridged carbocation, particularly the presence of a broad peak at δ -6.85, a unique high-field

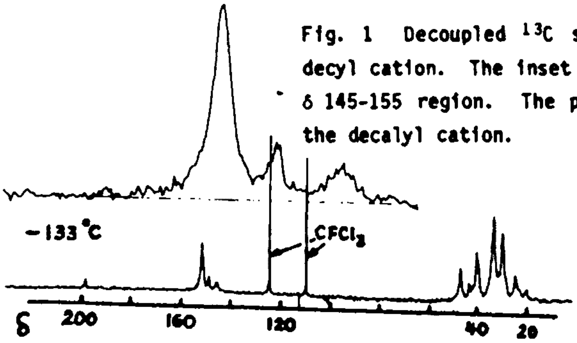


Fig. 1 Decoupled ^{13}C spectrum of the cyclodecyl cation. The inset is an expansion of the δ 145-155 region. The peak near δ 200 is from the decalyl cation.

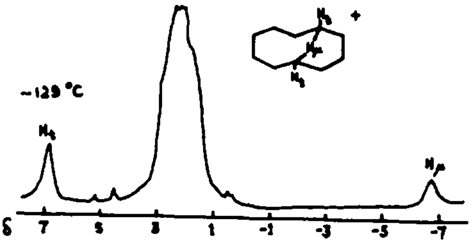
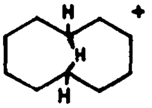
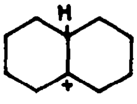


Fig. 2 ^{1}H NMR spectrum of the cyclodecyl cation. The area ratio of the peaks at δ 6.80 and -6.85 is almost exactly 2:1 but the combined ratio of these protons to the remaining ^{1}H area is 1:8.2 (theoretical 1:5.33).

position shown previously to be characteristic for bridging hydrogen[2] (see Experimental for chemical shifts and coupling constants). In the preliminary communication of this work[1], this carbocation was assigned a 1,6-μ-hydrido-bridged structure 1. This was based on the fact that the cation rearranged at higher temperatures to the decalyl cation 2 and dihydrogen, a reaction that we felt suggested the 1,6-bridging structure. Also, at this point in time, the only previously known μ-hydrido-bridged carbocation also possessed a 1,6-bridging structure, i.e., cation 3[2a,c]. However it is now apparent that the cyclodecyl cation must be assigned a 1,5-μ-hydrido-bridged structure 4. This is based on the following pieces of evidence, which will be elaborated in turn:



1



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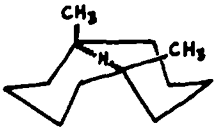

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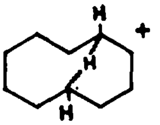
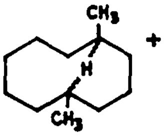


4



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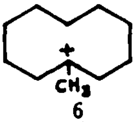
(1) the ^{13}C peak position for the terminal carbons of the bridge structure fits much closer to a 1,5-bridging model than to that expected for a 1,6-bridge.

(2) work with both the bridged 1,5-dimethyl-1,5-bridged carbocation 5 and with 3 shows that 5 is somewhat more stable than 3[2c].

(3) carbocation 5 is an observable mixture of three conformers at low temperatures. Similarly, the cyclodecyl cation is also an apparent mixture of three isomers and the most obvious assignment of these involves differing conformational structures of 4.

(4) work involving the 1-methylcyclodecyl cation 6 shows conclusively that this molecule prefers a 1,5-transannular interaction over the competing 1,6-process, both interactions being freely available to this cation.



6

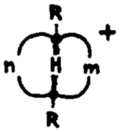
(5) the ^{13}C chemical shift data for ring carbons are consistent only with the 4 structure.

^{13}C Peak Position

In Table 1, we have gathered together ^{13}C chemical shift data for various di-secondary- and di-tertiary-bridged carbocations. It is readily apparent that the "fit" for the 1,5-structure 4 is much better than for 1. The δ 125 ppm region where 1 might have been expected is blank except for a $CFCl_3$ peak at δ 124.7 (see Fig. 1). This latter peak is very sharp in most spectra and even if a cation peak is obscured in the decoupled spectra, one would have seen peaks in the off-resonance mode.

Table 1

^{13}C Chemical Shift Data[a] For the Terminal Carbons (•) of μ-Hydrido-bridged Carbocations



n CH_2	m CH_2	R	δ	$\delta_{R=CH_3} - \delta_{R=H}$
3	3	H	151.7	
3	3	CH_3	172.0	20.3
4	3	H	137.2	
4	3	CH_3	156.4	19.2
4	4	H	(est. 125±3)	
4	4	CH_3	142.0	-10.8[b]
5	3	H	146.6,150.1,152.8	
5	3	CH_3	162.5,165.3,167.6	15.9,15.2,14.8

a. this data can be found in References 2b,c,e.

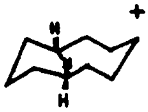
b. the calculated value if the observable cyclodecyl cation were assigned the 1,6-μ-H structure 1.

Comparison With The 1,5-Dimethyl- 5 And 1,6-dimethylcyclodecyl 3 Cations

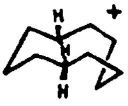
When the title cations are allowed to equilibrate, the 1,5- structure 5 predominates (K = 5/3 = 2.8 at -84°C)[2c]. This is consistent with the present assignment of 4, except that the equilibrium constant for 4/1 must be > 10.

Conformational Aspects of 5 and 4

Cation 5 shows both ^1H and ^{13}C evidence indicating a mixture of three conformational isomers (backed-up by line-broadening observations at higher temperatures)[2c]. With cation 4 one has much less data to work with. The ^{13}C NMR spectra clearly show three low-field peaks, a major one and two minor (Fig. 1). As opposed to 5, these minor peaks occur at higher field than that for the major isomer. Conceivably, the minor peaks could be due to a single carbocation with non-equivalence at the bridging end carbons. However, in 5, each conformer appears to be symmetrical and this should then also be true for 4. Additionally, the two minor peaks in the spectrum of 4 differ in width (see inset of Fig. 1). In the ^1H NMR spectrum (Fig. 2), there is no indication of more than one bridged species, although the broadness of the proton peaks in question could easily obscure small chemical shift differences. Because of this, we cannot with certainty show that these minor peaks are μ-hydrido-structures. However, overall it is most probable that the three peaks in Fig. 1 correspond to three conformers of 4 and these structures are shown as 4a-d (three of these).

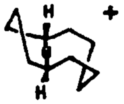


4a



4b

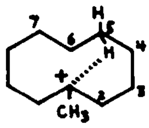
4c



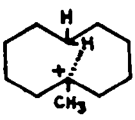
4d

The 1-Methylcyclodecyl Cation 6

The 1-methylcyclodecyl cation 6[3] at low temperatures (-130°C) shows one unique proton at -0.85 (Fig. 3, upper spectrum). This slightly high-field position is consistent with a weak transannular interaction similar to that reported for substituted cyclooctyl cations[2d] and could conceivably involve a 1,5- or 1,6-interaction, i.e., 6a or 6b. That 6a is involved is



6a



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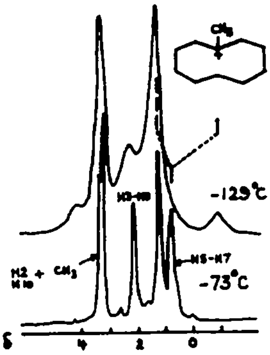
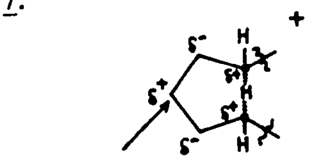


Fig. 3 ^1H NMR spectrum of the 1-methylcyclodecyl cation showing the single high field proton at δ -0.85 (-129°C). At higher temperatures this proton averages with three other protons (lower spectrum).

shown conclusively by the subsequent NMR line-broadening and coalescence behaviour, in which this proton exchanges <u>with three other protons</u> (see Fig. 3, lower spectrum), a process which could not have occurred if the proton in question were one of the <u>two</u> C-6 protons. The actual coalescence data for <u>6a</u> suggest that the conformational movement which averages the C-5 and C-7 sites has a similar barrier (about 7.2 kcals/mole) to a process which averages the two geminal protons on C-5 and C-7. The ^{13}C data for <u>6</u> are also consistent with a 1,5-interaction. At low temperatures, two different α-carbons are observed, which coalesce at the same rate as the process which equilibrates the unique proton in the ^1H spectra.

^{13}C Data For Ring Carbons

Previous work involving 9-membered μ-hydrido-bridged cations[2b] has shown that the β-carbon on the five-membered partial structure has an uniquely low-field ^{13}C chemical shift (δ 46.0 in the di-secondary cation). In the present case, a one carbon peak at δ 47.8 (Fig. 1) is easily assigned on the basis of structure <u>4</u>, but very hard to reconcile with structure <u>1</u>. Verhoeven[4] has suggested that "inphase" charge alternation can account for these results, i.e., partial structure <u>7</u>.



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In conclusion, we feel confident that the observable cyclodecyl cation is a 1,5-μ-hydrido-bridged structure, most probably involving at least three conformational isomers (structures <u>5a-d</u>).

The Rearrangement of 4 to The Decalyl Cation 2 and H_2

The evolution of H_2 from <u>4</u> is very facile[5], $t_{1/2}$ = <u>ca</u>. 1 h at -130°C, $\Delta G^{\neq}$ = 10-11 kcals/mole. The rate is also essentially the same in the various acidic solvent systems used. A large number of experiments (various temperatures) were conducted in which the cation was prepared under conditions in which the evolved gas could be quantitatively measured, and in the best cases, was about 75% of the theoretical based on 1-chlorocyclodecane.

The preparation of <u>4</u> for NMR analysis is also somewhat less than stoichiometric if one uses the areas of the very diagnostic μ-hydrogen (or the two terminal hydrogens) and compares these to the area of the total protons in the δ 1-3 region. For example, in Fig. 2, the ratio is ca. 8.2 to 1, which, assuming the extra area derives from some sort of chlorocyclodecane-derived products, corresponds to about 65% of theory. Some of the extra area in the δ 1-3 region is accounted for by variable small amounts of decalyl cation already present in the mixture but, after allowing the 4 → 2 + H_2 reaction, the formed decalyl cation 2 spectrum is also not completely clean and some extra area is present in the δ 1-3 region. It is difficult to be completely quantitative but it appears to us that the actual cyclodecyl cation → decalyl cation + H_2 is a stoichiometric reaction.

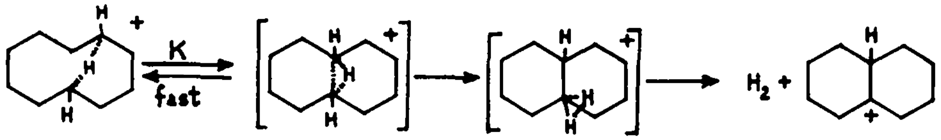
Possible Mechanisms For the Cation 4 Dehydrogenation

The dehydrogenation behaviour of 4 is unique amongst μ-hydrido-bridged secondary carbocations since in all other cases, a ring contraction to yield a normal tertiary carbocation is the eventual rearrangement process[2b]. One can ask several questions concerning the dehydrogenation reaction: (1) which hydrogens in the total system are the source of the dihydrogen? (2) why does this reaction only occur with the 10-membered ring? (3) what is the actual transition-state "structure" for the dehydrogenation reaction?

Several possibilities exist for the H_2 sources. One could envision a proton removal from 4 (via 1) leading to decalin, and then C-H protonation of decalin to yield the decalyl cation and H_2. This mechanism is excluded however on several grounds: (a) when 4 was prepared from the chloride in a large excess of FSO_3D-SbF_5-SO_2ClF solution, only H_2 gas was produced. If a decalin protonation step had occurred, HD should have been the main product. (b) in preparing the decalyl cation from decalin and various superacid mixtures, we have been unable to detect any H_2 gas production. Previous work by Olah et al.[6] also apparently failed to find significant H_2 production in this reaction. These authors however believed their reaction to involve a C-H bond protonation and attributed the lack of H_2 production to a "nascent hydrogen" argument (see later).

We believe that the most reasonable "mechanism" for the dehydrogenation of 4 is that shown in Equation 1. As explained earlier, it is reasonable to believe that 1 would have a

Eq. 1



4 1 3 2

steady-state existence and also that it would not lie very much above 4 in energy (although not close enough to form an observable equilibrium). The unique behavior of 1, as opposed to 4 and other secondary cations, in forming H_2 is probably associated with the stable decalin-like structure and the fact that there may already be significant C---C transannular bonding in the structure of the μ-hydrido cation 1[7]. The transition-state is pictured to involve a shortening of the transannular C---C bond and eventually the formation of an H---H bond. We have made a preliminary study[8], at the 4-31 G level, of the reaction of

$H_3C\cdots H\cdots CH_3^+$

$\rightarrow C_2H_5^+ + H_2$. The μ-H and the terminal hydrogens are initially antibonding and these become bonding only after one has nearly complete C---C bonding in place. One cannot therefore picture the process as concerted. The key factor in this reaction involving 1 is not the fact that we have a μ-hydrido structure per se, but that we probably have a bent μ-hydrido structure in which for geometric reasons significant C---C bonding is also present[7].

Relevance of The Dehydrogenation of 4 (1) to the Question of Alkane Protonation in Superacids

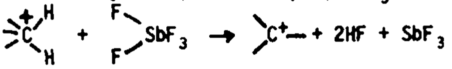
If one were to protonate the C-H bond of decalin with a superacid, one would almost certainly reach a structure identical to that postulated in Eq. 1 for the cyclodecyl cation dehydrogenation, i.e., a pentacoordinate structure 8[9]. One should then also obtain a stoichiometric yield of H_2 in a second step, based on our experience with 4 (1).

The question of the protonation of alkanes in superacid media has been the subject of a number of publications and it is not our intent to review this area in detail. In fact, readers of this literature must by now be thoroughly confused by conflicting claims. At the heart of the matter is the generally grossly non-stoichiometric production of H_2 according to Equation 2 (in a recent review,[10] it is argued that K is >1, but it is also possible to argue that RH_2^+ is simply a transition-state in an electrophilic substitution process[11b]).

Eq. 2 $$RH + H^+ \overset{K}{\rightleftharpoons} [RH_2^+] \rightarrow R^+ + H_2$$

Various researchers[11] have suggested that H^+ is not an important oxidizing agent, although the recent review (1982) by Fabre *et al*[10] ends a section with the statement "in the following sections, we shall consider that H^+ ion is the principle oxidant of alkanes".

Olah *et al*[12] originally described the non-stoichiometric formation of H_2 in Eq. 2 as due to the production of "nascent hydrogen". The latter was postulated to then reduce solvent or acid species, e.g., $Sb^V \rightarrow Sb^{III}$. Since "normal" hydrogen is unreactive [11j] with superacid solvents under low temperature conditions, the use of the term "nascent hydrogen" is very much in keeping with the original meaning of this term[13], albeit that the original "nascent hydrogen" concept is no longer tenable. More recently, the "nascent hydrogen" concept has been put in more chemically acceptable terms by the suggestion of Ledford[11j] that a pentacoordinate cation could react directly with, for example, SbF_5, as shown below:



The importance of our present observations vis-a-vis this controversial area is to throw very considerable doubt on any "nascent hydrogen" postulate. Indeed, if our speculation concerning the mechanism of H_2 production from 4(1) is correct, then we would conclude that one should always get essentially stoichiometric H_2 production from the breakdown of a pentacoordinated carbocation $R_3\overset{+}{C}H_2$ in any of the common superacid media, *with no reason to exclude those supposedly formed by solution C-H bond protonation reaction*. Since such stoichiometric H_2 producing reactions are virtually unknown when one adds alkanes to superacids like SbF_5-FSO_3H[14], we (like others) cannot really accept that the solution C-H protonation of alkanes, as shown in Eq. 2, is an important pathway in the RH → R^+ reaction.[15]

Experimental

1-chlorocyclodecane[16], *cis*- and *trans*-cyclodecene[16] were prepared as reported. The decalyl cation was conveniently synthesized from spiro[4.5]decan-6-ol[17] using an *in situ* preparation of the chloride prior to making the cation. 1-Methylcyclodecan-1-ol [18] was used directly in cation preparations. General procedures, including peak calibration, for making carbocations have been described[19], as well as the procedure for temperature calibration. Most ^1H spectra were obtained at 90 MHz. and ^{13}C spectra at 22.56 MHz. using a Bruker WH-90 NMR spectrometer equipped with a ^{19}F lock channel, however the ^1H decalin → decalyl cation work employed a Varian XL-200 instrument.

Cyclodecyl Cation 4

The SbF_5-SO_2ClF-SO_2F_2-RCl system was used in most preparations and gave the cleanest spectra. However, the *cis*- or *trans*-cyclodecene with 1:1 SbF_5-FSO_3H-SO_2ClF (SO_2F_2) also gave the cation. The ^1H NMR spectrum is shown in Fig. 2, H_μ is found at δ -6.85, the H_T protons at 6.80, with the remaining protons forming the unresolved broad peak from *ca*. δ 1-3. The ^{13}C assignments for the major conformer are: δ 152.8, C1-C5; 47.8, C3; 41.2 and 34.3, the C2-C4 and C6-C10 pairs (specific assignment in doubt); 30.8, C7-C9 and 34.3 (overlapped), probable position of C8. Smaller peaks assignable to the minor conformers of 4 are found at δ 150.1, 146.6, 44.5, 25.6 and *ca*. 20. Selective ^1H decoupling experiments give the coupling constants $J_{C_T-H_T}$ = 158±5 Hz. and $J_{C_T-H_\mu}$ = 32±5 Hz. Coupling constants for the remaining carbons were difficult to obtain because of the broadness of the peaks. The rearrangement of 4 to the decalyl cation was followed by both ^{13}C NMR spectroscopy (open tube!) and by volumetric techniques. H_2 (HD) was determined by mass spectrometry. Quenching experiments were performed by adding the cyclodecyl cation solution to a vigorously stirred 2-methylbutane-K_2CO_3 slurry at -130°C. In all cases, a mixture of *cis*- and *trans*-decalin (*ca*. 1:2 ratio) was recovered in good yield, indicating that H_2 was given off prior to hydride capture.

1-Methylcyclodecyl Cation 6

The ^1H spectrum of this cation is shown in Fig. 3. At -73°C, five peaks are seen, δ 3.37, CH_3; 3.25, H2 and H10 protons; 2.16, H3 and H9; 1.26, H4, H6 and H8; 0.78, H5 and H7. At low temperatures, one freezes out a conformational averaging and all ring protons become non-equivalent. The averaged ^{13}C spectrum shows: δ 324.5, C1; 56.6, C2, C10; 39.2, CH_3; 32.0, 30.0 and 24.5, the C3-C9, C4-C8 and C5-C7 carbons; 25.3, C6. By -115°C, the peak at 56.6 has split into two peaks at 58.4 and 54.6, the methyl carbon remains sharp and the remaining carbons are poorly resolved. Standard NMR line-broadening analysis gives a $\Delta G^{\ddagger}$ barrier of *ca* 7.2 kcals/mole for this conformational averaging process.

Decalyl Cation 2 Preparations From Decalin

In a closed system resembling a hydrogenation apparatus, *cis*- and *trans*-decalin were separately added to solutions of 1:1 FSO_3H-SbF_5 in SO_2ClF (various ratios) and to other superacid systems. Initially the superacid solutions were kept at dry-ice temperatures but occasional warming was necessary because the decalin tended to freeze on the stirrer bar and at the edges of the flask. Stirring was continued for several hours after the decalin addition was complete. In experiments where *ca*. 20 ml of H_2 was expected, within the limits of our volumetric apparatus (est. as ±0.2 ml) no gas evolution was observed. The solutions were then monitored by ^1H NMR spectroscopy, the decalyl cation having three characteristic peaks. Some small high-field peaks were also generally present.

Acknowledgements

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We interpret these differences as a reflection of the linearity of the C---H---C$^+$ system, the higher field the peak the more linear the bonds and the less (if any) C---C interaction.

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12. A good historical introduction to this area is given in Reference 11(b). As far as we are aware, Olah et al were the first to postulate "nascent hydrogen" to explain the nonstoichiometry of the H_2 production, G.A. Olah, Y. Halpern, J. Shen and Y.K. Mo, J. Am. Chem. Soc., 95, 4960 (1973).
13. The term "nascent hydrogen" (newborn) has been in use for at least 180 years and was formerly the subject of much speculation, J.H. Reedy and E.D. Biggers, J. Chem. Educ., 19, 403 (1942). J.W. Mellor in "Modern Inorganic Chemistry", Longmans, Green and Co., London, p. 103, writes in 1916 "Hydrogen at the moment of its formation is more chemically active than ordinary hydrogen. For instance, ordinary hydrogen can be passed into an acidified solution of ferric chloride without producing any appreciable change, but if metallic zinc be placed in the solution, the brisk evolution of hydrogen is soon attended by the reduction of the ferric chloride to ferrous chloride.... Hence, hydrogen in the nascent condition-in statu nascendi - can do chemical work which ordinary gas cannot do". Today one recognizes that this hypothesis is no longer needed. As expected, Olah et al were much more explicit in their descriptions of what their "nascent hydrogen" was, i.e., essentially a vibrationally excited state of dihydrogen.
14. There is some indication that SbF_5-HF systems may produce more H_2 gas, see Ref. 11(b). Quantitative hydrogen production has been found in a specialized case involving a perhydrotriazaphenalene system, J.D. Wuest and J.M. Erhardt, J. Am. Chem. Soc., 102, 6364 (1980).
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