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Solvent Effects in the Oxidation of Hydrocarbons. I. Chain Initiation by Azobisisobutyronitrile

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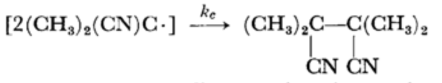
The effects of solvents on the rate of decomposition and the efficiency of radical production by AIBN were studied by measuring the rate of evolution of nitrogen from AIBN and the inhibition time in the oxidation of tetralin. The rates of decomposition of AIBN were larger in aromatic solvents than in aliphatic solvents. The efficiency of AIBN was found to depend more on the viscosity of the medium than on the polarity of the solvents. The requirements for the determination of the inhibition time are discussed.

Azobisisobutyronitrile (AIBN) is one of the most widely used initiators for the radical reactions such as autoxidation and polymerization. The mechanism for the initiation by AIBN has been thoroughly studied by numerous investigators and confirmed to proceed by the following equations, where brackets indicate pairs of radicals which have not been separated by diffusion.[1]

$$\mathrm{AIBN} \xrightarrow{k_i} [2(\mathrm{CH_3})_2(\mathrm{CN})\mathrm{C}\cdot] + \mathrm{N_2} \qquad (1)$$



$$[2(\mathrm{CH_3})_2(\mathrm{CN})\mathrm{C}\cdot] \xrightarrow{k_c} (\mathrm{CH_3})_2\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\!-\!\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}(\mathrm{CH_3})_2 + \text{disproportionation products} \qquad (2)$$

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[1] C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3233 (1955).

$$[2(\mathrm{CH_3})_2(\mathrm{CN})\mathrm{C}\cdot] \xrightarrow{k_d} 2(\mathrm{CH_3})_2(\mathrm{CN})\mathrm{C}\cdot \xrightarrow{\mathrm{O_2}} \text{initiate chains} \tag{3}$$

It is known that the efficiency of the radical production by the thermal decomposition of AIBN, which can be expressed as $e=k_d/(k_c+k_d)$, is smaller than unity. This phenomenon has been explained as being due to the geminate recombination of demethylcyanomethyl radical in the solvent cage to from tetramethylsuccinonitrile and the disproportionation product, ketenimine. The solvent effects on the decomposition of AIBN have been studied by several investigators,[2] but a definite conclusion has not yet been obtained. In the course of our study on the solvent effects in the autoxidation of hydrocarbons, the effects of solvents in the initiation step by AIBN had to be elucidated. The rate of decomposition and the efficiency of radical production of AIBN were studied in the various solvents.

Theoretical

The mechanism of the autoxidation of hydrocarbons in the liquid phase at moderate temperature under sufficient oxygen pressure is represented as follows.

$$\mathrm{RH} \rightarrow \mathrm{R}\cdot \qquad R_i = 2ek_i[\mathrm{AIBN}] \tag{4}$$

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{RO_2}\cdot \tag{5}$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_p} \mathrm{ROOH} + \mathrm{R}\cdot \tag{6}$$

$$\mathrm{RO_2}\cdot + \mathrm{RO_2}\cdot \xrightarrow{k_t} \text{non-radical products} + \mathrm{O_2} \tag{7}$$

When the inhibitor IH is added to the system, the following fast termination step replaces the normal termination reaction (7).

$$\mathrm{RO_2}\cdot + \mathrm{IH} \xrightarrow{k_{inh}} \mathrm{ROOH} + \mathrm{I}\cdot \tag{8}$$

$$\mathrm{RO_2}\cdot + \mathrm{I} \xrightarrow{\text{fast}} \mathrm{ROOI}\cdot \tag{9}$$

In this case, the values of ek_i can be obtained by measuring the inhibition time, t_{inh}, using the equation[1]

$$t_{inh} = n[\mathrm{IH}]/R_i = n[\mathrm{IH}]/2ek_i[\mathrm{AIBN}], \tag{10}$$

where n represents the number of peroxy radicals which are scavenged by each inhibitor molecule.

This inhibition method is useful not only for determination of the rate or efficiency of intiation but also for comparing the activities of various inhibitors for polymers, oils, *etc.* It is important to confirm the validity and accuracy of this technique. The two reactions (7) and (8) are competitive and Eq. (10) is applicable only when reactions (8) and (9) replace completely reaction (7). The ratio of the rate of reaction (8) to that of (7) is given by

$$\frac{V_8}{V_7} = \frac{k_{inh}[\mathrm{IH}][\mathrm{RO_2}\cdot]}{2k_t[\mathrm{RO_2}\cdot]^2} = \frac{k_{inh}[\mathrm{IH}]}{2k_t[\mathrm{RO_2}\cdot]} \tag{11}$$

where V_8 and V_7 represent the rates of reactions (8) and (7) respectively. The steady state treatment for the elementary steps (4), (5), (6), (7), (8) and (9) gives the concentration of the peroxy radical as

$$[\mathrm{RO_2}\cdot] = \{-k_{inh}[\mathrm{IH}] + (k_{inh}^2[\mathrm{IH}]^2 + 2k_tR_i)^{1/2}\}/2k_t \tag{12}$$

Substitution of Eq. (12) into Eq. (11) yields

$$\frac{V_8}{V_7} = \frac{1}{-1+\{1+4ek_ik_t[\mathrm{AIBN}]/k_{inh}^2[\mathrm{IH}]^2\}^{1/2}} \tag{13}$$

Therefore, the importance of reactions (8) and (7) in the specific reaction system is determined by the value of [AIBN]/[IH]^2, and the contribution of reaction (8) decreases with the increase in this value.

TABLE 1. CONTRIBUTION OF THE TWO TERMINATION STEPS IN THE OXIDATION OF TETRALIN AT 70°C WITH 1.00×10^{-2}M AIBN

[IH] M	[AIBN]/[IH]	[AIBN]/[IH]^2 M^{-1}	V_8/V_7	Percent of reaction (8)
5.00×10^{-3}	2.0	4.0×10^{2}	292	99.7
2.00×10^{-3}	5.0	2.5×10^{3}	48.3	98.0
1.00×10^{-3}	10	1.0×10^{4}	12.3	92.5
5.00×10^{-4}	20	4.0×10^{4}	3.40	77.3
2.00×10^{-4}	50	2.5×10^{5}	0.782	43.9
1.00×10^{-4}	100	1.0×10^{6}	0.311	23.7
1.00×10^{-5}	1000	1.0×10^{8}	0.0250	2.45

IH: 2,6-di-*t*-butyl-4-methylphenol

In Table 1 are summarized the calculated values of V_8/V_7 for the oxidation of tetralin at 70° with 1.00×10^{-2}M of AIBN at various concentrations of 2,6-di-*t*-butyl-4-methylphenol (BMP), a well known inhibitor. n was assumed to be 2.0.[3] The value of k_t was taken as 8.0×10^6 *l*/mol/sec, k_{inh} as 7.0×10^3 *l*/mol/sec, e as 0.65, and k_i as 3.96×10^{-5} sec^{-1}, respectively, from literature values.[4] Table 1 shows how the relative contribution of the termination reaction (8) decreases with the decreases in the concentration of the inhibitor. When the relative importance of the termination reaction (7) is not small enough, Eq. (10) is not applied and the value of ek_i thus measured may be unreliable.

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[2] a) L. M. Andronof and G. E. Zaikov, *Kinetika i Kataliz*, **8**, 270 (1967); b) O. Yamamoto, J. Yamashita and H. Hashimoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **71**, 223 (1968), and the papers cited therein.

[3] E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 263, 269, 985 (1966).

[4] E. Niki, Y. Kamiya and N. Ohta, This Bulletin, in press.

TABLE 2. REQUIRED CONCENTRATIONS OF THE INHIBITOR IN THE OXIDATION OF TETRALIN, α-METHYLSTYRENE AND CUMENE AT 70°C, $V_8/V_7 \geqq 40$

[AIBN] M	[IH]≧, M ([AIBN]/[IH]≦)		
	Tetralin	α-Methylstyrene	Cumene
1.00×10^{-1}	5.74×10^{-3} (17.4)	3.04×10^{-3} (32.9)	5.28×10^{-4} (189)
4.00×10^{-2}	3.63×10^{-3} (11.0)	1.92×10^{-3} (20.8)	3.33×10^{-4} (120)
2.00×10^{-2}	2.57×10^{-3} (7.78)	1.36×10^{-3} (14.7)	2.36×10^{-4} (84.7)
1.00×10^{-2}	1.81×10^{-3} (5.52)	9.62×10^{-4} (10.4)	1.67×10^{-4} (59.9)
1.00×10^{-3}	5.74×10^{-4} (1.74)	3.04×10^{-4} (3.29)	5.28×10^{-5} (18.9)

IH: 2,6-*t*-butyl-4-methylphenol

As is clear from Eq. (13), the relative importance of reaction (8) depends also on the value of k_t, *i. e.*, on the hydrocarbons. In Table 2 are shown the calculated concentrations of the inhibitor required to make the value of V_8/V_7 larger than 40, corresponding to 97.5% termination by inhibitor, in the oxidation of tetralin ($k_t=8.0\times10^6$ *l*/mol/sec), α-methylstyrene ($k_t=1.0\times10^6$ *l*/mol/sec), and cumene ($k_t=3.0\times10^4$ *l*/mol/sec) at 70°C with various concentrations of AIBN. The values of k_{inh} for the oxidation of α-methylstyrene and cumene were taken as 4.7×10^3 and 1.6×10^3 *l*/mol/sec, respectively, from the fact that the relative reactivities of tetralylperoxy, α-methylstyrylperoxy and cumylperoxy radicals are in the ratios of 4.5 : 3.0 : 1.0.[4] Table 2 suggests that the required concentration of the inhibitor is largely dependent on the hydrocarbons and the concentration of the initiator.

As described above, the concentrations of AIBN and the inhibitor used in the determination of the inhibition time should be carefully chosen in order to satisfy the above requirements and to obtain accurate and reasonable data. These important conditions seem to have been overlooked until now, and the inhibition time has been determined with an insufficient amount of inhibitor.

Results and Discussion

The rate constant for the unimolecular decomposition of AIBN was determined by measuring the rate of nitrogen evolution. The inhibition time was measured in the oxidation of tetralin using 2,6-di-*t*-butyl-4-methylphenol (BMP) as an inhibitor assuming that 2 radicals reacted with one molecule of inhibitor.[3]

Equation (10) suggests that the inhibition time is proportional to the concentration of the inhibitor and inversely proportional to the concentration of AIBN. Figure 1 shows that the inhibition time in

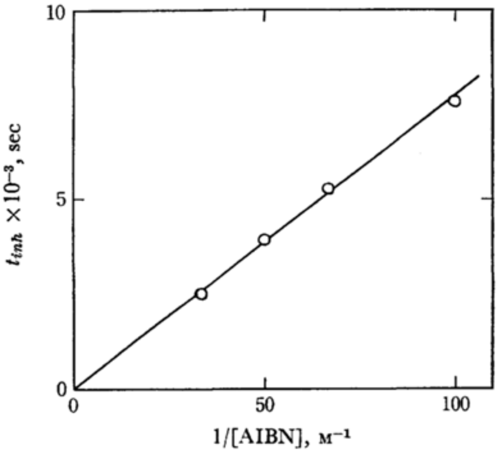

Fig. 1. Inhibition time in the oxidation of tetralin in chlorobenzene at 70°C.
[Tetralin]=1.47M, [BMP]=2.00×10^{-3}M

TABLE 3. INHIBITION TIME IN THE OXIDATION OF TETRALIN IN CHLOROBENZENE AT 70°C, [tetralin]=1.47 M

$[\mathrm{AIBN}]\times10^2$ M	$[\mathrm{BMP}]\times10^3$ M	t_{inh} sec	$t_{inh}/([\mathrm{IH}]/[\mathrm{AIBN}])$ $\times10^{-4}$, sec
10.0	6.04	2140	3.54
4.00	3.67	3280	3.57
3.00	2.00	2350	3.53
2.00	2.00	3730	3.73
1.50	2.00	5100	3.82
1.00	2.00	7360	3.68

TABLE 4. INHIBITION TIME, RATE CONSTANT FOR DECOMPOSITION AND EFFICIENCY OF AIBN IN THE OXIDATION OF TETRALIN IN THE VARIOUS SOLVENTS AT 70°C, [tetralin]=1.47M

Solvent	$D^{a)}$	$\eta^{b)}$ centipoise	$t_{inh}{}^{c)}$ sec	$ek_i\times10^5$ sec⁻¹	$k_i\times10^5$ sec⁻¹	e
Chloro-benzene	4.440	0.5568	2140	2.82	4.10	0.688
Anisole	3.651	0.6232	2350	2.55	3.89	0.656
Nitro-benzene	21.10	0.9694	2200	2.73	4.70	0.581
Acetophe-none	11.21	0.8958	2390	2.51	4.41	0.569
Butyric acid	2.937	0.8232	2920	2.05	3.64	0.563
n-Decane	2.069	0.5633	3790	1.58	3.05	0.518
Diethyl maleate	5.811	1.211	3370	1.78	3.64	0.489
Tetralin[d]	2.657	0.9869	2935	2.02	4.22	0.483
Butyl stearate	2.857	2.337	5020	1.20	3.67	0.327

a) Dielectric constant of the solution measured at 70°C.
b) Viscosity of the solution measured at 70°C.
c) Inhibition time measured at 70°C in the presence of 0.100M AIBN and 66.00×10^{-3}M BMP.
d) Pure tetralin.

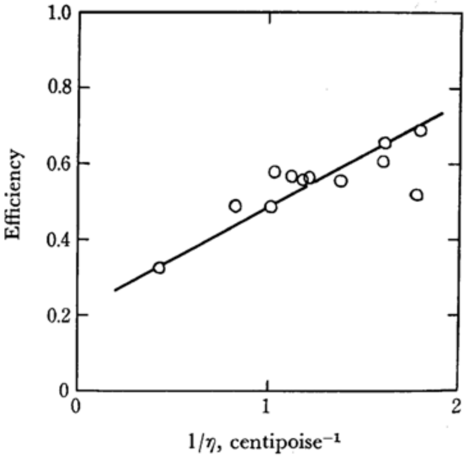

Fig. 2. Plots of efficiency of AIBN as a function of viscosity of the solution.

the oxidation of tetralin in chlorobenzene solvent is inversely proportional to the concentration of AIBN. In addition, Table 3 indicates that the inhibition time is proportional to [IH]/[AIBN]. Since all the solvents used in this study were found to be really inert under the reaction conditions employed here and since sufficient amount of inhibitor was used in the measurement, it may be said that Eq. (10) applies for solvents other than chlorobenzene.

The inhibition time in the oxidations of tetralin in various solvents with added AIBN and BMP is summarized in Table 4. The values of ek_i calculated from Eq. (10), the measured rate constant for the decomposition of AIBN, and calculated efficiency of chain initiation are also included in Table 4. Both k_i and e were reproducible within an experimental error of about 5%. The results indicate that both k_i and e are dependent on the reaction medium. The rate of decomposition of AIBN differs by a factor of 1.54, and is a little higher in an aromatic than in an aliphatic solvent. The efficiency of initiation differs by a factor of 2.10 ranging from 0.33 to 0.69. It depends mostly on the viscosity of the oxidizing solution and is a nearly linear function of the reciprocal of the viscosity, as shown in Fig. 2. Such a correlation has been observed in other systems.[5] However, there is also some contribution to this efficiency from the dielectric constant of the solution: the three solvents that give the greatest positive deviations from the indicated line, nitrobenzene, acetophenone, and diethyl maleate, also have the highest dielectric constants, and in the same order. *n*-Decane, which gives the greatest negative deviation, has the lowest dielectric constant.

TABLE 5. INHIBITION TIME, RATE CONSTANT FOR DECOMPOSITION AND EFFICIENCY OF AIBN IN THE OXIDATION OF TETRALIN IN CHLOROBENZENE AT 70°C, [AIBN]=0.100M, [BMP]=6.00×10^{-3}M

[Tetralin] M	D	η centipoise	t_{inh} sec	$ek_i\times10^5$ sec^{-1}	$k_i\times10^5$ sec^{-1}	e
7.35	2.657	0.9869	2935	2.02	4.22	0.483
5.88	3.086	0.8424	2650	2.26	4.04	0.559
4.41	3.509	0.7238	2410	2.49	4.47	0.557
2.94	4.017	0.6257	2290	2.62	4.33	0.605
1.47	4.440	0.5568	2140	2.82	4.10	0.668

The effect of dilution by chlorobenzene was also studied. As shown in Table 5, the effect of medium change on k_i is less than the experimental error, and e is approximately a linear function of the reciprocal of the viscosity (Fig. 2).

Experimental

Tetralin and various solvents used were the same as in the previous paper.[6] AIBN and 2,6-di-*t*-butyl-4-methylphenol were recrystallized from methanol several times.

The inhibition time was determined by performing the oxidation of tetralin in a variety of solvents with added inhibitor under atmospheric pressure of oxygen in a constant pressure closed system. The rates of decomposition of AIBN in the various solvents were determined by measuring the rate of nitrogen evolution using a buret connected to the constant closed system under atmospheric pressure of nitrogen. Oxygen which might possibly interfere with the accurate measurement of the nitrogen evolution was carefully eliminated from the system. The viscosity was measured at 70°C with a modified Ostwald viscometer.

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5) O. Dobis, J. M. Pearson and M. Szwarc, *J. Am. Chem. Soc.*, **90**, 278 (1968).

6) E. Niki, Y. Kamiya and N. Ohta, This Bulletin, in contribution.