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The Effects of Solvents and Metal Halides upon Radical Decompositions of Alkyl α, α' -Azobisisobutyrate

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SUMMARY

The radical decompositions of eight kinds of alkyl α, α' -azobisisobutyrate in various solvents, such as cyclohexane, benzene, acetonitrile, methanol, and acetic acid, and in methanol solution of stannic chloride or zinc chloride were investigated. It was found that the methyl α, α' -azobisisobutyrate decomposed through first-order kinetics in these solvents, but the resulting rate constants changed significantly with the kind of solvent or metal chloride used. These rate constants were also observed to correlate with the polarities and the proton-donating abilities (E_T values) of the solvents used. The activation enthalpies and entropies at 60°C were determined; the former values were kept constant independent of the reaction medium, but the latter values were changed.

It was found that the decompositions of alkyl α, α' -azobisisobutyrate having methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, and n-amyl ester groups in methanol also fit first-order kinetics, while the resulting rate constants were unchanged by their ester alkyl groups.

INTRODUCTION

It is known that α, α' -azobisisobutyronitrile (AIBN) decomposes thermally via first-order kinetics independent of the type of solvent used [1]. Recently, however, the importance of solvent effect on the thermal decomposition of AIBN was pointed out by Olivé and

Olivé [2] and Moroni [3], but the rate constants did not differ by more than a factor of 2. An increase in the rate of decomposition of AIBN by complex formation with organoaluminum compounds and silver perchlorate was noted by Hirano et al. [4] and Bamford et al. [5], respectively.

Although alkyl azobisisobutyrate (RAIB) has been known to serve as a radical initiator for vinyl polymerization, the systematic effects on its radical decomposition have not been described except in some studies by Lewis and Matheson [6], Bickel and Waters [7], and Hammond and Fox [8].

In previous papers [9-11], it was reported that some metal halides such as zinc chloride and stannic chloride markedly affected the radical polymerization and copolymerization of methyl methacrylate through the complex formation. Since the radical resulting from the decomposition of methyl α, α' -azobisisobutyrate (MAIB) is also a model for the poly(methyl methacrylate) radical, some solvents or metal halides are expected to affect the thermal decomposition step. The present paper describes the results obtained under these conditions.

On the other hand, we have stated that the reactivities of alkyl methacrylates toward polymer radicals are dependent upon the polar nature of their ester alkyl groups [12, 13]. This study also deals with the effects of the ester alkyl groups in RAIB.

EXPERIMENTAL

Materials

RAIB's having methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, and n-amyl ester groups, supplied from Wako Pure Chemicals Co., Ltd., were used. Methanol, acetic acid, acetonitrile, benzene, and cyclohexane, used as solvents, were dried and then purified by fractional distillations. Stannic chloride was used after distillation from the commercial reagent. Reagent grade zinc chloride was also used without further purification.

Rate Determinations

The rate of thermal decomposition of RAIB in solvent was determined from the change in optical density of RAIB at 365 μ due to the azo group. This λ_{\max} was not dependent on the types of alkyl groups in RAIB, and Lambert-Beer's law in all solvents used was established even if the metal halides were present. Then the rate constants for the decompositions of RAIB were calculated from the integrated form for the first-order rate equation, as follows:

$$2.303 \log D_0/D_t = kt$$

where D_0 and D_t denote the optical densities at zero and t hours, respectively, and k is the first-order rate constant.

The decompositions of RAIB, whose concentration was kept at about 0.03 mole/liter, were carried out in individual sealed glass tubes in a thermostat maintained at a given temperature without diffused light. During certain intervals, the optical density of the reaction mixture at $365\text{ m}\mu$ was measured by using a Hitachi EPU-2U spectrophotometer.

RESULTS

Decomposition of MAIB

Table 1 shows the extinction coefficients of MAIB at $365\text{ m}\mu$ in the solvents used. It was found that the extinction coefficients remained almost unchanged in the solvents and stannic chloride used.

Table 1. Extinction Coefficients of MAIB in the Solvents Used

No.	Solvent	ϵ_{365}
1	$\text{CH}_3\text{OH}-\text{SnCl}_4$	20
2	CH_3COOH	21
3	CH_3OH	19
4	CH_3CN	19
5	C_6H_6	21
6	$\text{Cyclo}-\text{C}_6\text{H}_{12}$	19

Figure 1 shows the change in ultraviolet spectra during the thermal decomposition of MAIB in acetic acid at 60°C . From this figure, it was found that the optical densities of MAIB at $365\text{ m}\mu$ decreased as a function of the reaction time. Similar results were obtained for the other RAIB and solvents used.

When $\log(D_0/D_t)$ for the decomposition of MAIB in various solvents at 60°C was plotted with the reaction time, straight lines through the origin were obtained, as shown in Fig. 2. This result indicates that the thermal decomposition of MAIB in these solvents and even in the presence of metal halides follows first-order kinetics. Table 2 shows the first-order rate constants at temperatures ranging from 40 to 70°C . It was found that these rate constants, for the same temperature, were changed by the solvents or metal halides.

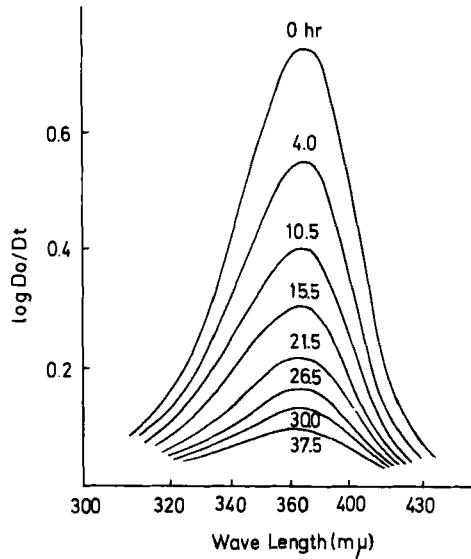


Fig. 1. Relationship between ultraviolet spectra of MAIB in acetic acid and the reaction time at 60°C.

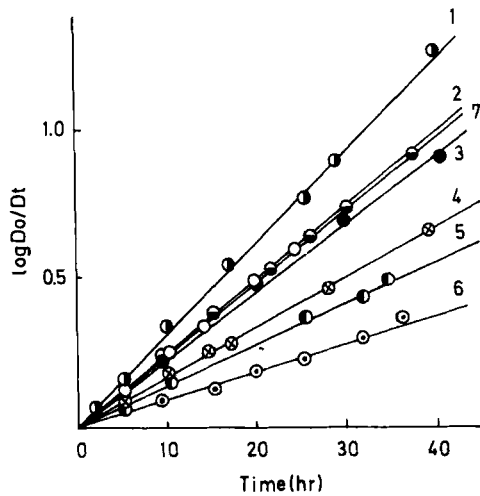


Fig. 2. First-order rate plots for the decompositions of MAIB in various solvents at 60°C. Numbers indicate the solvents listed in Table 2.

Table 2. First-Order Rate Constants for the Thermal Decomposition of MAIB in Various Solutions

No.	Solvent	Reaction temp., °C	$k \times 10^3$, hr ⁻¹
1	CH ₃ OH—SnCl ₄ ^a	40	4.34
		50	16.05
		55	30.90
		60	71.28
2	CH ₃ COOH	40	3.10
		50	11.37
		60	56.31
		70	197.7
3	CH ₃ OH	40	2.47
		50	11.22
		55	21.56
		60	51.80
		65	78.81
4	CH ₃ CN	40	1.96
		50	9.66
		55	19.01
		60	36.35
		70	128.7
5	C ₆ H ₆	50	8.00
		55	17.52
		60	31.87
		70	117.6
6	Cyclo—C ₆ H ₁₂	40	1.04
		50	4.97
		60	21.08
		70	80.05
7	CH ₃ OH—ZnCl ₂ ^b	60	54.40

^a[SnCl₄] = 1.5 moles/liter.

^b[ZnCl₂] = 1.6 moles/liter.

For comparison, the effect of stannic chloride on the thermal decomposition of AIBN in methanol was investigated. The result is shown in Fig. 3, from which we can see that the first-order rate plots were not changed in the presence or absence of stannic chloride.

The Arrhenius plots of these rate constants are shown in Fig. 4, from which the activation parameters at 60°C were determined as shown in Table 3.

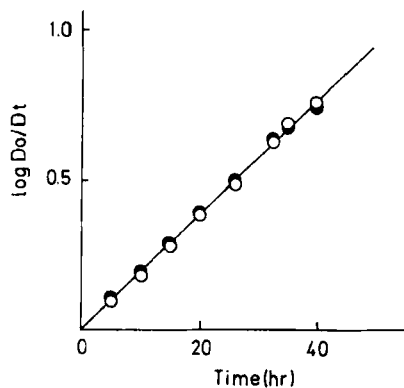


Fig. 3. First-order rate plots for AIBN in the presence (●) and absence (○) of stannic chloride in methanol at 60°C.

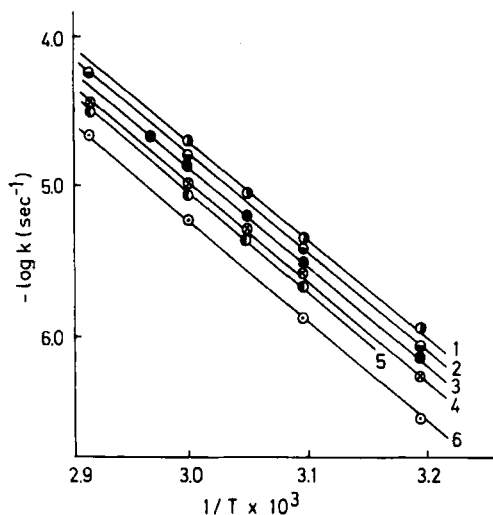


Fig. 4. Arrhenius plots for thermal decomposition of MAIB in various solvents. Numbers indicate the solvents listed in Table 2.

Decomposition of RAIB

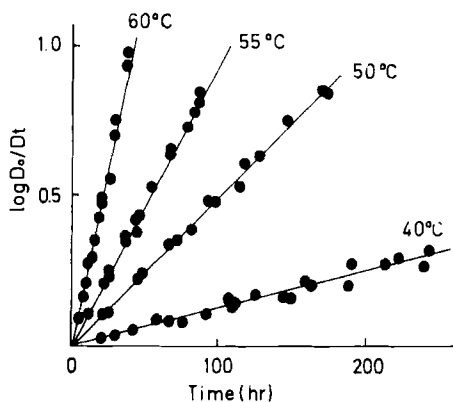
Although all RAIB's have absorption maxima at 365 μ due to the azo group, their thermal decompositions in methanol were analyzed by the same method as described above. The first-order rate plots at 40-60°C are shown in Fig. 5. These plots include data for RAIB's which contain ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, and n-amyl ester groups.

Table 3. Activation Parameters for Thermal Decomposition of MAIB at 60°C

No.	Solvent	$k \times 10^3$ at 60°C, hr^{-1}	ΔH^\ddagger , kcal/mole	ΔS^\ddagger , e.u.
1	$\text{CH}_3\text{OH}-\text{SnCl}_4^a$	71.28	28.7	5.2
2	CH_3COOH	56.31	28.7	5.1
3	CH_3OH	51.80	28.7	5.0
4	CH_3CN	36.35	28.7	4.4
5	C_6H_6	31.87	28.7	4.1
6	Cyclo- C_6H_{12}	21.08	28.7	3.3
7	$\text{CH}_3\text{OH}-\text{ZnCl}_2^b$	54.40	—	—

^a $[\text{SnCl}_4] = 1.5$ moles/liter.

^b $[\text{ZnCl}_2] = 1.6$ moles/liter. Since the reaction mixture was somewhat cloudy, the accurate value was not determined.

**Fig. 5.** First-order rate plots for thermal decompositions of RAIB in methanol.

As can be seen from this figure, the first-order rate constant for thermal decomposition of RAIB at a given temperature is not dependent on the ester alkyl groups. Accordingly, the rate constants and the activation parameters for various RAIB's were the same as those for MAIB indicated in Tables 2 and 3.

DISCUSSION

As can be seen from Table 2, MAIB decomposed three or four times faster in methanol-stannic chloride than in cyclohexane. Such an effect was quite different from that observed for AIBN, which was found to decompose at the same rate in the solvents used except for cyclohexane [1]. It is interesting to note that a pronounced effect of solvents and metal halides on the thermal decomposition of MAIB was observed, as compared with that of AIBN.

From the results of the activation parameters shown in Table 3, the activation enthalpies were kept constant at 28.7 kcal/mole but the activation entropies increased from 3.3 to 5.2 e.u. as the solvent was changed and the stannic chloride was added. These observations were also different from those of thermal decompositions of AIBN [3] and phenylazotriphenylmethane [14], for which an isokinetic relationship was observed as the result of both the solvation in the ground state and the desolvation in the transition state; i.e., the increase in the activation enthalpy was compensated for by the decrease in the activation entropy.

Since the absorption maxima and the extinction coefficients of MAIB at 365 $m\mu$ were almost constant in these solvents, as shown in Table 1, it might be assumed that the electronic state of the azo group was not largely affected by the nature of the solvents used. However, the interaction between the carbonyl oxygen in MAIB and the solvent might be changed by the kind of solvent used. The complexes of AIBN with some metal halides have been isolated by Haas [15] and Hirano et al. [4], and those of methyl methacrylate, whose polymer radical has a similar structure to the model radical from MAIB, were isolated by the present authors [9-11].

From Table 3, the solvent effect on thermal decomposition of MAIB was found to be entropy-determining and hence the activation entropies decreased with the solvents used in the following order: $\text{CH}_3\text{OH}-\text{SnCl}_4 > \text{CH}_3\text{COOH} > \text{CH}_3\text{OH} > \text{CH}_3\text{CN} > \text{C}_6\text{H}_6 > \text{cyclo-C}_6\text{H}_{12}$. This order does not coincide with the dielectric constants of the solvents, but it is the same as that of the decreasing E_T values of solvents, which are a measure of the polarities and the proton-donating abilities of the solvents [16]. Such a correlation is shown in Fig. 6, in which the E_T value for cyclohexane is the same as that for *n*-hexane. A similar correlation was observed between the relative reactivities of methyl methacrylate toward the polystyryl radical in the monosubstituted benzene solvents [17].

The fact that the rate constant was correlated with the polarities and the proton-donating ability of the solvent might suggest that the interaction between the carbonyl oxygen and the solvent predominantly affected the decomposition rate of azoester. The addition of stannic chloride or zinc chloride, which was expected to form the

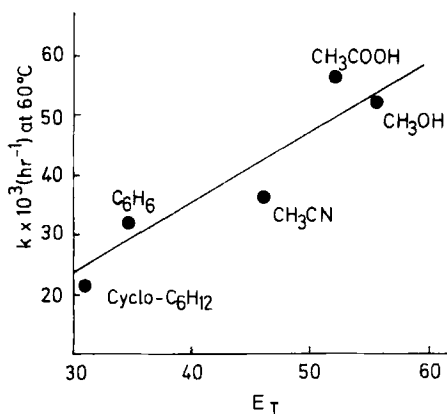


Fig. 6. Relationship between the first-order rate constants for the decomposition of MAIB at 60°C and the E_T values of the solvents used.

complex with MAIB, might have strengthened the solvation in the ground state of MAIB to increase the activation entropy.

A possible explanation for these entropy-controlled solvent effects on decompositions is as follows: In the ground state of MAIB the solvent interacts with its carbonyl oxygen by dipole-dipole interaction or by hydrogen bonding, as shown in Fig. 7. Such interaction might be weakened to some extent by the delocalization of its unpaired electron in the transition state. Accordingly, it might be considered that the increased solvation of MAIB in the ground state would lead to increase in its activation entropy.

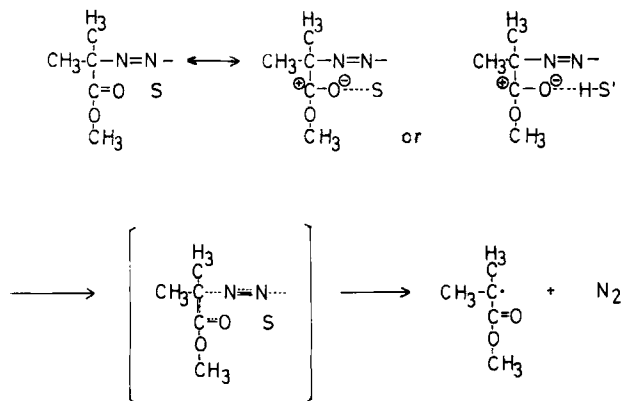


Fig. 7. Reaction scheme for thermal decomposition of MAIB.

However, the effect of the ester alkyl groups in RAIB on their thermal decomposition in methanol was not observed. This finding might suggest that the structural change in the ester group of RAIB was not significant. Hence it was noted that the effect of the solvents on the thermal decomposition of RAIB was greater than the effect of their ester alkyl groups.

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