

# CHEMICAL KINETICS OF CETANE NUMBER IMPROVING AGENTS

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## INTRODUCTION

The increasing demand for diesel fuels has resulted in the use of greater percentage of cracked distillates having poor ignition properties. The ignition properties of diesel fuels can be rated in terms of their cetane number and diesel fuels having low cetane number may have poor ignition properties such as diesel knock, difficulties to start engines in the cold weather and so on. Such diesel fuels need cetane number improving agents. In the 1940s and 1950s alkyl nitrates, alkyl nitrites and organic peroxides were found to be effective cetane number improving additives (1). Our recent study suggests that free radicals produced from thermal decomposition just before ignition should have an important role to improve their ignition properties (2). However no studies on the reaction mechanism for improving effect of these additives have been attempted because of complex nature of spontaneous ignition reaction of hydrocarbons. In order to clarify the reaction mechanism for improving effects of cetane number improving agents. We here have attempted to simulate the spontaneous ignition of n-butane as a model compound in the presence of alkyl nitrites as cetane number improving agents.

## CALCULATION METHOD

Calculations are performed using Chemkin and Senkin programs from the Sandia National Laboratories. Simulation reactions are assumed to be carried at under adiabatic condition at constant volume. Kozima's model (3) partly revised by adding thermal decomposition of cetane number improving agents was used for spontaneous ignition of n-butane in the presence of cetane number improving agents. Batt and the other's kinetic data (4) were used for simulation of the thermal decomposition of alkyl nitrites. Unknown thermochemical data were estimated by using the THERM program (5).

## RESULT AND DISCUSSION

Addition effects of n-amyl nitrite addition on ignition delay period of n-butane are shown in Fig.1. Fig.1 shows that n-amyl nitrite addition to n-butane reduces ignition

delay period suggesting that this reaction model can simulate the effect of cetane number improving agents on ignition delay period.

Fig.2 shows the mechanism for thermal decomposition of n-amyl nitrite. In the thermal decomposition of n-amyl nitrite, weak N-O bond is dissociated to produce n-amyloxy radical and nitric oxide. Then beta-fission of n-amyloxy radical immediately produce n-butyl radical. Under the preignition conditions of n-butane, n-amyl nitrite may be thermally decomposed to induce complex radical reactions that enhance the n-butane ignition reactions. Thus n-amyl nitrite would reduce the ignition delay period of n-butane spontaneous ignition.

Fig.3 and Fig.4 show effects of initial pressure and temperature on ignition delay period of n-butane in the presence of n-amyl nitrite respectively.

Table 1 shows additive effect of n-amyl nitrite, n-propyl nitrite and t-amyl nitrite on ignition delay of n-butane. The effect of n-amyl nitrite is larger than that of n-propyl nitrite and t-amyl nitrite. Our previous experimental results (2) show that the effect of n-amyl nitrite on cetane number is larger than that of n-propyl nitrite and t-amyl nitrite. The present calculation results would be much in agreement with the experimental results.

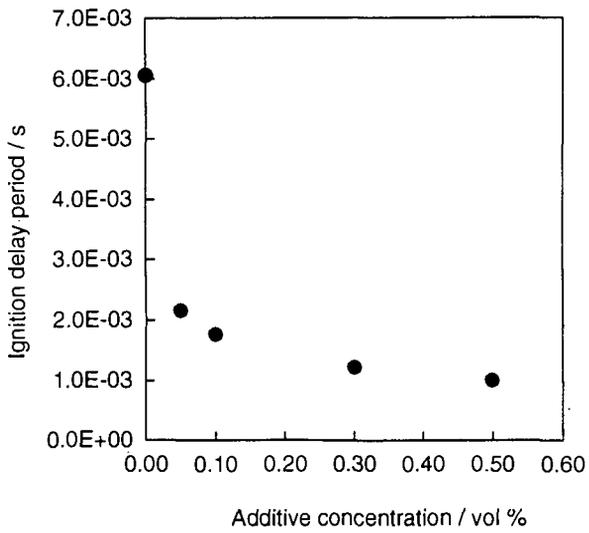
Fig.5 shows the mechanism for thermal decomposition of n-propyl nitrite and t-amyl nitrite. Thermal decomposition of n-propyl nitrite and t-amyl nitrite can produce ethyl radical. We suggest that larger ignition delay reduction effect of n-amyl nitrite than that of n-propyl nitrite and t-amyl nitrite should be due to larger reactivity of n-butyl radicals than ethyl radicals under the preignition condition of n-butane.

## CONCLUSION

In order to clarify the reaction mechanism for improving effects of cetane number improving agents, we have attempted to simulate the spontaneous ignition of n-butane in the presence of alkyl nitrites. As a result, it is shown that n-alkyl nitrite can reduce the ignition delay period of n-butane. It is known that cetane number improving agents decompose to produce alkyl radicals under operation conditions of diesel engine. We suggest that alkyl radicals produced would enhance the pre-ignition reactions of hydrocarbons to reduce ignition delay period. And it is also shown that the cetane number improving agents having higher cetane number can reduce the ignition delay period of n-butane more effectively. We also suggest that more reactive radicals should have larger effects on reduction of ignition delay period.

#### LITERATURE CITED

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- (3) Kojima, S., Combust. Flame, 99, 87(1994)
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**Fig.1 Ignition delay period vs additive concentration**

Additive : n-Amyl nitrite

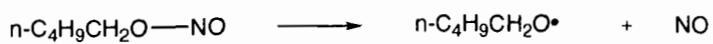
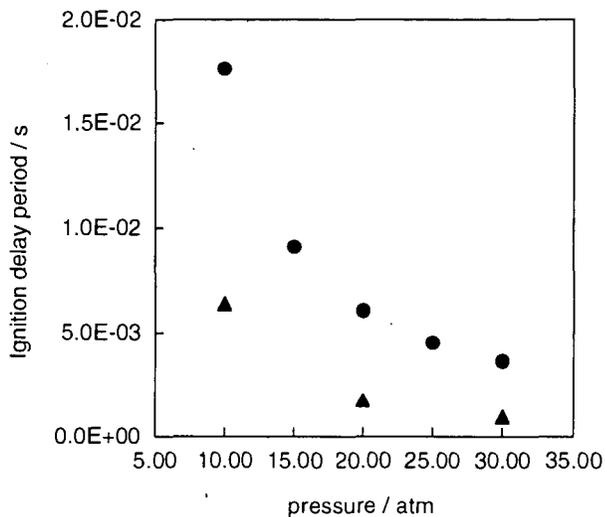


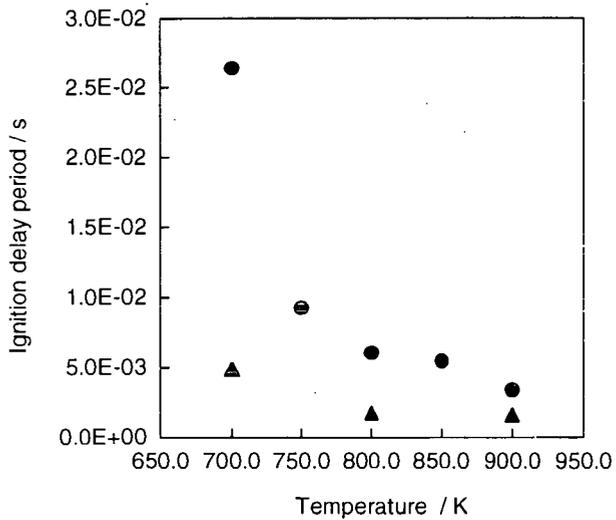
Fig.2 Mechanism for thermal decomposition n-amyI nitrite



**Fig.3 Ignition delay period vs initial pressure**

Initial temperature : 800K

- No additive
- ▲ n-Amyl nitrite 0.1 vol %



**Fig.4 Ignition delay period vs initial temperature**

Initial pressure : 20atm

- No additive
- ▲ n-Amyl nitrite 0.1 vol %

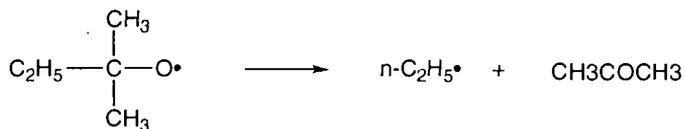
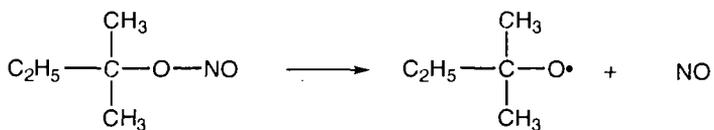


Fig.5 Mechanism for thermal decomposition of n-propyl and t-amyl nitrite

Table 1 Ignition delay period in spontaneous ignition of n-butane  
in the presence of additives

Additive concentration : 0.1 vol %

Initial temperature : 800K

Initial pressure : 20atm

Additives	Ignition delay period / $10^3$ s
n-Amyl nitrite	1.76
t-Amyl nitrite	1.92
n-Propyl nitrite	1.92