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Computer simulation study on the conversion of spirolactone to enones over H-Y zeolite

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We report here the results of computer modeling studies and quantum chemical calculations on the spirolactone-to-enone conversion reaction over the zeolite catalysts, especially H-Y zeolite. We studied the adsorption mode of the molecules inside the supercage of H-Y and the mechanism of electron transfer between organic molecules and the framework of zeolite H-Y by density functional theory (DFT) calculations. Because the organic molecules considered in the present study are less symmetrical we docked the molecule inside the supercage of H-Y and energy minimization was then applied to these docked structures to yield representative low-energy binding sites for the molecules within the host structure. The interaction energy results show that the major interaction is between the methylene hydrogen of the molecule and the oxygen of the framework. The molecular electrostatic potential maps show that the ketonic oxygen of the reactant molecules abstract proton from Brönsted acid site. Thus the mechanism proposed by DFT calculation matches well with the experimental observations. © 1998 by Elsevier Science Inc.

Keywords: spirolactone, enone, conversion, zeolite H-Y, density functional theory (DFT), mechanism

INTRODUCTION

The acyclic enones are important intermediates in the total synthesis of natural products and complex organic molecules.[1,2] The conventional procedure is the acid-catalyzed intramolecular transformation of spirolactones over a methanesulfonic acid–P_2O_5 mixture to obtain enones.[3] There have been few reports wherein hazardous catalysts are replaced by environmentally friendly zeolite catalysts for important organic reactions.[4,5] In this background, Sreekumar and co-workers reported the application of various zeolite catalysts for the title reaction.[6] It was shown[7] that large amounts of zeolite were required to adsorb all the reactant molecules for the successful conversion, and that the product could be recovered only by extraction of the catalyst after the reaction, using methanol. At present there is not much correspondence with the amount of reactant required with reference to product, but still the product must be extracted from the zeolite. We are thus now interested in working out the role of the zeolite framework and mechanism of this interesting reaction with the help of computer simulation, and propose here a plausible explanation of this unusual phenomenon occurring inside zeolite pore.

In the present article we apply computer simulation techniques such as Monte Carlo, density functional theory (DFT), and so on, to model the spirolactone-to-enone conversion. The electronic interactions between the organic molecules (molecules 1–10 shown in Figure 1) and the zeolite H-Y host lattice (the zeolite determined to be most effective in the conversion) are studied to understand the reaction governing the conversion. The mechanism of the conversion is studied by density functional theory, by calculating the interaction energy of the zeolite framework with reactant and product molecules after optimizing the organic molecules inside a fixed zeolite framework. Beforehand, a Monte Carlo simulation was adopted to determine the initial configuration of the organic molecules inside the zeolite framework. The results have been further compared with the experimental observations.

METHOD AND MODEL

DFT calculations were performed using the DMOL package, version 3.00 (Biosym, MSI Inc., USA). The geometry optimization calculations were carried out using a minimal numerical basis set.[8] The total energy for the final optimized geometry was then evaluated using a double-numerical polarization basis set.[8] A JMW local type functional[9] was used for the exchange-correlation energy terms in the total energy expression. The

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The Color Plate for this article is on page 259.

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Received 18 April 1997; revised 21 July 1997; accepted 27 August 1997.

Journal of Molecular Graphics and Modelling 15, 216–220, 1997
© 1998 by Elsevier Science Inc.
655 Avenue of the Americas, New York, NY 10010

1093-3263/97/$17.00
PII S1093-3263(97)00079-X

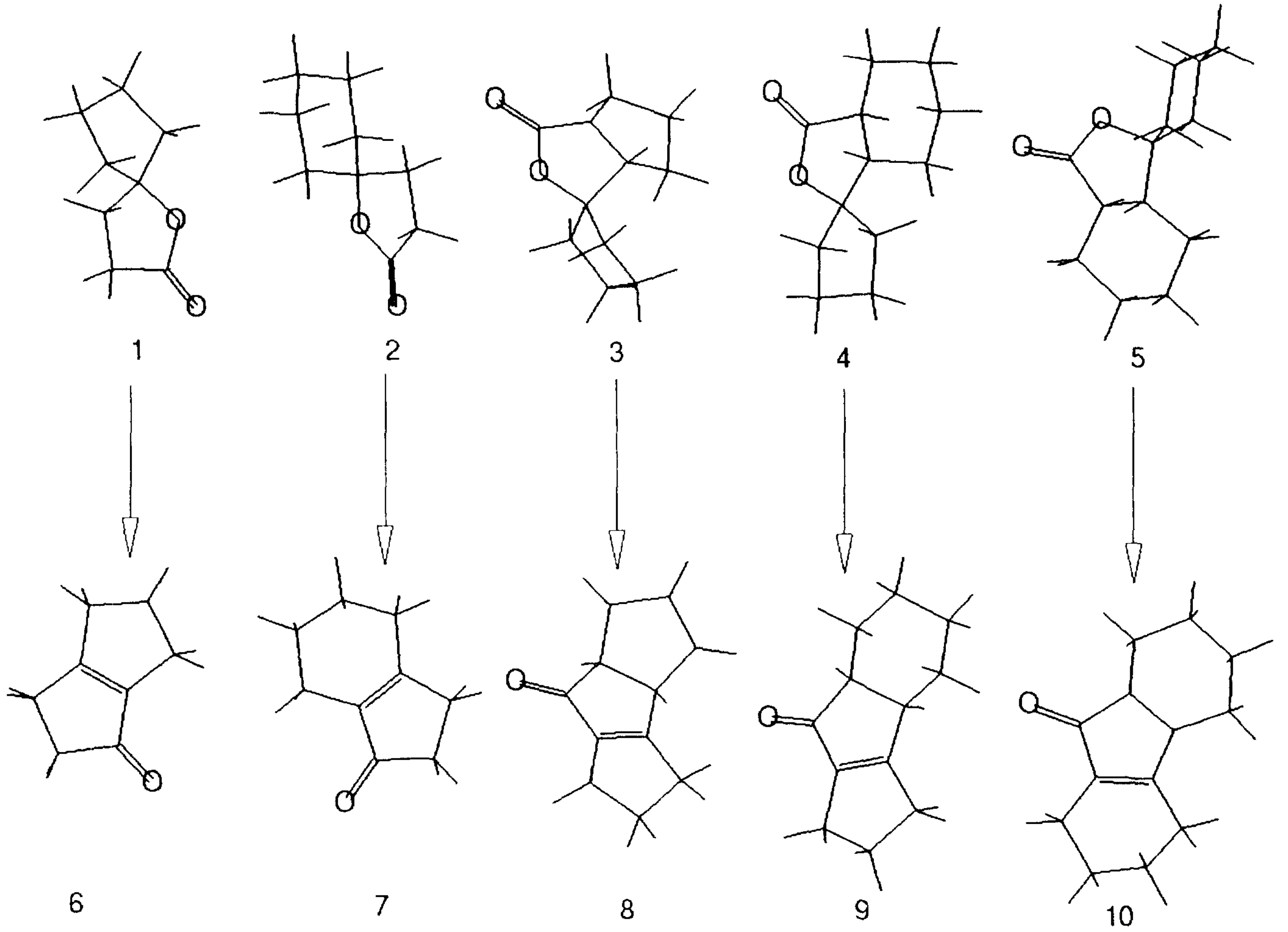


Figure 1. The three-dimensional structure of spirolactone and enone molecules, as derived from density functional calculations.

static visualization of molecular configurations and the optimized molecular geometries were made with the InsightII code of Biosym on a Silicon Graphics Indigo 2 workstation.

The H-Y lattice was modeled from the structure reported by X-ray crystallographic studies.[10] The 12-membered pore opening in zeolite H-Y has C_{6v} symmetry along the pore opening. Localized cluster model approaches to the study of crystal lattice properties were used.[11,12] As we know, all zeolites are formed by corner sharing of SiO_4 and TO_4 tetrahedra (where T is Al, B, P, Ti, V, Fe, etc.). In the H-Y zeolite there are 12 T sites in its 12-membered pore. Here we have chosen a dimer cluster, owing to CPU limitations. The cluster model was chosen from the Monte Carlo simulation results, as from this calculation we obtained the minimum energy conformation of the interacting molecule; we cut the nearest framework from the 12-membered pore of H-Y and modeled it as the acid site model for our density functional calculation. The dimer cluster model consists of two TO_4 groups bridged by a commonly shared oxygen. To mimic the Brönsted acid site in the zeolite framework we have chosen a cluster with formula $SiAlO_7H_7$ with all the hydrogens at the crystallographic position of the nearest T-site, except the hydrogen bonded to the bridging oxygen (it is at water distance). All the calculations were performed with a fixed dimer cluster and the interacting molecule was optimized with respect to the fixed cluster.

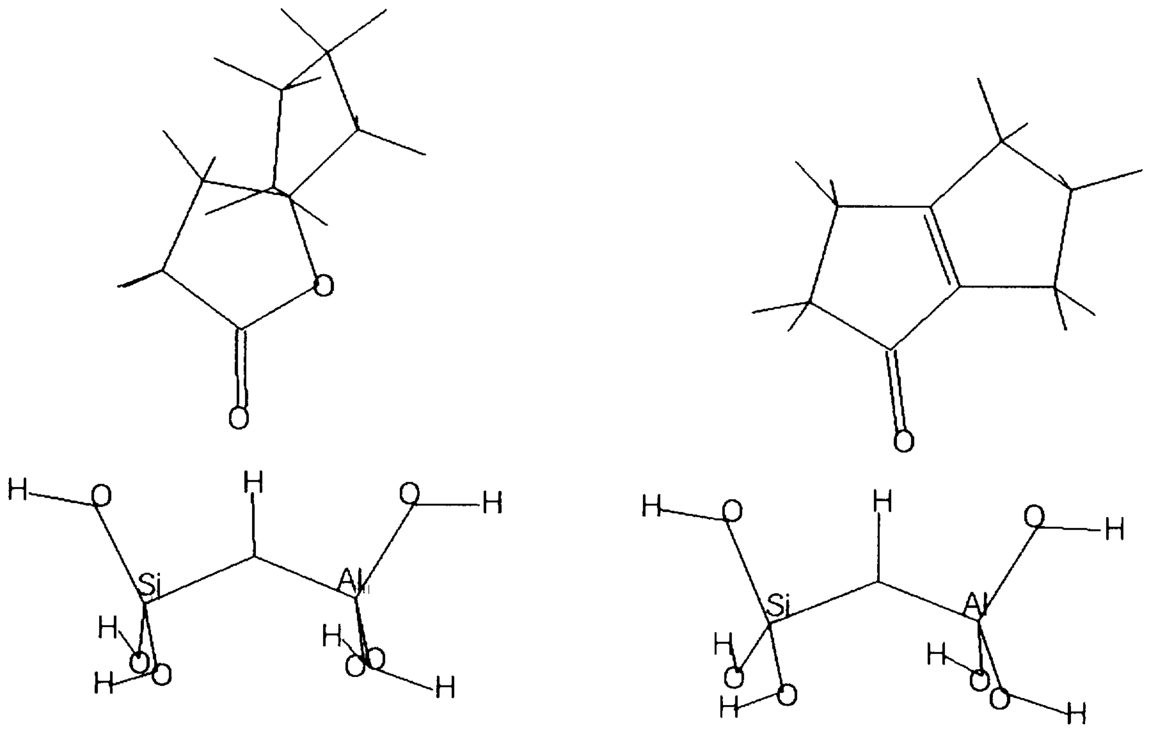
RESULTS AND DISCUSSION

Electronic factors are also important in explaining the shape-selective behavior of zeolites. As the product molecule is extracted by organic solvents it seems that the molecule has a strong adsorption complex inside the framework, suggesting the reaction may not be happening on the surface. The solvent effect is complicated and it is difficult to probe it with computational techniques at this stage. We therefore studied the adsorption mode of the molecules inside the supercage of H-Y, and the mechanism of electron transfer between organic molecules and the framework of zeolite H-Y, by DFT calculations. The total energy of the minimized reactant and the product molecules as calculated by DFT is given in Table 1. The total energy values in Table 1 are presented in the order product + water < reactant. The reaction is a dehydration type, so we added the energy of a water molecule to the energy values given in Table 1, to see the effect. The net charges calculated

Table 1. Electronic properties of reactants and products (optimized) calculated using density functional theory

Molecule	Total energy (kcal/mol)	Charge on oxygens		Bond order between C and O	
		Ring	Ketonic	Ring	Ketonic
1	−287915.46	−0.33	−0.36	0.927	1.831
6	−240209.06	—	−0.37	—	1.875
2	−312372.95	−0.33	−0.36	0.914	1.816
7	−264667.47	—	−0.38	—	1.878
3	−360103.58	−0.32	−0.35	0.912	1.812
8	−312414.39	—	−0.37	—	1.872
4	−384974.12	−0.34	−0.39	0.915	1.814
9	−337253.45	—	−0.37	—	1.880
5	−409422.14	−0.34	−0.39	0.913	1.826
10	−361321.12	—	−0.40	—	1.882

by Mulliken population analysis indicate that the ketonic oxygen atoms are expected to interact with the proton of the Brönsted acid site of zeolite. Table 1 also presents the bond order of the C–O bond in the ring as well as the ketonic bond. It is observed that the bond order is affected more in the case of reactants than products; the bond order of the ring oxygen also changes for the reactants, showing the existence of another interacting site in the reactants.



REACTANT (1)

PRODUCT (6)

Figure 2. The orientation of typical spirolactone (1) and enone (6) molecules with respect to the zeolite framework cluster model. These cluster models were chosen to study the electronic interaction between the molecule and zeolite framework.

Table 2. Interaction energy of reactants and products with acid site cluster

Molecule	Total energy (kcal/mol)	Interaction energy (kcal/mol)	Charge on oxygens		Bond order between C and O (ring)
			Ring	Ketonic	
Bare acid site dimer cluster (FW)	−663 030.98				
Water molecule	−47 634.541				
FW + 1	−950 929.84	16.60	−0.28	−0.32	0.916
FW + 2	−975 385.26	18.67	−0.28	−0.32	0.903
FW + 3	−1023 118.9	15.66	−0.27	−0.31	0.906
FW + 4	−1047 985.2	19.86	−0.29	−0.35	0.907
FW + 5	−1072 434.9	18.22	−0.29	−0.35	0.904
FW + 6	−903 247.18	−7.14	—	−0.33	—
FW + 7	−927 704.44	−5.99	—	−0.34	—
FW + 8	−975 450.21	−4.84	—	−0.33	—
FW + 9	−1000 292.5	−8.07	—	−0.33	—
FW + 10	−1024 359.7	−7.60	—	−0.36	—

The organic molecules have a considerable amount of dynamic freedom inside the supercage of the faujasite framework. The preferred low-energy binding sites were investigated by Monte Carlo internal energy calculations. These calculations were carried out using the catalysis software modules of Biosym. The molecule is placed at the center of the supercage. The simulation box consists of eight (2 × 2 × 2) unit cells. The molecule is moved toward the framework in +x, −x, +y, −y, +z, and −z directions and orientation is chosen by giving a rotation in a random direction. The molecules are moved in steps of 0.5 Å and the energy minimization was carried out with the central valence force field (CVFF) method.[13] The interactions of organic molecules with the cluster model are studied. The adsorption complex formed between the molecules and the zeolite is simulated by the cluster model. As typical examples, the conformation of the adsorption complex between the zeolite framework and spirolactone (1) as well as enone (6) are shown in Figure 2a and b, respectively. The interaction energies between the molecule and the acid site cluster model given in Table 2 are calculated according to the following relation:

Interaction energy = total energy of complex − [total energy of independent acid site model + total energy of free molecules (both reactant and product)]

The organic molecules are found to have multisite interactions with the framework. In the zeolite cluster: organic molecule complex, it was found that the major interaction was between the methylene hydrogens of the organic molecule and the oxygens of the framework. The net charges calculated by Mulliken population analysis (Table 2) show that the product molecules are more polar than the reactant molecules. Consequently, the interaction energies of the enones with the framework are favorable relative to those of the spirolactones.

Little importance can be attributed to the actual numerical values due to confined cluster models. However, the qualitative trends predicted for the interaction of various molecules will be reliable. Chemically, the conversion of spirolactone to enone is a dehydration process. The solvation by water molecules as well as their interaction with the framework of hydrophilic zeolites such as H-Y are poorly understood phenomena. In spite of these complications, comparison of the electronic properties of free and adsorbed molecules given in Tables 1 and 2, respectively, shows some small but subtle changes. The bond order of the C–O bond in the ring shows a decrease due to adsorption, indicating a tendency toward weakening. The net negative charges in the rings remain constant or there is a slight increase, whereas the negative charge on the ketonic oxygen decreases. The ketonic oxygen atoms in the product molecules have less negative charge than the reactant molecules. Thus the electron redistributions predicted by the present calculations indicate that the ketonic oxygens of the reactant molecules abstract the proton from the Brönsted acid site, although the ring oxygen is removed during dehydration. During the interactions between any two chemical systems, the major contribution for the interaction energy comes from the electrostatic interaction. Because the attractive and repulsive terms are canceled by each other in the shorter intermolecular distances, electrostatic energy can be approximated as the interaction energy. Approximate electrostatic properties can be computed even without detailed, self-consistent field quantum chemical calculations. The MESP (molecular electrostatic potential) maps derived from accurate wavefunctions are able to reproduce the activity of catalyst surface for the adsorption and dissociation of molecules.[14] The MESP map at a given point r in space represents a first-order approximation to the interaction energy of the molecular charge distribution with the probe of unit charge at that point. The MESP map for the enone framework complex (Color Plate 1) shows that the positive MESP around the molecules is smeared with the negative potentials created by the zeolite cluster model. This shows the point of interaction between the molecule and zeolite. It was found that the ketonic oxygen of spirolactone faces a strong interaction with the proton of the framework, which results in the abstraction of proton from the Brönsted acid site, resulting in the favorable formation of enone.

CONCLUSIONS

In the zeolite cluster:organic molecule complex, it was found that the major interaction was between the methylene hydrogens of the organic molecule and the oxygens of the framework. Geometric optimization calculations have been performed to simulate the realistic bond fission process. It is observed that the net negative charge on oxygen in the rings increases whereas the negative charge on the ketonic oxygen decreases. The ketonic oxygen atoms in the product molecules have less negative charge than the reactant molecules. The MESP maps show that the ketonic oxygens of the reactant molecules abstract proton from Brönsted acid sites of the framework. This fact supports the observed phenomenon that the spirolactone undergoes strong interaction with the zeolite framework, which results in the favorable formation of enone. Now the resulting enone becomes more polar and thus tends to stay inside the zeolite cage, which results in extraction of the product. The results of DFT match well with experimental observations.

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