

Calculation of the Reaction of Ethylene, Propene, and Acetylene on Zeolite Models

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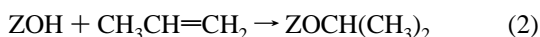
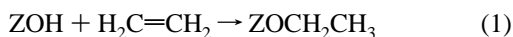
The reactions of ethylene, propene, and acetylene with two different zeolite models are computationally characterized using both semiempirical and ab initio methods. The MP2/6-31G* level calculations give activation energies which appear too high in comparison with the estimated experimental values. The DFT values seem more reasonable. The AM1 and PM3 transition state structures appear dubious with respect to both ab initio results and generally accepted intuitive descriptions.

1. Introduction

The ab initio quantum mechanical modeling of the interaction of simple molecules like water, ammonia, and methanol^{1–6} at the Bronsted acid sites in zeolites has evolved to the stage where simple addition or exchange reactions with ethylene,⁷ formaldehyde,⁸ [2H]methane,^{9–11} propene,¹² and more recently methanol¹³ have been investigated. Earlier semiempirical studies were of indeterminate energetic value but developed mechanistic ideas that will influence future theoretical ab initio studies.¹⁴

One of the features of the evolution of complexation and reaction ab initio computations is the study of the role of oxygen atoms surrounding the active acidic site, ZOH. The reaction calculations have been carried out on $\text{—OAlH}_2\text{OH—}$ or $\text{—OAl(OH)}_2\text{OH—}$ zeolite models with the unspecified bonds usually occupied by —H , —SiH_3 , or —Si(OH)_3 groups. First, one can hypothesize that several framework oxygens complex the hypothetical cation intermediate or transition state, RH^+ , generated by the proton transfer from the zeolite to the reacting molecule R.¹⁵ Alternatively, concerted mechanisms can be invoked in which the oxygen at one site aids the proton transfer process from another oxygen site in such a way that zwitterionic intermediates or transition states need not be proposed.⁷ Since the energy difference between zwitterionic and concerted mechanisms of reactions so far investigated can be small,^{8,9} it is not yet known whether these mechanistic differences are of real importance or zeolite model size dependent. Within the context of ab initio calculations, large molecules interacting with large zeolite models are computationally intensive if large basis sets are employed and if geometry optimizations are performed. Therefore, it is useful to know if small basis set or semiempirical calculations can give qualitatively satisfactory results.

The main emphasis of the reactions investigated here are the activation energies for ethylene, propene, and acetylene alkylating a zeolite acid site.



Reaction 1 has been already theoretically investigated at the SCF/3-21G level by Senchenya and Kazansky,⁷ who found a very low activation energy, 8.5 kcal/mol, as computed from *gaseous ethylene* which corresponds to the experimental conditions.¹⁶ Senchenya and Kazansky used a $\text{HOAl(OH)}_2\text{OH}_2$ zeolite model, and their calculations were performed using a planar geometry constraint. Our own fully optimized computations⁸ showed a higher SCF/3-21G activation energy (16 kcal/mol). As shown here, a $\text{HOAlH}_2\text{OH}_2$ model (model I and referred to here as Z_1OH) yields a comparable activation energy (19.0 kcal/mol, thermodynamically uncorrected). The SCF/3-21G calculations of Viruela-Martin et al.¹² on propene and isobutene yield higher SCF activation energies (30 and 26 kcal/mol, respectively, as calculated from gaseous substrates), using a larger zeolite model, $\text{H}_3\text{SiOHAlH}_2\text{OSiH}_3$ (Z_2OH). These activation energies were significantly reduced at the MP2/3-21G//3-21G level to 19.9 and 19.1 kcal/mol, respectively. Although these calculations were performed using planar geometry restraints in the Z_2OH portion of the structure, we will show that full relaxation of the propene transition states does not significantly alter these results.

The experimental work of Cant and Hall¹⁶ showed the activation energy for deuterium exchange of ethylene on a Y zeolite of 16 kcal/mol with a complexation energy of the order 9 kcal/mol. Senchenya and Kazansky⁷ cite Jacobs' determination¹⁷ of similar activation energies (15–20 kcal/mol) for double bond isomerization. The recent experimental determination of complexation of both acetylene and ethylene on a H-ZSM5 zeolite by Haw and co-workers¹⁸ mentions that deuterium isotope exchange with ethylene occurs within several hours at room temperature. However, exchange with acetylene takes several days. In addition, the equilibrium constants of both substances with H-ZSM5 are 7 equiv^{−1}. Assuming that the complexation entropy change is between −20 and −30 eu, the complexation enthalpy can be bracketed between −5 and −10 kcal/mol, which is in qualitative agreement with the work of Cant and Hall. Gorte and co-workers¹⁹ also found that acetylene on H-ZSM5 is unreactive at room temperature but becomes reactive above 425 K. All of this work implies that activation energies for isotope exchange of ethylene are lower than for acetylene. We speculate that these probably range between 15 and 20 kcal/mol for the former and between 20 and 25 kcal/mol for the latter. Methylated olefins have

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activation energies on aluminum silicate materials for double bond migration in some cases below or well below 15 kcal/mol.²⁰ Haw and co-workers²¹ find that both propene and isobutene react with the H-ZSM5 at temperatures well below 300 K. Viruela-Martin et al. computed MP2/3-21G activation energies (ca. 20 kcal/mol, as calculated from gaseous substrates) for both propene and isobutene. These may be too high by 5–10 kcal/mol to explain the below room temperature reactions of the methylated olefins. In addition, the SCF/3-21 activation energies for propene and isobutene using the Z₂OH model are much larger than ethylene reacting with the Z₁OH model. This creates some question as to the validity of using either zeolite model. Additional technical questions revolve around the basis set and the use of correlation.

2. Technical Details

The calculations reported here used the Gaussian 92 and 94 programs^{22,23} for geometry optimizations and energy determinations, and the semiempirical calculations employ AMPAC 5.0.²⁴ Since we are principally interested in the activation energies for the transition state of the addition reactions, we make no estimation of the basis set superposition error for the complexation of these substances. We will report the sum of thermal energies at 300 K so that the reader can compute the thermodynamically corrected activation energies. Since the theoretical literature we cite does not make those corrections, we will avoid confusion and report only the electronic energy changes which are comparable to those results. The thermodynamic corrections generally will add about 2 kcal/mol to the activation energies, and this correction is less than the other uncertainties discussed here (effect of larger zeolite model size and larger basis sets and the nature of the correlation correction based on a single SCF parent configuration). The DFT calculations were carried out using Gaussian 94, using the BLYP option for the Becke functional and the Lee, Yang, and Parr correlation functional.²³ Gaussian 94 imposes by default a Int = FineGrid integration. The DFT calculations were initiated from 6-31G* optimized geometries and used the same basis set.

Full geometrical details of the structures discussed here are provided in the Supporting Information in the form of the archive files recoverable either directly from the journal or its WWW site. This information can also be provided by e-mail by contacting ev@lct.jussieu.fr.

The key problem studied here is the activation energies as estimated from the reaction of the zeolite model with gaseous substrates. Therefore, the intermediate complexes and products were not computed in every case. The transition state optimizations for cyclic transition states is sometimes a difficult procedure. The near linearity of some bonds creates a problem of connectivity in **Z**-matrix optimizations. In the cases treated here, the O–H–C of the proton transferring from the zeolite model to the carbon atom of the attaching organic moiety creates a problem in near linearity. One way of avoiding this is to directly join the O to the C atom in the **Z**-matrix. In several instances the transition state optimizations were accomplished using Cartesian coordinate optimizations. Obtaining geometries near the transition state structures proved to also be a major problem. Our starting points assumed a 30% or extension of the O–H bond and near equivalence for the O–H and H–C bonds. This procedure did not work in the case of acetylene. However, using Gaussian 92/94 the opt = (ts,noeig,calcfc) starting point often gave us the single negative eigenvalue required in a transition state search if the initial geometry was near the final region. The active components of the ab initio force constant eigenfunction were generally the O–H and H–C

TABLE 1: Ab Initio Energies of Species Involved in the Addition of Ethylene, Propene, and Acetylene to Zeolite Model I, Z₁OH = HOAlH₂OH₂

structure	basis	SCF, au	MP2, au	STE, ^a kcal/mol
ethylene	3-21G	–77.600 99	–77.780 13	36.2
	6-31G*	–78.031 71	–78.284 42	
	6-31G*	–78.031 69	–78.284 10 ^b	
Z ₁ OH	3-21G	–392.457 54	–392.736 61	38.9
	6-31G*	–394.587 47	–395.012 57	
	6-31G*	–394.580 28	–395.007 12 ^b	
Z ₁ OH–C ₂ H ₄ π -complex	3-21G	–470.071 66	–470.533 13	77.1
	6-31G*	–472.626 83	–473.307 82	
TS	3-21G	–470.028 22	–470.494 20	73.3 ^c
	6-31G*	–472.562 57	–473.257 91	
Z ₁ OCH ₂ CH ₃ product	3-21G	–470.097 15	–470.554 60	79.0
	6-31G*	–472.654 09	–473.334 84	
propene	3-21G	–116.424 01	–116.693 41	56.3
	6-31G*	–117.071 47	–117.454 73	
	6-31G*	–117.071 40	–117.454 44 ^b	
TS	3-21G	–508.854 00	–509.411 23	93.8 ^d
	6-31G*	–511.609 14	–512.431 16	
	6-31G*	–511.601 43	–512.430 85 ^b	
acetylene	3-21G	–76.395 96	–76.576 76	20.1
	6-31G*	–76.817 86	–77.064 63	
Z ₁ OH–HCCH complex	6-31G*	–471.415 74	–472.091 10	60.8
TS	3-21G	–468.825 82	–469.289 35	59.0 ^e
	6-31G*	–471.358 24	–472.039 81	
	6-31G*		–472.044 52 ^f	
Z ₁ OCH=CH ₂ product	6-31G*	–471.457 17	–472.126 19	62.6

^a STE = sum of thermal energies, including zero point, at 300 K.

^b Geometry optimized at HF/3-21G. ^c Single negative frequency at –1162 cm^{–1}. ^d Single negative frequency at –1111 cm^{–1}. ^e Single negative frequency at –518 cm^{–1}. ^f Optimized at MP2 level.

bonds rather than the C–O bond undergoing formation. As shown below, the ab initio picture was that of proton transfer occurring before C–O bond formation in the cases of ethylene and propylene. The picture in the case of acetylene is more complicated,

3. Results and Discussion

A. Complexation of Acetylene and Ethylene at the Acid Site. Although the main interest in this article is in estimating the reaction activation energies of acetylene, ethylene, and propene reacting with zeolite models, we will discuss the complexation energetics and geometry. On the basis of the ab initio energies shown in Table 1, the technically best levels (MP2/6-31G*) yield values of –7.6 and –5.4 kcal/mol, respectively, for acetylene and ethylene complexing to zeolite model I. A more accurate estimation of these values as a function of basis set size, BSSE, and correlation corrections on larger zeolite models was not considered sufficiently interesting to warrant a study.

As shown in Figure 1, there is structural difference between the complexation of acetylene and ethylene to ZOH model I. Acetylene shows double H-bonding of the CH bond of acetylene with the oxygen of the zeolite model, while maintaining π -bonding with the ZOH. Only the latter occurs in ethylene. CH–O bonding occurs in the acetylene–water gas phase complex while H– π -bonding occurs in the ethylene–water complex.²⁵ The water–acetylene complex has a CH–O* bond distance of 2.23 Å, while the H– π -bond distance is 2.48 Å in the case of the ethylene–water complex. These are essentially the values shown for the corresponding zeolite complexes (Figure 1). In Haw and co-workers' NMR study,¹⁷ both structures were assumed to have ZOH π -H bonded structures (2.4 Å).

The computed unscaled C–C vibrational frequencies of the acetylene and ethylene zeolite complexes are shifted from their

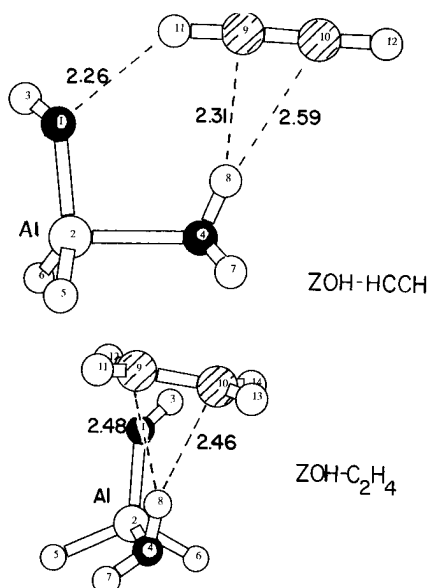


Figure 1. Complex structures of acetylene and ethylene with $Z_1\text{OH}$. Only the critical distances with of the complexation sites are shown. The complete geometries of these structures are given in the Supporting Information.

gas phase values of 2247 and 1858 cm^{-1} to 2225 and 1838 cm^{-1} , respectively. These only represent red shifts of about 20 cm^{-1} and have not been experimentally observed. Small shifts of this magnitude are found in ethylene complexed to other cationic species on zeolites.²⁶ The infrared intensities of these C—C vibrations, being zero in the gas phase, remain relatively weak (3 and 5 km/mol) when complexed to $Z_1\text{OH}$. With regard to the O—H vibrations of the ZOH species, its unscaled frequency, 3991 cm^{-1} , is computed to be only weakly perturbed on complexation, 3942 (acetylene) and 3923 (ethylene) cm^{-1} . The computed red shifts (60–70 cm^{-1}) are nowhere near the 300–400 cm^{-1} values reported by Cant and Hall¹⁶ for ethylene (3648 $\text{cm}^{-1} \rightarrow$ 3300 cm^{-1}). However, Haber et al.²⁷ report no perturbation.

B. Products of the Addition of Acetylene and Ethylene at the $Z_1\text{OH}$ Acid Site. Both reactions 1 and 2 yield alkylated zeolite sites which, in turn, are susceptible to reaction. Both reactions 1 and 2 are expected and computed to be mildly exothermic (10–20 kcal/mol) which is generally true for additions of ROH substances to a multiple bond (e.g., the hydration of ethylene has an enthalpy of reaction of –11 kcal/mol ;³⁰ see also ref 7). These addition structures are without great interest, and if the reader wishes to know greater structural detail, these can be obtained from the Supporting Information in the form of archive files.

C. Transition States for the Alkylation of $Z_1\text{OH}$ and $Z_2\text{OH}$. 1. *Energy Analysis.* The main emphasis of this paper deals with the activation energies of the alkylation of a ZOH site by ethylene, propene, and acetylene. In particular, since the propene appears reactive at lower temperatures than ethylene, one seeks a theoretical activation energy which reflects this difference as well as the apparent fact that acetylene is less reactive. Tables 1 and 2 contain the ab initio energies computed for these reactions on the $Z_1\text{OH}$ and $Z_2\text{OH}$ models. Table 3 gives AM1 and PM3 computed heats of formation of the various components. Table 4 contains the DFT-BLYP/6-31G* results. Finally, Table 5 shows comparative electronic activation energies using all methods.

First, it should be pointed out that semiempirical calculations on this size of system take little time and could have been extended to much larger systems. In fact, this was done but

TABLE 2: Ab Initio Energies of Species Involved in the Addition of Ethylene and Propene to Zeolite Model II, $Z_2\text{OH} = \text{H}_3\text{SiOH}_2\text{OHSiH}_3$

structure	basis	SCF, au	MP2, au	STE, ^a kcal/mol
ethylene	all	Table 1		
	6-31G*	–78.031 69	–78.284 10 ^b	
$Z_2\text{OH}$	3-21G	–969.661 20	–970.046 49	62.7
	6-31G*	–974.836 24	–975.407 85	63.3
TS	6-31G*	–974.831 78 ^b	–975.405 87	
	3-21G	–1047.216 57	–1047.795 88	
	6-31G*	–1052.812 33 ^c	–1053.654 14	97.6
	6-31G*	–1052.801 89	–1053.655 77 ^b	
propene	all	Table 1		
TS	3-21G	–1086.039 63	–1086.708 48	117.6 ^d
	6-31G*	–1091.862 83	–1092.831 81	117.4 ^e
	6-31G*	–1091.848 639 ^b	–1092.830 89	
acetylene	all	Table 1		
TS	3-21G	–1046.015 79 ^f	–1046.590 05	82.3
TS	6-31G*	–1051.597 48 ^g	–1052.433 84	

^a STE = sum of thermal energies, including zero point, at 300 K.

^b Calculated at 3-21G geometry. ^c Single negative frequency at –973 cm^{-1} . ^d Single negative frequency at –1269 cm^{-1} . ^e Single negative frequency at –517 cm^{-1} . ^f Single negative frequency at –616 cm^{-1} . ^g Single negative frequency at –677 cm^{-1} .

TABLE 3: Semiempirical Heats of Formation Data for the Addition of Ethylene to Various Zeolite Models

structure	AM1	PM3
$\text{CH}_2=\text{CH}_2$	16.5	16.6
$\text{CH}_3\text{CH}=\text{CH}_2$	6.6	6.4
HCCH	54.8	50.7
$Z_1\text{OH} = \text{H}_2\text{OAlH}_2\text{OH}$	–136.2	–106.0
$Z_1\text{OH}-\text{CH}_2=\text{CH}_2$ complex	–121.8	–90.8
complexation enthalpy	–2.1	–1.4
$Z_1\text{OH}-\text{CH}_2=\text{CH}_2$ TS	–90.0	–68.7
$Z_1\text{OH}$ –propene TS	–96.0	–75.7
$Z_1\text{OH}$ –acetylene TS	–47.2	–34.9
$Z_2\text{OH} = \text{H}_3\text{SiOH}-\text{AlH}_2-\text{OSiH}_3$	–138.9	–124.9
$Z_2\text{OH}$ –ethene TS	–106.0	–88.2
$Z_2\text{OH}$ –propene TS	–110.0	–93.9
$Z_2\text{OH}$ –acetylene TS	–63.2	–54.6

TABLE 4: DFT BLYP/6-31G* Energies for the Zeolites Models $Z_2\text{OH}$ with Ethylene and Propene

structure	energy, au
ethylene	–78.537 12
propene	–117.829 57
acetylene	–77.291 29
$Z_1\text{OH}$	–395.872 35
TS $Z_1\text{OH}$ with ethylene	–474.38702 ^a
TS $Z_1\text{OH}$ with propene	–513.68185 ^a
TS $Z_1\text{OH}$ with acetylene	–473.148 04 ^a
$Z_2\text{OH}$	–977.274 26
TS $Z_2\text{OH}$ with ethylene	–1055.787 81 ^a
TS $Z_2\text{OH}$ with propene	–1095.083 56 ^a
TS $Z_2\text{OH}$ with acetylene	–1054.546 64 ^a

^a One negative force constant.

will not be reported here since those results, as well as what is presented here, are in conflict with the ab initio geometries. The SCF/6-31G* geometry optimizations were very time consuming, taking days on an IBM work station. SCF/3-21G optimizations are less computationally intensive and would be the preferred ab initio procedure if it were demonstrated that this level of treatment seems adequate. This turned out not to be the case. The DFT-BLYP/6-31G* optimizations were as time consuming as those using classical ab initio methods.

Using the same ab initio or semiempirical method, we expected that the $Z_1\text{OH}$ and $Z_2\text{OH}$ models would give nearly the same activation energies for the same substrate. As shown in Table 4, this turned out not to be the case for the AM1

TABLE 5: Activation Energies (kcal/mol) for Ethylene, Propene and Acetylene Reacting with Zeolites Models Z₁ and Z₂

reaction	AM1	PM3	SCF/ 3-21G	MP2/ 3-21G	SCF/ 6-31G*	MP2/ 6-31G*	BLYP/ 6-31G*
ethylene + Z ₁ OH	29.7	20.7	19.0	14.1	35.5	25.0	14.1
						24.0 ^a	
ethylene + Z ₂ OH	16.4	20.1	28.6	19.3	34.9	23.9	14.8
					38.6	21.5 ^b	
propene + Z ₁ OH	33.6	23.9	17.3	11.7	31.2	22.7	12.6
					31.5	19.3 ^b	
propene + Z ₂ OH	22.3	24.6	28.6	19.7	28.1	19.1	12.9
					34.2 ^b	18.4 ^b	
acetylene + Z ₁ OH	34.2	20.4	17.3	15.0	29.5	23.5	9.8
						20.5 ^a	
acetylene + Z ₂ OH	20.9	19.6	26.0	20.8	35.5	24.2	11.9

^a Optimized at MP2/6-31G* level. ^b Geometries optimized at HF/3-21G level.

TABLE 6: Geometrical Parameters for the Critical Components of the Transition States

structure	method	O—H	H—C	C—O
ethylene + Z ₁	HF/3-21G	1.142	1.485	1.911
	HF/6-31G*	1.296	1.327	2.089
	MP2/6-31G*	1.227	1.390	1.942
	BLYP/6-31G*	1.286	1.365	2.099
	AM1	1.078	1.596	1.657
	PM3	1.001	1.721	1.776
propene + Z ₁	HF/3-21G	1.163	1.453	1.975
	HF/6-31G*	1.381	1.272	2.336
	BLYP/6-31G*	1.337	1.321	2.661
	AM1	1.104	1.543	1.689
	PM3	0.996	1.774	1.764
ethylene + Z ₂	HF/3-21G	1.203	1.412	1.993
	HF/6-31G*	1.448	1.251	2.421
	BLYP/6-31G*	1.367	1.297	2.220
	AM1	0.965	2.315	1.672
	PM3	0.960	2.324	1.741
propene + Z ₂	HF/3-21G	1.286	1.317	2.167
	HF/6-31G*	1.528	1.231	2.973
	BLYP/6-31G*	1.501	1.224	2.431
	AM1	0.960	2.385	1.696
	PM3	0.966	1.774	1.764
acetylene + Z ₁	HF/3-21G	1.042	1.688	1.987
	HF/6-31G*	1.024	1.719	1.937
	MP2/6-31G*	1.099	1.558	1.937
	BLYP/6-31G*	1.135	1.517	2.086
	AM1	1.060	1.611	1.716
	PM3	1.060	1.721	1.716
acetylene + Z ₂	HF/3-21G	1.059	1.637	1.979
	HF/6-31G*	1.072	1.580	1.917
	BLYP/6-31G*	1.211	1.397	2.167
	AM1	1.004	1.799	1.668
	PM3	1.000	1.761	1.792

activation energies, which dropped from 29.7 to 16.4 kcal/mol for ethylene, 33.6 to 22.3 kcal/mol for propene, and 34.2 to 20.9 kcal/mol for acetylene in going from Z₁OH and Z₂OH. In addition, the activation energy for propene was marginally higher than for ethylene, which is in disagreement with our interpretation of the experimental results. However, the PM3 activation energies were all nearly invariant with regard to Z₁OH and Z₂OH. However, as with AM1, the propene activation energy was still larger than for ethylene.

The 3-21G calculations behaved in an inverse fashion compared to the AM1 calculations. For both ethylene and propene, the MP2/3-21G and SCF/3-21G activation energies increased by as much as 10 kcal/mol in going from Z₁OH to Z₂OH. This was not the case for the SCF/6-31G*, MP2/6-31G*, and DFT-BLYP/6-31G* activation energies which are individually invariant in going from Z₁OH to Z₂OH. The largest effect occurs in comparing the SCF/6-31G*, MP2/6-31G*, and DFT-

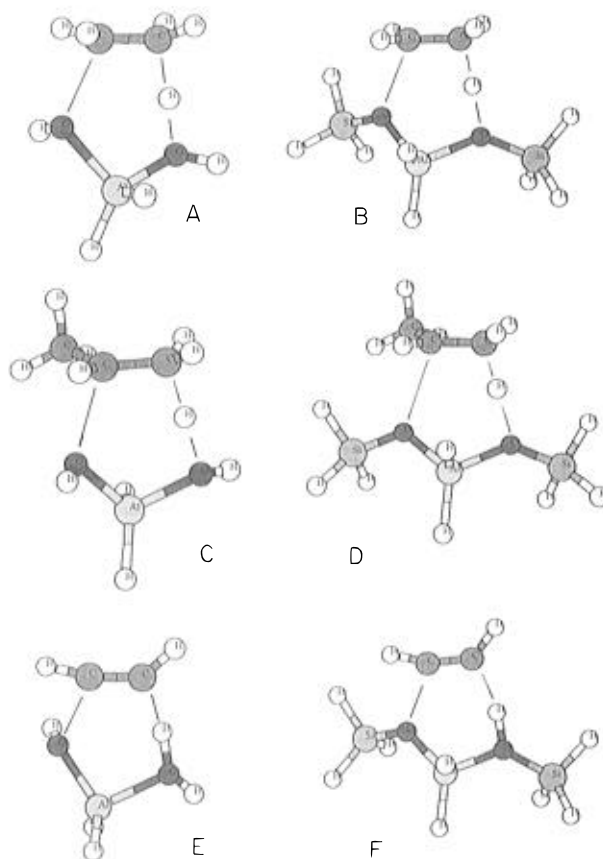


Figure 2. (A and B) Transition state structures for the addition of ethylene to Z₁OH and Z₂OH. (C and D) Transition state structures for the addition of propene to Z₁OH and Z₂OH. (E and F) Transition state structures for the addition of acetylene to Z₁OH and Z₂OH. A–E are all DFT-BLYP/6-31G* structures, but these are close to the SCF/6-31G* structures. The F structure is HF/6-31G*, which is somewhat different than DFT-BLYP/6-31G*. The geometrical details of these structures are given in the Supporting Information. section. The critical O—H, C—H, and C—O bond distances are given in Table 6. These geometrical parameters are shown here by lines.

BLYP/6-31G* activation energies for a single substrate. For each substrate the activation energy decreases in order of the sequence SCF/6-31G* → MP2/6-31G* → DFT-BLYP/6-31G*. Using the latter methodology, the computed activation energies using Z₁OH and Z₂OH models are the same for the same substrate and approach the energies found experimentally.

One compromise procedure of using HF/3-21G optimized geometries to compute the HF and MP2/6-31G* energies gives approximately the same results as those using the optimized HF/6-31G* geometries. This result is possibly fortuitous since the critical 3-21G transition state O—H, C—H, and C—O bond distances are significantly different from those obtained at the 6-31G* level (Table 6). In every case, the 3-21G transition state showed O—H distances shorter than the C—H and a higher degree of C—O bond formation than found in the 6-31G* calculations. However, the error involved in using 3-21G geometries to calculate MP2/6-31G* activation energies is between 1 and 3 kcal/mol.

Finally, the comparative activation energies for the reaction of acetylene are irregular and depend on the method used in comparison with those found for ethylene and propene. The DFT method employed indicates a lower activation for acetylene than for the two other materials. The MP2/6-31G* results indicated comparable activation energies. Our interpretation of the experimental work indicates that acetylene should have a higher activation than for the other two materials.

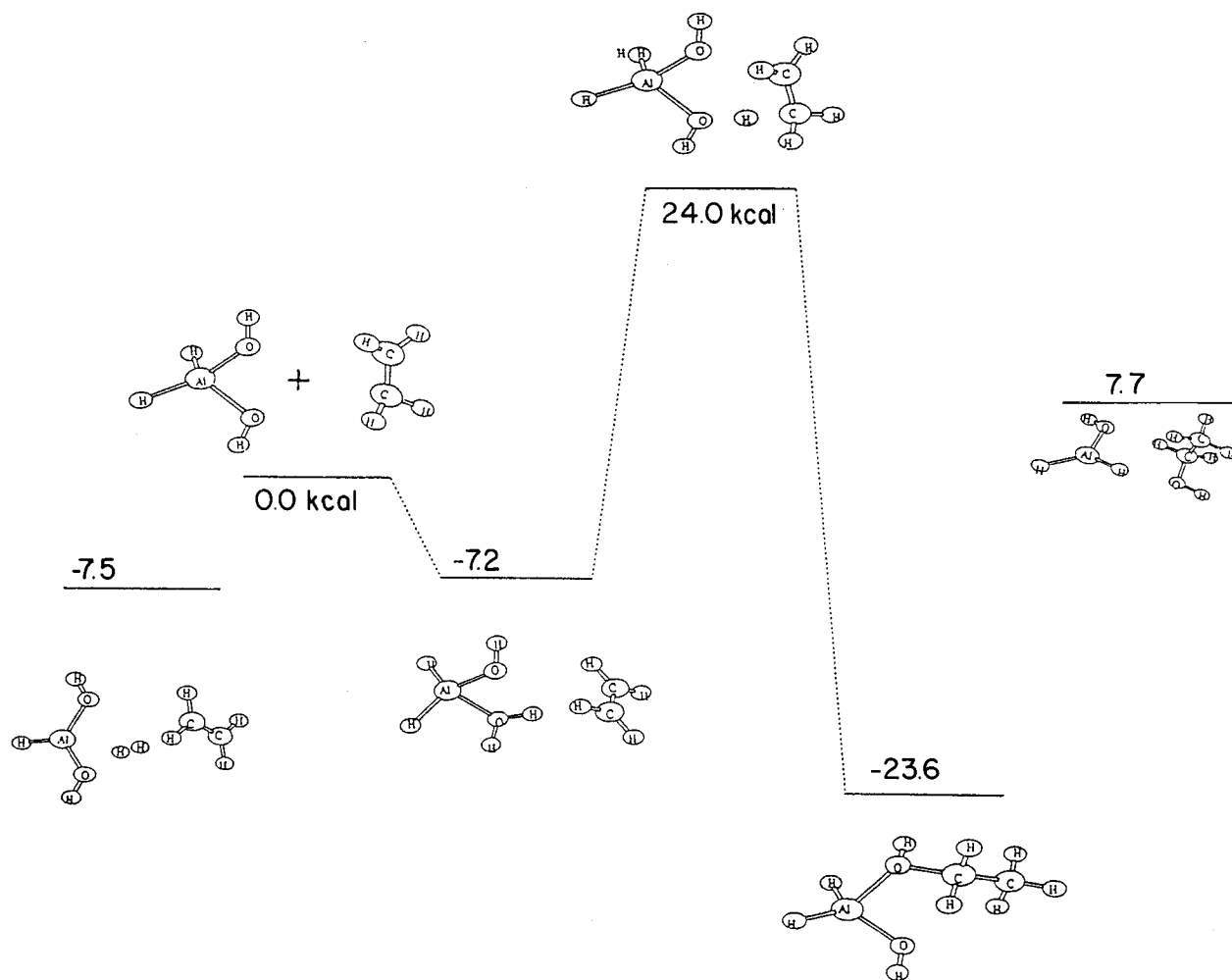


Figure 3. MP2/6-31G* optimized reaction surface for the reaction of ethylene with $Z_1\text{OH}$. The main reaction sequence takes the separate components, $\text{H}_2\text{OAlH}_2\text{OH}(\text{Z}_1\text{OH}) + \text{H}_2\text{C}=\text{CH}_2$, to a complex (Figure 1), with a binding energy of -7.2 kcal/mol, through a transition state ($+24.0$ kcal/mol) to the addition product, -23.6 kcal/mol. Two model dependent side reactions occur. One reaction is the dative bond rupture to give ethanol + H_2AlOH ($+31.3$ kcal/mol as measured from the product). Another hypothetical reaction involves H_2 elimination from $\text{H}_2\text{OAlH}_2\text{OH}$, which is 7.5 kcal/mol exothermic. An addition reaction can occur with the hydrogenation of ethylene to give ethane. These latter two reactions are completely deceptive since in real zeolite materials no $\text{Al}-\text{H}$ bonds occur. The MP2 geometry optimized energies (atomic units) of the various components are as follows: Z_1OH , $-395.014\ 80$; AlH_2OH , $-318.770\ 62$; $\text{AlH}(\text{OH})_2$, $-393.882\ 61$; C_2H_6 , $-79.494\ 74$; C_2H_4 , $-78.285\ 03$; H_2 , $-1.144\ 14$; $\text{Z}_1\text{OH}-\text{C}_2\text{H}_4$, $-473.311\ 25$; TS, $-473.261\ 60$; $\text{ZO}-\text{C}_2\text{H}_5$, $-473.337\ 37$.

2. *Analysis of the Structure of the Transition States.* What structure does one anticipate for the transition states? First, in the case of a proton acceptor molecule interacting with the acidic site of a zeolite, one could anticipate nearly complete proton transfer at the transition state before addition of the organic to the ZO^- moiety. In the case of acetylene, ethylene, and propene, this would produce transition states looking like $\text{ZO}^-\cdot\text{CH}=\text{CH}_2$, $\text{ZO}^-\cdot\text{CH}_2\text{CH}_3$, and $\text{ZO}^-\cdot\text{HC}(\text{CH}_3)_2$, respectively.¹⁵ However, in the case of the concerted description of the transition state, one anticipates structures in which both proton transfer and $\text{C}-\text{O}$ bond formation are occurring simultaneously in the transition state. Figure 2 shows the approximate ab initio structures determined for the these transition states. The geometrical details of these structures are obtainable from Supporting Information. However, the key geometrical parameters are the $\text{O}-\text{H}$, $\text{C}-\text{H}$, and $\text{C}-\text{O}$ bond distances shown in Table 6. The active components if the eigenfunction of the negative force constant of the transition state are these internal coordinates, especially the $\text{O}-\text{H}$ bond breaking and $\text{C}-\text{H}$ bond formation.

In the case of the Z_1OH and Z_2OH -acetylene transition states (Figure 2E,F) there is little $\text{ZO}-\text{H}$ bond breaking occurring except in the case of the DFT calculation (Table 6). As seen in Figure 2, in the cases of ethylene and propene adding to Z_1OH

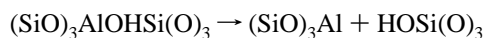
and Z_2OH the position of the proton visually appears about halfway between the zeolite model and the acceptor molecule. However, Table 6 shows that the proton transfer is more for propene than ethylene. The key factor (Table 6) is whether the $\text{O}-\text{H}$ distances are smaller or larger than the $\text{H}-\text{C}$ distances. Except in the case of the Z_1OH -ethylene transition state, all of the SCF/6-31G* optimizations showed that the $\text{O}-\text{H}$ distances were larger than the forming $\text{C}-\text{H}$ bonds for the cases of ethylene and propene. This result was not changed qualitatively at the DFT-BLYP/6-31G* level. This information, together with the computed long $\text{C}-\text{O}$ bonds, gives a picture of $\text{ZO}^-\cdot\text{CH}_2\text{CH}_3$, and $\text{ZO}^-\cdot\text{HC}(\text{CH}_3)_2$ like transition states. The Mulliken charge analyses showed the same picture (not presented here); the structural data suffices in qualitatively assigning zwitterionic character to the transition states of the ethylene and propene additions. The same type of transition states is only encountered at the DFT-BLYP/6-31G* for acetylene reacting with Z_2OH .

This above picture is nuanced. It was also found that in the region of the Z_1OH -ethylene transition state that full MP2 optimization (while holding the $\text{C}-\text{O}$ bond distance at 2.20 Å) yielded an authentic $\text{ZO}^-\cdot\text{CH}_2\text{CH}_3$ -like structure (full proton transfer) having the same MP2 energy (-473.2616 au) as the fully optimized transition state. Therefore, whether one assigns

partial or full proton transfer to the transition state has little energetic consequence. Visual examination of these transition states (Figure 2A–D) gives a picture of a nearly halfway proton transfer in which the proton could be positioned on one side or the other of the transition state without changing the picture significantly. In fact, the MP2/6-31G*//HF/3-21G activation energies discussed above indicate that there is little energetic consequence in doing this. Therefore, we recommend prudence in claiming either zwitterionic or concerted character to these kinds of transition states. Different basis sets and methodology may give different geometrical results, but they are essentially the same.

Another feature of Table 5 is that partial proton transfer is more extensive in the case of propene than ethylene and acetylene. This is expected on the basis of their respective gas phase proton affinities (propene, 180 kcal/mol; ethylene, 163 kcal/mol; acetylene, 153 kcal/mol).³⁴ However, this order is not reflected in the activation energies and is unexplained in the work presented here.

One final feature of the calculations that must be pointed out is shown in Figure 3 and its caption. A number of other reactions can be calculated to occur in the the preference for Al–O bond rupture over the retroreaction transition state in regenerating Z₁OH + ethylene. The Al–O rupture is equivalent in a real zeolite to the reaction



This type of reaction yields a Lewis acid site on a trigonal Al structure. The energies shown in the caption of Figure 3 demonstrate that it is easier to generate Al–O rupture from the alkylated product (i.e. $\text{HOAlH}_2\text{OC}_2\text{H}_5 \rightarrow \text{HOAlH}_2 + \text{C}_2\text{H}_5\text{OH}$, a reaction energy in the order of 31 kcal/mol) than the retroreaction generating the $\text{ZO}^-\text{CH}_2\text{CH}_3$ -like structure (48 kcal/mol). Therefore, on the basis of the calculations presented here, one cannot exclude Lewis acid type reaction mechanisms playing a role in determining the course of high activation energy reactions.

4. Conclusions

First, AM1 and PM3 semiempirical methods in computing the activation energies of olefins adding to small zeolite models give results in conflict with the ab initio methods employed here. The structures of the semiempirical transition states are also in conflict. Second, the 3-21G basis set gives energetic results which are also in conflict with the next basis set level (6-31G*) normally used in ab initio methods. The pursuit of the ever better basis set is a constant in computational chemistry, and given past experience further work will be done using those larger than employed here. The other factor is the methodological level at which the geometries of the system were optimized. The geometries change, the essential features of the transition state seem to change, but the overall picture remains the same. It was shown here, as expected, that correlation has a significant effect on the activation energies. This is reflected in the difference between the HF/6-31G* and MP2 and DFT results. The orbital sizes of the Z₂OH–propene system prevents using higher order MP methods, and the difference between the MP2 and DFT results may reside in correlation effects. On the other hand, the DFT methods have their particular methodological traps (grid size, choice of correlation functionals) which force one to be prudent about the results presented here.

With regard to the degree of proton transfer in the transition state, the calculations indicate that while this varies with the method used, there is little energetic significance to whether

one has full or partial transfer. Therefore, using a qualitative zwitterionic model to rationalize the character of the transition state is acceptable even if a particular calculation shows a concerted transfer structure.

Supporting Information Available: Tables giving geometries of the structures presented in Tables 1–6 in the form of Gaussian archive files (8 pages). Ordering information is given on any current masthead page.

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