

A Study on Polymerization of Oxocane High Explosives

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Abstract

Oxocane high explosives substituted to explosive group such as azide (-CH₂N₃), nitrate (-CH₂ONO₂), and hydrazine (-CH₂N₂H₃) are investigated theoretically the acid catalyzed reaction using the semiempirical MINDO/3, MNDO and AM1 methods to use as the guidelines of high explosives. The nucleophilicity and basicity of oxocane high explosives can be explained by the value of negative charge on oxygen atom of oxocane and the reactivity in propagation step can be represented by the value of positive charge on carbon atom and low electrophile LUMO energy. It was known that carbenium ion was favorable due to the stable energy (11.745~25.461 Kcal/mol) between oxonium ion and carbenium ion in the process of cyclic oxonium ion of oxocane high explosives being converted to open carbenium ion in oxocane high explosives. The value of concentration of cyclic oxonium ion and open carbenium ion in equilibrium status was found to be a major determinant of mechanism, it was expected to react faster in the prepolymer propagation step in SN1 mechanism than in that of SN2.

Key words: Oxocane, High Explosives, Polymerization, Oxonium Ion, Carbenium Ion

1. Introduction

It is in 5th hazardous materials and open prepolymer of the monomer was applied as a combiner of high explosion as these compounds of substitution (-CH₂ONO₂, -CH₂N₃, -CH₂N₂H₃) product which are part of energized binding are explosive^[1].

Reactive mechanism and active chemical species are influential to the polymerization when cyclic ether and acetal series react with open copolymer under the acid catalyzed reaction in the propagation step and there are steric hindrance effect of a substitute, polar effect and the thermodynamic effect of ring strain which could effect to the nucleophilic monomer^[2]. Penczek *et al.*^[3] explained the copolymerization of acetal and cyclic ether under the acid catalyzed polymerization as the additional reaction by the electrostatic effect when the protonated monomer reacts to the polymer.

The reactive velocity of the polymerization and the equilibrium of oxonium-carbenium ion which is one of active chemical species in the propagation step was con-

sidered as S_N1 and S_N2 mechanism due to the competitive reaction of the growth of polymer. Chien *et al.*^[4] mentioned that -oxycarbenium ion that is active chemical species in the propagation step in 2-butyl-1,3-dioxepane and 2-butyl-1,3,6-trioxocane which are 2-substitutional acetal does an important role in reactive mechanism. And the nucleophilic and basicity which are a degree of reactivity between two monomers in the polymerization are possible to study in IR and NMR^[5].

On the other hand, the polymerization^[6-8] of energized substitutive oxetanes and oxepanes monomer was studied under the acid catalyst and it brought the result^[9] of the polymerization between energized oxetane monomers. It was possible to know that the nucleophilic and basicity that is a degree of reactivity between two monomers of energized substitutive oxetane through getting the most normal alternating copolymer when the product of reactivity ratio between two monomers approaching to 1.

Also, it was known that the nucleophilic and basicity of monomer and the changeable reactivity due to transition of substitute, when compared to contra reactivity of copolymerization when the substitutes change.

The issue for energized bonding materials improving the weakness of the mechanical property^[10,11] contrary to high energy has constantly been studied for their

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Table 1. Formal charges of oxocane high explosives by MINDO/3, MNDO, and AM1 methods

Oxocanes	MINDO/3				MNDO				AM1			
	O	C ₃	C ₅	C ₇	O	C ₃	C ₅	C ₇	O	C ₃	C ₅	C ₇
Oxocane	-0.316	0.366	0.087	0.289	-0.343	0.141	0.138	0.127	-0.286	-0.022	-0.288	-0.019
MNO	-0.312	0.371	0.096	0.356	-0.324	0.149	0.149	0.134	-0.279	-0.027	-0.192	-0.034
MAO	-0.307	0.388	0.133	0.401	-0.318	0.152	0.153	0.147	-0.270	-0.033	-0.187	-0.012
MHO	-0.301	0.396	0.236	0.408	-0.304	0.157	0.157	0.152	-0.266	-0.038	-0.190	-0.022

practical usage. Exothermic reaction could be emerged when the energized bonding materials get heated according to the chemical structure or disassembled by contact with combustibles material, heat of fire, humidity, shock and friction when it is carried or stored.

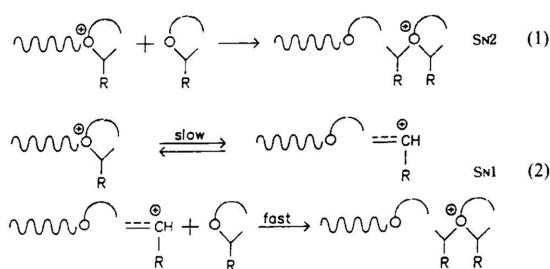
This study was investigated to know the reactivity, reactive mechanism and the process of reactivity of oxocane high explosives including MNO, MAO, MHO, which were explosive energized bonding materials and also in 5th hazardous matters under the acid catalyst polymerization. And formal charge, heat of formation and energy level were used to get a conclusion using MINDO/3, MNDO, AM1 which were semiempirical molecular orbital methods.

2. Calculation

The program used in this study was, restricted Hartree-Fock of AM1 (austin model 1), MINDO/3 (modified intermediate neglect of differential overlap), and MNDO (modified neglect of differential overlap) which was a semiempirical methods^[12-14]. Calculated monomers of oxocane high explosives are oxocane, MNO (methyl nitrate oxocane), MAO (methyl azide oxocane), and MHO (methyl hydrazine oxocane). Especially MNO, MAO, MHO are monomers of oxocane high explosives including explosive groups of nitrate, azide and hydrazine. The least condition of energy of the monomer structure of every molecule has been taken by normal value and this structure has been used to the monomer structure of cyclic open compound. The monomer of oxocane high explosives was calculated as normal, oxonium and carbenium type and also safe general type was used to calculate in the normal status between monomers.

3. Results and Discussion

Polymerization of oxocane high explosives monomer



Scheme 1. Reaction process in propagation step.

under the acid catalyst changes its mechanism due to the concentration of cyclic oxonium ion and open carbenium ion, which are chemical species in the propagation step. And transferring the charges of reactive centered atom of monomer due to the substitute effect, steric hindrance effect and molecular orbital energy level are dominant elements on the decision of the reactivity^[3]. The process of reactivity in propagation step has been issued^[3] because of (1), (2) in Scheme 1.

Charge value to the monomer of oxocane high explosives calculated by semiempirical method of MINDO/3, MNDO and AM1 was summarized in Table 1. The investigation of the nucleophilic and basicity of cyclic monomer was known by IR and ¹³C-NMR^[5] and these properties of monomer were directly proportional to the value of a negative charge of oxocane-oxygen atom due to the calculation of Table 1. And it was expected that the reactivity of monomer would get larger as the positive charge of centered-carbon atom when these monomers were attacked by electrophilic agent because hard-hard type reactivity was dominant charge-adjusting one according to hard and soft acid and base principle^[15].

There was contradiction that a charge of carbon atom appeared to positive charge in MINDO/3 and MNDO methods but it did to negative charge in AM1 method when the value of charge of oxocane monomers was observed. It

had turned out that the value of negative charge of oxygen atom among monomers has changed little due to the change in substitute in every positive charge of carbon atom that was attack calculation methods in Table 1 and the value of centered electrophile of monomer appeared in order of value, MHO > MAO > MNO > oxocane. Under the acid catalyst polymerization, as the negative charge of oxygen atom that was nucleophile among monomers increased, the interaction of electrostatic attraction increased proportionally among molecules and so did the reactivity.

The heat of formation of oxocane high explosive monomers was resulted in Table 2. Also, it was showed that the stability of the molecule itself decreased while the heat of formation made a marked energy as it had positive value of energy. It had been investigated the calculation of the heat of formation by AM1 method had an approximate value to experimental value^[13], especially it appeared a complete positive charge in MAO and MHO, and the heat of formation had the potential to change to positive value in MNO monomer

Table 2. Heat of formation (ΔH_f) of oxocane high explosives by MINDO/3, MNDO, and AM1 methods

Oxocanes	Heat of formation (kcal/mol)		
	MINDO/3	MNDO	AM1
Oxocane	-52.223	-52.372	-44.904
MNO	-48.314	-3.980	8.341
MAO	-45.197	66.319	61.278
MHO	-33.563	101.017	128.225

Table 3. Formal changes of oxocane high explosives by AM1 method

Oxocanes	Normal form				Oxonium ion				Carbenium ion			
	O	C ₃	C ₅	C ₇	O	C ₃	C ₅	C ₇	O	C ₃	C ₅	C ₇
Oxocane	-0.275	-0.042	-0.166	-0.047	-0.289	0.170	0.191	0.192	-0.278	0.172	0.199	0.206
MNO	-0.272	-0.038	-0.189	-0.042	-0.277	0.192	0.197	0.198	-0.273	0.198	0.213	0.223
MAO	-0.268	-0.031	-0.193	-0.041	-0.271	0.263	0.243	0.244	-0.268	0.269	0.242	0.248
MHO	-0.256	-0.030	-0.184	-0.044	-0.262	0.278	0.275	0.274	-0.256	0.280	0.287	0.294

Table 4. Formal charges of oxocane high explosives by MNDO method

Oxocanes	Normal form				Oxonium ion				Carbenium ion			
	O	C ₃	C ₅	C ₇	O	C ₃	C ₅	C ₇	O	C ₃	C ₅	C ₇
Oxocane	-0.253	0.127	0.122	0.122	-0.271	0.177	0.188	0.189	-0.247	0.251	0.253	0.253
MNO	-0.242	0.135	0.131	0.132	-0.263	0.201	0.203	0.199	-0.243	0.271	0.278	0.278
MAO	-0.233	0.142	0.137	0.139	-0.232	0.256	0.256	0.254	-0.216	0.338	0.342	0.340
MHO	-0.227	0.146	0.140	0.141	-0.211	0.279	0.281	0.283	-0.192	0.362	0.363	0.364

including nitrate group.

Table 3 showed the electric charge value calculated by AM1 method for every monomer of oxocane high explosives and it is explained that was calculated by MNDO method in Table 4. The charge of every chemical species showed noticeably the positive charge of carbon that was substituted to explosive group like -CH₂ONO₂, -CH₂N₃, -CH₂N₂H₃ in Table 3 and 4 and it showed that the positive charge of reactive centered carbon showed a large value to open carbenium ion than to cyclic oxonium ion in comparison with protonated cyclic oxonium ion and open carbenium ion. It implied that the chemical species to the substitute group was proportional to the value of the positive charge of reactive centered carbon. It suggested S_N1 mechanism has more potential in open cyclic status since the positive charge of reactive centered carbon is advanced in open carbenium ion. This implied the electrostatic attraction of two chemical species in transition state reacted generally better in open carbenium ion than in cyclic oxonium ion when it comes to electrophilicity and also was advanced in MNDO method than in AM1.

On the other hand, Klopman^[16] explained the change in energy (reactivity between molecules) that happens when a molecular orbital overlaps with molecules that has another energy level including electrostatic attraction term and perturbation term. Regarding the reactivity of acetal series and cyclic ether is as same as the energy of ring strain suited to the change of substitute group under the acid catalyst polymerization, it could be presented to formula (3) that considered with perturba-

tion term and electrostatic attraction term, since this combine ionic bonding and covalent bonding. First paragraph is directly proportional to the product of reactive centered charge in electrostatic attraction term, and second one is in inverse proportional to the gap of energy level ($\Delta E_j = E_{HOMO} - E_{LUMO}$) between two molecules in perturbation term and is proportional to the value of resonance integral (β) and matrix element which is a factor (C) of reactive centered atomic orbital.

$$\Delta E = \frac{Q_{HOMO} \cdot Q_{LUMO}}{\epsilon R} + \frac{2(C_{HOMO} \cdot C_{LUMO} \cdot \beta)^2}{E_{HOMO} - E_{LUMO}} \quad (3)$$

In perturbation term, the bigger the reactivity is, the bigger matrix element is, but the smaller the gap of energy of two orbitals (ΔE_j) is. The main reactivity by the gap of charge of reactivity substance is controlling the charge and ΔE_j influences the reactivity to the control of the gap of energy as the effect of ΔE_j is outstanding when the gap of energy charge is relatively small between two elements of perturbation term and matrix elements decides the reactivity when the factor of orbits of two atoms gets bigger.

It is summarized in Table 5 and 6 by calculating the energy level of HOMO and LUMO of oxocane high explosives in AM1 and MNDO methods. It was expected that the reactivity between monomer and equilibrium of open carbenium ion or activated cyclic oxonium ion in polymerization was in better position when the HOMO (highest occupied molecular orbital) energy, which was nucleophilic of monomer was high, and the reactivity increased as the value of perturbation term

from the formula (3), since the gap of energy (ΔE_j) got lower when the LUMO (lowest unoccupied molecular orbital) energy, which was electrophilic of carbenium ion or activated oxonium ion in propagation step. It was more reactive in MNDO method than in AM1 one, in carbenium ion than in oxonium ion and it also represented that the order of substitutive oxocane, which MHO > MAO > MNO was relatively coincident to that of the heat of formation of Table 2. It was known that the reactivity of open carbenium ion was advantageous when compared to the action between activated electrophiles like cyclic oxonium and open carbenium ion and monomers like electrophile oxocane, MNO, MAO and MHO. Thus, the reactivity to the polymerization of oxocane high explosives went after to the HSAB principle, which happened at the same time controlling reaction of energy gap of perturbation term that was soft-soft interaction and hard-hard one, an electrostatic effect when the positive charge of reactive centered carbon atom showed large value. Especially, in case of MNO, MAO, MHO, which were explosive monomers in Table 3 to 6, the concentration of carbenium and oxonium ion that were species under the acid catalyst polymerization in propagation step influenced the reactivity mechanism but carbenium ion type showed an active movement in controlling charge reactivity and energy level control that were electrostatic interactions.

Calculation about the heat of formation of oxocane high explosive monomer by AM1 method in Table 7 and MNDO method was mentioned in Table 8. It could be known that the low value of the energy

Table 5. Energy levels (eV) of HOMO and LUMO of oxocane high explosives by AM1 method

Oxocanes	Normal form		Oxonium ion		Carbenium ion	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
Oxocane	-12.341	-0.073	-17.367	-5.332	-16.621	-8.445
MNO	-11.873	-0.104	-15.730	-5.025	-14.390	-7.831
MAO	-11.027	-0.149	-12.661	-5.184	-13.672	-7.669
MHO	-10.420	-0.242	-10.829	-4.128	-11.454	-6.896

Table 6. Energy levels (eV) of HOMO and LUMO of oxocane high explosives by MNDO method

Oxocanes	Normal form		Oxonium ion		Carbenium ion	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
Oxocane	-11.331	-2.878	-16.984	-6.327	-15.662	-8.441
MNO	-10.209	-1.862	-13.789	-5.781	-11.867	-6.390
MAO	-9.978	-2.077	-11.634	-6.135	-10.319	-6.514
MHO	-8.689	-2.021	-10.742	-6.012	-9.434	-6.572

Table 7. Heat of formation (ΔH_f) of normal form, protonated oxonium ion, and open carbenium ion of oxocane high explosives by AM1 method

Oxocanes	Heat of formation (kcal/mol)			$\Delta H_f (\Delta H_c - \Delta H_o)$ kcal/mol
	Normal form (ΔH_f)	Oxonium ion (ΔH_o)	Carbenium ion (ΔH_c)	
Oxocane	-44.904	156.221	167.263	11.042
MNO	8.341	158.067	146.322	-11.745
MAO	61.278	228.890	211.312	-17.578
MHO	128.225	304.413	280.841	-23.572

Table 8. Heat of formation (ΔH_f) of normal form, protonated oxonium ion, and open carbenium ion of oxocane high explosives by MNDO method

Oxocanes	Heat of formation (kcal/mol)			$\Delta H_f (\Delta H_c - H_o)$ kcal/mol
	Normal form (ΔH_f)	Oxonium ion (ΔH_o)	Carbenium ion (ΔH_c)	
Oxocane	-52.372	147.864	154.673	6.809
MNO	-3.980	177.092	163.302	-13.790
MAO	66.319	251.313	231.370	-19.943
MHO	101.017	335.906	310.445	-25.461

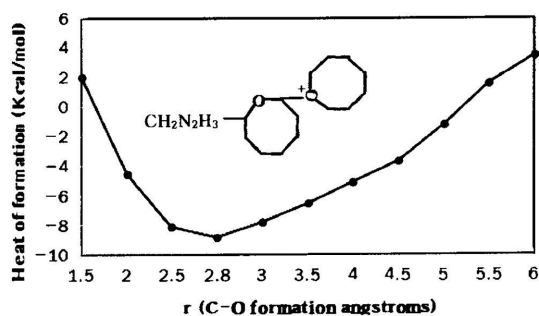


Fig. 1. C-O bond formation of MHO oxonium ion and oxocane.

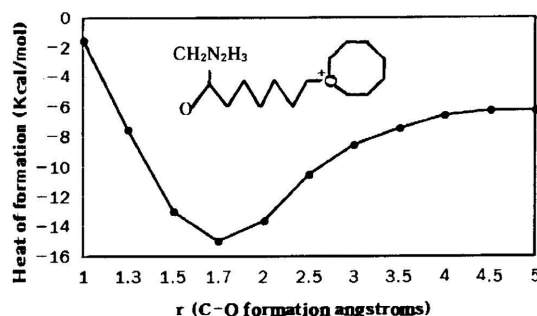


Fig. 2. C-O bond formation of MHO carbenium ion and oxocane.

(11.745~25.461 kcal/mol) in carbenium ion including explosive group ($-\text{CH}_2\text{ONO}_2$, $-\text{CH}_2\text{N}_3$, $-\text{CH}_2\text{N}_2\text{H}_3$) made it stabilized in the equilibrium of oxonium and carbenium ion of oxocane high explosives. This is the evidence that carbenium ion, which is explosive in propagation step was much more stabilized than oxonium ion was and this expected the mechanism had converted $\text{S}_{\text{N}}2$ to $\text{S}_{\text{N}}1$. And the values to use these methods had proved out similar result that was studied by Cheun *et al.*^[6].

Fig. 1 represented the change of heat of formation according to the C-O formation of nucleophilic oxocane monomer to activated cyclic oxonium ion and that formation with nucleophilic oxocane to MHO that has the largest heat of formation and reacts greatest among oxocane high explosives. The transition state of C-O for-

mation when the monomer attacks the cyclic oxonium ion was the most stabilized form when the complex was observed at 2.80 Å.

On the other hand, the additional activating transition state of nucleophilic oxocane monomer to open carbenium ion on Fig. 2 became stable when the length of C-O formation was 1.70 Å. The length of C-O formation was longer by 1.43 Å^[17] in C-O formation among molecules and shorter than 2.80 Å of C-O formation when monomer attacks oxonium ion. This meant the prepolymer was formed by additional reactivity in propagation step. The aspect of prepolymer in propagation step appeared the length of the stabilized C-O formation was 2.80 Å when oxocane monomer was added to activated cyclic oxonium ion while the length of formation with monomer in open carbenium ion was 1.70 Å.

And MNO, MAO and MHO, which were substituted to high explosives in Table 7 and 8 were much more stabilized by 11.745–25.461 kcal/mol of carbenium ion between oxonium and carbenium ion in equilibrium. It was expectable that this polymerization mechanism would converse to S_N1 , since it was influenced by stabilized energy, the concentration value of chemical species, and this led to the thick concentration of carbenium ion.

4. Conclusion

Oxocane high explosives of 5th hazardous materials which are substituted to explosive azide group ($-\text{CH}_2\text{N}_3$), nitrate group ($-\text{CH}_2\text{ONO}_2$), and hydrazine group ($-\text{CH}_2\text{N}_2\text{H}_3$) has been studied to know their reactivity, reactive mechanism and the process of reactivity under the acid catalyst polymerization using semiempirical MINDO/3, MNDO and AM1 methods to investigate the formal charge, heat of formation and energy level.

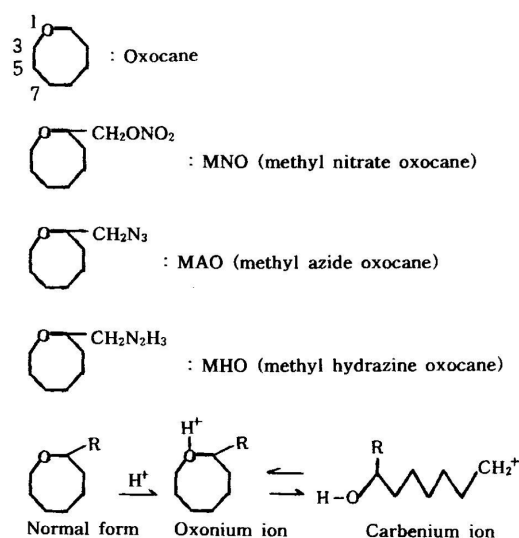
1) Oxocane high explosives had similar reactivity and the reactivity was proportional to the value of negative charge of oxygen atom, to the value of positive charge of carbon atom in propagation step, was bigger when the low LUMO energy of oxonium and carbenium ion.

2) The heat of formation of oxocane high explosives changed to positive mark as it became energized while the stabilization of molecule gets lower. It was expected that mechanism would converse S_N2 to S_N1 as the stabilized energy of carbenium ion in oxocane ring-opening reaction in propagation step would become more stable by 11.745–25.461 Kcal/mol.

3) The attack of monomer to carbenium ion would made prepolymer form easier in propagation step because the length of C-O formation of oxonium ion when complex attacked by nucleophilic monomer formed in oxonium ion and carbenium ion of oxocane high explosives was 2.80 Å and that of carbenium ion was 1.70 Å.

This study has led that it might be much safer in reactivity and mechanical character when oxocane high explosives are carried or stored if they are made to convert over to carbenium ion than to oxonium ion in the manufacturing process.

Monomer and reaction progress of oxocane high explosives



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