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H/D isotope exchange between methane and magic acid ($HSO_3F–SbF_5$): an *in situ* NMR study

Stéphane Walspurger, Alain Goeppert, Mohamed Haouas and Jean Sommer*

Laboratoire de Physico-chimie des Hydrocarbures (CNRS UMR 7513), Faculté de Chimie,
Université Louis Pasteur, 4, rue Blaise Pascal, 67070, Strasbourg cedex, France.
E-mail: sommer@chimie.u-strasbg.fr; Fax: +33 390241487; Tel: +33 390241486

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The kinetics of hydron exchange between methane and a series of $DSO_3F–SbF_5$ superacids were measured by *in situ* ^2H decoupled ^1H NMR spectroscopy. The rates of exchange showed a strong dependence on antimony pentafluoride concentration, with the free energy of activation $\Delta G^{\#}$ (30 °C) decreasing from 97 to 84 kJ mol^{-1} over the range of concentration 19 to 49 mol % SbF_5. The constant free enthalpy of activation $\Delta H^{\#}$ (*ca.* 65 kJ mol^{-1}) and the decreasing entropy of activation $\Delta S^{\#}$ seem to indicate that an increase in acidity of the superacid system does not substantially change the nature of the transition state but rather acts on its solvation.

Introduction

Methane is the major component of natural gas and one of the largest organic carbon reserves.[1] Unfortunately, methane is almost inert and for this reason mainly used as a clean and inexpensive burning fuel. The large number of papers dealing with the conversion of methane testify to the great economical efforts to transform it into more valuable chemicals such as methanol, formaldehyde, *etc.* Indirect conversion of methane to heavier hydrocarbons *via* syn-gas, such as Fischer–Tropsch synthesis,[2] has been well-developed, especially during the oil crisis. Recent reviews summarize progress in direct transformations such as oxidative coupling and conversion under nonoxidative conditions in heterogeneous catalysis.[3,4] Periana *et al.* reported excellent yields in methane to methyl bisulfate catalytic conversion in sulfuric acid media using a Pt catalyst[5] and more recently with iodine.[6] Carbonylation of methane under superacidic conditions has also been reported recently.[7] These promising studies, among others, make direct catalytic transformation of methane into more reactive molecules an exciting challenge for chemists. Although conversion of methane is more thermodynamically favorable under oxidative conditions, it is interesting to understand the mechanisms involved in the presence of electrophilic species and particularly strong acids and superacids.[8]

The activation of methane requires a C–H bond cleavage that can be monitored by H/D exchange between CH_4 and a source of deuterium such as D_2 gas, deuteride (D^-) or deuteron (D^+) in the presence of neutral, basic or acidic catalysts. For this reason, numerous studies have been carried out using the isotope exchange technique to clarify mechanisms. Hogeveen and Gaasbeek[9] have observed protium/deuterium exchange between CH_3D and $HF–SbF_5$ (8.4% SbF_5) at moderate pressure (7 atm) in the −10 to 25 °C temperature range. Olah and Schlosberg[10] have made similar observations by reacting CH_4 with $DSO_3F–SbF_5$ (1:1) (Magic Acid®) at room temperature. These authors suggested that methane can be considered as a σ-base[11] in superacidic media and proposed a methonium ion as the intermediate or transition state for the reversible protonation to explain the exchange process. This penta-coordinated ion, first discovered by mass spectrometry,[12] has been widely studied by theoretical approaches.[13–17] Nowadays, it is well-admitted that it takes part in the exchange mechanism in superacidic media. Recently, we reinvestigated the behavior of methane in superacid and strong liquid acid media. H/D exchange was observed when methane was recirculated in D_2SO_4 at temperatures of 250 °C and above and an apparent activation energy of 176 kJ mol^{-1} was measured.[18] In the strongest superacid, $HF–SbF_5$, we experimentally determined that the secondary kinetic isotopic effect for the H/D exchange, $k(CH_4)/k(CH_3D)$, is very close to unity;[19] moreover, high level computational studies using H_2F^+, more or less solvated by excess HF as the superacid species, suggested that $CH_5{}^+$ was not an intermediate in the exchange reaction but acted rather as a part of the activated complex strongly solvated by $(HF)_x$.[19] The apparent activation energy of 75 kJ mol^{-1} measured by Hogeveen and Gaasbeek[9] shows the large difference of stability of this activated complex between strong acidic media and superacid media. In another paper, the same group reported that exchange in $HF–SbF_5$ was 100 times faster than in $HSO_3F–SbF_5$.[20] Thus, we found it of interest to re-examine the H/D exchange between methane and $DSO_3F–SbF_5$ in a more quantitative way by *in situ* NMR measurements and to determine the relation between exchange rates and acidity of the superacid medium.

Experimental

Synthesis of deuterated fluorosulfonic acid (DSO_3F)

DSO_3F was prepared by reaction of sulfur trioxide with a 5 mol % excess of DF at −30 °C and then distilled three times through a short Vigreux column under vacuum [(bp(15 mmHg) = 85 °C]; the yield was 79% and the isotopic purity determined by NMR using a $CDCl_3–CHCl_3$ external reference was 96%.

DF was obtained by hydrolysis of benzoylfluoride with D_2O (99.90% D, SDS). Benzoylfluoride was synthesized by reaction of benzoylchloride with HF (Aldrich Chemicals). Methods of synthesis were already described elsewhere.[21] Methane as N35 grade was purchased from Messer and used without further purification.

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NMR experiments

Mixtures of $DSO_3F–SbF_5$ were prepared in a Teflon tube flushed with argon. After transfer of the superacid into the NMR tube under argon, 10 mL of methane were bubbled through the superacid mixture using a syringe equipped with a capillary Teflon tube. NMR spectra were recorded after 4–8 min of temperature equilibration in the NMR probe.

NMR experiments were carried out with a Bruker Avance 400 spectrometer operating at 400 MHz for ^1H. ^1H NMR experiments were performed with deuterium decoupling in order to suppress overlapping of the $J(^1H–^2H)$ coupling pattern of the different signals of isotopologues.

Results and discussion

Methane is only slightly soluble in superacid solution and preliminary NMR experiments showed that its solubility decreases with increasing temperature as expected for a gas. However, it was found to be soluble enough (0.0007 mole per mole of HSO_3F in 1:1 $HSO_3F–SbF_5$ at 25 °C) for time-resolved NMR observation. This allows us to use the same *in situ* NMR technique used earlier for H/D exchange studies in the $HF–SbF_5$ system.[19] Separate ^1H NMR signals of CH_4, CH_3D, CH_2D_2 and CHD_3 isotopologues were obtained thanks to the deuterium decoupling technique. Real time observation of the evolution of each species could then be monitored. *In situ* NMR analysis provides a real advantage by measuring the catalytic system without perturbation, whereas *ex situ* analysis like GC/MS requires preliminary separation of the products from the reactive medium. No by-products were detected during these *in situ* experiments.

Fig. 1 shows a typical evolution of the $^1H\{^2H\}$ decoupled NMR spectrum during the H/D exchange reaction. Signals of the different isotopologues CH_4, CH_3D, CH_2D_2 and CHD_3 can be easily identified by their order of appearance with reaction time; therefore, each substitution of protium by deuterium leads to a high-field shift of the signals.

The spectra were deconvoluted using a modified version of the Bruker Winfit program.[22] The distribution of isotopologues as a function of reaction time verified a pseudo-first-order kinetic model, since superacid is in large excess over methane. The following equations describe the consecutive H/D exchange reactions:

$$CH_4 + DSO_3F/SbF_5 \xrightarrow{k_1} CH_3D + HSO_3F/SbF_5$$

$$CH_3D + DSO_3F/SbF_5 \xrightarrow{k_2} CH_2D_2 + HSO_3F/SbF_5$$

$$CH_2D_2 + DSO_3F/SbF_5 \xrightarrow{k_3} CHD_3 + HSO_3F/SbF_5$$

$$CHD_3 + DSO_3F/SbF_5 \xrightarrow{k_4} CD_4 + HSO_3F/SbF_5$$

Investigation of the effect of the molar ratio of antimony pentafluoride on the H/D exchange was carried out at 25 °C with different $DSO_3F–SbF_5$ mixtures containing 20.7, 33.4, 36.0 and 49.0 mol % SbF_5. Fig. 2 shows a typical evolution of the isotopologue distribution plot *versus* reaction time obtained in a $DSO_3F–SbF_5$ mixture of 36 mol % SbF_5. Simulation of the experimental points with the following theoretical curves based on first-order kinetic law allows a determination of the successive rate constants k_1 to k_4:

$$[CH_4] = [CH_4]_0\, e^{-k_1 t} \tag{1}$$

$$[CH_3D] = \frac{k_1[CH_4]_0}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right] \tag{2}$$

$$[CH_2D_2] = k_1 k_2 [CH_4]_0 \left[\frac{e^{-k_1 t}}{(k_2-k_1)(k_3-k_1)} + \frac{e^{-k_2 t}}{(k_1-k_2)(k_3-k_2)} + \frac{e^{-k_3 t}}{(k_1-k_3)(k_2-k_3)}\right] \tag{3}$$

$$[CHD_3] = k_1 k_2 k_3 [CH_4]_0 \left[\frac{e^{-k_1 t}}{(k_2-k_1)(k_3-k_1)(k_4-k_1)} + \frac{e^{-k_2 t}}{(k_1-k_2)(k_3-k_2)(k_4-k_2)} + \frac{e^{-k_3 t}}{(k_1-k_3)(k_2-k_3)(k_4-k_3)} + \frac{e^{-k_4 t}}{(k_1-k_4)(k_2-k_4)(k_3-k_4)}\right] \tag{4}$$

$$[CD_4] = [CH_4]_0 - [CH_4] - [CH_3D] - [CH_2D_2] - [CHD_3] \tag{5}$$

Experimental points for $[CD_4]$ were deduced by subtracting the integrated spectra from the integration value of the first spectrum recorded in the early stages of the reaction. All our results verified the following statistical relationship ($k_1 = 4/3k_2 = 2k_3 = 4k_4$) within 7%. The probability of exchange (1, 0.75, 0.5 and 0.25 for CH_4, CH_3D, CH_2D_2 and CHD_3, respectively) is only dependant on the number of exchangeable protons in the isotopologues and there is no perturbation due to the presence of deuterium in the molecule. This points out clearly that secondary isotopic effects can be neglected. This is in agreement with our previous study in $HF–SbF_5$ where experimental and calculated secondary kinetic isotopic effects were very close to one for each isotopologue.[19]

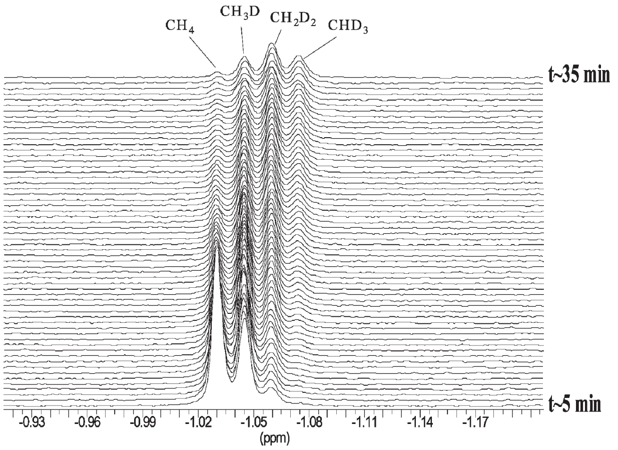

Fig. 1 Deuterium-decoupled proton ($^1H\{^2H\}$) NMR spectra during the reaction between methane and a mixture of $DSO_3F–SbF_5$ (41 mol % SbF_5) at 30 °C.

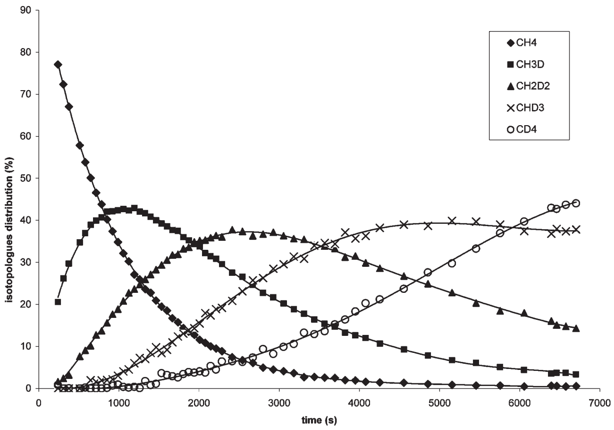

Fig. 2 Distribution percentages of methane isotopologues plotted *versus* exchange reaction time between methane and $DSO_3F–SbF_5$ (36 mol % SbF_5) at 25 °C.

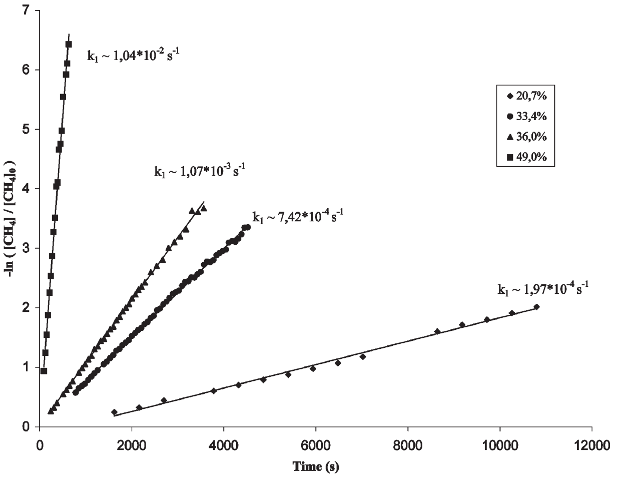

Fig. 3 Determination of the rate of incorporation of deuterium in CH_4 and correlation with SbF_5 concentration at 25 °C.

The rate of the first H/D exchange reaction step (eqn. 1) at 25 °C is reported in Fig. 3 as a function of the SbF_5 concentration in the DSO_3F–SbF_5 mixture. Its intrinsic acidity depends on the molar ratio between the Brønsted acid and the Lewis acid and it is well-known that the acidity increases with increasing Lewis acid concentration.[23] Thus, it appears clearly that the rate of H/D exchange increases with the acidity in agreement with an acid-base type mechanism.

The rate constant k_1 at −20 °C in a DSO_3F–SbF_5 (49% SbF_5) was found to be 8.14×10^{-5} s^{-1}, much lower than was found previously in DF–SbF_5 (15% SbF_5) at −20 °C (1.28×10^{-3} s^{-1}).[19] Rates of H/D exchange are faster in HF–SbF_5 than in HSO_3F–SbF_5 as earlier claimed by Hogeveen and Bickel.[20] Further investigations on the reaction kinetics as a function of temperature and composition of the acid system have been carried out, but limited as follows: (1) at lower concentration of SbF_5, temperature has to be increased for observable exchange and solubility of methane at more than 50 °C was the limiting factor of the method; (2) at higher concentration it was the viscosity of the media at low temperatures. Rates of exchange were measured for several temperatures for 5 mixtures containing from 49% to 19% molar SbF_5. An illustration of the effect of temperature on the exchange rate is given in Fig. 4. The corresponding Gibbs free energy of activation $\Delta G^{\#}$, enthalpy of activation $\Delta H^{\#}$ and entropy of activation $\Delta S^{\#}$ were estimated from the plot based on the Eyring equation:[24]

$$k = \frac{k_B}{h} \cdot T \cdot e^{\frac{-\Delta H^{\#}}{RT}} \cdot e^{\frac{-\Delta S^{\#}}{R}} \qquad (6)$$

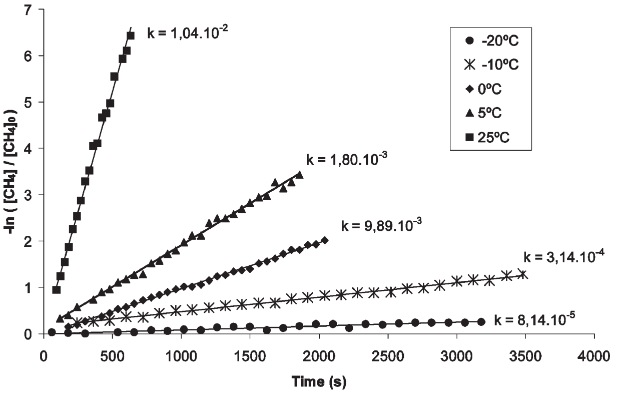

Fig. 4 Determination of the rate of incorporation of deuterium in CH_4 in DSO_3F–SbF_5 (49 mol % SbF_5) at several temperatures.

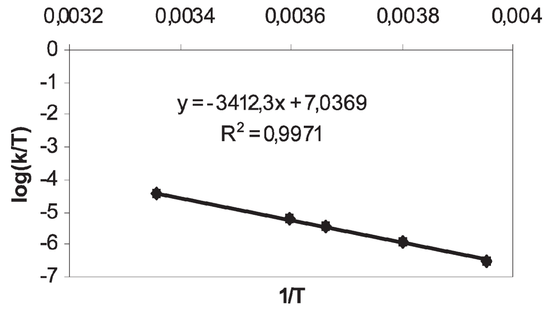

Fig. 5 Eyring plot for the H/D exchange between CH_4 and DSO_3F–SbF_5 (49 mol % SbF_5).

Fig. 5 presents a typical plot for the determination of the activation parameters. The numerical results for various concentrations are collected in Table 1.

It appears that an increase in concentration of SbF_5 from 19 to 49 mol % in HSO_3F–SbF_5 leads to a decrease of the free energy of activation from 97 to 84 kJ mol^{-1}, respectively, whereas the free enthalpy of activation $\Delta H^{\#}$ remains constant 64.5 ± 1 kJ mol^{-1}. Correspondingly, the importance of the free entropy of activation decreases from −25 to −15 J mol^{-1} K^{-1}. In comparison with the value found by Hogeveen *et al.*[9] ($\Delta H^{\#} = 75$ kJ mol^{-1}) for the H/D exchange between monodeuterated methane and HF–SbF_5, the $\Delta H^{\#}$ value found here is surprisingly lower despite the higher acidity of HF based superacids. It is, however, difficult to compare the reactivity of both systems, in which the ionic and cationic compositions differ substantially. While in the HF based superacid only 4 types of anions were detected,[25] more than 7 different anionic species were observable by ^{19}F NMR in HSO_3F superacids.[26] Comparison of the anionic part of both systems shows that the addition of SbF_5 to HF leads preferentially to the generation of larger ions instead of ionization of HF, whereas addition of SbF_5 to HSO_3F leads preferentially to ionization of HSO_3F. As a consequence HSO_3F is fully ionized in the presence of 50 mol % SbF_5[8] whereas HF can still be observed until the antimony pentafluoride concentration reaches 80 mol %.[25] Several theoretical studies on alkane protonation and reactivity in HF–SbF_5 superacid are available in the literature,[19,27–29] but no comparable studies have been published on HSO_3F–SbF_5 superacids. Increasing the concentration of the Lewis acid shifts the autoprotonation equilibrium towards the production of more acidic species:

$$SbF_5 + 2AH \rightleftharpoons SbF_5A^- + H_2A^+$$

Due to the large excess of acidic species in comparison with the amount of methane present in the system (molar ratio *ca.* 10^3:1) we cannot assign the increase in rate to an increase of concentration of the superacid when going from 19 to 49 mol % SbF_5. For this reason we suggest that the entropy factor due to a solvation effect is most probably at the origin of

Table 1 Activation parameters for H/D exchange between CH_4 and different mixtures of DSO_3F–SbF_5

DSO_3F–SbF_5/ mol % SbF_5	T_{expt}/ °C	$\Delta G^{\#}$ (30 °C)^a/ kJ mol^{-1}	$\Delta H^{\#a}$/ kJ mol^{-1}	$-\Delta S^{\#a}$/ J mol^{-1} K^{-1}
19	25–75	97	65.4	25
25	35–55	93^b	65.5	23
31	25–45	93	63.5	23
41	−10–30	90	64.5	20
49	−20–25	84^b	65.2	15

[a] Estimated errors within the limit of 10% of the corresponding values.
[b] Extrapolated

the observed variation. The hydrogen bonding of the methonium-ion-like transition state with the counter anion decreases as the acidity increases. The importance of solvation has been demonstrated by theoretical studies for HF-based systems. A computational study on methane protonation by $[H_2SO_3F^+]$-like species would be helpful to understand the nature of solvation of methonium ion and then to compare the activated complex involved in both systems. In line with these results it seems even more risky to relate the rate of exchange between methane and various deuterated solid acids to the acidity of such solid acidic catalysts as has been suggested recently.[30,31]

Conclusion

Kinetic studies of the H/D exchange between methane and DSO_3F–SbF_5 in the concentration range of 19 to 49 mol % SbF_5 were performed by means of *in situ* NMR spectroscopy. A relationship between the rates of the isotopic exchange and the acidity of the superacid was established. The free enthalpy of activation of the exchange process appears to be independent of the system's acidity, which seems to indicate only minor changes in the transition state in the studied acidity range. However, a substantial change in the entropy of activation is observed, related to solvation by the acid system. This is in line with results reported for the HF–SbF_5 system in which solvation of the methonium ion plays an important role.[27]

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