

CATALYTIC AND COMPUTER SIMULATION STUDIES OF CARBON–SULPHUR BOND CLEAVAGE OVER ZEOLITE-Y*

B. M. BHAWAL†

Division of Organic Chemistry (Synthesis), National Chemical Laboratory, Pune 411 008, India

R. VETRIVEL†

Catalysis Division, National Chemical Laboratory, Pune 411 008, India

T. INDRASENA REDDY, A. R. A. S. DESHMUKH AND S. RAJAPPA

Division of Organic Chemistry (Synthesis), National Chemical Laboratory, Pune 411 008, India

N-Substituted carbonimidodithioic acid dimethyl esters, when reacted with an active methylene compound such as nitromethane, undergo carbon–carbon bond formation followed by carbon–sulphur bond cleavage in the presence of zeolite catalysts to give 1-substituted amino-1-methylthio-2-nitroethenes. This carbon–sulphur bond cleavage is facilitated by the presence of rare earth cations in the zeolite-Y framework. The shape selectivity of the zeolite also plays an important role in this cleavage reaction. Force field calculations adopted for the molecules involved in the reaction indicate the geometry and conformational flexibility of these molecules. The computer-simulated model for the zeolite-Y is correlated with the conformation and shape of the reactant and product molecules to explain the variation in yields obtained in the conversion of substituted dimethyl esters.

INTRODUCTION

Synthetic zeolite-Y has the framework structure of the naturally, albeit rarely, occurring mineral faujasite. The structure of zeolite-Y is established and well described in the literature.¹ Zeolite-Y is the most widely used catalyst in petroleum refining processes and in many other useful chemical processes.² We have reported the efficient use of zeolite-Y catalyst in a novel condensation reaction^{3,4} of nitromethane with *N*-substituted carbonimido dithioates (**1a–i**) leading to variable yields of nitro ketene *S,N*-acetals [1-substituted amino-1-methylthio-2-nitroethenes (**3a–i**)] with elimination of methanethiol by C–S bond cleavage (Scheme 1).

The comparison of the cage dimensions with the molecular dimensions can rationalize the yield and product selectivity of the reaction. The nature and location of cations also play a crucial role in controlling the stability, acidity, shape selectivity and thus the catalytic activity of zeolite-Y.⁵ In this work, we adopted a computational methodology to rationalize and understand the C–S bond cleavage reaction of *N*-substituted car-

bonimido dithioates taking place in presence of RE(70%)NaY (RE = rare earth).

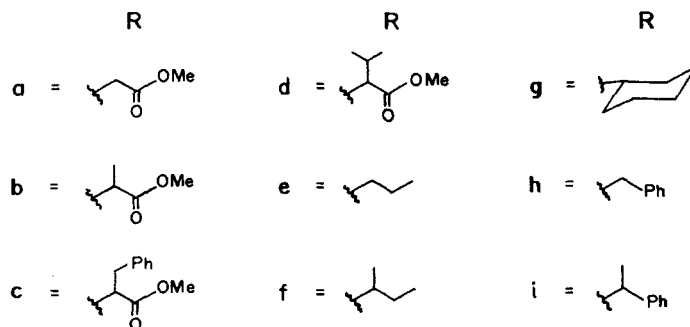
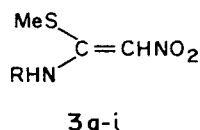
EXPERIMENTAL

Reactions. The reactions were carried out using RE(70%)NaY (Si/Al = 4.2) as reported previously.^{3,4} The yields were determined by isolation of products (**3a–i**) in pure form. The products were characterized by GC, IR, NMR and mass spectral analysis.

The typical procedure for the preparation of 1-methylthio-1-*n*-propylamino-2-nitroethene (**3e**) was as follows. To a mixture of **1e** (10 mmol) and nitromethane (50 mmol), freshly activated RE(70%)NaY (0.5 g) was added at room temperature and the suspension was refluxed with stirring for 24 h. The reaction mixture was then cooled to room temperature and the catalyst was filtered and washed with methylene chloride (2 × 30 ml). The filtrate was concentrated at reduced pressure. The residue was taken up in *n*-hexane and stirred for few minutes to solidify the product. The final purification was carried out by column chromatography to give pure 1-methylthio-1-*n*-propylamino-2-nitroethene (**3e**) as a colourless crystalline solid in 76% yield, m.p. 63–64 °C. IR

* NCL Communication No. 5768.

† Authors for correspondence.



Scheme 1

developed by Gelin and Karplus.⁹ The total strain energy for the molecules is expressed by the following equation:

$$E_{\text{total strain}} = E_{\text{bond length}} + E_{\text{bond angle}} + E_{\text{dihedral angle}} + E_{\text{improper torsion}} + E_{\text{electrostatic}} + E_{\text{van der Waals}} \quad (1)$$

$$E_{\text{bond length}} = K_b(r - r_0)^2 \quad (2)$$
$$E_{\text{bond angle}} = K_{\theta} (\theta - \theta_0)^2 \quad (3)$$
$$E_{\text{dihedral angle}} = K_{\phi} [1 + \cos (n\phi_0 - \delta)] \quad (4)$$
$$E_{\text{improper torsion}} = Kt (t - t_0)^2 \quad (5)$$
$$E_{\text{elec}} = \sum_{i,j>i} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (6)$$

Methods. The equilibrium geometry of the molecules was obtained by the molecular mechanics method

where $q_i q_j$ = automatic partial charges, E_0 = dielectric constant, r_{ij} = inter-atomic distance; and

$$E_{VDW} = \sum_{ij} \frac{[A_{ij}]}{r_{ij}^{12}} - \frac{[B_{ij}]}{r_{ij}^6} \quad (7)$$

where A and B are non-bonded parameters derived from effective number of outer-shell electrons and polarizability of interacting atoms.

Typical parameters used for the energy calculation are given in Table 1.

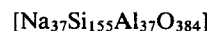
Table 1. Significant force field parameters used for bond length, bond angle and dihedral angle functions

Bond length parameters			
Bond	K_b (kcal mol ⁻¹ Å ⁻²)	r_0 (Å)	
C=N	390.0	1.47	
C=O	640.0	1.23	
N-O	469.0	1.21	
C=C	565.0	1.34	
C-S	237.0	1.80	
Bond angle parameters			
Bond	K_θ (kcal mol ⁻¹ deg ⁻²)	Θ (°)	
S-C-S	60.0	121.00	
S-C-N	60.0	120.00	
C-C-N	65.0	109.47	
S-C-C	60.0	120.00	
Dihedral angle parameters			
Bond ^a	K_φ (kcal mol ⁻¹)	φ (°)	n
X-S-C-X	0.8	0.0	3
X-O-C-X	3.0	180.0	2
N-C-C-N	1.6	0.0	3
X-C-C-X	1.0	0.0	3
Partial charges of various atoms			
Atoms	partial charge		
sp ³ -C	-0.0903		
sp ² -C	-0.0903		
sp-C	-0.0903		
Carbonyl-O	-0.1591		
Nitro-O	-0.1591		
Thioether-S	-0.0430		
Amine-N	-0.2384		
Nitro-N	-0.2384		
Aromatic-H	-0.0045		
Aliphatic-H	-0.0498		

*X represents any bonded atom.

The visualization and the calculations of energy were performed using QUANTA/CHARMM software packages distributed by Molecular Simulations Inc. The strain energy of the molecule was minimized by the steepest descent method to eliminate initial bad contacts and then later by the conjugate gradient and Powell method. A thermodynamically stable conformation corresponds to the minimum strain energy geometry which is obtained according to the equation (1).

Model. The three largest dimensions of the molecules were determined as length, breadth and width ($a \times b \times c$) of the molecules. The hydrogen atoms at edges were considered as point charges and the dimensions of the molecules were determined from the nuclei of the hydrogen atoms. The zeolite-Y lattice was modelled from the crystal structure reported by x-ray crystallographic studies.¹⁰ The unit cell of faujasite containing 192 T sites with an Si/Al ratio of 4.2, used in the present study, can be described as



when it is in the 100% sodium form (NaY) and for the 70% rare earth-exchanged form [RE(70%)NaY], the unit cell composition will be



RESULTS

Model of cages and windows in zeolite-Y

There are many distinct types of sites, three of which are significant for cation occupancy in faujasite-type zeolites described as I, II and III (Figure 1).¹¹ The electrostatic field strength felt by the cations in each type of site is different and hence the catalytic activity induced by them will also be different. Further, the presence of cations in different types of sites will alter the dimensions of windows opening to the cages. Therefore, shape selectivity can be visualized as a function of the nature and location of cations.

There are 16 type I, 32 type II and 48 type III cationic positions in the faujasitic structure. For NaY with an Si/Al ratio of 4.2, all type I sites and nearly two thirds of type II sites will be occupied by Na. It is known that Na in type I sites is very stable and it is difficult to pull it out from the small cage. Hence in RE(70%)NaY, the large tripositive lanthanide ions will occupy type II sites.¹³

It should be noted that among the 32 type II sites available in the unit cell, only one fifth will be occupied by rare earth cations. This corresponds to a maximum of one rare earth ion per supercage. However, it is possible that the lanthanides may also occasionally enter the sodalite cage and hence may not have any influence on

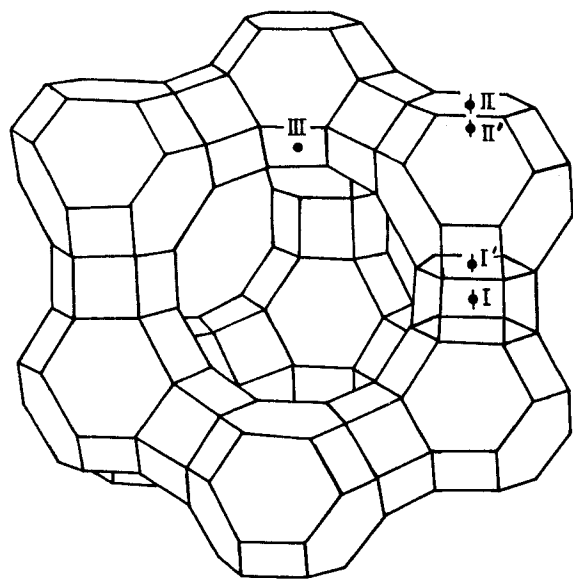


Figure 1. Zeolite-Y framework with the different possible cationic sites

the shape selectivity. As shown in Figure 1, each supercage has four 12-T ring windows. Among these four windows, one or none of them may be blocked by rare earth cations. However, the other 12-T windows are fully open for molecular traffic. The dimensions of the 12-T window and the supercages with different cationic contents are given in Table 2.

Model of reactant, intermediate and product molecules

The molecular mechanic energy calculations were performed for all the reactants (1a–i) and products (3a–i) and also the proposed intermediate molecules (2a–i) shown in Scheme 1. The total energy values for the molecules in their favourable conformations are given in Table 3. From Scheme 1, it can be seen that in the reac-

tant molecules, the substituent R is far from the other of the atoms and the conformation is little affected by varying R. In contrast, the substituent R is closer to nitro and SME groups in the intermediate and product molecules, respectively, and hence the conformation is found to depend on the nature of the substituent R. The actual conformations of the proposed intermediate molecules are shown in Figure 2, which clearly indicates the effect of R on the conformation. The three largest dimensions ($a \times b \times c$) for the minimum energy conformation of the molecules are given in Table 3. The efficiency of zeolite-Y catalyst in bringing out these conversion reactions is shown as the percentage yield obtained (Table 3).

Correlation of molecular dimensions to zeolite-Y void dimensions

It was found that the efficiency of NaY was very low for these conversions. NaY will correspond to case 4 as shown in Table 2, because only 50% occupancy in type I sites is possible owing to overcrowding. Accordingly, the diameter of the void space in a supercage will be reduced to 10.4 Å from 12.4 Å. More crucially, the diameter of 12-T windows which are the entry points to supercages is also reduced. Comparing the dimensions of the molecules given in Table 3, it is clearly evident that the entry and exit of reactant and product molecules to the supercage through 12-T window is severely restricted.

However, when there is 70% exchange of Na^+ by rare earth cations to form RE(70%)NaY catalyst, the situation will correspond to case 3 shown in Table 2, since three Na^+ are replaced by one RE cation. When correlating the molecular dimensions with the zeolite void dimensions, it is customary to neglect the largest dimension (length) of the molecule. This is because the molecule can and does energetically prefer to enter the cages through its smaller dimensions. There are more detailed analyses on the effect of shape of the molecules in the selectivity of conversions in the literature. The model proposed by Choudhary and Akolekar¹⁴ is a

Table 2. Reduction in dimensions of the 12-T window and the supercage in zeolite-Y due to different cation occupancy

Case	Presence of extra framework cations ^a	Dimensions of 12-T window (Å)	Dimensions of supercage (Å)
1	None	7.4 × 7.4	12.4 × 12.4 × 12.4
2	16 cations/u.c. in type I site	7.4 × 7.4	12.4 × 12.4 × 12.4
3	8 cations/u.c. in type II site	7.4 × 6.4	12.4 × 12.4 × 10.4
4	33 cations/u.c. in type II site	7.4 × 5.4	10.4 × 10.4 × 10.4

^a Cation radii are assumed to be 1.0 Å; u.c. = unit cell.

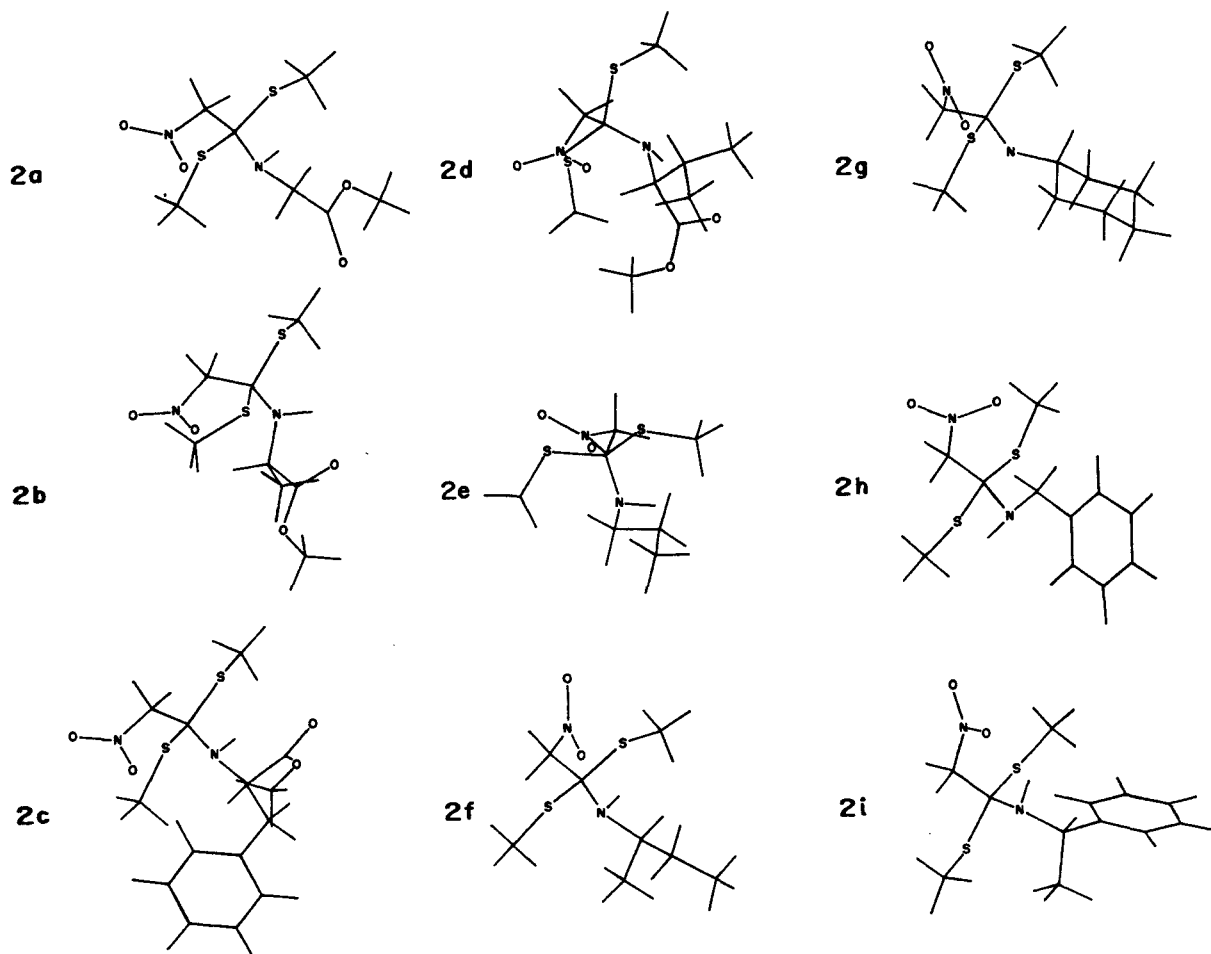


Figure 2. Energy-minimized conformations of the intermediate molecules (2a-i)

typical example which supports the fact that the molecules prefer to enter the pores through their smaller dimensions.

DISCUSSION

Several criteria could be assigned to the observed efficient C—S bond cleavage reaction over RE(70%)NaY. The reactant and product molecules have to be smaller than the 12-T member windows, because they have to enter or leave supercages through these windows. The active sites are inside the supercages since the proposed intermediates can be formed only inside the supercages owing to their large dimensions. The molecules can enter the cages in certain preferred orientations, which are graphically visualized by matching the reactants with the windows.

As discussed in the previous section, the largest dimension of the molecule does not matter. On this basis, when the reactant molecule is too small, say as in the case of 1d, then the products are formed in very low yield, probably because of their short residence time inside the cage due to free diffusion of the molecules. When the reactant molecule is too large, say as in the case of 1c, then the yield also decreases. Actually the size of 1c (8.4×5.6 Å) is slightly larger than the 12-T window and the size of 1d (5.6×4.75 Å) is slightly smaller than the 12-T window, but for all the other reactants the second largest dimension is in the range 6.0 – 6.5 Å. However in the case of 3a, although the molecule is small, the product yield is low. The low yield is due to the formation of a cyclic product⁴ by self-condensation of two reactant molecules (1a). The self-condensation reaction occurs only with reactant 1a

Table 3. Total strain energy and the dimensions of various molecules calculated for the equilibrium structures

No. of atoms	Molecule No.	Powell (kcal mol ⁻¹)	Dimensions (Å) <i>a</i> × <i>b</i> × <i>c</i>	Yield (%)
22	1a	-02.96	9.75 × 6.40 × 1.75	
25	1b	-07.12	9.75 × 6.25 × 3.75	
35	1c	09.74	10.10 × 8.40 × 5.60	
31	1d	-00.93	10.60 × 5.60 × 4.75	
29	2a	02.37	8.40 × 7.40 × 4.10	
32	2b	05.07	7.60 × 6.10 × 4.50	
42	2c	17.48	9.10 × 8.00 × 7.50	
38	2d	09.66	9.20 × 7.10 × 6.75	
23	3a	-03.97	10.60 × 6.40 × 3.50	25.00 ^a
26	3b	-10.65	9.80 × 7.00 × 3.60	65.00
36	3c	-01.28	8.75 × 7.75 × 5.60	45.00
32	3d	-10.10	10.00 × 7.50 × 4.00	00.00
22	1e	-03.26	8.50 × 6.40 × 1.75	
25	1f	-05.82	7.75 × 6.50 × 3.80	
29	1g	-02.85	8.10 × 5.90 × 4.10	
26	1h	00.59	10.75 × 6.25 × 1.80	
29	1i	02.55	10.25 × 6.40 × 4.00	
29	2e	13.26	7.10 × 7.10 × 4.50	
32	2f	07.50	7.75 × 7.50 × 4.40	
36	2g	11.02	9.25 × 7.40 × 3.40	
33	2h	11.09	9.25 × 7.25 × 4.80	
36	2i	08.25	9.25 × 7.50 × 5.70	
23	3e	-00.88	8.30 × 7.40 × 3.25	76.00
26	3f	-04.74	8.90 × 6.20 × 3.00	82.00
30	3g	-02.86	8.75 × 6.70 × 4.25	75.00
27	3h	00.70	9.50 × 7.25 × 3.50	80.00
30	3i	-00.50	10.30 × 8.30 × 3.75	50.00

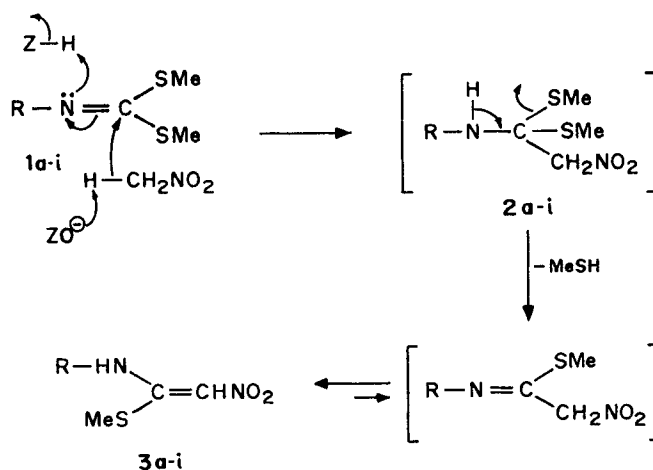
^a A cyclic product from self-condensation of 1a was also obtained in 53% yield along with this compound.

because of the presence of an active methylene group, with a highly acidic proton. The dimensions of the product molecules are close to the diameter of 12-T windows. The yields obtained are found to be a function of their sizes and those with comparatively larger dimensions such as 3c and 3i are obtained in lower yields. Hence, there is a kind of molecular recognition mechanism by the pore entries to the cages which decide the efficacy of the reaction.

The cooperative acid-base catalysis that can take place inside the cage is unique in zeolite catalysts compared with other catalysts as shown in Scheme 2. Hence, the formation of the intermediate and cleavage of the C—S bond in this intermediate occur ideally inside the supercage. The dimensions of the proposed intermediates are such that they easily fit in the supercage of RE(70%)NaY. The geometric strains are maximum in the intermediates (2a–i) as can be seen from the E_{angle} values given in Table 4. However, the electrostatic energy (E_{electro}) is favourable for the

intermediates and this electrostatic force will lead to specific orientations of these intermediates inside the supercages.

In Table 4, the contributions of individual energy terms to the total strain energy are given. It was found that the dimensions of the molecules are not dependent on just the number of atoms but more on their conformation. The conformations themselves are controlled by the attractive electrostatic interaction (E_{electro}) and the non-bonded van der Waals interactions (E_{VDW}), as can be seen from the values given in Table 4. The intermediates were always found to have greater strain energies than the reactants or products. There are also many degrees of conformational freedom for these molecules. The exact conformation adopted by the molecule may be influenced by external factors such as electronic interactions between the molecule and the zeolite, the electrostatic field inside the cages, solvents used for the reaction medium and the temperature of the reaction. In some conformations, there is a possibility of the



Scheme 2

Table 4. Contributions of individual energy terms (kcal mol⁻¹) to the total strain energy for the final energy minimized molecules

Molecule	$E_{\text{bond length}}$	$E_{\text{bond angle}}$	$E_{\text{dihedral angle}}$	$E_{\text{electrostatic}}$	E_{VDW}	$E_{\text{improper torsion}}$	E_{total}
1a	0.05	0.21	0.00	-3.56	0.33	0.00	-2.96
1b	0.07	0.29	0.30	-8.15	0.35	0.00	-7.12
1c	0.35	2.07	5.35	-0.44	2.39	0.02	9.74
1d	0.18	1.26	4.63	-7.00	-0.02	0.03	-0.93
1e	0.02	0.12	0.00	-3.30	-0.09	0.00	-3.26
1f	0.02	0.22	0.21	-6.07	-0.21	0.00	5.82
1g	0.07	0.36	0.20	-3.28	-0.21	0.00	-2.85
1h	0.18	0.34	0.00	-2.78	2.86	0.00	0.59
1i	0.19	1.09	4.39	-5.77	2.64	0.01	2.55
2a	0.15	11.13	1.21	-8.23	-1.88	0.00	2.37
2b	0.30	14.02	2.62	-10.19	-1.69	0.00	5.07
2c	0.51	14.48	2.82	0.37	-0.06	0.10	17.48
2d	0.45	15.58	3.62	-7.69	-2.46	0.16	9.66
2e	0.31	14.42	2.86	-2.96	-1.37	0.00	13.26
2f	0.18	11.50	1.44	-3.63	-1.99	0.00	7.50
2g	0.23	11.55	1.00	0.12	-1.89	0.00	11.02
2h	0.30	10.94	0.39	-1.56	1.02	0.00	11.09
2i	0.35	11.55	1.66	-6.25	0.92	0.02	8.25
3a	0.02	0.15	1.08	-3.70	-1.83	0.32	-3.97
3b	0.01	0.29	0.98	-10.17	-2.03	0.25	-10.65
3c	0.27	1.41	1.04	-1.10	-3.07	0.15	-1.28
3d	0.12	0.61	0.60	-9.82	-1.64	0.03	-10.10
3e	0.08	0.39	2.06	-2.90	-1.11	0.60	-0.88
3f	0.02	0.31	0.15	-3.27	-1.97	0.01	-4.74
3g	0.05	0.42	0.13	—	-3.52	0.24	-2.86
3h	0.15	0.04	0.58	-0.93	-0.53	0.34	0.70
3i	0.15	0.49	2.30	-5.04	1.38	0.23	0.50

reacting group being sterically shielded, resulting in non-reactivity of the reactant molecules. This may be the reason for the absence of a 1:1 correlation of molecular dimensions to the yield obtained. Electronic structure calculations on suitable cluster models will further help in understanding the reaction mechanism.¹⁵

From the present study, the following conclusions can be drawn: the supercages in zeolite-Y have the requisite characteristics for catalysing the condensation of nitromethane with *N*-substituted carbonimido dithioates; the effect of the Si/Al ratio and the nature of extra framework cations in modifying the cage and window dimensions have been elucidated; and, the molecular mechanics energy calculations predict the equilibrium configuration of molecules, and the shape and size of these molecules provide the rationalization of the yields obtained for the reactions involving these molecules. Hence computer simulation studies such as these are able to improve our understanding of the catalytic reaction of molecules inside the supercages of zeolite-Y.

REFERENCES

1. W. J. Mortier and H. J. Bosmans, *J. Phys. Chem.* **75**, 3327 (1971).
2. N. Y. Chen and T. F. Degnan, *Chem. Eng. Prog.* February, 32 (1988).
3. A. R. A. S. Deshmukh, T. I. Reddy, B. M. Bhawal, V. P. Shiralkar and S. Rajappa, *J. Chem. Soc., Perkin Trans. I* 1217 (1990).
4. T. I. Ruddy, B. M. Bhawal and S. Rajappa, *Tetrahedron* **49**, 2101 (1993).
5. J. A. Rabo, C. L. Angell, P. H. Kasai and V. Shomaker, *Discuss. Faraday Soc.* **41**, 328 (1966).
6. J. F. Lindsay, *US Pat.* 4 125 591 (1978).
7. V. P. Shiralkar and S. B. Kulkarni, *Indian J. Chem.* **16A**, 665 (1978).
8. D. Hoppe and L. Beckman, *Liebigs Ann. Chem.* 2066 (1979).
9. B. R. Gelin and M. Karplus, *Biochemistry* **18**, 1256 (1979).
10. W. J. Mortier, H. J. Bosmans and J. B. Uytterhoeven, *J. Phys. Chem.* **76**, 650 (1972).
11. D. W. Breck, *J. Chem. Educ.* **48**, 678 (1964).
12. H. W. Haynes, *Cat. Rev. Sci. Eng.* **17**, 273 (1978).
13. P. B. Venuto and P. S. Landis, *Adv. Catal.* **18**, 259 (1968).
14. V. R. Choudhary and D. B. Akolekar, *J. Catal.* **117**, 542 (1989).
15. S. Prasad and R. Vetrivel, *J. Phys. Chem.* **96**, 3092 (1992).