

## Theoretical Study on Polymerization of Oxepane High Explosives

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### Abstract

Oxepane high explosives substituted to explosive group such as azido, nitrate and hydrazino 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 oxepane high explosives can be explained by the value of negative charge on oxygen atom of oxepane 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 (19.507~32.101 Kcal/mol) between oxonium ion and carbenium ion in the process of cyclic oxonium ion of oxepane high explosives being converted to open carbenium ion in oxepane 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 S<sub>N</sub>1 mechanism than in that of S<sub>N</sub>2.

**Key words** : High Explosives, Oxepane, Polymerization, Oxonium Ion, Carbenium Ion

### 1. Introduction

It was studied for the useful possibility of oxepane being an energized binding to the polymer<sup>[1-2]</sup> when monomer is grafted to the reactivity of open prepolymer as the synthesis method of cyclic ether was introduced. 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 (-CH<sub>2</sub>ONO<sub>2</sub>, -C H<sub>2</sub>N<sub>3</sub>, -CH<sub>2</sub>N<sub>2</sub>H<sub>3</sub>) product which are part of energized binding are explosive.

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<sup>[3]</sup>. Penczek et al.<sup>[4]</sup> 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 considered as S<sub>N</sub>1 and S<sub>N</sub>2 mechanism due to the competitive reaction of the growth of polymer. Chien et al.<sup>[5]</sup> mentioned that  $\alpha$ -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<sup>[6]</sup>.

On the other hand, the polymerization of energized substitutive oxetane<sup>[7,8]</sup> monomer was studied under the acid catalyst and it brought the result of the polymerization<sup>[9]</sup> 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<sup>[10,11]</sup> contrary to high energy has constantly been studied for their

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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.

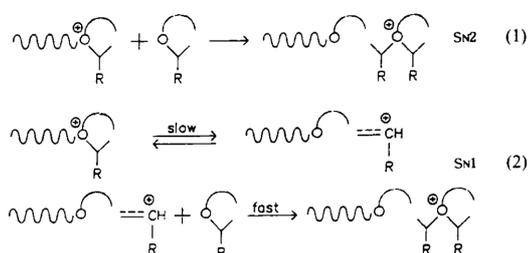
This study was investigated to know the reactivity, reactive mechanism and the process of reactivity of oxepane high explosives including MNO, MAO, MHO, which were explosive energized bonding materials and also in 5th hazardous matters under the acid catalyst polymerization. And formal charge, heat of 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<sup>[12,13]</sup>. Calculated monomers of oxepane high explosives are oxepane, MNO (methyl nitrate oxepane), MAO (methyl azide oxepane), and MHO (methyl hydrazine oxepane). Especially MNO, MAO, MHO are monomers of oxepane high explosives including explosive groups of nitrate, azido and hydrazino. 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 oxepane 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. Result and Discussion

Polymerization of oxepane high explosives monomer



Scheme 1. Reaction progress 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<sup>[4]</sup>. The process of reactivity in propagation step has been issued<sup>[4]</sup> because of (1), (2) in Scheme 1.

Charge value to the monomer of oxepane 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 <sup>13</sup>C-NMR<sup>[6]</sup> and these properties of monomer were directly proportional to the value of a negative charge of oxepane-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<sup>[14]</sup>.

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 oxepane monomers was observed. It had turned out that the value of negative charge of oxygen atom among monomers has changed

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

Oxepanes	MINDO/3				MNDO				AM1			
	O	C <sub>2</sub>	C <sub>4</sub>	C <sub>6</sub>	O	C <sub>2</sub>	C <sub>4</sub>	C <sub>6</sub>	O	C <sub>2</sub>	C <sub>4</sub>	C <sub>6</sub>
Oxepane	-0.339	0.372	0.091	0.375	-0.319	0.131	0.134	0.134	-0.281	-0.035	-0.216	-0.032
MNO	-0.327	0.380	0.115	0.383	-0.302	0.145	0.145	0.142	-0.277	-0.033	-0.177	-0.029
MAO	-0.320	0.401	0.124	0.411	-0.298	0.146	0.148	0.146	-0.273	-0.030	-0.165	-0.023
MHO	-0.313	0.415	0.236	0.415	-0.281	0.147	0.152	0.148	-0.262	-0.027	-0.134	-0.024

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 > oxepane. 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 oxepane 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<sup>[13]</sup>, 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 including nitrate group.

Table 3 showed the electric charge value calculated

Table 2. Heat of formation ( $\Delta H_f$ ) of oxepane high explosives by MINDO/3, MNDO, and AM1 methods

Oxepanes	Heat of formation (kcal/mol)		
	MINDO/3	MNDO	AM1
Oxepane	-49.338	-62.056	-51.378
MNO	-61.426	-8.343	11.817
MAO	-46.652	41.891	59.322
MHO	-35.971	117.240	136.319

Table 3. Formal charges of oxepane high explosives by AM1 method

Oxepanes	Normal form				Oxonium ion				Carbenium ion			
	O	C <sub>2</sub>	C <sub>4</sub>	C <sub>6</sub>	O	C <sub>2</sub>	C <sub>4</sub>	C <sub>6</sub>	O	C <sub>2</sub>	C <sub>4</sub>	C <sub>6</sub>
Oxepane	-0.281	-0.035	-0.216	-0.032	-0.213	0.163	0.181	0.185	-0.203	0.166	0.197	0.198
MNO	-0.277	-0.033	-0.177	-0.029	-0.203	0.180	0.192	0.195	-0.192	0.182	0.201	0.205
MAO	-0.273	-0.030	-0.165	-0.023	-0.195	0.224	0.236	0.236	-0.181	0.229	0.239	0.241
MHO	-0.262	-0.027	-0.134	-0.024	-0.188	0.256	0.268	0.269	-0.172	0.261	0.271	0.278

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

Oxepanes	Normal form				Oxonium ion				Carbenium ion			
	O	C <sub>2</sub>	C <sub>4</sub>	C <sub>6</sub>	O	C <sub>2</sub>	C <sub>4</sub>	C <sub>6</sub>	O	C <sub>2</sub>	C <sub>4</sub>	C <sub>6</sub>
Oxepane	-0.319	0.131	0.134	0.134	-0.284	0.165	0.184	0.187	-0.244	0.246	0.246	0.246
MNO	-0.302	0.145	0.145	0.142	-0.275	0.193	0.198	0.198	-0.223	0.265	0.267	0.267
MAO	-0.298	0.146	0.148	0.146	-0.247	0.241	0.246	0.245	-0.201	0.319	0.319	0.320
MHO	-0.281	0.147	0.152	0.148	-0.222	0.268	0.271	0.271	-0.181	0.351	0.352	0.352

by AM1 method for every monomer of oxepane 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 -CH<sub>2</sub>ONO<sub>2</sub>, -CH<sub>2</sub>N<sub>3</sub>, -CH<sub>2</sub>N<sub>2</sub>H<sub>3</sub> 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<sub>N</sub>1 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<sup>[15]</sup> 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 perturbation term and electrostatic attraction term, since this combine ionic bonding and covalent bonding. First par-

agraph 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 ( $\beta$ ) and matrix element which is a factor (C) of reactive centered atomic orbital. In perturbation term, the bigger the reactivity is, the bigger matrix element is, but the smaller the gap of energy of two orbitals ( $\Delta E_j$ ) is. The main reactivity by the gap of charge of reactivity substance is controlling the charge and  $\Delta E_j$  influences the reactivity to the control of the gap of energy as the effect of  $\Delta E_j$  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.

$$\Delta E = \frac{Q_{HOMO} \cdot Q_{LUMO}}{\epsilon R} + \frac{2(C_{HOMO} \cdot C_{LUMO} \cdot \beta)^2}{E_{HOMO} - E_{LUMO}} \quad (1)$$

It is summarized in Table 5 and 6 by calculating the energy level of HOMO and LUMO of oxepane 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 ( $\Delta E_j$ ) 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 oxepane, 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 oxepane, MNO, MAO and MHO. Thus, the reactivity to the polymerization of oxepane 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 oxepane 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 (19.507~

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

Oxepanes	Normal form		Oxonium ion		Carbenium ion	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
Oxepane	-10.691	2.889	-17.914	-5.658	-16.023	-8.123
MNO	-11.286	-0.095	-15.990	-5.317	-14.562	-7.537
MAO	-9.773	-0.173	-12.965	-5.142	-13.719	-7.514
MHO	-8.046	-0.261	-10.278	-4.983	-11.675	-6.863

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

Oxepanes	Normal form		Oxonium ion		Carbenium ion	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
Oxepane	-11.006	-3.101	-17.871	-5.363	-16.277	-8.028
MNO	-11.393	-0.821	-14.135	-5.278	-12.385	-6.702
MAO	-9.780	-1.256	-10.397	-5.127	-11.351	-6.811
MHO	-8.802	-1.986	-9.673	-5.722	-9.157	-6.646

**Table 7.** Heat of formation ( $\Delta H_f$ ) of normal form, protonated oxonium ion, and open carbenium ion of oxepane high explosives by AM1 method

Oxepanes	Heat of formatoin (kcal/mol)			$\Delta H_f (\Delta H_c - \Delta H_o)$ kcal/mol
	Normal form ( $\Delta H_f$ )	Oxonium ion ( $\Delta H_o$ )	Carbenium ion ( $\Delta H_c$ )	
Oxepane	-32.647	141.276	153.243	11.967
MNO	15.242	182.346	158.261	-24.085
MAO	84.590	253.912	223.091	-30.821
MHO	107.604	338.788	306.687	-32.101

**Table 8.** Heat of formation ( $\Delta H_f$ ) of normal form, protonated oxonium ion, and open carbenium ion of oxepane high explosives by MNDO method

Oxepanes	Heat of formation (kcal/mol)			$\Delta H_f (\Delta H_c - \Delta H_o)$ kcal/mol
	Normal form ( $\Delta H_f$ )	Oxonium ion ( $\Delta H_o$ )	Carbenium ion ( $\Delta H_c$ )	
Oxepane	-21.461	159.363	172.715	13.352
MNO	13.110	134.492	114.985	-19.507
MAO	67.418	235.317	211.312	-24.005
MHO	91.242	310.435	287.257	-23.178

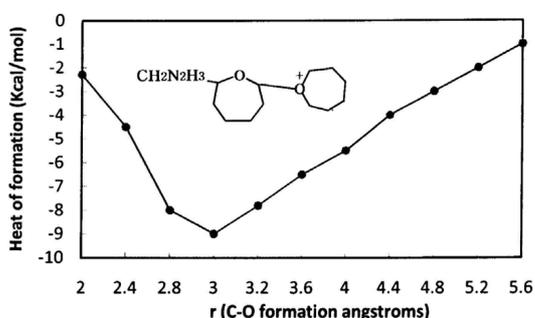
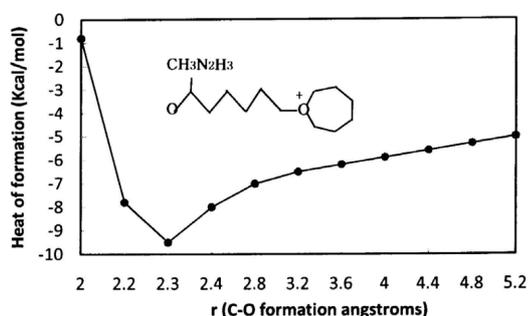
32.101 kcal/mol) in carbenium ion including explosive group ( $-\text{CH}_2\text{ONO}_2$ ,  $-\text{CH}_2\text{N}_3$ ,  $-\text{CH}_2\text{N}_2\text{H}_3$ ) made it stabilized in the equilibrium of oxonium and carbenium ion of oxepane high explosives. This is the evidence that carbenium ion, which is 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<sup>[7]</sup>.

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

formation when the monomer attacks the cyclic oxonium ion was the most stabilized form when the complex was observed at 3.00 Å.

On the other hand, the additional activating transition state of nucleophilic oxepane monomer to open carbenium ion on Fig. 2 became stable when the length of C-O formation was 2.30 Å. The length of C-O formation was longer by 1.43 Å<sup>[16]</sup> in C-O formation among molecules and shorter than 3.00 Å of C-O formation when 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 3.00 Å when oxepane monomer was added to activated cyclic oxonium ion while the length

**Fig. 1.** C-O bond formation of MHO oxonium ion and oxepane.**Fig. 2.** C-O bond formation of MHO carbenium ion and oxepane.

of formation with monomer in open carbenium ion was 2.30 Å.

And MNO, MAO and MHO, which were substituted to high explosives in Table 7 and 8 were much more stabilized by 19.507~32.101 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. Conclusions

Oxepane high explosives of 5th hazardous materials which are substituted to explosive azido group ( $-\text{CH}_2\text{N}_3$ ), nitrate group ( $-\text{CH}_2\text{ONO}_2$ ), and hydrazino 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.

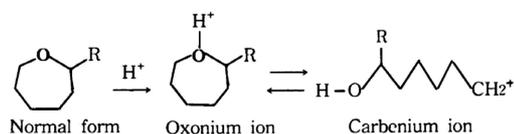
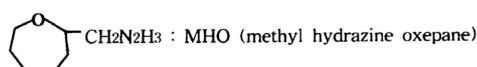
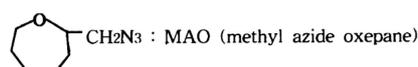
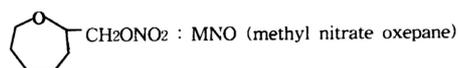
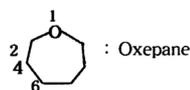
1) Oxepane high explosives had similar reactivity and the reactivity was proportional to the value of negative charge of oxygen atom, to the value of positive charge of carbon atom in propagation step, was bigger when the low LUMO energy of oxonium and carbenium ion.

2) The heat of formation of oxepane 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 oxepane ring-opening reaction in propagation step would become more stable by 19.507~32.101 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 oxepane high explosives was 3.00 Å and that of carbenium ion was 2.30 Å.

This study has led that it might be much safer in reactivity and mechanical character when oxepane 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 oxepane high explosives



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