

Theoretical Study on the Nitration of Methane by Acyl Nitrate Catalyzed by H-ZSM5 Zeolite[†]

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A theoretical study on the nitration of methane by acyl nitrate catalyzed by HZSM-5 zeolite is reported. The zeolite was represented by a “double ring” 20T cluster. The calculations were performed at the DFT/X3LYP/6-31G** and MP2/6-31G** levels. The first step of the mechanism involves the protonation of the acyl nitrate by the zeolite and the formation of a nitronium-like ion. The reaction proceeds through a concerted step with the attack of the methane molecule by the nitronium-like ion and the simultaneous transfer of a proton from the methane molecule to the zeolite, thus reconstructing the acidic site. The activation energies for the first and second steps of this reaction are, respectively, 14.09 and 10.14 kcal/mol at X3LYP/6-31G** level and 16.68 and 13.85 kcal/mol at the MP2/6-31G**.

1. Introduction

Although the nitration of saturated hydrocarbons can be considered a fundamental and important reaction in synthetic and industrial chemistry,¹ it is not as well studied as the nitration reaction of aromatic hydrocarbons. The first attempt at obtaining nitroalkanes was performed by Meyer and Stüber in 1872.² They observed that the reaction between amyl iodide and silver nitrite produced nitropentane and amyl nitrite. This kind of reaction has been known since then as the Victor–Meyer reaction. Several other nitro compounds, such as nitro alcohols, nitro olefines, and nitro ethers,³ have been obtained using this reaction. However, the first report on the production of a nitroalkane by direct nitration of a hydrocarbon in liquid phase was by Beilstein and Kurbatov in 1880,⁴ and subsequently by Konovalov⁵ and Markonikov.⁶ Some important conclusions came from these studies,³ the most important ones being (a) high temperatures and dilute nitric acid are needed to achieve nitration of saturated aliphatic hydrocarbons, (b) a large percent of oxidized products is formed, (c) the sulfur–nitric acid mixture is not suitable for saturated hydrocarbons and (d) aluminum nitrate seems to be the best catalyst for liquid-phase nitration.

The nitration of saturated hydrocarbons was carried out by Hass et al.³ and Grundmann.⁷ Hass in the 1930s developed a practical procedure for the gas-phase nitration of light linear and branched hydrocarbons using nitric acid vapor at 350–400 °C. Heavier hydrocarbons were studied by Grundmann by carrying out the reaction at 160–180 °C in the liquid phase, with superheated nitric acid vapor or with nitrogen dioxide. These and other studies suggest, and it was generally accepted, that the reactions proceed via a free radical, with NO₂ as the nitrating agent.⁸ However, only light saturated hydrocarbons are efficiently converted to their corresponding nitroalkanes. For example, the nitration of propane with NO₂ at 300 °C produces nitropropanes and 26% of byproduct such as nitroethane and nitromethane, which result from the C–C bond cleavage.

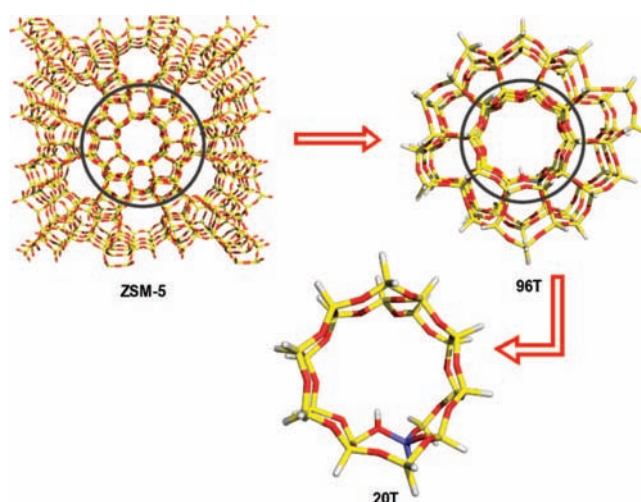


Figure 1. Process of constructing the 20T and 96T clusters from the crystal structure of the HZSM-5 zeolite.

A new method of nitration of alkanes with nitronium salts was developed by Olah⁹ in the 1970s. This new method is based on the electrophilic substitution of hydrogen by the nitro group, therefore excluding the possibility of a free-radical mechanism. The salts generally employed are hexafluorophosphate NO₂⁺PF₆⁻, hexafluoroantimonate NO₂⁺SbF₆⁻ and tetrafluoroborate NO₂⁺BF₄⁻. The accepted mechanism for these reactions considers a three-center bond transition state formed by the nitronium ion attacking the two-electron covalent σ bonds, forcing them into electron-pair sharing. Despite providing a new route for nitration, this method still gives poor conversion and selectivity.

Other procedures for nitration of alkanes have been developed in the last two decades. A laser-induced one was used by Umstead et al.¹⁰ for the production of 2-nitro-2-methylpropane from the reaction between isobutane and NO₂ radical. This procedure has been used by Godbey¹¹ for other alkanes. Minkov et al.¹² have obtained nitroalkanes by treating alkanes with HNO₃ over metal nitrates.

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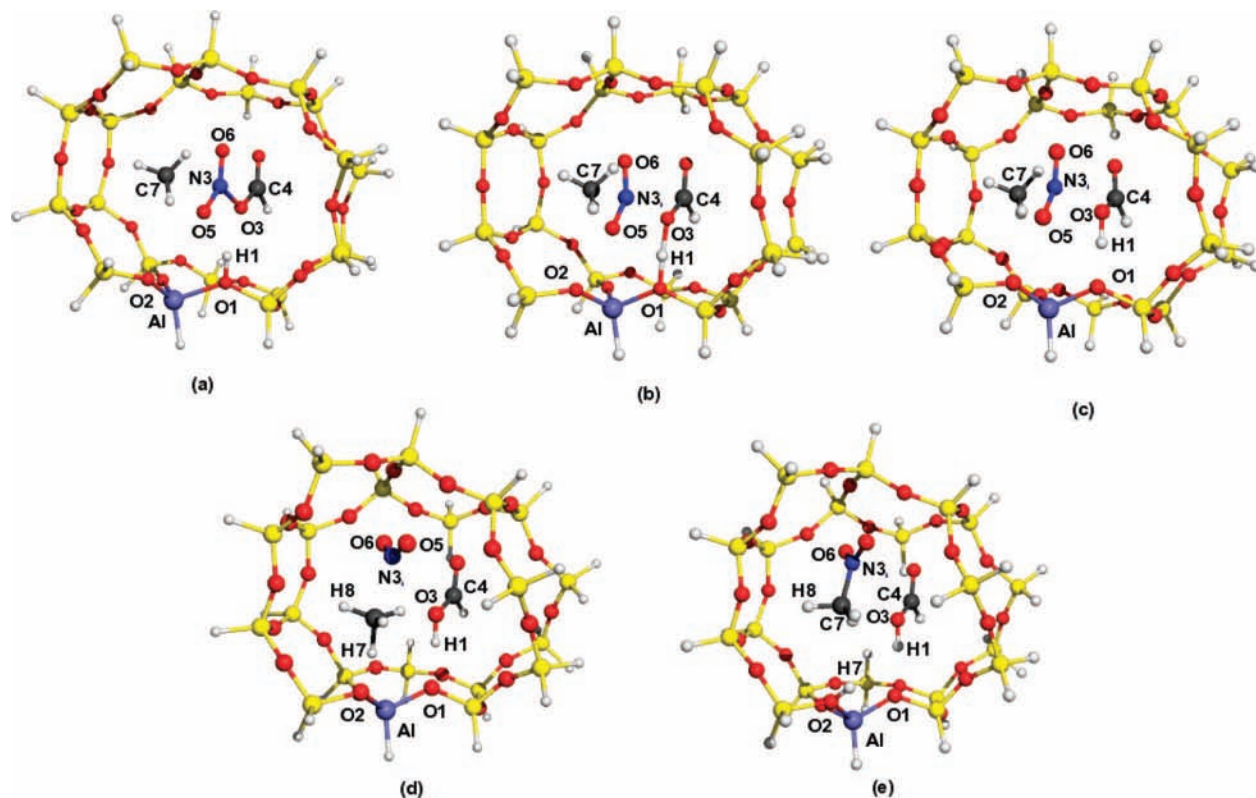


Figure 2. Stationary points of the potential energy surface: (a) adsorbed reactants; (b) first transition state; (c) intermediate; (d) second transition state; (e) adsorbed products.

TABLE 1: Relevant Geometrical Parameters at the X3LYP/6-31G level for the Adsorbed Reactants (React.), Transition States (First TS and Second TS), Intermediate (Int), and Adsorbed Products (Prod.) in the Cluster 20T**

parameters	structures				
	react.	first TS	int	second TS	prod.
Distances (Å)					
Al–O1	1.97	1.89	1.87	1.80	1.77
Al–O2	1.73	1.76	1.80	1.85	1.96
O1–H1	0.98	1.14	1.50	1.61	1.81
H1–O3	1.77	1.27	1.01	1.01	0.99
O3–C4	1.38	1.35	1.33	1.33	1.34
O3–N3	1.57	1.90	2.74	3.23	
N3–O5	1.19	1.16	1.17	1.18	1.22
N3–O6	1.18	1.16	1.17	1.18	1.22
N3–C7				2.08	1.49
C7–H8	1.09	1.09	1.09	1.09	1.07
C7–H7	1.09	1.09	1.09	1.25	
O2–H7				1.42	0.96
Angles (deg)					
O2–Al–O1	99.1	101.8	102.3	103.4	96.3
Al–O1–H1	114.0	118.6	119.0	119.9	
H1–O3–C4	123.5	117.1	113.8	113.1	112.4
N3–O3–C4	123.7	124.8			
O6–N3–O5	135.6	146.9	142.0	138.2	126.1
H8–C7–N3				85.2	106.2
H7–C7–H8		108.3		99.8	

Recently Nishiwaki et al.¹³ have developed a catalytical method for the nitration of light alkanes and the alkyl side chain of aromatic compounds by NO_2 or HNO_3 with *N*-hydroxyphthalimide (NHPI) as the catalyst. In this method, it is possible to achieve selective nitration but only reasonable yields are obtained (~60%) for the nitration of light alkanes at 100 °C, under aerobic conditions and during 14 h.

As discussed above, those methods directly employing nitric acid reveal some problems such as over nitrated and/or oxidized

products. Moreover, the acid waste produced represents a serious operational and environmental problem. To overcome these problems, new methods employing solid-acid catalysts have been extensively studied. Silica gel,¹⁴ sulfonated polyoxanes,¹⁵ acid resins,¹⁶ modified clays,¹⁷ sulfated zirconia,¹⁸ supported sulfuric and sulfonic acids,¹⁹ and zeolites²⁰ are some of solid-acid catalysts investigated.

In their protonated forms, zeolites have been employed in the oil and petrochemical industries for catalytic cracking, isomerization and alkylation of hydrocarbons. Some studies have employed these catalysts and several nitrating agents (NO_2 , N_2O_3 and N_2O_4 , HNO_3) for the nitration of aromatic hydrocarbons.^{21,22}

Acyl nitrates have also been used as nitrating agents for aromatic nitration since the early 1950s.²³ Considering the similarity between the results obtained with acyl nitrates and the ones using nitronium cation precursors, these species could also be viewed as NO_2^+ precursors.^{24,25} In a recent paper,²⁶ we have shown that at least for the nitration of aromatics the reaction involves a nitronium-like-ion species, produced after the protonation of the acyl nitrate by the acidic site of the zeolite.

The aim of this work is a detailed theoretical study of alkanes nitration reaction with acyl nitrate catalyzed by zeolites. For this purpose, we have chosen the methane molecule as the substrate prototype, and a 20T cluster as the model for the protonated ZSM-5 zeolite.

2. Theoretical Basis

The cluster used to simulate the ZSM5 zeolite was obtained directly from its largest cavity. The H-ZSM5 acid site was simulated with a 20T cluster, composed of nineteen silicon atoms and one aluminum atom arranged in two parallel rings. The initial cluster was obtained through the process indicated in Figure 1, using the database from the CERIUS² v.4.0 program.²⁷ The dangling bonds were terminated with hydrogen

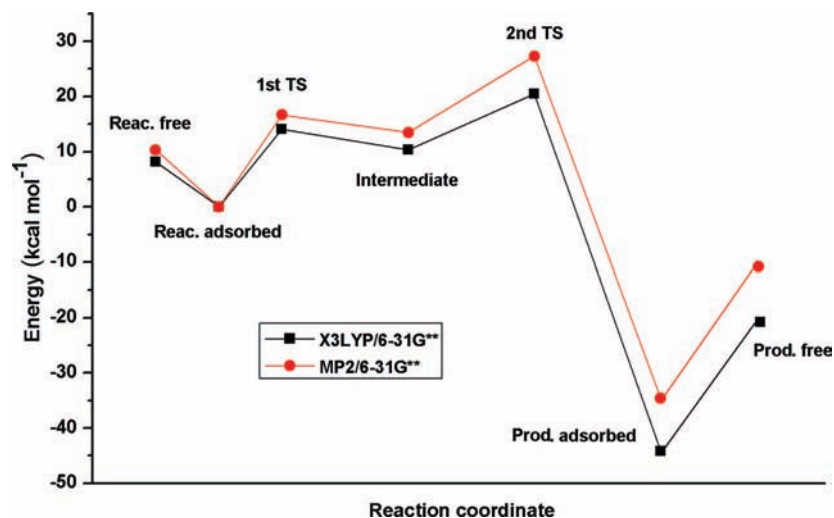


Figure 3. Energy profile of the reaction.

atoms and the site of the aluminum atom was chosen according to suggestion of NMR²⁸ and previous quantum-mechanical studies.²⁹

The geometry optimization of all reagents, products, intermediates and the search for saddle points were performed with the program JAGUAR v.7.0.³⁰ The calculations were performed at the DFT/X3LYP³¹ and also at the second-order Moeller–Plesset perturbation theory (MP2)³² levels, along with the 6-31G** basis set. For this basis set the BSSE computed with the counterpoise method³³ is of 0.8 and 0.2 kcal at the X3LYP and MP2 levels, respectively. A DFT-based method was chosen because, among the methodologies for which calculations on smaller clusters are feasible, it is one that gives the best results when compared to the ab initio methods.³⁴ The X3LYP functional was chosen because, among the presently available functionals, it seems to give a better description of dispersion interactions, and hence, of the physical adsorption. However, to obtain more reliable adsorption energies, calculations at the using MP2 level were also performed.

The vibration frequencies have been calculated to check the character of the stationary points obtained after the geometry optimization. It is expected only positive frequencies for reactants, intermediates and products, and only one negative frequency for transition states (TS). Unscaled frequencies were used to calculate the ZPE corrections. This correction was not determined for the calculations at MP2/6-31G** level because of the extremely high computational costs involved in the calculation of the full Hessian matrix from scratch. The ZPE corrections computed at X3LYP/6-31G** level were used to correct the MP2/6-31G** results. The geometry optimizations and the search for saddle points have all been performed with no restrictions imposed. Structures along the reaction path have been obtained through a intrinsic reaction coordinate (IRC) calculation.³⁵

3. Results and Discussion

The chemical reactions, at the active sites of the zeolite, are preceded by the diffusion and adsorption steps.³⁶ The resulting structure of the adsorbed complex is shown in Figure 2a. In this structure the acid proton of the cluster is at a distance of 1.77 Å from the oxygen atom O5 of the nitrate group (Table 1). It can be seen that the geometry of the adsorbed formyl nitrate molecule is practically indistinguishable from that of the free molecule. The adsorption energy of the reactants in the

20T cluster, i.e., the difference in energy of the complex reactants-20T cluster and the sum of the energies of the reactants and the cluster at infinity separation, is of 8.15 and 10.30 kcal mol⁻¹ at X3LYP/6-31G** and MP2/6-31G** levels, respectively (Figure 3). Similarly, the adsorption energy of the products has been computed as the difference in energy between the complex products-20T cluster and the sum of the energies of the products and the cluster infinitely apart. For the products, the adsorption energy is of 23.8 and 25.4 kcal mol⁻¹ at the X3LYP and MP2 levels, respectively. The value obtained at the DFT/X3LYP/6-31G** should be considered just as an estimate because of the failure of the functional to describe weak interactions dominated by dispersion forces. The MP2 result seems more reasonable when compared to the adsorption energy of small linear hydrocarbons on ZSM5.

The saddle point corresponding to the first step of the reaction (formyl nitrate's protonation) is depicted in Figure 2b and its most relevant geometric parameters are shown in Table 1. The reaction barrier for this step is 14.09 and 16.68 kcal mol⁻¹ at X3LYP/6-31G** and MP2/6-31G** levels, respectively. The H1 atom is at a distance of 1.14 Å from the O1 atom of the 20T cluster and at 1.27 Å of the O3 atom of the nitrate group. The N3–O3 distance is 1.90 Å. The saddle point exhibits one imaginary frequency at -227.7 cm⁻¹, which is clearly associated with the breaking of the O1–H1 bond, the simultaneous formation of the H1–O3 bond and with a weak N3–O3 stretching. The O5–N3–O6 group, already dissociated from the original reactant molecule, could be considered as a nitronium-ion-like species. Thus, the transition state is composed of a practically formed formic acid molecule and a nitronium-like-ion. This step is similar to that of the reaction of benzene nitration previously reported.²⁶

An IRC calculation with this transition state structure shows that the nitronium-like-ion NO₂^{δ+} moves away from the formic acid, which remains adsorbed in the cluster along the entire reaction coordinate mainly due to the electrostatic interaction between the H1 and O1 atoms. A possible intermediate species is shown in Figure 2c. The energy of this structure is 10.35 and 13.45 kcal mol⁻¹ at X3LYP/6-31G** and MP2/6-31G** levels, respectively, above those of the adsorbed reactants energy.

The geometry of the second transition state is shown in Figure 2d. In this structure, the NO₂ group is at a distance of 2.08 Å from the carbon atom C7 of the methane molecule, and at 3.23

Å from the oxygen atom O3 of the formic acid (Table 1). The major change in this group relative to the first transition state is the reduction of the O5–N3–O6 angle from 146.9 to 138.2°.

The imaginary frequency associated with this transition state is -785.8 cm^{-1} , which is related to the attack of the NO₂ group on the methane and the simultaneous proton transfer from the methane molecule to the oxygen atom O2 of the cluster, thus regenerating the acidic site of the zeolite. The reaction barrier for this step is 10.14 and 13.85 kcal mol⁻¹ at X3LYP/6-31G** and MP2/6-31G** levels, respectively, considering the intermediate structure mentioned before as the reactant complex.

The difference between the transition barriers for first and the second steps transitions, at both the DFT and MP2 levels, is smaller than the degree of accuracy expected from levels of calculation employed. Therefore, although the MP2 favors the second step, at the present levels of calculation one cannot determine which step is the rate determining one of the reaction.

Once formed, the products (nitromethane and formic acid) remain adsorbed in the 20T cluster, as shown in Figure 2e. From Table 1 it can be seen that the geometry of the clusters changes accordingly to reflect that the proton, initially bound to the O1 atom, is now bound to the O2 atom of the cluster.

Comparison of the adsorption energies of reactants and products shows that the latter are more strongly adsorbed than the reactants by 15.65 and 15.10 kcal mol⁻¹ at X3LYP/6-31G** and MP2/6-31G** levels, respectively. Therefore, the nitration of methane by formyl nitrate catalyzed by zeolite is an exothermic reaction, like the benzene nitration.²⁶ This could be one of the reasons for the low yields of nitro products reported for the benzene nitration.^{26,37}

4. Conclusions

In this work, the nitration reaction of methane by acyl nitrate on a model cluster zeolite has been investigated, at the DFT/X3LYP and MP2 levels of calculation. The adsorption takes place with practically no changes in the geometry of the reactant molecules. The adsorption energy of the reactant molecules (formyl nitrate and methane) in the 20T cluster is 8.15 kcal mol⁻¹ at X3LYP/6-31G** and 10.30 kcal mol⁻¹ at the MP2/6-31G** level, and that of the products (nitromethane and formic acid) in the cluster is 23.8 and 25.4 kcal mol⁻¹ at the X3LYP/6-31G** and MP2/6-31G** levels of calculation.

This reaction involves a nitronium-like-ion species, produced after the protonation of the formyl nitrate by the zeolite. The estimated reaction barrier for this step is 14.09 kcal mol⁻¹ at X3LYP/6-31G** and 16.68 kcal mol⁻¹ at the MP2/6-31G** level.

The second step of the reactions involves the attack of the nitronium-like ion on the methane molecule. The reaction barrier for this step is 10.14 kcal mol⁻¹ at X3LYP/6-31G** and 13.85 kcal mol⁻¹ at MP2/6-31G**.

The results also shown that the products are more strongly adsorbed to the 20T cluster zeolite than the reactants, and that the reaction is exothermic.

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