

MODELLING OF ETHER SYNTHESIS OVER NAFION-H

Kinetic results suggest that the mechanism of the ether-forming reaction on WZ is the same as on SZ and Nafion-H. We are examining the dual-site S_N2 reaction pathway theoretically *via ab initio* DFT (BP86, DN**) calculations [18] of the prototype system $2S + M + B$ ($S \equiv CF_3SO_3H$, $M \equiv CH_3OH$, $B \equiv (CH_3)_2CHCH_2OH$). These computations are being extended to DME synthesis for comparison.

Geometries have been optimized and true global minima have been found. The transition state (TS) has been found that satisfies the criteria of one imaginary frequency with root mean square gradient of 0.00023 hartree/Å. The calculated total energies are $\Delta E(S) = -962.4218$, $\Delta E(M) = -115.7793$, and $\Delta E(B) = -194.4431$ hartrees, respectively, and energy differences on the reaction pathway are given in Table 10.

The calculated energies for MIBE synthesis are shown in Table 10, and the results demonstrate that:

- (1) the TS barrier from free reactants, $E^\ddagger \approx 16$ kcal/mol, is comparable to the experimental 15 kcal/mol obtained with Nafion-H [6,14],
- (2) the overall reaction is nearly thermally neutral ($E_{(reaction)} \approx -6$ kcal/mol), in agreement with thermochemical data ($\Delta H = -5.53$ kcal/mol) [14],
- (3) sorbed intermediates involve hydrogen-bonded methanol and more strongly held hydrogen-bonded isobutanol, in agreement with the pattern derived from kinetic data [6],
- (4) MIBE is more weakly bonded than the precursor alcohols but H_2O is more strongly held, and

(5) weak (≈ 4 kcal/mol) cooperative complex formation between the sorbed methanol and isobutanol reactants or the sorbed products is predicted.

Table 10. Energetics of the dual-site S_N2 pathway $M + B \rightarrow TS \rightarrow MIBE + W$ over sulfonic acid sites.^a

1	2		3	4	5	6		7
	2a	2b				6a	6b	
M + B	M	B	M·····B	TS	MIBE·····W	MIBE	W	MIBE + W
+ 2S	 S	 S	⋮ S·····S		⋮ S·····S	⋮ S	⋮ S	+ 2S
0	-14.81	-13.68	-22.44	-6.63	-28.58	-12.53	-10.92	-1.44

^aAll energies are in kcal/mol, DFT (BP86, DN**) optimized. M \equiv CH₃OH, B \equiv (CH₃)₂CHCH₂OH, MIBE \equiv (CH₃)₂CHCH₂OCH₃, W \equiv H₂O, S \equiv CF₃SO₃H, and TS \equiv the transition state. The columns represent:

1. Separated alcohol reactants and two acid sites;
2. Alcohols adsorbed on two separate acid sites;
3. Sorbed precursor complex of alcohols and two proximal acid sites;
4. Transition state;
5. Sorbed complex of product MIBE and water on two proximal acid sites;
6. MIBE and water adsorbed on two separate acid sites; and
7. Separated products and two acid sites.

The above features, in conjunction with experimental results, suggest a pathway in which the alcohols are brought together by hydrogen bonding to the proximal sites and the sorption complexes are transformed into the TS by a concerted methyl transfer between the two alcohol oxygens and three protons transfer among the methanol and two sulfonic groups.

The TS structure is shown in Figure 18 with two pathway-driving orbitals involving the carbon C_o of the CH₃ group of MeOH. The i-BuO(H)·····CH₃·····OH₂ angle is 175.3° and the CH₃ group is planar as the configuration of the H atoms is being inverted from that in

MeOH to that in MIBE. The σ -TS orbital (Figure 18A; -32.33 hartree) connects the two Os adjacent to CH₃ as O 2p σ -C 2s-O 2p σ , and the π -TS orbital (Figure 18B; -18.56 hartree) as O 2p π -C 2p π -O 2p π in an antarafacial fashion. These orbitals are nearly symmetric and are very sensitive to the movement of the CH₃ toward one O or another, tantamount to breaking one C-O bond and strengthening the other.

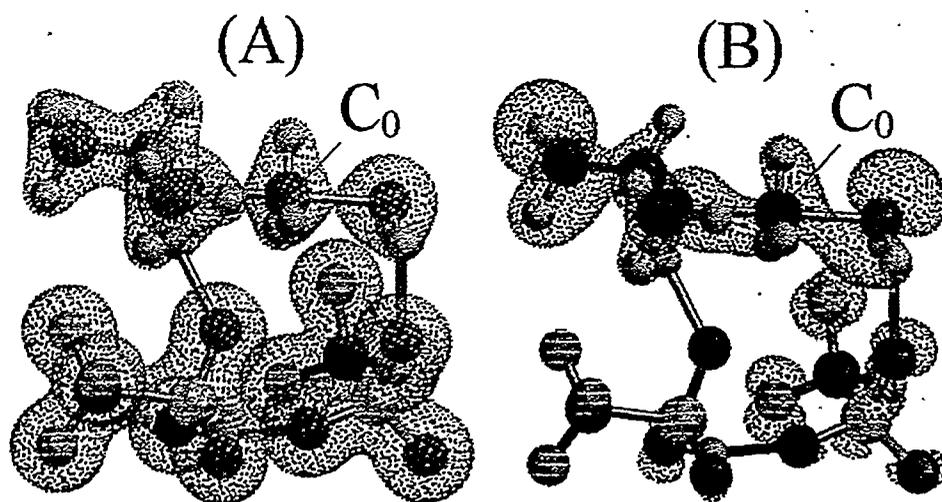


Figure 18. The dual site TS structure for the MeOH + i-BuOH \rightarrow MIBE + H₂O reaction pathway showing (A) the σ -TS orbital and (B) the π -TS orbital as the methyl group of MeOH moves toward forming the ether linkage. The atoms represented by colors are: red for O, gray for H, black for C, green for F, and blue for S.

Sulfated zirconia and tungstated zirconia have been established as very strong acids [9,13], as have the fluorocarbon sulfonic acids [1,14]. Furthermore, evidence based on hydrocarbon isomerizations indicates that WO₃/ZrO₂ possesses stronger acid sites than SO₄/ZrO₂ [9]. We have herein quantified at the DFT/BP/DN** level [19] the relative acidities of SO₄/ZrO₂ and CF₃SO₃H and the basicities of pyridine and ethylenediamine (EDA) by calculating acid-base interaction energies. Reactants and products were fully

optimized to rms gradient <0.0005 hartree/Å. The SO_4/ZrO_2 catalyst site was modeled as $(\text{HO})_3\text{ZrOSO}_3\text{H}$. The interaction energies are summarized in Table 11, which show that (1) SO_4/ZrO_2 (SZ) is a slightly stronger acid than $\text{CF}_3\text{SO}_3\text{H}$ by 1.3-1.4 kcal/mol, (2) EDA is a stronger base than pyridine by 4.1-4.2 kcal/mol, and (3) the SO-H and H-N distances reflect the strength of the acid-base interaction.

Table 11. Energies (kcal/mol) of acid-base interactions and the SO-H-N distances (Å)^a derived from the computational models.

ACID	BASE	
	Pyridine	EDA
SZ	-18.54 (1.49, 1.10)	-22.72 (1.52, 1.09 ₆)
$\text{CH}_3\text{SO}_3\text{H}$	-17.23 (1.37, 1.16)	-21.29 (1.67, 1.07)
$(\text{CH}_3\text{SO}_3\text{H})_2^b$	-----	-21.61 (3.87, 1.04) ^d
$(\text{CH}_3\text{SO}_3\text{H})_2^c$	-----	-33.69 (1.12, 1.44) ^e

^aEntries in parentheses are the (SO-H distance, H-N distance) involving hydrogen between the SO- and -N= groups;

^bEDA bound with one nitrogen to the acid group with hydrogen transfer;

^cEDA bonded symmetrically to both acid groups;

^dOnly one of the two nitrogens is a proton acceptor; and

^eBoth nitrogens are bonded