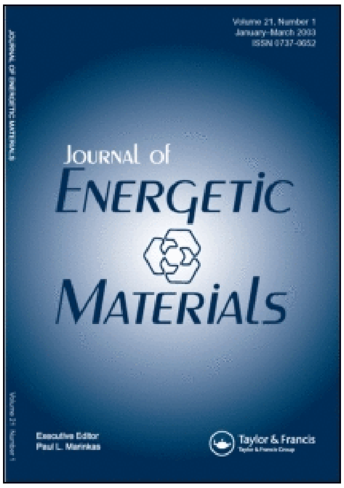

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AM1 STUDIES ON S_N2 HYDROLYSIS OF METHYL NITRATE IN ALKALINE SOLUTION

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ABSTRACT

The semi-empirical MO AM1 method has been employed to investigate the mechanism of the alkaline S_N2 hydrolysis of methyl nitrate and the influence of the solvent on the hydrolysis reaction. The activation energy calculated is 50.61 kJ/mol for the hydrolysis in gas phase, however when the solvent effect is taken into account, it is increased to 89.65 kJ/mol and in agreement with the experimental result(82.42 kJ/mol). It is shown that the solvation energy is an important source of the activation energy.

INTRODUCTION

Methyl nitrate(CH_3ONO_2) is the simplest one of organic nitric esters — a series of energetic materials. Studies on this compound will help us to understand some common characteristics of these materials. A number of investigations, through either experimental or theoretical methods, have

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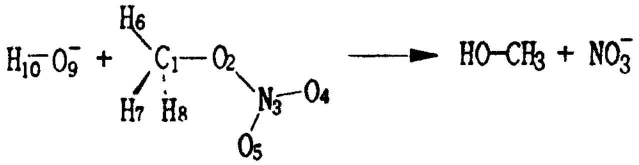
mainly focused on its ground-state properties such as geometry [1] and IR spectra [2,3] etc. Relatively few studies have been performed on the hydrolysis of this compound. The available experimental results [4] showed that methyl nitrate is hydrolysed mainly because of the attacking of the nucleophile OH^- on carbon atom in alkaline media, proceeding a bimolecular nucleophilic substitution(S_N2) reaction. The Arrhenius activation energy for this reaction is 82.42 kJ/mol at 60°C. But theoretical studies carried out by Wang etc.[5] using ab initio method at HF/STO-3G level and semi-empirical MINDO/3 method showed that no barrier or just a very small barrier are required, respectively. Therefore the authors utilized a combined method (MM2 + MINDO/3) to study the solvent effect and concluded that the solvation energy is the main source of the activation energy. However, systematic studies [6] on about 50 nitric esters showed that the calculated energies of these compounds are quite sensitive to the method used. MINDO/3 and ab initio calculation at STO-3G level can't give satisfactory results, whereas AM1 results are reasonably good [7,8,9]. Though it is a good way to study the reaction in solution using a combined method, the results based on the MINDO/3 calculation may be unreliable. In this paper, AM1 method [10] has been used to investigate the alkaline hydrolysis of CH_3ONO_2 and the effect of solvent on this reaction, the satisfactory results are obtained as expected.

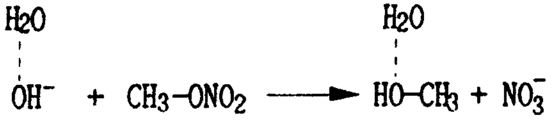
CALCULATION METHOD

The calculations have been performed with the AM1 method implemented in the MOPAC 6.0 program package on HP9000 computer.

The processes of the hydrolysis reactions(reactions 1, 2 and 3) are simulated as the backside attacking on the carbon atom in CH_3ONO_2 by the oxygen atom in OH^-. The reactant complexes(R) and product complexes(P) are fully optimized using the energy gradient method. The transition states(TS) are optimized using NLLSQ or TS algorithms and confirmed by the vibration frequency analysis with the presence of only one imaginary frequency.

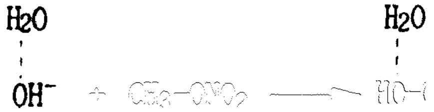


(1)



$$\begin{array}{c}H_2O\\ \vdots\\ OH^-\end{array} + CH_3\text{–}ONO_2 \longrightarrow \begin{array}{c}H_2O\\ \vdots\\ HO\text{–}CH_3\end{array} + NO_3^-$$

(2)



$$\begin{array}{c}H_2O\\ \vdots\\ OH^-\end{array} + CH_3\text{–}ONO_2 \longrightarrow \begin{array}{c}H_2O\\ \vdots\\ HO\text{–}\end{array}$$

RESULTS AND DISCUSSIONS

AM1 calculations are first carried out at RHF and UHF levels respectively to study the alkaline hydrolysis in gas phase (Reaction 1). Table 1 lists the heats of formation (ΔH_f) for the R, TS and P complexes .

We can easily find that the calculated results at UHF and RHF levels are same , which implys that the alkaline S_N2 hydrolysis of CH_3ONO_2 is the reaction in which the systems involved are closed-shell systems and that the calculations performed at RHF level instead of UHF level not only give reasonable results but also also save CPU time. The following discussions are all based on the results of the calculations at RHF level.

Calculations show that the hydrolysis reaction proceeds in a concerted way. When the nucleophile OH^- approaches the substrate CH_3ONO_2, the energy decreases first and goes through a minimum, and then increases gradually. When the distance between the oxygen in nucleophile and the carbon atom in CH_3ONO_2 is 1.90 Å , the energy reaches its maximum, which corresponds to the TS which is confirmed by the presence of only one negative eigenvalue in the force constant matrix, and the corresponding length of breaking bond r_{C1O2} increases from 1.45 Å to 1.64 Å. As the reaction proceeds, the energy decreases rapidly and Walden inversion occurs. Meanwhile, a O_9-C_1 bond is formed and C_1-O_2 broken. From the energies of R and TS at their optimized geometries(including the correction of zero point energies for both), the activation energy(Ea) required for the reaction is calculated to be 50.61 kJ/mol. And the reaction is exothermic.

The changes in bond lengths are shown in Fig.1. The TS appears closer to the R than to the P according to Hammond postulation [11] , since the increase of the bond length of C-ONO_2 from R(1.45Å) to TS (1.64Å) is 0.19 Å, whereas the decrease in the HO-C bond length from the TS(1.90 Å) to P(1.44Å) is 0.46 Å. The changes of net charges in OH and

ONO_2 groups are also shown in Fig.1. It is obvious that along the reaction path, charges transfer from OH group to ONO_2 group.

Though the activation energy(50.61 kJ/mol) in gas phase computed with AM1 is much higher than the MINDO/3 result(5.70 kJ/mol) given by reference [5], it is still too low as compared to the experimental result(82.42 kJ/mol). The substantial difference(31.81 kJ/mol) between calculated and experimental activation energies may come from the neglection of solvation energy in gas-phase.

2 Study on Solvent Effect

The experimental activation energy[4] for the hydrolysis of CH_3ONO_2 is Arrhenius energy of activation, obtained by measuring the velocity coefficients at different temperatures in aqueous alcohol and interpolating Arrhenius equation. However, the Ea obtained by theoretical calculation is the energy barrier of reaction in gas-phase. In aqueous solution, the existence of solvent may interfere the reaction, even change the procedure of reaction. To investigate the reaction in solution, the solvent effect should be taken into account. Therefore, reactions (2) and (3) are designed to study the influence of the solvent water on the hydrolysis of methyl nitrate. For the maximum coordination number of oxygen is four, at most two water molecules have been involved in the calculation.

Table 2 lists the calculated heats of formation and the activation energies(Ea) for the reactions. Some main geometric parameters and atomic charges are given in Table 3.

It shows in Table 2 that when one H_2O molecule is considered (reaction 2), the Ea calculated is 71.02 kJ/mol, which is 20.41 kJ/mol higher than the Ea required for the reaction in the absence of solvent. When another H_2O is involved(reaction 3), the calculated Ea is increased to 89.65 kJ/mol, which is rather consistent with the experimental activation energy(82.42kJ/mol) . Hence, the contribution of solvation energy is determined to be 39.04 kJ/mol, which is 43 percent of the calculated Ea. One H_2O molecule increases the energy barrier by about 19.5 kJ/mol.

As what happen in the energies, the geometries and atomic charges also change somewhat under consideration of the solvent effect. As the numbers of H_2O molecules increase (from 0 to 2), the length of forming bond r_{O9C1} of R and breaking bond r_{C1O2} of TS increase, while the breaking bond length r_{C1O2} of P and angle θ_{H8C1O2} of TS decrease, which seems to show that the solvent effect moves TS towards the direction of the product.

Our calculated results also show that the solvent water affects the hydrolysis of CH_3ONO_2 in the alkaline solution mainly by forming hydrogen bond with nucleophile OH^-. When H_2O interacts with OH^- , a hydrogen bond is formed(HO···H distance equals 1.99 Å), which lowers the total energy greatly and decreases the negative charge on O atom of OH^-. This may decrease the nucleophilicity of OH^- and therefore make S_N2 reaction proceed more difficultly. On the other hand, the formation of hydrogen bond changes the energy level of HOMO in OH^-(Fig.2). When a water molecule is added to OH^-, the energy level E_{HOMO} of OH^- is decreased by approximately 1.0 eV, and therefore the energy difference between E_{LUMO} of CH_3ONO_2 and E_{HOMO} of OH^- is increased($\Delta E3 > \Delta E2 > \Delta E1$) which means that electron transfers from HOMO of

OH^- to LUMO of CH_3ONO_2 more difficultly, i.e., the S_N2 reaction proceeds with more difficulty.

CONCLUSIONS

Our AM1 calculations show that the alkaline S_N2 hydrolysis of CH_3ONO_2 is a concerted reaction. The activation energy calculated in the absence of solvent is 50.61 kJ/mol. When the effect of solvent is considered, the result is increased to 89.65 kJ/mol, which is in good agreement with the experimental result. The contribution of solvation energy to the activation energy is calculated to be 39.04 kJ/mol, which implys that it is an important component(43 percent) of the activation energy, but not the main source.

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TABLE 1 Heats of formation calculated at RHF and UHF levels(kJ/mol)

Method	R	TS	P
RHF-AM1	-261.70	-211.74	-647.98
UHF-AM1	-261.70	-211.49	-647.98

TABLE 2 Heats of formation and activation energies(kJ/mol)

Reactions	R	TS	P	Ea$^{a,b)}$
1	-261.70	-211.74	-647.98	50.61
2	-589.42	-519.24	-930.77	71.02
3	-914.95	-820.58	-1233.88	89.65

a) Zero-point energies have been corrected by 0.65, 0.84 and -5.72 kJ/mol for reactions (1), (2) and (3), respectively. b) experimental Ea is 82.42 kJ/mol

TABLE 3 Calculated geometric parameters and atomic charges[a)]

Reactions		R	TS	P
1	r_{C1O2}	1.45	1.64	3.27
	r_{O9C1}	2.47	1.90	1.41
	θ_{H8C1O2}	105.5	88.2	14.5
	q_{C1}	−0.036	0.194	−0.073
	q_{O9}	−1.013	−0.747	−0.377
2	r_{C1O2}	1.45	1.67	3.20
	r_{O9C1}	2.52	1.89	1.41
	θ_{H8C1O2}	109.1	86.8	19.9
	q_{C1}	−0.072	0.197	−0.071
	q_{O9}	−0.990	−0.759	−0.404
3	r_{C1O2}	1.45	1.72	3.04
	r_{O9C1}	2.55	1.88	1.41
	θ_{H8C1O2}	105.1	85.2	40.1
	q_{C1}	−0.044	0.199	−0.072
	q_{O9}	−0.988	−0.762	−0.377

a) bond length(r) in Å; angle(θ) in ° ; charge(q) in e

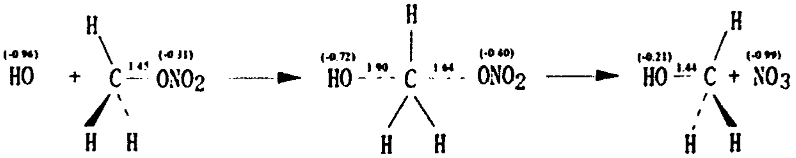

FIGURE 1 Changes in bond lengths(Å) and charges(in parentheses) from R to TS and P

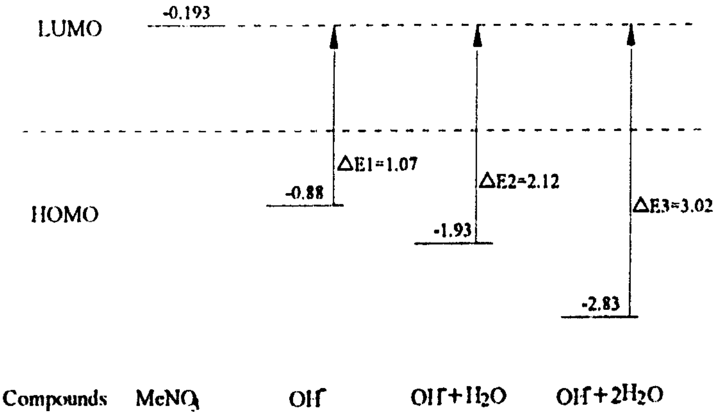

FIGURE 2 Schematic diagram of energy levels(eV) of HOMOs and LUMO