Solvated CH_5^+ in Liquid Superacid

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Abstract: The transition states for methane activation in liquid superacid have been studied by experimentally determined secondary kinetic deuterium isotope effects (SKIEs) and computational chemistry. For the first time, the SKIEs on hydrogen/deuterium exchange of methane have been measured by using the methane isotopologues in homogeneous liquid superacid ($^2HF/SbF_5$). To achieve high accuracy of the SKIEs, the rate constants for pairs of methane isotopologues were simultaneously measured in the same superacid solution by using NMR spectroscopy. Density functional theory (DFT) and high-level ab initio methods have been employed to model possible intermediates and transition states, assuming that the superacids involved in the exchange reactions are H_2F^+ ions solvated by HF. Only the unsolvated superacid H_2F^+ is found to be strong enough to protonate methane, yielding the methonium ion solvated by HF as a potential energy minimum. In contrast, the $(HF)_x$-solvated H_2F^+ superacids ($x = 1-4$) do not appear to be strong enough to yield stable solvated methonium ions. However, such ions show up as parts of the transition states of the exchange in which the methonium ions are solvated by $(HF)_x$. The calculated DFT activation barrier is in good agreement with that experimentally observed.

Keywords: density functional calculations · isotope effects · methane · methonium ion · superacidic systems

Introduction

Methane is abundant on earth. It is the major component of natural gas and is produced on a short timescale through the biological conversion of biomass.[1] During the last decades, much effort has been applied to the challenge of converting methane into useful products.[2–5] One approach is electrophilic activation, which relies on the σ basicity of the C–H bond, that is, its ability to react with strong electrophiles.[6, 7] In liquid superacid[8] Hogeveen and co-workers[9, 10] and Olah and co-workers[11, 12] have observed protium/deuterium exchange with methane, and the methonium ion was suggested as an intermediate or transition state [Eq. (1)].

$$C^1H_4 + {}^2HF/SbF_5 \rightarrow C^1H_3{}^2H + {}^1HF/SbF_5 \qquad (1)$$

Olah and co-workers have also reported ESCA (electron spectroscopy for chemical analysis) evidence for the presence of the methonium ion in a superacid matrix.[13] Hogeveen and co-workers studied the exchange reaction with mono-deuterated methane in a HF/SbF_5 solution (9 mol% SbF_5) at a high pressure (7 atm) over a temperature interval (−10–25 °C). Deviations in methane solubility were experienced upon changing the temperature. Olah and co-workers observed the hydrogen exchange with both C^1H_4 and C^2H_4 under atmospheric pressure at room temperature in $FSO_3{}^1H/SbF_5$ and $FSO_3{}^2H/SbF_5$ (1:1). Upon elevation of the temperature to 140 °C, the dissociation products CH_3^+ and H_2 were suggested to have formed.

The methonium ion (CH_5^+) was first discovered by mass spectrometry.[14, 15] A number of theoretical studies have shown its shallow potential-energy surface.[16–21]

The eclipsed C_s conformer, C_s(e) (Figure 1), is now accepted as being the lowest on the potential-energy surface, although the barriers for rearrangements are extremely small. The barrier for methyl rotation to a staggered C_s conformation, C_s(s), is approximately 0.1 kcal mol^{-1}, and the exchange between two eclipsed C_s structures via a flipped transition

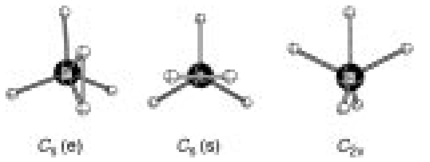

Figure 1. Calculated conformations of the methonium ion, CH_5^+.

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0947-6539/01/0709-1936 $ 17.50+.50/0

structure (TS) with C_{2v} symmetry is approximately 0.8 kcal mol^{-1}. Addition of zero-point energy (ZPE) suggests that the energy difference is almost negligible.[16] A recent high-resolution infrared spectrum in the gas phase seems to confirm that the parent alkonium ion CH_5^+ is highly fluxional and that its structure may not be described by a single nuclear configuration, although no assignment of peaks was possible.[22] Retardation of the degenerate rearrangement has been achieved by trapping CH_5^+ in clusters with H_2, CH_4, Ar or N_2.[23–35] Characterisation of such clusters, both theoretically and by spectroscopy, have been performed, and the results have supported the C_s structure for the parent CH_5^+ ion. A mass spectrometry study by Heck et al. on the other hand indicates that the isotopologues $CH_4{}^2H^+$ and $C^2H_4H^+$ do not rearrange.[36–39] Schreiner et al. has reported a theoretical study of methane and the electrophile NO^+.[40] However, little is still known about the detailed reaction mechanism for the hydrogen exchange in liquid solution.

To obtain information about the rate-limiting activated complexes involved in the hydrogen exchange we have, in the present study, experimentally determined the secondary kinetic isotope effects (SKIEs) for the exchange by NMR spectroscopy by using the methane isotopologues in homogeneous liquid $^2HF/SbF_5$. In order to achieve the required SKIE accuracy, experiments were designed in which rate constants for pairs of methane isotopologues were measured simultaneously in the same superacidic solution. To interpret the results, a theoretical study of possible intermediates and activated complexes has been performed by using density functional theory (DFT: B3LYP) and ab initio methods (MP2, QCISD). The theoretical results show that in the activated complexes, the methonium ions are strongly hydrogen bonded by $(HF)_x$ polymers.

Computational Details

Compounds were optimised at B3LYP/6-311++G(3df,2p),[41–45] here denoted B3LYP/BS2, MP2(full)/6-311+G(d,p), here denoted MP2/BS1,[46] or QCISD(full)/BS2[47–49] levels of theory, as implemented in Gaussian 98.[50] Optimisations with a very tight convergence criteria, as well as a finer grid (grid = −96032), were used for the SKIE calculations with DFT. All geometries were characterised as minima or saddle points on the potential-energy surface (PES) by using the sign of the eigenvalues of the force-constant matrix obtained from a frequency calculation. Transition states with one imaginary frequency were confirmed to describe the correct movement on the PES by a mode analysis. IRC (intrinsic reaction coordinate) calculations[51, 52] were performed, in selected cases, to connect the TS with its corresponding reactant and product. Secondary kinetic isotope effects (SKIE) were calculated by using Gibbs free-energy values from the Gaussian program. A scaling factor of 1.00 was applied to the frequency calculations. Different scaling factors were tested at B3LYP/BS2 (0.96) and MP2/BS1 (0.94) as suggested by Scott and Radom[53] leading to changes in the secondary kinetic isotope effects of less than 1%. Energies given in the text refer to B3LYP/BS2.

Results and Discussion

The superacid solutions that were used for the methane activation in the present work are mixtures of HF and SbF_5. Experimentally, it has been shown that such mixtures ionise into $(HF)_x$ solvated H_2F^+ ions and SbF_6^- or larger anionic species ($Sb_2F_{11}^-$ or $Sb_3F_{16}^-$).[54–57] The number, x, of HF solvate molecules per H_2F^+ has been found to decrease with increasing SbF_5 concentration. The composition of the superacids is thus determined by the concentration ratio of HF and SbF_5 through a complex set of equilibria. Studies of $(HF)_x$-solvated H_2F^+ ions by various techniques (X-ray diffraction, molecular dynamics and ab initio methods) have shown that they form linear, zigzagged chains held together by strong hydrogen bonds.[58–61] Recent ab initio molecular dynamics simulations by Kim and Klein show that the solvated H_2F^+ ion and the SbF_6^- counterion are parts of a fully separated ion pair.[62]

Protium/deuterium exchange reactions of alkanes catalysed by superacids have been studied by a number of groups.[8, 63] In the strongest superacid system HF/SbF_5, the hydrogen exchange rate has been shown to be much larger than the ionisation rate of isobutane.[64] Hogeveen and co-workers have reported the activation parameters for the exchange of methane.[65] In the literature, we have not been able to find any kinetic isotope effects (KIE) for the exchange reaction of alkanes in superacids,[10, 66, 67] but equilibrium isotope effects on carbocations have been reported.[68–73] Kinetic isotope effects for the protonation of isotopologues of bicyclo[4.4.4]-tetradecane with trifluoromethanesulfonic acid ($CF_3SO_3{}^1H$/$CF_3SO_3{}^2H$) and the accompanying dissociation of the carbocation to H_2 and a carbenium ion has been reported by McMurry and co-workers. Their results are supportive of a pentacoordinated, nonlinear, activated complex with a carbonium ion as intermediate.[74–76] Erhardt and Wuest, on the other hand, have reported a linear activated complex or intermediate upon protonation of perhydro-3a,6a,9a-triazaphenalene, followed by H_2 dissociation.[77] Schoofs et al. have reported KIE for hydrogen exchange in the solid phase.[78] We have now determined the secondary kinetic deuterium isotope effects (SKIEs) for exchange of the parent alkane methane, revealing information on the transition states and possible intermediates. SKIEs have been shown to be useful in excluding proposed reaction mechanisms and transition-state structures.[79]

Neutral methane has been reported to be, at best, sparsely soluble in superacids, if at all.[13] However, methane is found to be soluble enough (approximately 0.005 M) for direct kinetic studies by NMR spectroscopy, for example, of isotope exchange.

Rate constants for protium/deuterium exchange of the isotopologous methanes shown in Equations (2)–(5) have been determined in the superacid $^2HF/SbF_5$ (15 mol% SbF_5)

$$^{13}C^1H_4 + {}^2HF/SbF_5 \xrightarrow{4k_a} {}^{13}C^1H_3{}^2H + {}^1HF/SbF_5 \tag{2}$$

$$^{12}C^1H_3{}^2H + {}^2HF/SbF_5 \xrightarrow{3k_b} {}^{12}C^1H_2{}^2H_2 + {}^1HF/SbF_5 \tag{3}$$

$$^{12}C^1H_2{}^2H_2 + {}^2HF/SbF_5 \xrightarrow{2k_c} {}^{12}C^1H^2H_3 + {}^1HF/SbF_5 \tag{4}$$

$$^{12}C^1H^2H_3 + {}^2HF/SbF_5 \xrightarrow{k_d} {}^{12}C^2H_4 + {}^1HF/SbF_5 \tag{5}$$

at −20 °C and the SKIEs have been calculated. The rate constants k_a, k_b, k_c and k_d are defined as rate constants per protium available for exchange with deuterium in the methane isotopologue. The rate constants for the two pertinent methane isotopologues were measured simultaneously in the same superacidic solution in order to improve SKIE accuracy. No condensation products could be detected during the reaction.

Figure 2 shows one-pulse ^2H decoupled 600 MHz ^1H NMR spectra, obtained at different reaction times, of a solution containing initially approximately equimolar amounts of $^{13}C^1H_4$ and $^{12}C^1H_3{}^2H$. Spectrum a, obtained after 8 min, shows three major signals: the doublet originating from $^{13}C^1H_4$ and a singlet from $^{12}C^1H_3{}^2H$, in addition to product signals from $^{13}C^1H_3{}^2H$ and $^{12}C^1H_2{}^2H_2$. These latter signals appear upfield of the corresponding signals from the starting materials due to deuterium-induced shifts. In spectrum b, recorded after 15 min, additional signals from the new products $^{13}C^1H_2{}^2H_2$ and $^{12}C^1H^2H_3$ have appeared. In spectrum c, the most abundant isotopologues are no longer the starting materials. After 35 min, the product $^{13}C^1H^2H_3$ is visible in spectrum d. The molar percentages (mol %) of the reagents and products in the reaction mixture were calculated from the integrated spectra and are plotted as a function of time in Figure 3a.

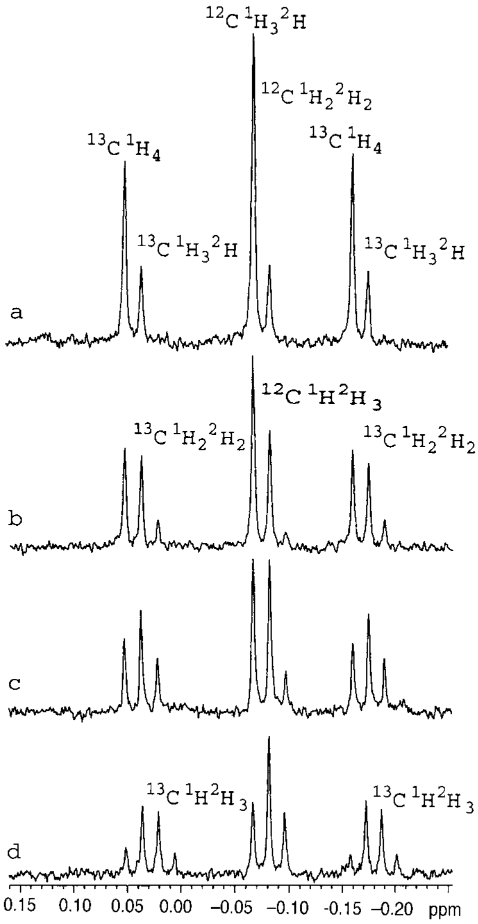

Figure 2. ^1H NMR spectra of a reaction mixture at different reaction times, see text.

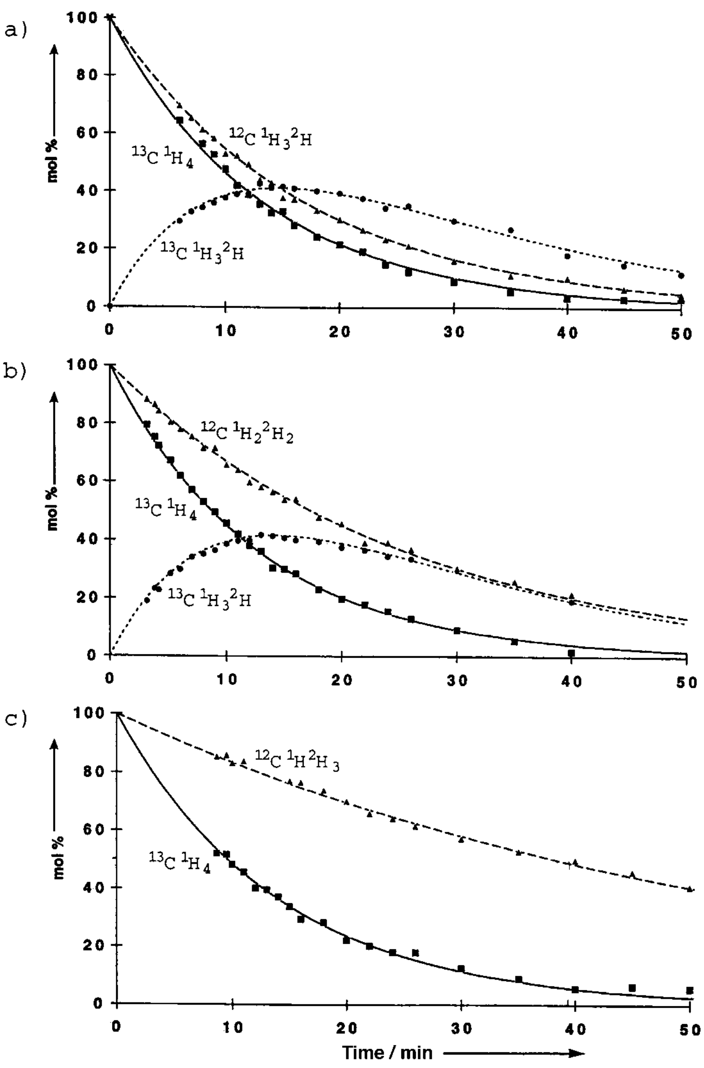

Figure 3. Molar percentages (mol %) of methane isotopologues plotted against time for the exchange reactions shown in Equations (2)–(5). The reaction mixtures were initially composed of equimolar amounts of pairs of labelled methanes. The following pairs were used in the experiments: a) $^{13}C^1H_4$ and $^{12}C^1H_3{}^2H_1$; b) $^{13}C^1H_4$ and $^{12}C^1H_2{}^2H_2$; c) $^{13}C^1H_4$ and $^{12}C^1H^2H_3$. The curves were simulated by using the rate constants shown in Table 1.

The two starting materials, $^{13}C^1H_4$ and $^{12}C^1H_3{}^2H$, are both found to disappear by first-order reactions, with rate constants $4k_a$ and $3k_b$, respectively. The rate constants k_a and k_b are defined as rate constants per protium available for exchange with the particular methane isotopologue (Table 1). The SKIE k_a/k_b was calculated to be 0.96.

Similarly, by using the reagent pairs $^{13}C^1H_4/^{12}C^1H_2{}^2H_2$ and $^{13}C^1H_4/^{12}C^1H^2H_3$ as starting materials, the results shown in Figures 3b and c, respectively, were obtained. The calculated, and statistically corrected first-order rate constants, k_c and k_d, are also given in Table 1. The estimated SKIEs are 1.00 and 1.02, respectively.

At first glance we found the above-observed isotope effects surprisingly small in view of the expected dramatic structural

Table 1. Experimentally determined rate constants at −20 °C.

Substrate pair	k_a [s^{-1}]	k_b [s^{-1}]	k_c [s^{-1}]	k_d [s^{-1}]
$^{13}C^1H_4/^{12}C^1H_3{}^2H$	3.21×10^{-4}	3.33×10^{-4}	–	–
$^{13}C^1H_4/^{12}C^1H_2{}^2H_2$	3.33×10^{-4}	–	3.33×10^{-4}	–
$^{13}C^1H_4/^{12}C^1H^2H_3$	2.99×10^{-4}	–	–	2.92×10^{-4}

change in going from methane to the presumed carbonium-ion-like activated complex. To interpret the results, DFT and ab initio methods were used in order to optimise the structures, energies of intermediates, activated complexes and SKIEs. HF-solvated H_2F^+ superacids, with 0–4 HF molecules in the solvating linear polymer, are the superacids that have been employed in the present study. The theoretical methods used were first verified on calculated systems in the literature related to this study. These systems include the CH_5^+ (C_s(e) conformer), an adduct between CH_5^+ and H_2, and the HF dimer. The geometrical parameters are compared in Table 2 and Figure 4.

Table 2. Theoretical geometrical parameters at various levels of theory.

CH_5^+ (C_s(e))	CCSD(T)/TZ2P + f[a]	CCSD(T)/BS2[b]	B3LYP/BS2[b]
C-H_1	1.198	1.193	1.186
C-H_2	1.197	1.192	1.182
C-H_3	1.106	1.104	1.109
H_1-H_2	0.945	0.949	0.988
$CH_5^+ \cdot H_2$	CCSD(T)/TZ2P + d[c]	MP2/aug-ccPVTZ[d]	B3LYP/B2[b]
C-H_1	1.213	1.200	1.210
C-H_2	1.187	–	1.169
C-H_3	1.103	1.110	1.107
H_1-H_2	0.947	0.989	1.005
H_1-H_6/H_7	1.854	1.880	1.825
H_6-H_7	0.749	–	0.751
H_2F_2	CCSD(T)/TZ2P(f,d)[e]	CCSD(T)/TZ2P(f,d)[f]	B3LYP/BS2[b]
H_1-F_1	0.921	0.921	0.925
H_2-F_2	0.923	0.923	0.929
F_1-F_2[g]	2.732	2.742	2.735

[a] Ref. [16]. [b] This work, BS2 = 6-311++G(3df,2p). [c] Ref. [32]. [d] Ref. [33]. [e] Ref. [80]. [f] Ref. [81]. [g] Experimental value taken from ref. [80]: 2.72 ± 0.03 Å.

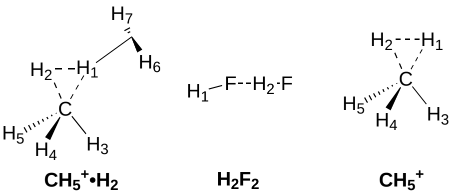

Figure 4. Calculated structures of $CH_5^+ \cdot H_2$, the HF dimer, and CH_5^+.

In CH_5^+, the H_1–H_2 bond length is slightly overestimated with B3LYP, compared to the CCSD(T) structures optimised by Schreiner et al.: 0.988 and 0.945 Å, respectively.[16] This underestimation of interaction makes the corresponding C–H bonds too strong and thus too short by 0.012 and 0.015 Å for C–H_1 and C–H_2, respectively. The $CH_5^+ \cdot H_2$ adduct was found by Kim et al. to have a dissociation energy (D_e) of 3.48 kcal mol^{-1} at the CCSD(T)/TZ2P + d level of theory.[32] With B3LYP/BS2 we estimate this energy value to be 3.67 kcal mol^{-1}. Roszak and Leszczynski estimated values of 3.69, 3.16, and 2.80 kcal mol^{-1}, using MP2/aug-cc-pVTZ, MP4/aug-cc-pVTZ, and CCSD(T)/6-311 + G(d,p), respectively.[33] The experimental D_0 value was found to be 1.88 ± 0.10 kcal mol^{-1}.[30] Kim et al. determined this to be 1.46 kcal mol^{-1}, while the present study gave 1.60 kcal mol^{-1}. The B3LYP results are thus in agreement with CCSD(T) and experimental results. The geometrical deviations (Figure 4 and Table 2) between these CCSD(T) and B3LYP calculations are similar to those for the parent CH_5^+. The distance between the H_2 moiety and H_1 in the CH_5^+ moiety is underestimated by DFT by 0.029 Å. As a result, the H_1–H_2 bond length is 0.058 Å longer and that of C–H_2 is 0.018 Å shorter.

The HF dimer has been investigated by Schaefer III and coworkers at the CCSD(T)/TZ2P(f,d) level of theory in two studies, and the D_e values were determined to be 4.94/4.73 kcal mol^{-1}, while the D_0 values were found to be 3.07/2.94 kcal mol^{-1}.[80, 81] The present work yields the energies 4.81 and 2.98 kcal mol^{-1}, respectively. The experimental D_e value and D_0 values are estimated to be 4.47 and 3.04 kcal mol^{-1}, respectively.[81] The energetics for the HF dimer are thus in agreement with both CCSD(T) and experimental values. The H–F bond lengths are slightly longer at B3LYP-level compared to the CCSD(T) level, (+0.004 and +0.006 Å for H_1–F_1 and H_2–F_2, respectively). The F–F distance is overestimated by 0.003 Å. In summary, the comparison of the methods show that the energetics of B3LYP are in agreement with the highest levels of theory and experiment. The structure of the HF dimer is also in agreement with CCSD(T) results, while the H_1–H_2 interaction in CH_5^+ is underestimated by B3LYP.

Structures (Figure 5), potential energies (Figure 6) and free energies have been calculated for intermediates and activated complexes involved in the hydrogen exchange with the different superacids.

The protonation of methane by H_2F^+ (**1**) to yield the strongly HF-hydrogen-bonded CH_5^+ ion (**2**) (Figure 5) was found to be barrierless by B3LYP/BS2 and MP2/BS1, and lowered the potential energy by 29.0 kcal mol^{-1}. The activated complex **3** for the hydrogen exchange has been identified and has a potential energy of only 1.9 kcal mol^{-1} higher than that of **2**, that is, the exchange takes place without dissociation within the complex. In **2**, and in particular in **3**, the methonium ion moiety has a structure closely similar to the C_s structure of CH_5^+. In **2**, HF forms hydrogen bonds predominantly to one of the hydrogens in the H_2 moiety of the ion; however, in the activated complex **3**, both of these hydrogens are hydrogen-bonded by HF. Relative free energies are given in Table 3.

In contrast, B3LYP/BS2 and MP2/BS1 models $H_3F_2^+$ (**4**) as an acid not strong enough to protonate methane. However, strong hydrogen bonds are found to form between methane and $H_3F_2^+$, yielding the asymmetric complex **5** as an intermediate. All attempts to calculate the hydrogen-bonded

Table 3. Relative (B3LYP/BS2//B3LYP/BS2) free energies [kcal mol^{-1}] of $(HF)_xH^+ \cdot CH_4$ and $((HF)_x \cdot CH_5^+)^+$ relative to $(HF)_xH^+$ + CH_4.

x	$(HF)_xH^+$ + CH_4	$(HF)_xH^+ \cdot CH_4$	$((HF)_x \cdot CH_5^+)^+$
1	0	−24.31	−23.71
2	0	−6.36	+0.45
3	0	−2.40	+11.88
4	0	+0.38	+19.48
5	0	+1.65	+23.62

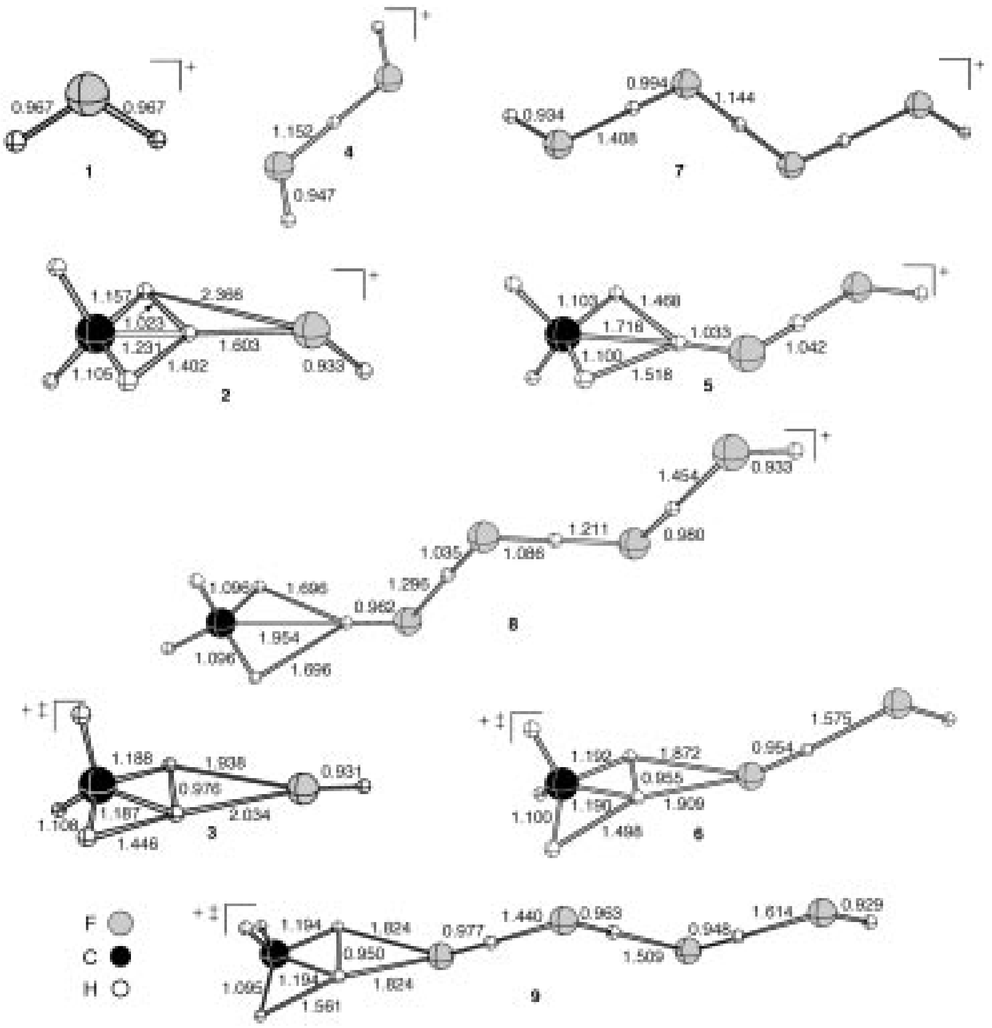

Figure 5. DFT-optimised structures of superacids, intermediates and activated complexes in the exchange reactions studied. Selected bond lengths [Å] are displayed. Relative Gibbs free energies are given in Table 3 and potential energies in Figure 6.

methonium ion as a potential energy minimum failed. The hydrogen-exchange activated complex **6** is 7.9 kcal mol^{-1} less stable than **5**. In **6**, the two hydrogens in the H_2 moiety are hydrogen-bonded by a HF dimer. In Figure 5, results with the acid $H_5F_4^+$ are also shown. The structures of the CH_5^+ moieties of all the activated complexes are similar. Thus, increased solvation by HF only results in small structural changes. In a superacidic solution of HF containing 15 mol % of SbF_5, the most abundant acids are presumably $H_5F_4^+$ and $H_6F_5^+$. The calculated free-energy barriers at 298 K of $H_5F_4^+$ and $H_6F_5^+$ are 19.1 kcal mol^{-1} and 22.0 kcal mol^{-1}, respectively. From the free species ($H_5F_4^+$ and $H_6F_5^+$ and CH_4) the barriers at 253 K are 18.7 and 22.9 kcal mol^{-1}, respectively. These barriers are in agreement with the barrier (18.8 kcal mol^{-1} at 253 K) calculated from the experimentally determined first-order rate constant by using standard transition-state theory. The potential energy diagrams for hydrogen exchange between methane and all different superacids studied are shown in Figure 6.

For the two isotopomers of $C^1H_4{}^2H^+$ with deuterium in the H_2 moiety we find a ZPE difference of 0.02 kcal mol^{-1}. The fluxionality of the CH_5^+ ion is found to be retained in the transition-state structure. As an estimate of this, we have calculated the barrier for methyl rotation and hydrogen flip in the TS and compared with the corresponding barriers for the free CH_5^+ ion, leading to the C_s(s) and C_{2v} structures, respectively (see Figure 1). For CH_5^+ we calculate the potential energy barriers to be +0.07 and +0.50 kcal mol^{-1}, respectively. The corresponding values with HF coordinated are +0.00 and −1.37 kcal mol^{-1}, respectively, relative to **3**. The transition state that resembles the C_{2v} transition state contains only one hydrogen bond and which connects the complexes **2** and **2′** without any hydrogen exchange is more stable than transition state **3**.

Marx and Parrinello have pointed out that for fluxional molecules, harmonic analysis may be a severely limited tool. Nevertheless, they found it instructive to compare—within the Born–Oppenheimer approximation—the harmonic zero-point vibrational energies of various isotopomers in the ground-state C_s structure of $C^1H_4{}^2H$.[39] They report ZPE differences of 0.25–0.45 kcal mol^{-1} between the isotopomers, and our calculations give 0.25–0.42 kcal mol^{-1}, in good agreement with their results. Below, results of deuterium isotope effect calculations are presented and compared with those obtained experimentally. The SKIE depends on the number of deuterium atoms and their positions within the activated

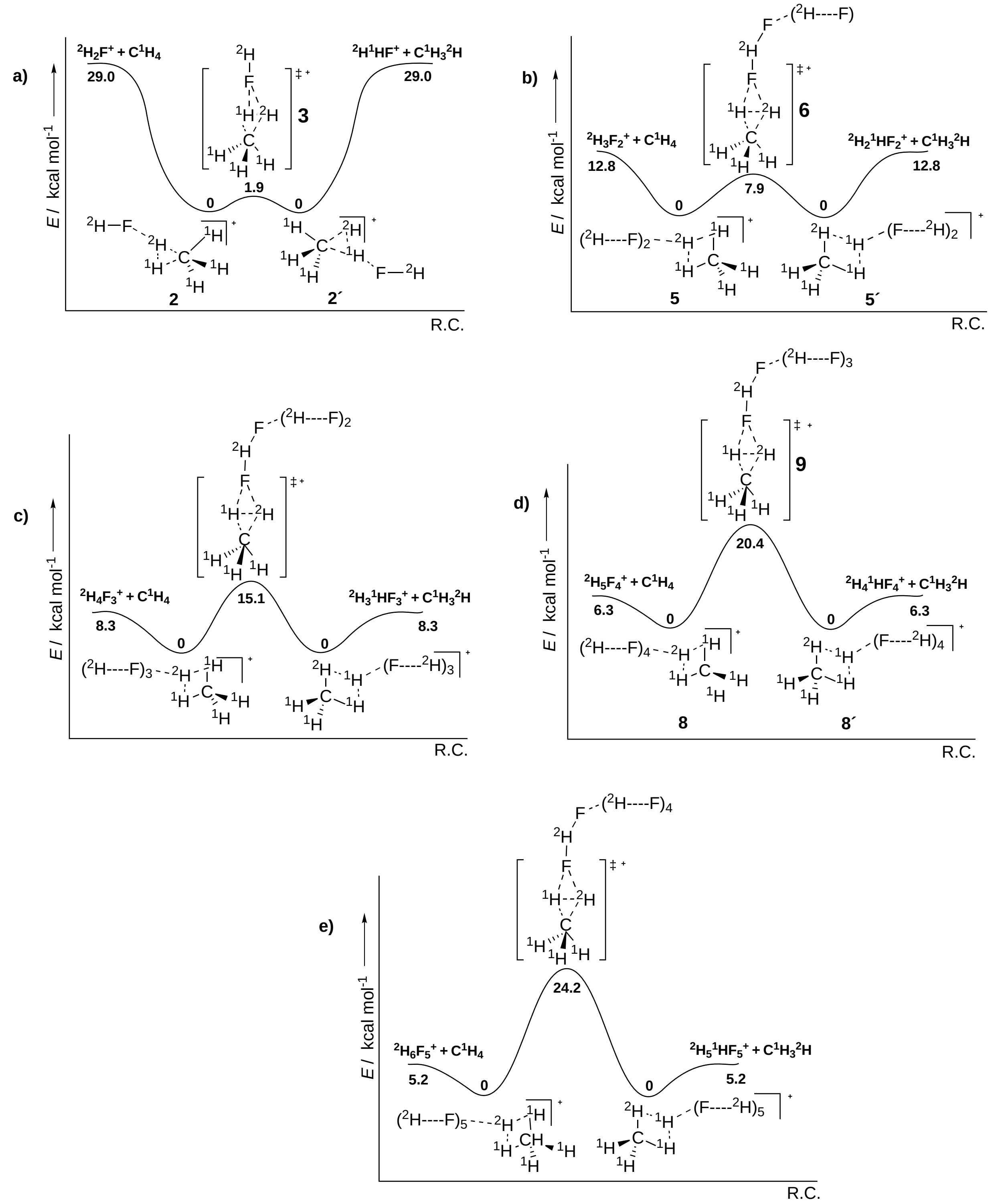

Figure 6. Potential energy diagrams for hydrogen exchange of CH_4 with different deuterated superacids.

complexes. SKIEs have been calculated for each of the isotopomeric activated complexes containing one, two or three deuteriums, respectively. The weighted-average values are shown in Table 4 together with the experimentally measured SKIEs. The calculated SKIEs are similar for all superacids, both at DFT and MP2 levels (1.03–1.04, 1.07–1.10 and 1.11–1.15, respectively). The corresponding experimentally determined values are 0.96, 1.00 and 1.02. With QCISD, the calculated SKIE for H_2F^+ is reduced and if a similar reduction in isotope effect applies to the longer acids, the agreement with the experimental values would be closer. Due to the computational demand, larger acids were not studied with QCISD. However, the calculated values are systematically somewhat higher than those measured, a finding that could result from a number of factors. In our calculations we have used a semiclassical treatment, but in view of the

Table 4. Experimental and calculated secondary kinetic isotope effects (SKIE).

Acid	k_a/k_b	k_a/k_c	k_a/k_d
Experimental superacid	0.96	1.00	1.02
$H_6F_5^+$	1.02[a]	1.06[a]	1.10[a]
	1.03[b]	1.09[b]	1.13[b]
$H_5F_4^+$	1.03[a]	1.07[a]	1.11[a]
	1.03[b]	1.09[b]	1.13[b]
$H_4F_3^+$	1.03[a]	1.08[a]	1.13[a]
	1.03[b]	1.09[b]	1.13[b]
$H_3F_2^+$	1.03[a]	1.08[a]	1.13[a]
	1.04[b]	1.10[b]	1.15[b]
H_2F^+	1.04[a]	1.10[a]	1.15[a]
	1.04[b]	1.10[b]	1.15[b]
	1.01[c]	1.04[c]	1.07[c]

[a] Calculated using B3LYP/BS2. [b] Calculated using MP2/BS1. [c] Calculated using QCISD/BS2.

presence of shallow parts of the potential-energy surface, the nuclear quantum effects should be included. Such studies have been performed on CH_5^+, $C^1H_4{}^2H^+$, $C^1H^2H_4^+$ and hydrogen fluoride by Marx and Parrinello and co-workers,[17, 19, 39, 82–84] and on protonated hydrogen fluoride polymers by Kim and Klein.[60] Also, solvation of the CH_3 moiety of the methonium ion may contribute to the observed isotope effect. Due to computational demands, investigation into the effect of the presence of anion has not been performed.

The calculated free energy of association of CH_5^+ and $(HF)_4$ to yield the activated complex for the hydrogen exchange is $-13.7\ \mathrm{kcal\,mol^{-1}}$. Thus, our results indicate that CH_5^+ is not an intermediate in the exchange reaction, but rather it acts as a part of the activated complex and is strongly solvated by $(HF)_x$.

Experimental Section

The spectra in Figure 2 are one-pulse ^2H decoupled 600 MHz spectra of a mixture initially containing approximately equimolar amounts of $^{13}C^1H_4$ and $^{12}C^1H_3{}^2H_1$ in $^2HF/SbF_5$ (15 mol% SbF_5) at $-20 \pm 0.5\,^{\circ}C$. Spectra a, b, c and d were recorded after 8, 15, 22 and 35 min of reaction, respectively, by using a Varian INOVA 600 instrument equipped with four channels and a 5 mm triple resonance PFG probe. The low-temperature system was composed of a FTS system XR401 Air-Jet Crystal Cooler and a TC-84 controller. Sample temperatures in the probe were measured with a calibrated methanol thermometer supplied by Varian. One-dimensional proton spectra were recorded with a standard ^1H pulse sequence with deuterium decoupling during the acquisition by using channel 4. The spectra were acquired with nonspinning tubes without deuterium field-frequency locking. The following parameters were used: spectral width: 12000 Hz; number of transients: 1; acquisition time: 3 s. The NMR tubes were 5 mm quartz tubes 507-PP from Wilmad. The preparation of the NMR samples was performed in a nitrogen atmosphere. The NMR tube was connected to a Schlenk apparatus and then placed in an ion generation apparatus at a temperature set at $-20\,^{\circ}C$.

Typically, $^2HF/SbF_5$ solution (700 µL) was added through a thin Teflon tube to the NMR tube. An equimolar mixture of the labelled methanes was prepared and the gas mixture (10 mL) was bubbled through the superacid mixture by using a syringe. The void in the NMR tube was flushed with argon, and the tube was sealed. After transfer of the tube to the NMR probe, the first spectrum was recorded after 5 min of temperature equilibration. The labelled methanes $^{13}C^1H_4$ (99% ^{13}C), $^{12}C^1H_3{}^2H_1$ (98% ^2H), $^{12}C^1H_2{}^2H_2$ (98% ^2H) and $^{12}C^1H^2H_3$ (98% ^2H) were purchased from Cambridge Isotope Laboratories. ^1HF (>99.9%) was obtained from AGA Gas and ^2HF (>98% ^2H) was prepared as described earlier. SbF_5 (97%) from Allied Chemicals was triple distilled in a nitrogen atmosphere at normal pressure. The superacid solution $^2HF/SbF_5$ (15 mol% of SbF_5) was prepared in a Kel-F tube under nitrogen. Freshly distilled SbF_5 was transferred to the tube, which was then cooled to $-78\,^{\circ}C$. An appropriate amount of ^2HF was condensed in the Kel-F tube, which was then capped and allowed to reach ambient temperature. Mixing gave the homogeneous liquid superacid used in all the experiments. The error in the isotope effects are estimated to be less than 3%.

Acknowledgements

We thank the Swedish Natural Science Research Council for support, the National Supercomputer Centre in Sweden for computer time, the Swedish NMR Center for spectrometer time and F.K. Charlotta Damberg for assistance. A.G. is grateful for financial support from Loker Hydrocarbon Research Institute, U.S.C., Los Angeles.

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Received: October 5, 2000 [F2781]