Methane Activation and Oxidation in Sulfuric Acid

Alain Goeppert,[a] Peter Dinér,[b] Per Ahlberg,[b] and Jean Sommer*[a]

Abstract: The H/D exchange observed when methane is contacted with D_2SO_4 at 270 – 330 °C shows that the alkane behaves as a σ base and undergoes rapid and reversible protonation at this temperature. DFT studies of the hydrogen exchange between a monomer and a dimer of sulfuric acid and methane show that the transition states involved in the exchange are bifunctional, that is one hydrogen atom is transferred from a hydroxy group in sulfuric acid to methane, while one hydrogen atom is abstracted from methane by a non-hydroxy oxygen atom in sulfuric acid. All the transition states include a CH_5 moiety, which shows similarities to the methanium ion CH_5^+. The calculated potential activation energy of the hydrogen exchange for the monomer is 174 kJ mol^{-1}, which is close to the experimental value (176 kJ mol^{-1}). Solvation of the monomer and the transition state of the monomer with an extra sulfuric acid molecule, decrease the potential activation energy by 6 kJ mol^{-1}. The acid – base process is in competition, however, with an oxidative process involving methane and sulfuric acid which leads to CO_2, SO_2, and water, and thus to a decrease of acidity and loss of reactivity of the medium.

Keywords: density functional calculations · H/D exchange · methane · oxidation · sulfuric acid

Introduction

Methane, a principal component of natural gas, is an abundant hydrocarbon resource that is mainly used as a relatively inexpensive and clean burning fuel. Because of the enormous proven reserves of natural gas in the world (1.4×10^{14} m^3),[1] there is a strong economic incentive to develop a process that would convert methane into more valuable chemicals and fuel. The quest for such a process and the associated scientific challenge has stimulated a large amount of research in the last few decades on methods for direct conversion of methane into ethylene, methanol, formaldehyde, etc. However since methane is a very stable molecule, its activation is much more difficult than for other saturated hydrocarbons. Recently, most of the efforts have focused on the oxidative coupling of methane initiated by homolytic cleavage of a C–H bond.[2–4] High temperatures of usually more than 700 °C are required. However, Periana et al.[5] found that methane can be converted into a methanol derivative in more than 70 % yield for one cycle on a platinum-based catalyst in concentrated sulfuric acid between 180 °C and 200 °C. Another approach is electrophilic activation which relies on the σ basicity of the C–H bond, that is, its ability to react with strong electrophiles. Olah et al. have reported that the reaction of methane in a 1/1 FSO_3H/SbF_5 solution (superacid) at 80 to 140 °C leads to the formation of higher molecular weight hydrocarbon ions such as *tert*-butyl and *tert*-hexyl cations by protolytic condensation.[6, 7] In this medium, but also in HF/SbF_5,[8] H/D exchange in methane was observed. This suggests that in superacidic solutions, methane indeed behaves as a base. The methanium ion, CH_5^+, was suggested either as an intermediate or transition state accounting for the hydron exchange. As sulfuric acid with an H_0 of -12[7] is on the borderline between conventional acids and superacids, we found it of interest to investigate the probability of H/D exchange and reaction of methane in D_2SO_4 both theoretically and experimentally in the range between 270 and 330 °C.

Experimental Section

D_2SO_4 98 wt % solution in D_2O, 99.5 atom % D from Aldrich was used without further purification. Methane N35 was purchased from Messer.

Procedures: The reaction between methane and deuterated sulfuric acid was performed in an all-glass, grease-free recirculation set-up. D_2SO_4 (6 g, 0.06 mol; 99.5 % D) was introduced in the reactor and heated to 200 °C. The system was carefully evacuated and methane (80 mL, 0.00357 mol) introduced. The temperature was then rapidly but precisely increased to

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the desired temperature in the range 270 – 330 °C and methane bubbled at a rate of 10 mL min^{-1} (0.00045 mol min^{-1}) through the acid. Deuteration and formation of by-products were monitored by GC-MS as a function of time.

The same experimental procedure was used for the reaction of CO in D_2SO_4.

Mass spectrometry: MS analysis was performed on a Carlo-Erba QMD-1000 spectrometer with a JSW Scientific DB 624 column (∅ = 0.25 mm, film 1.4 µm, $l = 30$ m). The concentration of methane isotopologues (CH_xD_{4-x} with x = 0 – 4) must be related to the intensity of their respective molecular ion peaks analyzed by GC-MS. To determine the contribution of each methane isotopologue to the mass spectra, a correction is needed due to the superposition of various fragmentation peaks. The correction method is based on the work of Schoofs and co-workers,[9] namely the degree of fragmentation for all the methane isotopologues is supposed to be the same. The fragmentation pattern of unreacted methane was used as a reference. Once the concentration of the different isotopologues was known, the amount of deuterium incorporated into methane could be calculated and consequently the exchange rate.

The analysis of hydrocarbons was performed on a Girdel 300 with a FID detector using packed column HAYESED R (∅ = 1/8", $l = 2$ m). Helium was used as a carrier gas. The concentration of hydrogen was determined on an Intersmat IGC 112M provided with 5 Å molecular sieve. Argon was employed as a carrier gas. The results of our analysis were computed on a Delsi Instruments ENICA 21 recorder integrator.

Computational details: Reactants and transition states were optimized at B3LYP/6-311 + G(d,p)[10–13] and B3LYP/6-311 + + G(3df,2p)[14] levels of theory as implemented in Gaussian 98.[15] All structures were characterized as minima or saddle points on the potential energy surface (PES) by use of the sign of the eigenvalues of the force constant matrix obtained from frequency calculations. The imaginary frequencies of the transition states were confirmed to correspond to the right motion on the PES by a mode analysis. Intrinsic reaction coordinate (IRC) calculations[16, 17] of 24 points, followed by geometry optimizations were performed to connect the transition state with reactant and product at the B3LYP/6-311 + G(d,p) level of theory. The B3LYP/6-311 + G(d,p) and B3LYP/6-311 + + G(3df,2p) levels of theory were chosen since a previous investigation[18] at B3LYP/6-311 + + G(2d,2p) level reproduced high-level results of the geometry of sulfuric acid and studies[19] of the gas-phase acidities at B3LYP/6-311 + G(d,p) and B3LYP/6-311 + G(3df,3pd) had shown good agreement with experimental results. The energies and geometries in the text refers to the B3LYP/6-311 + + G(3df,2p) level of theory if not otherwise stated.

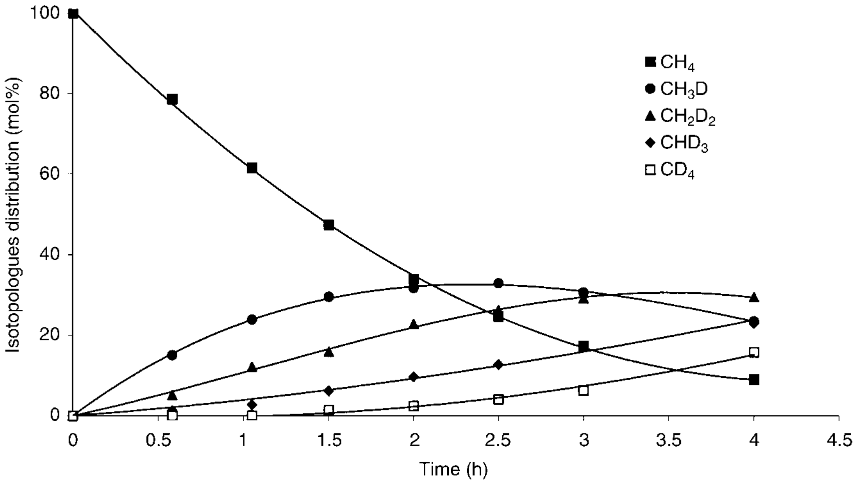


Figure 1. Distribution of the methane isotopologues [%] as a function of time in boiling D_2SO_4 (338 °C).

Results and Discussion

H/D exchange of methane in D_2SO_4

Experimental study: H/D exchange reactions on small alkanes is a very useful tool to gain insight into mechanisms of alkane activation in acidic media. In our work in recent years, we noted that depending on the acidity, the H/D exchange in superacids occurred either by reversible protonation of the alkane in the strongest acids such as HF/SbF_5[20, 21] or through reversible deprotonation of carbenium ions in weaker superacids such as HSO_3F,[22] CF_3SO_3H,[23] and solid acids. For these studies we found that isobutane is a convenient model as the main reaction, isotope exchange, is accompagnied by a negligible contribution of cracking. In DF/SbF_5, in agreement with the formation of carbonium ion intermediates, the reversible protonation occurs on all C–H bonds and contrasts markedly with the H/D exchange observed in D_2SO_4[24, 25] or triflic acid[23] in which case the methine proton is not exchanged. In these weaker acids, after activation by oxidation, H/D exchange takes place by deprotonation of the *tert*-butyl cation and reprotonation of isobutene. As the last step is a hydride transfer, the methine proton cannot be exchanged. Nevertheless, if we use methane, the oxidation is more difficult.

As the formation of carbonium ions from alkanes is a typical reaction for superacids, methane is not predicted to undergo H/D exchange in D_2SO_4, the strongest "conventional" acid. Nevertheless, when methane was allowed to react with a large excess of boiling D_2SO_4 (338 °C), extensive H/D exchange was observed. The methane isotopologue distribution (mol %) after mass spectral corrections is presented in Figure 1 as a function of time. It can be seen that the mono-, bis-, ter-, and perdeuterated isotopologues of methane are formed in a consecutive reaction pathway. The concentration of CH_4 decreases gradually with time, whereas the concentration of deuterated products increases. Similar features were observed not only in DF/SbF_5[26] but also on deuterated solid acids such as zeolites[9] and sulfated zirconias,[27] which are capable of exchanging protons in methane, albeit at higher temperature (300 – 500 °C).

The exchange rate between methane and deuterated catalysts is determined in the following way: The amount of deuterium in methane is obtained from mass spectrometric analysis at various time intervals. The rates are then expressed as moles of H replaced by D per mole of methane per unit of time (s^{-1}), which correspond to the slopes of the lines in Figure 2; the maximum value is 4. At temperatures up to 250 °C, no H/D exchange was observed under our conditions. However between 270 and 315 °C the observed rate constant of deuterium incorporation into methane increased steadily (Figure 2) going from 4.21×10^{-6} s^{-1} at 270 °C to 8.41×10^{-5} s^{-1} at

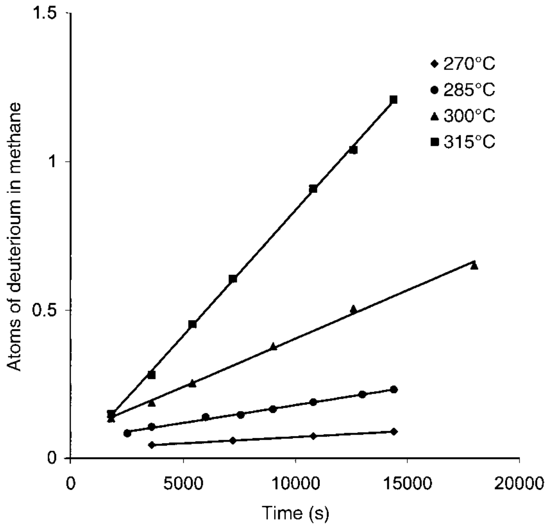


Figure 2. Average number of moles of D per mol of CH_4 versus time at different temperatures.

315 °C. This means that after reaction at 315 °C for 4 h, 30 % of the protons have been exchanged by deuterons in methane. The apparent activation energy for the H/D exchange of methane was estimated to be 176 $kJ\,mol^{-1}$ from the slope of the Arrhenius plot (Figure 3). The activation energy is much higher than the values obtained previously in the very strong superacid $H(D)F/SbF_5$. In a recent study of methane reactivity in DF/SbF_5 (15 mol% SbF_5) at −20 °C, we[26] found a free energy of activation of 78.6 $kJ\,mol^{-1}$ for this reaction. In the late 1960s Hogeveen and co-workers[8] reported an activation energy of 75 $kJ\,mol^{-1}$ for the inverse reaction of dedeuteration of CH_3D in HF/SbF_5 at high pressure (7 atm) over a temperature interval from −10 °C to 25 °C. This apparent activation energy for the H/D exchange reaction between methane and D_2SO_4 is also substantially higher than on zeolites (120 to 150 $kJ\,mol^{-1}$)[9, 28, 29] and different sulfated zirconias (93 to 96 $kJ\,mol^{-1}$).[27]

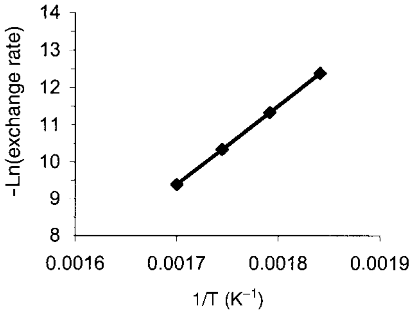


Figure 3. Arrhenius plot for the H/D exchange of methane in D_2SO_4

Computational results: To better understand the isotope exchange process observed experimentally, we have also investigated the hydrogen exchange between sulfuric acid (**1**) and methane (**3**) computationally. To model the solvation we have also investigated the hydrogen exchange in methane with the sulfuric acid dimer (**2**) (Figure 4).

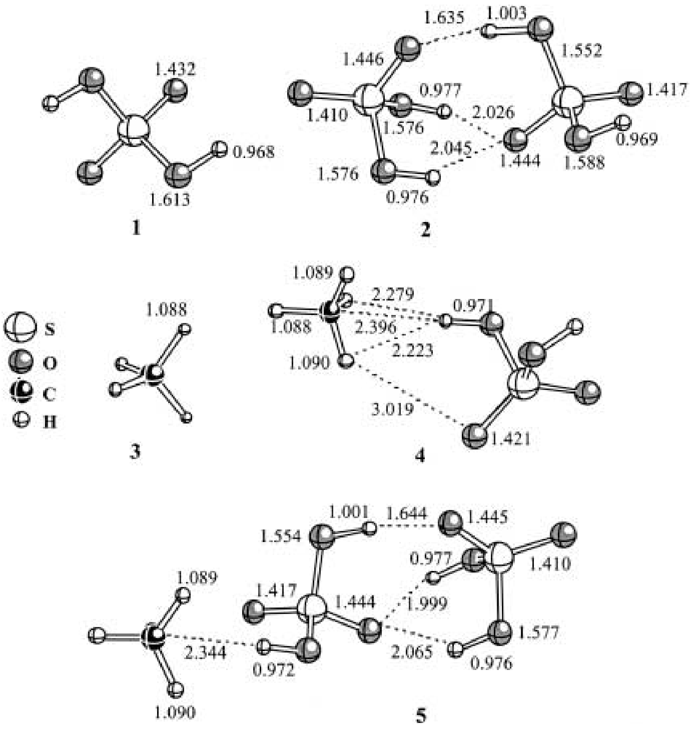


Figure 4. Geometries of sulfuric acid (**1**), dimer of sulfuric acid (**2**), methane (**3**), a complex between methane and sulfuric acid (**4**), and a complex between methane and dimer of sulfuric acid (**5**) at the B3LYP/6–311 ++ G(3df,2p) level of theory.

According to the DFT calculations, methane forms a weak complex (**4**) with sulfuric acid (Figure 4). The reaction potential energy of the complex is −4.6 $kJ\,mol^{-1}$ on the B3LYP/6–311 ++ G(3df,2p) potential energy surface. Inclusion of the zero-point energy and temperature correction gives an reaction enthalpy of 0.4 $kJ\,mol^{-1}$.

Both monofunctional and bifunctional transition states for the hydrogen exchange were investigated. In the monofunctional transition state (**TS2**), the exchange of protons takes place using a single oxygen atom in sulfuric acid, that is one hydrogen atom is transferred to the carbon atom in methane from one of the oxygen atoms in sulfuric acid, while another proton from methane is transferred to the same oxygen atom in sulfuric acid (Figure 5). In the bifunctional transition state (**TS1**), on the other hand, one hydrogen atom is tranferred from a hydroxy group in sulfuric acid to methane, while a hydrogen atom is abstracted from methane by a non-hydroxy oxygen atom in sulfuric acid (see Figure 5).

In the bifunctional transition state, the hydrogen atoms in flight are closer to the carbon atom (C–H 1.284 Å) than to the oxygen atom (O–H 1.418 Å) and the H–H distance is 1.167 Å (Figure 5). A comparison of the CH_5 part of the transition state structure with free CH_5^+, calculated at the B3LYP/6–311 ++ G(3df,2p) level of theory, shows that C–H bonds and the H–H bond in the bifunctional transition state structure **TS1** are 0.120 and 0.169 Å longer, respectively, than in the free CH_5^+ ion (Figure 5). The similarity with CH_5^+ indicates that the bifunctional transition state has some carbonium character. The calculated activation potential energy for the hydrogen exchange, relative to free methane and a monomer of sulfuric acid, is 174 $kJ\,mol^{-1}$ (Table 2). The experimentally

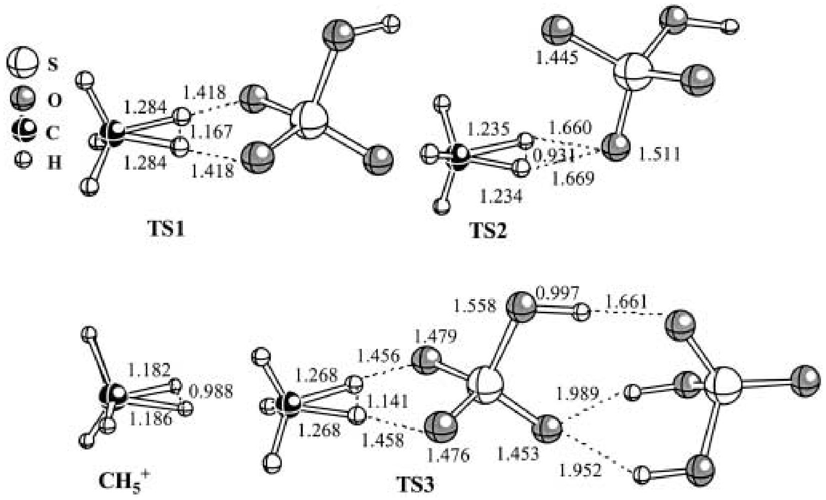


Figure 5. Geometries of the hydrogen exchange transition states **TS1** and **TS2** and **TS3** at the B3LYP/6-311++G(3df,2p) level of theory.

Table 1. Absolute energies (*E*) and enthalpies (*H*) of the calculated structures at the B3LYP/6-311+G(d,p) and B3LYP/6-311++G(3df,2p) level of theory.

	B3LYP/6-311+G(d,p)		B3LYP/6-311++G(3df,2p)	
	E [Hartree]	*H* [Hartree]	*E* [Hartree]	*H* [Hartree]
1	-700.33901	-700.29457	-700.42940	-700.38414
2	-1400.70313	-1400.61200	-1400.88129	-1400.78876
3	-40.53393	-40.48558	-40.53680	-40.48842
4	-740.87469	-740.78000	-740.96800	-740.87242
5	-1441.23930	-1441.09787	-1441.42031	-1441.27743
TS1	-740.80469	-740.71781	-740.89975	-740.81174
TS2	-740.77720	-740.68929	-740.87015	-740.78132
TS3	-1441.17157	-1441.03773	-1441.35401	-1441.21853

determined activation energy is 176 kJ mol^{-1}. However the fact that these values are extremely close is fortuitous as we should keep in mind that the theoretical approach does not completely take into account all the parameters controlling the interactions in the condensed state. On the other hand, the experimentally determined activation energy does not consider the difference of methane solubility in D_2SO_4 at various temperatures. Inclusion of the zero-point energy and temperature correction (298 K) gives an activation enthalpy of 159 kJ mol^{-1}. The activation enthalpy for the reaction of the isotopologue molecules D_2SO_4 and deuterated **TS1** is calculated at the B3LYP/6-311+G(d,p) level of theory to be 2.9 kJ mol^{-1} higher than for the corresponding protium compounds.

In the monofunctional transition state **TS2**, the C–H distances and the H–H distance are 1.23 and 0.93 Å, respectively, that is 0.054 and 0.237 Å, respectively, shorter than in the bifunctional transition state. The H–H distance in the monofunctional transition state is 0.058 Å shorter, and the C–H distances 0.048 Å longer than the corresponding distances in CH_5^+ (Figure 5). Thus the cationic part of the monofunctional transition state is more CH_5^+-like than that in the bifunctional transition state. The activation potential energy for the monofunctional hydrogen exchange reaction is 251 kJ mol^{-1}, which is 77.4 kJ mol^{-1} higher than for the bifunctional transition state (Table 2). Thus the reaction path via the monofunctional activated complex is probably not used for the hydrogen exchange.

Sulfuric acid is a media that can form strong intermolecular hydrogen bonds. To study the solvation effect upon the reactivity in the hydrogen exchange between methane and sulfuric acid, sulfuric acid in the initial state and the transition state was solvated by another sulfuric acid molecule. The solvated monomer, that is the dimer **2**, is found to be held together by three hydrogen bonds (Figure 1) and the corresponding potential energy stabilization is -59.0 kJ mol^{-1}, compared to two monomers of sulfuric acid. The distances in the dimer resembles the corresponding ones in the monomer, but with some deviations due to the hydrogen bonding (see Figure 4). Similar to the monomer of sulfuric acid, its dimer forms a weak complex with methane (**5**), which is stabilized by 5.9 kJ mol^{-1} compared to free methane and the dimer of sulfuric acid on the potential energy surface. The structure of the bifunctional activated complex for the dimer, (**TS3**), is similar to the bifunctional activated complex with the monomer of sulfuric acid, **TS1**. The C–H and the H–H distances in **TS3** are slightly shorter (0.016 and 0.026 Å, respectively) than in the **TS1**. The O···H distances, on the other hand, for the bifunctional dimer transition state are 0.040 Å longer than for the bifunctional transition state with the monomer. The calculated activation potential energy for the hydrogen exchange with the sulfuric acid dimer is 168 kJ mol^{-1} (Table 2), that is slightly lower than for the monomer.

Table 2. Relative energies ($\Delta\Delta E_{0\,K}$) and enthalpies ($\Delta\Delta H_{298.15\,K}$) of the calculated structures at the B3LYP/6-311+G(d,p) and the B3LYP/6-311++G(3df,2p) level of theory.

	B3LYP/6-311+G(d,p)		B3LYP/6-311++G(3df,2p)	
	$\Delta\Delta E$ [kJ mol^{-1}]	$\Delta\Delta H$ [kJ mol^{-1}]	$\Delta\Delta E$ [kJ mol^{-1}]	$\Delta\Delta H$ [kJ mol^{-1}]
1 + **3**	0.0	0.0	0.0	0.0
4	-4.60	0.40	-4.60	0.38
TS1	179	164	174	160
TS2	250	238	252	239
2 + **3**	0.0	0.0	0.0	0.0
5	-5.86	-0.75	-5.86	-0.63
TS3	172	157	168	154

The geometries of the bifunctional transition states of both the monomer (**TS1**) and the dimer (**TS3**) closely resemble the transition state previously found for hydrogen exchange with zeolite clusters.[29] The computationally determined activation potential energy (174 kJ mol^{-1} for the monomer) for the hydrogen exchange between sulfuric acid and methane is higher than the recently reported calculated activation potential energy (124-137 kJ mol^{-1})[29] for the zeolite cluster with inclusion of a Madelung potential. On the other hand, other computational studies[30] at the CISD/6–31G(d,p) level of theory using a smaller zeolite cluster has given an activation potential energy of 174 kJ mol^{-1}.

To compare the change in reactivity due to solvation, the reactants have to be on the same potential energy surface. By adding an extra non-solvating sulfuric acid molecule both to the reactants and the transition state, the monomer and the dimer cases are energetically comparable.

On solvation of the transition state of the monomer with an extra sulfuric acid molecule, the transition state of the dimer is stabilized by 59.5 kJ mol^{-1}, compared to the monomer transition state plus free sulfuric acid (**TS1**+**1**) (Figure 6). The Gibbs free energy stabilization of the monomer is -5.64 kJ mol^{-1}. The solvation of the monomer transition state is effected in a similar way as the monomer of sulfuric acid, that is the stabilization free energy is decreased to -12.9 kJ mol^{-1} due to solvation, which give a total lowering of the Gibbs free activation energy of 7.31 kJ mol^{-1}.

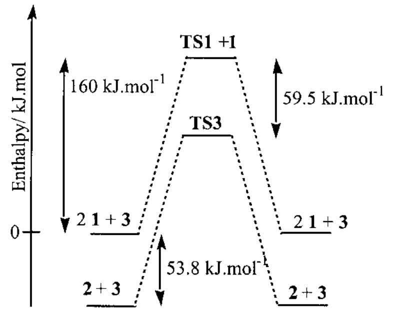


Figure 6. Enthalpy diagram of monomer **1** and dimer **2** of sulfuric and the hydrogen exchange transition states **TS1** and **TS3**.

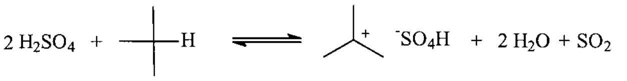
The hydrogen exchange between methane and other acidic species, such as H_3O^+,[31] $H_2F^+(HF)_n$,[26] SbF_5/HF,[32] Sb_2F_{11}/HF,[33] and zeolites,[29] have previously been investigated theoretically (Figure 7). The protonating species are both neutral and cationic species and the charge influences the structure of the exchange transition state. The structures of the CH_5^+ part of cationic transition states, that is H_3O^+ and $H_2F^+(HF)_n$, are similar to the structure of the free methanium CH_5^+ ion.

Secondary reactions of methane oxidation in D_2SO_4

Catalyst deactivation: When the same D_2SO_4 is used several times, we can observe a slower deuteration rate for methane (Table 3) the extent of which cannot be assigned to isotopic dilution. At 315 °C, three consecutive runs of 8 h duration show that the initial rate of deuteration observed in the first run is about 60 times faster than in the third one. This cannot be attributed to a depletion of deuterium in the catalyst because even after the last run less than 10% of the D_2SO_4 deuterium have been exchanged based on methane deuteration. In all experiments, no presence of hydrogen or higher alkanes—a sign of methane oligomerization—was found by GC, but SO_2 and CO_2 were detected by mass spectrometry, which arose from the reduction of D_2SO_4 and the oxidation of methane, respectively. For the formation of these species, we suggest a reaction similar to the one proposed for the activation of isobutane in H_2SO_4[34] [Eq. (1)]. The production of six molecules of water [Eq. (2)] during CO_2 and SO_2 formation could explain the loss in activity of the catalyst. The deactivation can thus be rationalized by the accumulation of water in the acid and the corresponding decrease in acidity. This is also in line with the acid–base character of the H/D exchange reaction under these conditions.

Table 3. Observed deuteration rate constants of methane in reused D_2SO_4 at 315 °C.

Run	Deuteration rate constant [s^{-1}]
1	8.41×10^{-5}
2	1.07×10^{-5}
3	1.28×10^{-6}



(1)

$$4 H_2SO_4 + CH_4 \longrightarrow CO_2 + 4 SO_2 + 6 H_2O \qquad (2)$$

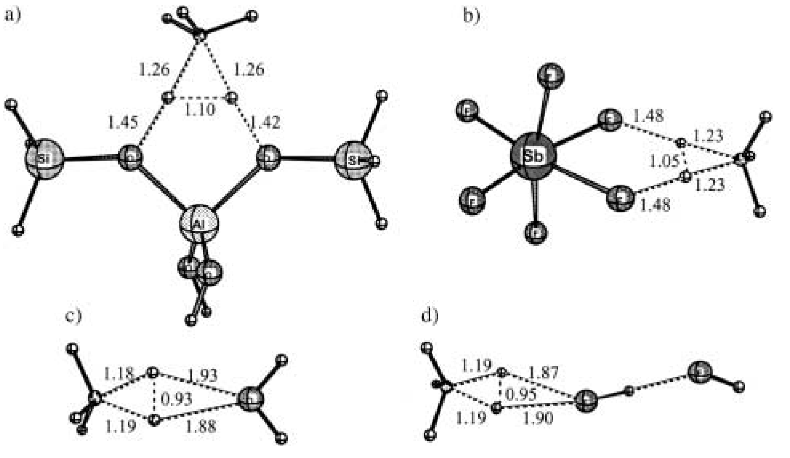


Figure 7. Previously investigated transition states for hydrogen exchange in methane: a) zeolites,[29] b) SbF_5/HF,[32] c) H_3O^+,[31] d) $H_3F_2^+$.[26]

Formation of CO_2 and SO_2: The formation of CO_2 from CH_4 attests an oxidation reaction parallel to the H/D exchange reaction. Activation of methane in sulfuric acid has been described by using radical initiators such as $PdSO_4$ or $HgSO_4$[35] or platinum complexes[5] but never in neat H_2SO_4. For this reason we found it of interest to study the oxidation reaction, not only qualitatively, but also quantitatively. The rate of CO_2 formation was measured by comparing the MS parent peak of CO_2 (m/z 44) with the peak m/z 40 of argon used as internal standard. This rate was found to be the same as the rate of decrease of the methane peak (m/z 12 to 20 considering all the isotopologues and their fragmentation). In Figure 8, we compare the oxidation reaction with the deuteration of methane in boiling D_2SO_4. We can see that the H/D exchange rate constant ($1.50 \times 10^{-4}\ s^{-1}$) is about 5.2 times faster than the rate of oxidation ($2.85 \times 10^{-5}\ s^{-1}$). Interestingly, the same ratio was also observed at 270 °C. On the other hand, the formation of SO_2 was also monitored by using the peak m/z 48 representing SO^+ and comparing this one to the internal m/z 40 argon reference peak. We can see from Figure 8 that the rate of SO_2 formation is about four times faster than the rate of CO_2 formation. This means that for each molecule of CO_2 we have at the same time four molecules of SO_2 appearing in the system. These results are in agreement with Equation (2), in which the same ratio of $1CO_2{:}4SO_2$ appears. The large amount of water formed during the oxidation reaction, six molecules for each methane molecule, may explain the observed deactivation of the catalyst.

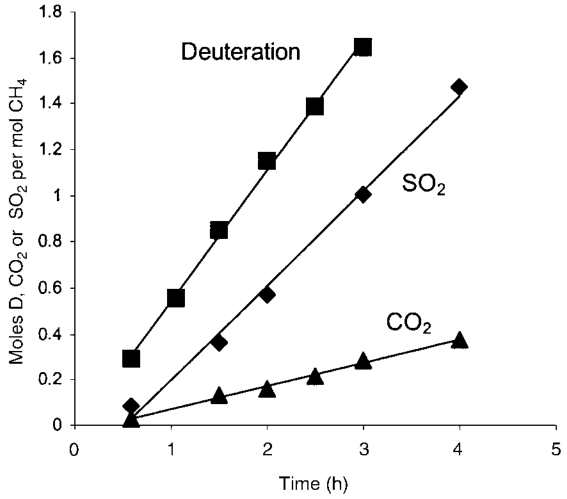


Figure 8. Deuteration and oxidation of methane in boiling D_2SO_4 (338 °C)

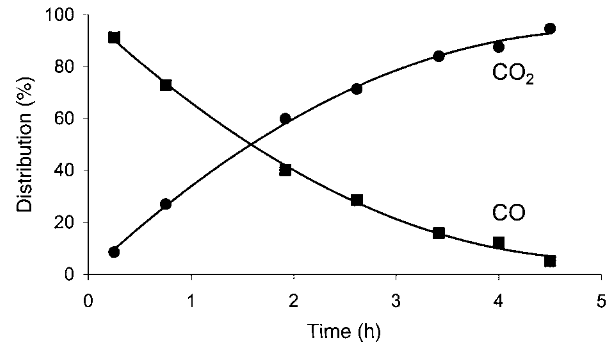


Figure 9. Oxidation of CO to CO_2 in D_2SO_4 at 315 °C (mol% of CO/(CO + CO_2)).

Oxidation of CO to CO_2 in sulfuric acid: In the reaction of methane with D_2SO_4, no carbon monoxide was detected. This could be due to the fact that no partial oxidation was taking place or, that the oxidation reaction of CO to CO_2 was too fast to be observed. For this purpose it was interesting to study the reaction of carbon monoxide in sulfuric acid. Figure 9 shows the conversion of CO into CO_2 versus time at 315 °C in H_2SO_4. The sulfuric acid oxidized rapidly CO into CO_2 and after 4.5 h 95 % of CO was converted to CO_2. If we assume that we are dealing with a pseudo-first-order reaction, owing to the large excess of sulfuric acid, the rate constant estimated for this reaction is $1.51 \times 10^{-4}\ s^{-1}$, which is about two times faster than the deuteration of methane at the same temperature and 10 times faster than the oxidation of methane to CO_2. At the same time we observed, as in the reaction of methane, the formation of sulfur dioxide. In this case, however, the rate of formation of SO_2 and CO_2 were found to be approximately the same. This suggests the formation of only one molecule of SO_2 per CO_2 molecule. Consequently, the reaction could be described most simply by Equation (3) in which H_2SO_4 reacts

$$H_2SO_4 + CO \longrightarrow CO_2 + SO_2 + H_2O \qquad (3)$$

with CO to form CO_2, SO_2, and H_2O. This equation was already proposed by Milbauer et al.[36] who observed at the beginning of this century that oxidation of CO does not occur to any appreciable extent below 200 °C. This reaction can however, be promoted by catalytic amounts of a large number of metals.

The fact that sulfuric acid oxidizes CO to CO_2 under our conditions is interesting per se but does not allow us to establish whether CO is a reaction intermediate in the formation of CO_2 as the reaction mechanism is still unknown.

Conclusion

Methane undergoes reversible protonation in sulfuric acid at 270 – 330 °C. This process competes with an oxidative process that yields CO_2, SO_2, and water, which slowly decreases the acidity of sulfuric acid. This indicates that methane behaves as a σ base even in concentrated sulfuric acid. The DFT calculations show that the exchange process may be of a bifunctional acid – base type with a transition state containing a CH_5 part, which shows similarities to CH_5^+.

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[1] *Oil Gas J.* **1993**, *52*, 37.
[2] R. Pitchai, K. Klier, *Catal. Rev.-Sci. Eng.* **1986**, *28*, 13.
[3] J. H Lunsford, *Angew. Chem.* **1995**, *107*, 1059; *Angew. Chem. Int. Ed.* **1995**, *34*, 970.
[4] E. N. Voskresenskaya, V. G. Roguleva, A. G. Anshits, *Catal. Rev.-Sci. Eng.* **1995**, *37*, 101.
[5] R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560.

[6] G. A. Olah, G. Klopman, R. Schlosberg, *J. Am. Chem. Soc.* **1969**, *91*, 3261.

[7] G. A. Olah, G. K. S. Prakash, J. Sommer, *Superacids*, Wiley, New York, **1985**.

[8] H. Hogeveen, C. J. Gaasbeek, *Rec. Trav. Chim.* **1968**, *87*, 319.

[9] B. Schoofs, J. A. Martens, P. A. Jacobs, R. A. Schoonheydt, *J. Catal.* **1999**, *183*, 355.

[10] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[11] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.* **1988**, *37*, 785.

[12] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650.

[13] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294.

[14] M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265.

[15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. Montgomery, J. A. , R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, GAUSSIAN 98, Rev. A3, Gaussian Inc., Pittsburgh, PA, **1998**.

[16] C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.* **1989**, *90*, 2154.

[17] C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.

[18] A. R. Bandy, J. C. Ianni, *J. Phys. Chem. A* **1998**, *102*, 6533.

[19] I. A. Koppel, P. Burk, I. Koppel, I. Leito, T. Sonoda, M. Mishima, *J. Am. Chem. Soc.* **2000**, *122*, 5114.

[20] J. Sommer, J. Bukala, S. Rouba, R. Graff, *J. Am. Chem. Soc.* **1992**, *114*, 5884.

[21] J. Sommer, J. Bukala, M. Hachoumy, R. Jost, *J. Am. Chem. Soc.* **1997**, *119*, 3274.

[22] J. Sommer, unpublished results.

[23] A. Goeppert, B. Louis, J. Sommer, *Cat. Lett.* **1998**, *56*, 43.

[24] J. W. Otvos, D. P. Stevenson, C. D.Wagner, O. Beeck, *J. Am. Chem. Soc.* **1951**, *73*, 5741.

[25] D. P. Stevenson, C. D. Wagner, O. Beeck, J. W. Otvos, *J. Am. Chem. Soc.* **1952**, *74*, 3269.

[26] P. Ahlberg, A. Karlsson, A. Goeppert, S. O. Nilsson Lill, P. Dinér, J. Sommer, *Chem. Eur. J.* **2001**, *7*, 1936.

[27] W. Hua, A. Goeppert, J. Sommer, *J. Cat.* **2001**, *197*, 406.

[28] G. J. Kramer, R. A. van Santen, C. A. Emeis, A. K. Nowak, *Nature*, **1993**, *363*, 529.

[29] J. M. Vollmer, T. N. Truong, *J. Phys. Chem. B.* **2000**, *104*, 6308.

[30] G. J. Kramer, R. A. van Santen, *J. Am. Chem. Soc.* **1995**, *117*, 1776

[31] Y. A. Borisov, Y. A. Zolotarev, *Russ. Chem. Bull.* **1999**, *48*, 1431.

[32] P. M. Esteves, A. Ramírez-Solís, C. J. A. Mota, *J. Braz. Chem. Soc.* **2000**, *11*, 345.

[33] P. M. Esteves, A. Ramírez-Solís, C. J. A. Mota, *J. Phys. Chem. B*, **2001**, *105*, 4331

[34] J. Sommer, A. Sassi, M. Hachoumy, R. Jost, A. Karlsson, P. Ahlberg, *J. Cat.* **1997**, *171*, 391.

[35] N. Basickes, T. E. Hogan, A. Sen. *J. Am. Chem. Soc.* **1996**, *118*, 13111.

[36] J. Milbauer, *J. Soc. Chem. Ind.* **1918**, *37*, 464.

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