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Kinetics of Radical Polymerization
35. The Effect of N-Nitroso Compounds on Free Radical Polymerization

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SUMMARY

The effect of N-nitroso compounds on free radical polymerization has been studied in the temperature range of 30 - 70 °C. The comparison with the effect of C-nitroso compounds shows that not only the inhibitor effectivity but the inhibition mechanism are different in the case of N-nitroso compounds. The detailed kinetic investigations proved that the thermal dissociation product of N-nitroso compounds can act as scavengers of macroradicals.

INTRODUCTION

In our previous paper it was shown that aromatic C-nitroso compounds act as strong inhibitors on free radical polymerization (KENDE et al. 1972). As further extension of this investigations we have studied the effect of N-nitroso compounds on the initiated polymerization of styrene.

The polymerization was followed by dilatometric measurements and the details of the experimental method applied was the same which was described in a previous paper (KENDE et al. 1972). Azoisobutironitrile has been used as initiator in the styrene polymerization.

RESULTS AND DISCUSSION

Comparison with the effect of aromatic C-nitroso compounds shows that three main deviations occur in the case of N-nitroso compounds. One of these deviations can be seen in Fig.1. which shows the effect of N-nitroso diphenylamine on the initiated polymerization of styrene at 50 °C.

Fig.1. clearly shows that N-nitroso diphenylamine can not suppress completely the polymerization of styrene during the inhibition period, in contrast to aromatic C-nitroso compounds which practically prevent the polymerization during this period. Similar behaviour was observed in the case of other N-nitroso compounds,too. This observation shows that the inhibitor activity of N-nitroso compounds are lower at this lower tamperature range.

The other significant deviation can be observed in the values of stochiometric coefficients (μ) which shows the number of macroradicals scavenged by one inhibitor molecule. This value can be measured by kinetic methods (TÜDÖS et al. 1963a). The value of μ

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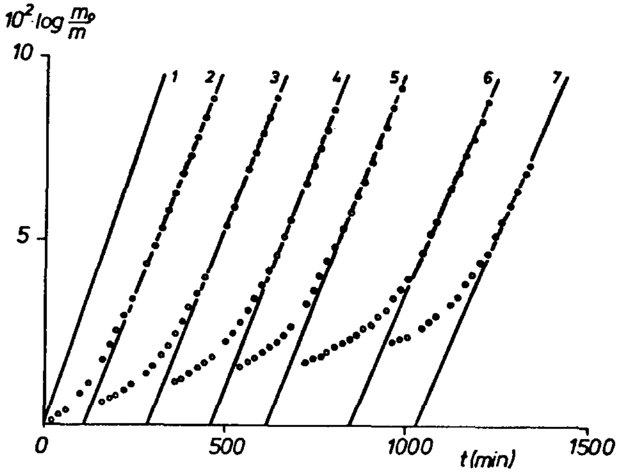


Fig.1. The log $m_0/m = f(t)$ dependence in the presence of the increasing concentration of N-nitroso diphenylamine. (For comparison No.1 shows the kinetic curve in the absence of inhibitor.)

turned out to be between 1 and 2 for the C-nitroso compounds (the theoretical value is equal to 2) but the N-nitroso compounds are more effective in the number of scavenged radicals. In the latter case the μ values were between 3 and 4. (It will be shown that the theoretical value would be 4 on the basis of the proposed mechanism.) For example this value is 3.85 ± 0.20 for N-nitroso diphenylamine.

The third particular behaviour appears in the temperature dependence of the relative reactivity which may be evaluated from the rate of polymerization during the inhibition period. Earlier detailed investigations (TÜDÖS et al. 1963b; TÜDÖS and SIMÁNDI 1962c; TÜDÖS et al. 1962b) showed that the relative reactivity of conventional inhibitors (quinones, nitro compounds etc.) had a negative temperature coefficient in contrast to the N-nitroso compounds where the temperature coefficient is positive, as can be seen in Fig.2.

Fig.2. shows that the rate of polymerization during the inhibition period is lower at higher temperatures which means that the efficiency of the inhibitor increase with increasing temperature.

These particular kinetic behaviour can be explained by the presence of a rather weak N-N bond of these N-nitroso compounds which can dissociate considerably above 50 °C (TÜDÖS and AZORI 1962a). Taking into account this possibility, two limiting cases should be considered in the interpretation of the kinetics

1) The effective inhibitor forms in a <u>preequilibrium</u> which determines the concentration of the true inhibiting species:

$$Ar_2N\text{-}N{=}O \underset{\overleftarrow{k}}{\overset{\vec{k}}{\rightleftharpoons}} Ar_2N^{\bullet} + NO^{\bullet} \xrightarrow[k_5]{R^{\bullet}} Ar_2NR + R_2NOR \qquad (1)$$

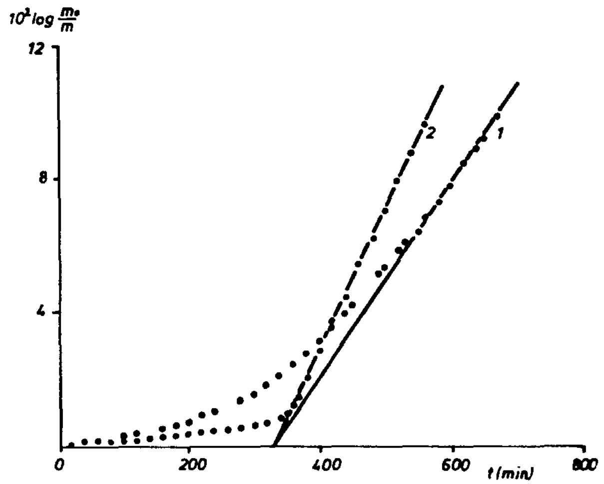
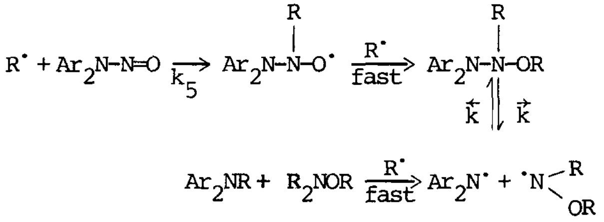


Fig.2. The comparison of kinetic curves at 70 °C (1) and 50 °C (2) in the presence of N-nitroso diphenylamine.

2) The second limiting case is when the macroradical attack is the first (rate determining) step and this is followed by a dissociation equilibrium as presented by the following scheme:



$$R^{\bullet} + Ar_2N\text{-}N{=}O \xrightarrow[k_5]{} Ar_2N\text{-}\underset{|}{\overset{R}{N}}\text{-}O^{\bullet} \xrightarrow[\text{fast}]{R^{\bullet}} Ar_2N\text{-}\overset{R}{N}\text{-}OR \quad \overleftarrow{k} \rightleftarrows \overrightarrow{k} \qquad (2)$$

$$Ar_2NR + R_2NOR \xrightarrow[\text{fast}]{R^{\bullet}} Ar_2N^{\bullet} + {}^{\bullet}N\begin{matrix} R \\ OR \end{matrix}$$

Using the usual simplifying kinetic assumptions, we derived following equation between the inhibitor (z) and the monomer (m) concentrations:

In the case of 1)

$$1 - \left(\frac{z}{z_o}\right)^{1/2} = \frac{\alpha}{2\sqrt{z_o}} \log \frac{m_o}{m} \tag{3}$$

where $\alpha = \frac{k_5}{k_2} \sqrt{\frac{\overrightarrow{k}}{\overleftarrow{k}}}$, and k_2 is the rate constant of propagation. z_o and m_o denote the inhibitor and monomer concentrations at $t = 0$.

In the case of 2) the usual kinetic relationship is valid:

$$\log \frac{m_o}{m} = \frac{k_2}{k_5} \log \frac{z_o}{z} \tag{4}$$

A comparison of eqs.(3) and (4) clearly shows that for cases where the real inhibitor is formed by dissociation equilibrium (eq.(3)) the kinetic expression is different from the usual,i.e. where the macroradical attack on the inhibitor molecule is the rate determining step (eq.(4)). This kinetic difference can be used to distinguish, between the two possible inhibition mechanisms. It is noteworthy that the activation energy of the α constant:

$$E_\alpha = E_5 + \frac{1}{2}\Delta H - E_2 \qquad (5)$$

Since ΔH can be estimated approximately as 120 k joule/mole (TÜDŐS and AZORI 1962a) and $E_5 - E_2 \sim -20$ k joule/mole (TÜDŐS et al. 1963a; TÜDŐS et al. 1963b; TÜDŐS and SIMÁNDI 1962c) which means that the value of E_α is significantly positive. This gives an explanation to the positive temperature coefficient of the relative reactivity.

The above kinetic treatments were applied to the experimental data of N-nitroso compounds. In the case of N-nitroso diphenylamine the real inhibition mechanism is between the two limiting cases in the temperature range 40 °C ÷ 60 °C. At 70 °C however, the dissociation equilibrium becomes predominant as can be seen in Fig.3. where the experimental data at different inhibitor concentrations are plotted according to eq.(3):

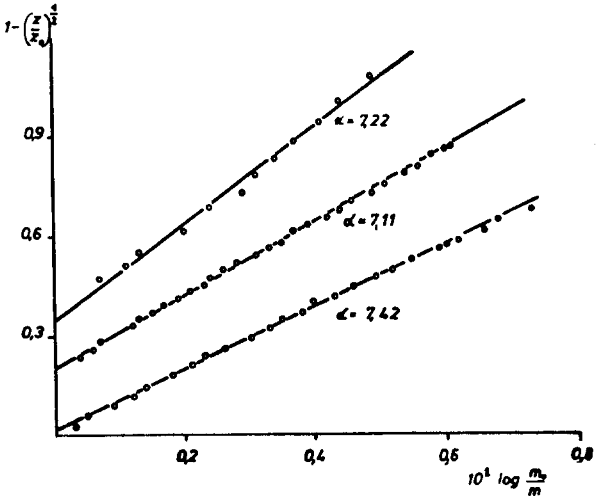


Fig.3. The experimental data of N-nitroso diphenylamine plotted according to the eq.(3). Temperature 70 °C.

For better seeing the $1-(z/z_0)^{1/2}$ - values had been shifted by 0.2 and 0.4 units at different inhibitor concentrations. Fig.3. shows that there is a fairly good linearity between the values $1-(z/z_0)^{1/2}$ and $\log m_0/m$. The computed α values are constant (within ± 5 %) irrespective of the different initial inhibitor concentrations applied.

Further investigations were aimed to obtaine informations on the bond strength of the N-N-bond i.e. the rate of dissociation if a phenyl-group is substituted by β-naphtyl- or methyl-group. Thes investigations showed that in the case of N-nitroso phenyl-naphtylamine at 60 °C the dissociation equilibrium becomes predominant but substitution of a phenyl-group by a methyl-group strongly stabilizes the N-N bond.

From these investigations some conclusion can be drawn on the reactivity and structure of the N-nitroso compounds. Since the -N=O bond of aromatic nitroso compounds has a rather strong double bond character these compounds are highly reactive in radical addition reactions. The double bond character of N-nitroso compounds on the other hand, is considerably weaker due to the following mesomeric structures:

$$>N-\bar{N}=O \longleftrightarrow\ >\overset{(+)}{N}=N-\overset{(-)}{\underline{\bar{O}}}| \longleftrightarrow\ >N-\overset{(+)}{N}-\overset{(-)}{\underline{\bar{O}}}|$$

Obviously, the decreased unsaturated character of the N=O bond in N-nitroso compounds may decrease the reactivity of these compounds.

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