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Mechanistic study of the acid catalyzed formation and hydrolysis of MTBE in nonpolar media

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Abstract

The acid catalyzed hydrolysis of MTBE using *p*-toluenesulfonic acid was studied in nonpolar medium to ascertain the effect of nucleophile upon reaction. NMR measurements showed protonation of both MTBE and methanol by *p*-toluenesulfonic acid in nonpolar medium but no nucleophile–electrophile interaction of MTBE with *p*-toluenesulfonic acid methyl ester as potential nucleophile. Addition or in situ generation of a nucleophile did not accelerate the reaction. At low conversions and low catalyst concentration the reaction exhibited pseudo zero order with respect to reactant concentration and second order with respect to catalyst concentration. The results suggest protonation of MTBE in a fast preequilibrium step in which the acid catalyst exhibits cooperative effect. No nucleophilic assistance in the transition state of MTBE hydrolysis in nonpolar medium occurs.

1. Introduction

The development of methyl *tert*-butyl ether (MTBE) into an important industrial commodity has led to a significant increase in the study of the mechanism of its synthesis from methanol (MeOH) and isobutene (IB) under acid catalysis [1]. The most commonly studied catalyst which is also used in commercial processes is a sulfonated ion exchange resin such as Amberlyst-15. Besides the large number of kinetic studies of MTBE formation on this catalyst some investigations targeting catalyst–substrate interactions have been published [2]. The mechanistic description which has widely gained acceptance postulates a change of mechanism depending upon the presence or absence of an excess of MeOH over IB [3]. In the former case, in which a polar medium exists around the acid site, protonated MeOH is formed in a fast step and reacts with IB in the rate-determining step, forming a carbocation which is trapped by MeOH to give protonated MTBE (Eq. 1–3). The acid–base reaction in Eq. 4 must also be fast. This mechanism is referred to as specific acid catalysis.

$$AH + MeOH \leftrightharpoons A^- + MeOH_2^+ \quad (1)$$

$$MeOH_2^+ + H_2C{=}CMe_2 \leftrightharpoons MeOH + Me_3C^+ \quad (2)$$

$$MeOH + Me_3C^+ \leftrightharpoons Me_3C{-}O(H)^+{-}Me \quad (3)$$

$$Me_3C{-}O(H)^+{-}Me + A^- \leftrightharpoons Me_3C{-}O{-}Me + AH \quad (4)$$

In the mechanism proposed for the nonpolar medium, the catalyst, or more specifically the active site, is claimed to play a dual role of proton

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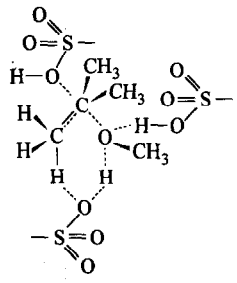

Fig. 1. Proposed transition state for MTBE formation from MeOH and IB on Amberlyst-15 [4].

donor (acid) and nucleophile toward the substrate [4]. No proton transfer step like Eq. 1 or 4 is said to be involved, however, instead, the catalyst interacts with the reactants and product exclusively by hydrogen bonding and the reaction is concerted. The proposed transition state for this mechanism comprises five participants (three SO_3H groups, MeOH, and IB) in a cyclic arrangement which subsequently dissociate into the reaction products, as shown in Fig. 1. This mechanism was described as general acid catalysis [4].

There are some troublesome features, however, in the mechanism proposed for the nonpolar medium. First, there is no aromaticity of the transition state proposed, therefore it represents a structure of high energy [5]. Second, the mechanism requires a pentamolecular collision. Such an aggregation, unheard of in solution, should be even more difficult to achieve on the solid, where proper orientation of sulfonic acid groups requires the distortion of the polymer chains. The highly oriented transition state is possible only if the polymer itself has the SO_3H groups properly oriented around a cavity of the right size and shape such that the two reacting molecules fit in like in enzyme catalysis. The necessary consequence would then be a high sensitivity to substrate size: a catalyst good for MeOH and IB should be totally unsuitable for ethanol (EtOH) and 2-methyl-2-butene. There is no report of such a reactivity pattern. Third, in the reverse pathway a nucleophilic attack by one of the sulfonic acid groups at the quaternary carbon of MTBE is required, which is sterically prohibited as shown long ago by the lack of reactivity of HO^- toward *tert*-butyl chloride [6], even though a combination of electrophilic and nucleophilic assistance by solvent was suggested for solvolyses involving carbocations as intermediates (S_N1) [7].

Much of the mechanistic problems stem from an unfortunate confusion of the meaning of general acid catalysis, which in fact does not mean absence of proton transfer, but its occurrence in the rate-determining step, rather than as a fast preequilibrium which is typical of specific acid catalysis [8]. As general acid catalysis obeys Brønsted's law of catalysis connecting catalytic rates with catalyst acid strengths, it now seems debatable whether hydrogen bonding is sufficient for manifestation of general acid catalysis [8](b), because it was found that there is no connection between hydrogen bond donor ability and acid strength [9].

We felt that a careful mechanistic study of MTBE formation and hydrolysis in nonpolar medium was necessary to solve these inconsistencies, either by amending the mechanism embodied by the transition state of Fig. 1, or by replacing it altogether. To avoid steric constraints and possible mass transfer limitations within the resin catalyst, which have been reported to occur under reaction conditions typical for MTBE synthesis [10], we conducted our study in solution with *p*-toluenesulfonic acid (TsOH) as catalyst, as a close analog of the resin catalyst. The nonpolar medium was ensured by the use of toluene as solvent. At the molecular scale these conditions appropriately simulate the reaction on the acid sites of Amberlyst-15.

In order to study the reaction in solution without the need of working under pressure we studied the hydrolysis of MTBE. The transition state structure should obviously be the same for reaction in either direction [4]. The study of hydrolysis rates is complicated, however, by the position of the equilibrium, heavily on the ether side at temperatures below 373 K, unless IB is removed from the solution. The best way to achieve this removal is by trapping IB with another molecule of alcohol, for example deuterated methanol. We preferred to use ethanol, which is less polar and allows the convenient measurement of conversion by GLC.

Macroscopically, the reaction is, therefore, a transetherification.

Three topics pertinent to the mechanism of interest were studied: the ability of TsOH to protonate the reactant and product, MTBE and MeOH; the reaction rates and kinetic reaction orders; and the effect of added nucleophiles upon the rate.

2. Experimental

Toluene (Fisher Scientific, A.C.S. grade), MeOH (Mallinckrodt, AR), MTBE (Aldrich, 99.9%), pyridine (Fisher Scientific, A.C.S. grade), and EtOH (AAPER Alcohol and Chemical Co., USP) were used as received. *p*-Toluenesulfonic acid (monohydrate, Aldrich, 99%) was recrystallized from toluene. Before use, the purified monohydrate was dried for 48 h at 321 K in the vacuum of a roughing pump and then capped under nitrogen atmosphere in order to allow addition of solvent and reactants to the reaction tube without contamination of the hygroscopic TsOH with water. *p*-Toluenesulfonic acid methyl ester (Aldrich, 98%) (TsOMe) was purified by recrystallization from 35–60° petroleum ether. Due to the low melting point crystallization was induced in an acetone–dry ice bath.

^{1}H and ^{13}C NMR spectra were recorded with a Bruker MSL 300 NMR spectrometer at ambient temperature (298 K) in 8 mm sample tubes placed in 10 mm outer tubes containing $CDCl_3$ as locking agent and TMS as external reference. ^{1}H spectra were run at 300 MHz, a sweep width of 5400 Hz, a pulse width of 9 μs, and a recycle delay of 2 s. For ^{13}C spectra, an irradiation frequency of 75.468 MHz with a spectral width of 20 kHz, a pulse width of 9 μs, a receiver blanking delay of 20 μs, and a recycle delay of 8.5 s was used. The ^{13}C spectra were recorded with irradiation at the proton frequency during acquisition for decoupling and for 1.5 s before excitation to establish NOE [11]. As discussed earlier [11], the resolution was 0.03 ppm; recording multiple spectra of the same sample gave a reproducibility of the same order.

Typically, a 0.5 M solution of dried TsOH in toluene was used as starting sample. The substrates, methanol, MTBE, and TsOMe were gradually added to obtain mixtures of varying stoichiometric ratios. The NMR spectra of the various catalyst–substrate solutions were compared with those of the pure substrate and catalyst solutions. For the determination of the equilibrium constant of protonation of pyridine by TsOH at 298 K, the chemical shifts of characteristic carbon atoms of pyridine were measured in the fully protonated and nonprotonated state [12] using pyridine and a 1:6 mixture of pyridine and trifluoromethanesulfonic acid (TFA), respectively, and were compared with those obtained for a 1:1 mixture of pyridine and TsOH in a solution mimicking that used for the kinetic measurements (MTBE, EtOH, and toluene as solvent).

For kinetic measurements, between 0.05 and 0.1 g of TsOH each were dried in glass tubes (130×7 mm) and capped under nitrogen with rubber septa. Calculated amounts of solvent and reactants were added to each tube through the septum using syringes (250, 100, and 10 μl) and the tube was weighed after each addition. The tubes were then immersed in an oil bath at 338 K where reaction was allowed to proceed. Samples (100 μl) were taken from the glass tubes at intervals, quenched in diluted aqueous KOH, and the organic layer was analyzed by GLC using a Hewlett Packard 5890 series II gas chromatograph equipped with FID and a 3 m×3 mm OD column packed with 10% methyl silicone SP2100 on 80/100 mesh Supelcoport. After 7 min isothermal operation at 308 K the GC oven was heated to 393 K with 20 K/min using 20 cm^3/min of nitrogen as carrier gas.

3. Results

3.1. Substrate–catalyst interaction

The results of the ^{13}C NMR measurements are compiled in Table 1 and those of the ^{1}H NMR

Table 1
Variation of the chemical shift [a] of carbon signals in ^{13}C NMR measurements of solutions of different reactant combinations in toluene at 298 K

	TsOH (ppm) [b]				TsOMe (ppm) [b]			MTBE/MeOH (ppm)		
	m-C	*p*-C	*o*-C	C-SO_3	O-CH_3	*o*-C	C-SO_3	(-CH_3)$_3$	O-CH_3	O-C-
TsOH [c]	126.81	129.58	134.77	144.25						
TsOMe					55.07	133.04	144.03			
MTBE								26.77	48.77	71.79
MeOH									49.76	
TsOMe + MTBE					55.09	133.10	144.06	26.77	48.79	71.94
TsOH + MTBE	126.77	n.o. [d]	n.o. [d]	142.73				25.99	48.77	76.10
TsOH + MTBE + TsOMe	126.75	n.o. [d]	n.o. [d]	142.86	55.26	132.79	144.24	26.01	48.78	76.11
TsOH + MTBE + 2 TsOMe	126.73	n.o. [d]	n.o. [d]	142.93	55.35	132.71	144.34	26.02	48.79	76.07
TsOH + 0.5 MeOH	126.63	129.39	136.86	143.08					50.59	
TsOH + MeOH	126.52	129.23	137.93	142.49					50.06	
TsOH + 2 MeOH	126.45	n.o. [d]	139.04	141.98					49.78	
TsOH + MeOH + TsOMe	126.47	129.58	137.84	142.63	55.27	132.72	144.26		50.07	
TsOH + MeOH + 2 TsOMe	126.47	129.64	137.47	142.70	55.38	132.64	144.38		50.05	
TsOH + 2 MeOH + TsOMe	126.36	n.o. [d]	138.93	142.13	55.29	132.73	144.29		49.80	

[a] Chemical shifts are reported with respect to TMS as external standard.
[b] The signals for ϕ-CH_3, *m*-C, and *p*-C of TsOMe and for ϕ-CH_3 of TsOH were not observable separately because they were covered by signals of toluene used as solvent (21.02, 125.29, 128.12, 128.95, 137.41 ppm).
[c] One equivalent corresponds to 0.5 M solution.
[d] The corresponding signal was not observable separately, see footnote b.

Table 2
Variation of the chemical shift [a] of proton signals in ^1H NMR measurements of solutions of different reactant combinations in toluene [d] at 298 K

	TsOH (ppm)						TsOMe (ppm)						MTBE/MeOH (ppm)		
	ϕ-CH_3	ArH				SO_3H	ϕ-CH_3	O-CH_3	ArH				(CH_3)$_3$	O-CH_3	-OH
TsOH [b]	1.90	6.71	6.74	7.71	7.74	11.25									
TsOMe							1.98	3.23	6.80	6.83	7.61	7.65			
MTBE													1.11	3.09	
MeOH														3.06	4.54
TsOMe + MTBE							1.99	3.25	6.83	6.85	7.65	7.67	1.11	3.08	
TsOH + MTBE	1.99	6.83	6.88	7.64	7.67	12.51							0.97	3.00	
TsOH + MTBE + TsOMe	2.01 [c]	6.85 [c]	6.89 [c]	7.83	7.86	12.37	2.01	3.26	6.85	6.89	7.62	7.65	0.98	3.00	
TsOH + MTBE + 2 TsOMe	2.03 [c]	6.88 [c]	6.91 [c]	7.82	7.85	12.17	2.03	3.29	6.88	6.91	7.62	7.65	0.99	3.01	
TsOH + 0.5 MeOH	1.95	6.80	6.83	7.81	7.84	11.78								3.31	
TsOH + MeOH	1.98	6.84	6.87	7.86	7.89	11.12								3.30	
TsOH + 2 MeOH	2.01	6.89	6.92	7.89	7.92	9.32								3.30	
TsOH + MeOH + TsOMe	1.99	6.89	6.91	7.83	7.86	10.89	2.02	3.25	6.82	6.85	7.60	7.63		3.31	
TsOH + MeOH + 2 TsOMe	2.02 [c]	6.92	6.96	7.82	7.85	10.57	2.02	3.28	6.86	6.89	7.61	7.64		3.31	
TsOH + 2 MeOH + TsOMe	2.01	6.90	6.94	7.89	7.91	9.63	2.06	3.27	6.84	6.87	7.62	7.65		3.31	

[a] Chemical shifts are reported with respect to TMS as external standard.
[b] One equivalent corresponds to 0.5 M solution.
[c] Not distinguishable from the signals of TsOMe.
[d] The signals of toluene used as solvent: 2.15, 6.99–7.13 (multiplet) ppm.

measurements in Table 2. The assignment of signals to specific carbon and hydrogen atoms, respectively, were done in accordance with literature [13].

Upon addition of 1 equiv. TsOH to MTBE, the quaternary carbon atom of the *tert*-butyl group of MTBE shifted from 71.94 to 76.10 ppm, the methyl groups from 26.77 to 25.99 ppm, whereas the methoxy carbon remained unaffected. At the same time, the α-carbon (ipso) of TsOH next to the SO_3H group shifted from 144.25 to 142.73 ppm. The β-carbon (ortho) was no longer separately observable but was shifted downfield and covered by a solvent peak at 137.40 ppm. The γ (meta) and δ-carbon (para) were only weakly affected. In the corresponding ^1H spectrum, the observed upfield shift of the signals for both types of methyl groups in MTBE indicates increased shielding of those protons as a consequence of the interaction with TsOH. While generally the changes in the shifts of the TsOH hydrogen atoms were small, the acidic proton showed a downfield shift from 11.25 to 12.51 ppm.

When methanol was added to TsOH the carbon signal of methanol shifted from 50.59 ppm for a 2:1 TsOH:MeOH mixture to 49.78 ppm for a 1:2 TsOH:MeOH mixture, a value almost identical with pure methanol. The α-carbon of TsOH was found some 1.2 ppm upfield from its original position for the 2:1 TsOH:MeOH mixture and about 2.2 ppm upfield for the 1:2 TsOH:MeOH mixture. Analogous changes were observed for the β-carbon which showed a downfield shift with increasing MeOH concentration. Only very subtle changes were observed in the proton spectra. The methyl protons of methanol shifted from 3.06 to 3.31 ppm, but were fairly insensitive to the methanol concentration. The acidic proton of TsOH, however, shifted downfield at first (from 11.25 to 11.78 ppm for the 2:1 TsOH:MeOH mixture) and then upfield again to 11.12 ppm for the 1:1, and to 9.32 ppm for the 1:2 TsOH:MeOH mixture.

Compared with the NMR spectra of the pure compounds, no significant changes in the carbon or proton signals were observed when MTBE and TsOMe were in solution simultaneously, suggesting at most a very weak interaction between these two compounds in solution. The addition of 1 equiv. of TsOMe to a 1:1 TsOH/MTBE solution also gave essentially identical NMR spectra. Minimal effects were observed for the signal of the acidic proton which shifted from 12.51 to 12.37 ppm and for the α, β, and methoxy carbon atom of TsOMe that exhibited shifts of 0.2 ppm. Besides a small upfield shift of the acidic proton by 0.2 ppm the addition of another equivalent of TsOMe to the solution did not yield any further changes in the NMR spectra.

The gradual addition of TsOMe to a 1:1 mixture of TsOH:MeOH again induced only minimal changes in the ^1H and ^{13}C NMR spectra. The α and β-carbon of TsOH were displaced in the usual manner from 141.98 to 142.70 ppm and from 139.04 to 137.47 ppm, respectively, whereas the changes of the signals for TsOMe compared to the pure solution were in the range of 0.2 ppm. In the proton spectra, the changes of the TsOMe signals were negligible, however, the signal for the acidic proton moved upfield for 1:1 TsOH:MeOH by 0.5 ppm after addition of 2 equiv. of TsOMe but downfield by 0.3 ppm after addition of 1 equiv. of TsOMe to a 1:2 TsOH:MeOH mixture. This last result shows that TsOMe does not enter acid–base interaction but only modifies the polarity of the solution.

3.2. Kinetic measurements

All reaction data obtained from our kinetic studies could be fitted by a zero order rate law regarding the reactants. A typical example of the linearization is shown in Fig. 2 for the reaction with varying catalyst concentration. The conversion was kept below 10% to avoid the influence of the backward reaction upon kinetics which is illustrated in Fig. 3. From this experiment, the equilibrium constant of transetherification at 338 K was determined as 0.774. Table 3 summarizes the results of the transetherification of MTBE with ethanol at 338 K, atmospheric pressure, and various catalyst–substrate ratios. The set of experiments indicated by A showed a more than

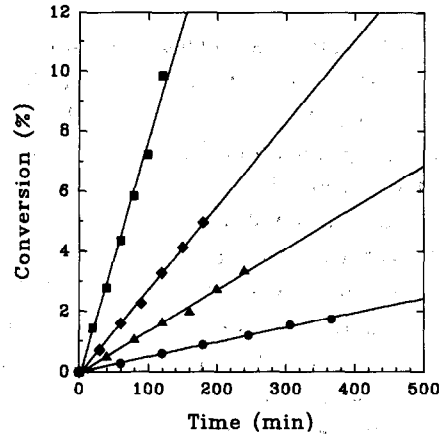

Fig. 2. Linearized plot of reaction results for the transetherification of MTBE with EtOH at 338 K at catalyst concentrations of (■) 0.369, (♦) 0.238, (▲) 0.161, and (●) 0.093 mol/l.

proportional increase of the reaction rate constant with increasing catalyst concentration. The reaction order with respect to the catalyst concentration, determined by plotting the logarithm of the catalyst concentration versus the logarithm of the reaction rate in Fig. 4, was 2.

The addition of TsOMe as potential nucleophile to the reaction mixture did not affect the reaction rates, as is shown by the constant values for the reaction rates in Table 3 for the experiments indicated by B1–B2. In a different approach, we attempted to replace part of the acid as nucleophile by the much more strongly nucleophilic tosylate anion which was generated by partial neutralization of the catalyst with pyridine. The reaction rate was determined for the reactant composition of

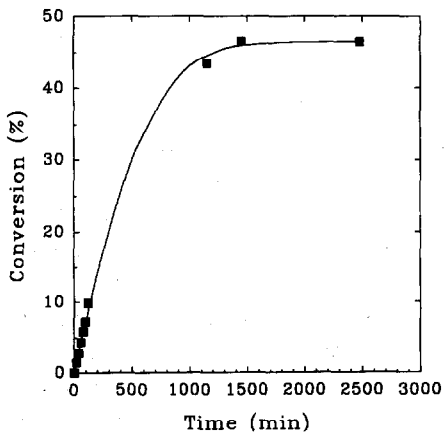

Fig. 3. Approach to equilibrium for the transetherification of MTBE with EtOH at 338 K.

experiment A4 in Table 3 with the addition of increasing amounts of pyridine. The values of the rate constant for experiments C1–C3 in Table 3 show clearly that the reaction rate decreased with increasing conversion of the acid to its anion (pyridinium salt, TsO^-PyH^+). The quantity of pyridine for experiments C1–C3 was chosen such that the remaining concentration of acid would be the same as in experiments A1–A3 if complete neutralization of pyridine occurred. Fig. 5 shows, however, that the reaction in each experiment in series C was faster than its corresponding experiment in series A.

3.3. Determination of the equilibrium constant of protonation of pyridine by TsOH

By interpolation of the ^{13}C NMR signals of pyridine, pyridine–TsOH mixtures, and pyridine fully protonated in a mixture with TFA (see Experimental) we determined the equilibrium constant of protonation K_{prot} of pyridine by TsOH. The results in Table 4 allowed calculation of $K_{prot} = 190 \pm 20$ l/mol at 298 K. From this value and the reaction enthalpy of -15.3 kcal/mol [14](a) we obtained $K_{prot} = 9.2$ l/mol at our reaction temperature of 338 K using the equation of van't Hoff. In view of the uncertainty in all the quantities employed and of the difference of the solvent composition between our experiments and those in the literature [14], the value is only a rough estimate.

It is also possible to calculate a value of the equilibrium constant of protonation from our reaction data taking that the decrease in the rate of reaction is due entirely to incomplete protonation. Knowing that the reaction rate depends upon the square of catalyst concentration one can calculate the concentration of free acid from the reaction rates obtained with the partially neutralized samples. This true concentration of free acid ([TsOH]) together with the initial concentration of TsOH (C^0_{TsOH}) and pyridine (C^0_{Py}) can be used to express the real concentration of pyridine ([Py]) and pyridinium salt ([TsO^-PyH^+]) in

Table 3
Zero order rate constants for the transetherification of MTBE with EtOH at 338 K, atmospheric pressure, and various catalyst and reactant concentrations

Experiment	C_{MTBE} [a] ($mol \cdot l^{-1}$)	C_{TsOH} ($mol \cdot l^{-1}$)	C_{TsOMe} ($mol \cdot l^{-1}$)	$C_{Pyridine}$ ($mol \cdot l^{-1}$)	$10^3 k$ [b] ($mol \cdot l^{-1} \cdot min^{-1}$)
A1	2.871	0.093	–	–	1.70±0.05
A2	2.866	0.161	–	–	4.72±0.14
A3	2.872	0.238	–	–	9.47±0.28
A4	2.872	0.369	–	–	26.50±0.80
B1	2.858	0.163	0.000	–	4.69±0.14
B2	2.858	0.163	0.167	–	4.70±0.14
C1	2.872	0.369	–	0.277	2.92±0.09
C2	2.872	0.369	–	0.207	5.90±0.18
C3	2.872	0.369	–	0.129	11.10±0.33

[a] Initial concentration of MTBE and EtOH in solution.
[b] The rate constant was determined by fitting a zero order rate law for conversions below 10%.

equilibrium. The equilibrium constant can be calculated according to Eq. 5.

$$K_{prot} = [TsO^-PyH^+]/([TsOH][Py]) =$$
$$= (C_{TsOH^0} - [TsOH])/\{(C_{Py^0}$$
$$- (C_{TsOH^0} - [TsOH]))[TsOH]\} \quad (5)$$

The equilibrium constant calculated in this way was 70±10 l/mol (average of three experiments), about 8 times higher than the estimated value.

4. Discussion

4.1. Protonation of reactants and products by TsOH

The significant downfield shift of the signal of the quaternary carbon atom of MTBE in interaction with TsOH is a clear indication for protonation of the ether by the acid. The signal of the methyl groups of the *tert*-butyl group was found at slightly higher field, by 0.8 ppm. A similar effect has been observed for the α and β-carbon of protonated mesityl oxide [11] and was related to the fact that the charge carrying carbon, which would be the quaternary carbon in MTBE, undergoes the most changes upon protonation. The changes in the carbon spectra of TsOH also concur with the suggested protonation of the ether since the upfield shift of the α-carbon indicates better shielding caused by the negatively charged SO_3^- group. The downfield shift of the acidic proton in the ^1H NMR spectra by 1.26 ppm to 12.51 ppm, a value which is close to that found for H_3O^+ and ROH_2^+ in organic solution [15], proves that MTBE was protonated.

A similar conclusion was reached for MeOH in contact with TsOH. The changes observed in the ^{13}C NMR spectra of the acid again indicate the loss of the proton while the small downfield shift of the MeOH carbon indicates a deshielded nucleus due to the charge at the neighboring atom. Clear evidence for methanol protonation is again

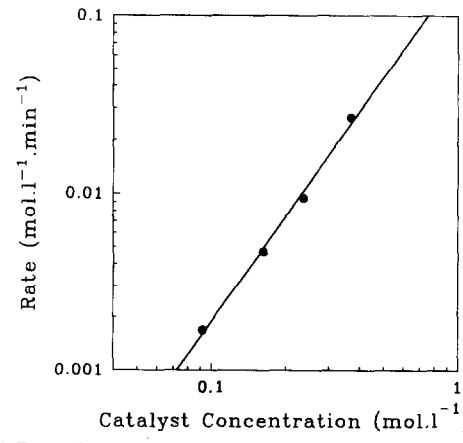

Fig. 4. Dependence of the rate of transetherification of MTBE with EtOH at 338 K upon catalyst concentration.

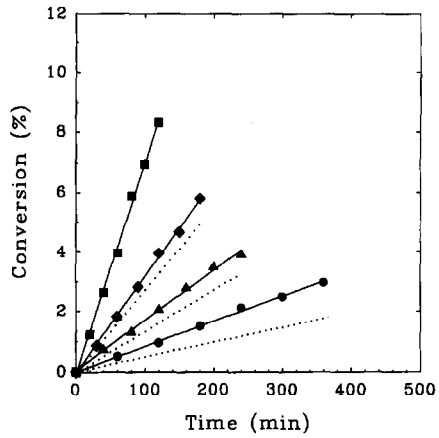

Fig. 5. Linearized plot of reaction results for the transetherification of MTBE with EtOH at 338 K, 0.369 mol/l TsOH and pyridine concentrations of (■) 0.0, (♦) 0.129, (▲) 0.207, and (●) 0.277 mol/l; the dashed lines correspond to the expected decrease in rate assuming complete neutralization (experiments A1–A3 in Table 3).

found from the combined changes of the protons of the alcohol hydroxyl group and the sulfonic acid group in the ^1H NMR spectra. The observation of only one signal for the proton of the alcohol hydroxyl group and the acid proton indicates rapid hydrogen exchange between the two groups which can only occur by protonation–deprotonation, as demonstrated before [13](c). Hence, protonation of methanol was established. The position of the average signal is determined by the amount of protonation in equilibrium. For negligible protonation, the signal would be found at 7.9 ppm, the average of the SO_3H and MeOH signals, whereas a downfield shift would indicate increased extent of protonation in equilibrium. The initial downfield shift observed at low MeOH:TsOH ratio demonstrates that the degree of protonation is substantial. In the presence of excess MeOH the signal moved upfield, as expected, but its position indicates that protonation was still significant. These observations contradict the proposed mechanism [4] which assumed that there was no protonation in nonpolar medium.

4.2. Reaction rates, reaction orders, and rate law

Because protonation of the ether occurs fast in a pre-equilibrium step, the formation of the carbocation and alcohol, as outlined earlier in Eq. 3, should represent the rate limiting step. For this type of mechanism one expects a first order dependence in MTBE and zero order in EtOH as quenching reagent. The rate, however, is proportional to the concentration of protonated MTBE. Because of the high substrate-to-catalyst ratio used (between 8 and 30) and the significant degree of protonation of MTBE the concentration of protonated MTBE changes negligibly at low conversions ($< 10\%$) which makes the reaction pseudo zero order with respect to MTBE.

The second order dependence of the reaction rate upon catalyst concentration is a very interest-

Table 4
Dependence of the shift [a] of ^{13}C NMR signals of pyridine upon extent of protonation

	TsOH (ppm) [b]				Pyridine (ppm) [c]		
	m-C	*p*-C	*o*-C	C-SO_3	α-C	β-C	γ-C
TsOH [d]	126.53	129.15	140.78	141.43			
Py					149.39	124.21	136.65
0.5Py + TsOH	126.46	128.99	140.61	142.24	142.00	127.63	146.74
Py + TsOH	126.37	128.89	140.03	143.28	143.01	127.20	145.42
Py + 6TFA	–	–	–	–	141.50	127.78	147.15
3Py + 6TFA	–	–	–	–	141.67	127.89	147.27

[a] Chemical shifts are reported with respect to TMS as external standard.
[b] The signal for ϕ-CH_3 was not observable separately because it was covered by the signals of toluene used as solvent: (21.02, 125.29, 128.12, 128.95, 137.41 ppm).
[c] The assignment of carbon signals of pyridine in dependence of pH was done in accordance with [12].
[d] One equivalent corresponds to 0.162 M solution.

ing result because it implies that two TsOH molecules participate in the rate determining step or in the step preceding it. According to the proposed mechanism [4] this could mean that the acid acts both as proton donor and as nucleophile toward the reactant. It has been shown, however, that in nonpolar media TFA forms aggregates with triflates of the structure $AH–A^-$, $(HA)_2–A^-$, and $(HA)_3–A^-$ [16] and that two molecules of acid are required to transfer a proton to a base [17], especially in nonpolar media (cooperative effect, Eq. 6) [17](c).

$$2AH + B \leftrightharpoons AH\text{-}\text{-}A^- + BH^+ \quad (6)$$

In our case, where we have quite a nonpolar medium, a similar effect could take place, meaning that the acid itself acts to stabilize the anion through hydrogen bonding. Since this is a necessary requirement for the dissociation it leads to a second order dependence of the rates upon the acid catalyst concentration. Analogously, a reaction order greater than one in catalyst concentration was observed for transalkylation reactions catalyzed by TFA [18] and Ancillotti et al. [3] reported a third order and higher dependence of MTBE formation rates upon the concentration of sulfonic acid groups in Amberlyst-15. Gates and coworkers suggested that a network of mutually hydrogen bonded sulfonic acid groups governs catalytic activity in Amberlyst-15 [2](b), [19], but Ancillotti et al. [3] argued that at high alcohol concentrations inside the resin this could not be the case. It is conceivable that sulfonic acid groups of the resin in close vicinity also exhibit cooperative effect in nonpolar medium and, thus, that a site could actually consist of two or more sulfonic acid groups. This may also lead to a better understanding of the proposed chemisorption of reactants on two sites and subsequently of the transition state on three sites as concluded from fitting reaction data by Langmuir–Hinshelwood–Hougen–Watson kinetics [4,20]. Because all the reactions considered involve in the critical step the interaction of an electrophile with a nucleophile and the adsorbate acquires a positive charge upon chemisorption on heterogeneous acid catalysts, it cannot be expected to observe a reaction between two chemisorbed species on acid catalysts as Langmuir–Hinshelwood kinetics would require.

4.3. Effect of nucleophile upon interactions and reaction

The lack of any effect of TsOMe upon the chemical shift of the methyl and quaternary carbon atoms of MTBE protonated at equilibrium indicates the absence of nucleophilic effects of the ester upon the substrate. This result was very well reflected in the kinetic experiments. The addition of TsOMe to the reaction mixture containing MTBE, EtOH, and TsOH should have increased the rate of reaction if the participation of the nucleophile in the transition state (see Fig. 1) was required because replacement of TsOH by TsOMe as nucleophile would increase the effective concentration of catalyst. The reaction rate remained unaffected by the addition of TsOMe, however, which suggests that the nucleophile does not play an important role in determining the overall reaction rate.

For the partial replacement of the acid as nucleophile by the much more strongly nucleophilic tosylate anion, one would expect to see a decrease in the rate of reaction equivalent to the amount of catalyst neutralized by pyridine, if there was no contribution of the nucleophile to the reaction. On the other hand, if the nucleophile had an effect, a less pronounced decrease or rather an increase in the rate of reaction would be expected. Indeed, if the two molecules of acid have different roles in the transition state the expression for the reaction rate can be written as in Eq. 7 where k_a relates to acidic strength and k_{Nu} to nucleophilicity.

$$r = k_a[AH]k_{Nu}[AH] = k_a k_{Nu}[AH]^2 \quad (7)$$

Let us consider that 20% of the acid catalyst was replaced by its anion. Because $[A^-] = 0.2$ [AH] Eq. 7 changes to Eq. 8.

$$r' = k_a 0.8[AH]k_{Nu}0.8[AH] + k_a 0.8[AH]k'_{Nu}0.2[AH] \quad (8)$$

In order to observe constant reaction rates $r = r'$ after partial neutralization it is necessary that the nucleophilicity of the anion, k_{Nu}', be equal to 2.25 k_{Nu}. The relative nucleophilicities for some acids and their anions were reported in the literature [21]. Thus, for H_2O/HO^- $k_{Nu}' = 10^{4.2} k_{Nu}$ [21](a), for $MeOH/MeO^-$ $k_{Nu}' = 10^{6.3} k_{Nu}$ [21](b), and for CH_3COOH/CH_3COO^- $k_{Nu}' = 10^{4.7} k_{Nu}$ [21](a). These values show that generally the anion is about 4 to 6 orders of magnitude more nucleophilic than the acid, from which it follows that in the case of the participation of the anion as nucleophile in the reaction the rate should be much higher. For instance, for 75% neutralization (experiment C1 in Table 3) we can estimate an acceleration of about three orders of magnitude. Comparing the data presented in Table 3 (A1–A3 and C1–C3) and in Fig. 5 we realize that this was clearly not the case.

Nevertheless, the decrease in the reaction rate was not as great as expected from the amount of pyridine added. Two factors may account for these differences. The first is a small acceleration due to the addition of an electrolyte (TsO^-PyH^+) to the solution, also known as salt effect [22]. The second is the possibility of incomplete protonation of pyridine in the reaction mixture, thus, increasing the amount of free acid available as catalyst. Although the value for the equilibrium constant of protonation could only be estimated to range between 9.2 and 70 l/mol it indicates, nevertheless, that protonation of pyridine is incomplete at the reaction temperature. An evaluation of the effect of incomplete protonation of pyridine is given in Fig. 6 which shows the rate of reaction without pyridine and with pyridine added under the assumption of complete protonation ($K_{prot} = \infty$), and of partial protonation according to $K_{prot} = 9.2$ l/mol as determined by NMR and extrapolated to 338 K. The experimental values were in between the limits of these two assumptions, thus, demonstrating the absence of any nucleophilic acceleration in the hydrolysis of MTBE in nonpolar medium.

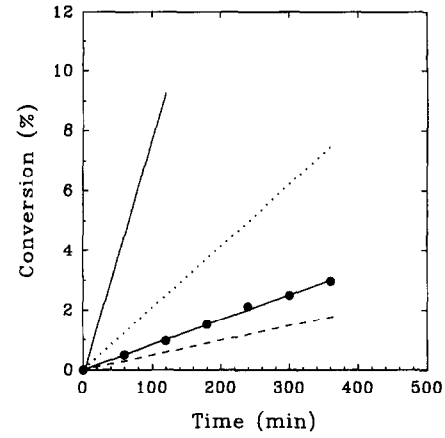

Fig. 6. Comparison of expected and measured rate of transetherification of MTBE with EtOH at 338 K after 75% neutralization with pyridine (Table 3, exp. C1), (●) measured data, (—) no protonation, (···) partial protonation ($K_{prot} = 9.2$ l/mol), (– – –) complete protonation ($K_{prot} = \infty$).

5. Conclusions

In nonpolar media both MeOH and MTBE were protonated by TsOH. NMR measurements showed that there was no nucleophile–electrophile interaction between TsOMe and $MTBE\cdots H^+$. The transetherification of MTBE with EtOH at 338 K in the presence of small amounts of catalyst exhibited pseudo zero order kinetics with respect to reactants and second order with respect to the catalyst. This is consistent with the rate determining step being the dissociation of equilibrium-protonated MTBE and manifestation of cooperative effect with formation of complex anions $AH–A^-$ in the proton transfer from the catalyst to the substrate. Addition of TsOMe as potential nucleophile had no effect upon reaction rate whereas conversion of a fraction of the catalyst to the corresponding anion resulted in a decrease in the reaction rate. Therefore, there is no nucleophilic assistance in the transition state of MTBE hydrolysis in nonpolar media.

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References

[1] G.J. Hutchings, C.P. Nicolaides and M.S. Scurrell, Catal. Today, 15 (1992) 23.

[2] (a) L.S. Frankel, J. Phys. Chem., 75 (1971) 1211; (b) R. Thornton and B.C. Gates, J. Catal., 34 (1974) 275; (c) E. Knözinger and H. Noller, Z. Phys. Chem., 55 (1967) 59.

[3] (a) F. Ancillotti, M. Massi Mauri and E. Pescarollo, J. Catal., 46 (1977) 49; (b) F. Ancillotti, M. Massi Mauri, E. Pescarollo and L. Romagnoni, J. Mol. Catal., 4 (1978) 37.

[4] J. Tejero, M. Cunill and M. Iborra, J. Mol. Catal., 42 (1987) 257.

[5] (a) R.B. Woodward and R. Hoffmann, Angew. Chem., 81 (1969) 797; (b) M.J.S. Dewar, Angew. Chem., Int. Ed. Engl., 10 (1971) 761.

[6] E.D. Hughes, J. Chem. Soc., (1935) 255.

[7] C.G. Swain and R.W. Eddy, J. Am. Chem. Soc., 70 (1948) 2989.

[8] (a) R.P. Bell, The Proton in Chemistry, Cornell University Press, Ithaca, NY, 1959, pp. 124–182; (b) F.A. Carey and R.J. Sundberg, Advanced Organic Chemistry, 2nd ed., Part A, Plenum Press, New York, 1984, p. 197; (c) M.L. Bender, Mechanisms of Homogeneous Catalysis from Protons to Proteins, Wiley-Interscience, New York, 1971, Ch. 5.

[9] D. Fărcaşiu and A. Ghenciu, Catal. Lett., 31 (1995) 351.

[10] (a) A. Rehfinger and U. Hoffmann, Chem. Eng. Sci., 45 (1990) 1605; (b) A. Rehfinger and U. Hoffmann, Chem. Eng. Sci., 45 (1990) 1619; (c) A. Rehfinger and U. Hoffmann, Chem. Eng. Technol., 13 (1990) 150.

[11] D. Fărcaşiu and A. Ghenciu, J. Am. Chem. Soc., 115 (1993) 10901.

[12] E. Breitmaier and K.-H. Spohn, Tetrahedron, 29 (1973) 1145.

[13] (a) E. Breitmaier and W. Voelter, ^{13}C NMR Spectroscopy, 2nd Ed., Verlag Chemie, Weinheim, 1978; (b) J.K.M. Sanders and B.K. Hunter, Modern NMR Spectroscopy, Oxford University Press, Oxford, 1990; (c) J.K.M. Sanders and B.K. Hunter, Modern NMR Spectroscopy, Oxford University Press, Oxford, 1990, p. 214.

[14] (a) E.M. Arnett, R.A. Haaksma, B. Chawla and M.H. Healy, J. Am. Chem. Soc., 108 (1986) 4888; (b) T.E. Mead, J. Phys. Chem., 66 (1962) 2149; (c) E.M. Arnett and B. Chawla, J. Am. Chem. Soc., 100 (1978) 217.

[15] J. Emsley, V. Gold and M.J.B. Jais, J.Chem. Soc., Chem. Commun., (1979) 961.

[16] (a) D. Souverain, A. Leborgne, G. Sauvet and P. Sigwalt, Eur. Polym. J., 16 (1980) 861; (b) P. Sigwalt and G. Sauvet, Polym. J., 12 (1980) 651.

[17] (a) I.M. Kolthoff and M.K. Chantooni Jr., J. Am. Chem. Soc., 87 (1965) 1004; (b) H.C. Brown and B. Kanner, J. Am. Chem. Soc., 88 (1966) 986; (c) D. Fărcaşiu, Nucleophilicity, in J.M. Harris and S.P. McManus (Eds.), Adv. Chem. Ser. 215, American Chemical Society, Washington, DC, 1987, Ch. 20.

[18] M. Fărcaşiu, T.R. Forbus and B.R. Rubin, J. Energy Fuels, 1 (1987) 28.

[19] B.C. Gates and W. Rodriguez, J. Catal., 31 (1973) 27.

[20] (a) F. Cunill, J. Tejero and J.F. Izquierdo, Appl. Catal., 34 (1987) 341; (b) J. Tejero, F. Cunill and S. Manzano, Appl. Catal., 36 (1988) 327; (c) J. Tejero, F. Cunill and J.F. Izquierdo, Ind. Eng. Chem. Res., 28 (1989) 1269; (d) M. Iborra, J. Tejero, J.F. Izquierdo and F. Cunill, Br. Polym. J., 23 (1990) 117.

[21] (a) P.E. Peterson and F.J. Waller, J. Am. Chem. Soc., 94 (1972) 991; (b) R.G. Pearson and J. Songstad, J. Am. Chem. Soc., 89 (1967) 1827; (c) P.L. Bock and G.M. Whitesides, J. Am. Chem. Soc., 96 (1974) 2826; (d) R.G. Pearson, H. Sobel and J. Songstad, J. Am. Chem. Soc., 90 (1968) 319.

[22] (a) L.C. Bateman, M.G. Church, E.D. Hughes, C.K. Ingold and N.A. Taher, J. Chem. Soc., (1940) 979; (b) A.H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78 (1956) 2763; (c) A.H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78 (1956) 2780; (d) A.H. Fainberg, G.C. Robinson and S. Winstein, J. Am. Chem. Soc., 78 (1956) 2777; (e) C.K. Ingold, Structure and Mechanism in Organic Chemistry, 2nd Ed., Cornell University Press, Ithaca, NY, 1969.