

## Thermal Decomposition of Additive Polymerization Initiators. I. Azobisisobutyronitrile

HIDEKI SASAKI and MASAKO NAGAYAMA, *Department of Industrial Chemistry, Faculty of Engineering, Chiba University, Chiba City, Japan*

### Synopsis

We measured the rate of thermal decomposition of azobisisobutyronitrile (AIBN) from the rate of loss of 2,2-diphenylpicrylhydrazyl (DPPH) on reaction of the free radicals formed by thermal decomposition of azobisisobutyronitrile (AIBN) in organic solvents with DPPH. There has been some doubt about the quantitative relation between AIBN and DPPH required to get the rate constant of thermal decomposition of AIBN. In the past, AIBN has been used in excess, and the rate constants measured by using DPPH are smaller than they ought to be. In our experiments we used as little of AIBN relative to DPPH as possible and obtained a value of  $3.8 \times 10^{-4} \text{ min.}^{-1}$  at  $50^\circ\text{C.}$  as the rate constant of the first-order reaction, which was shown satisfactorily by the linearity of the graph. We also obtained 32 kcal./mole as activation energy. We were also able to make clear the meaning of the result when a large quantity of AIBN was used.

### INTRODUCTION

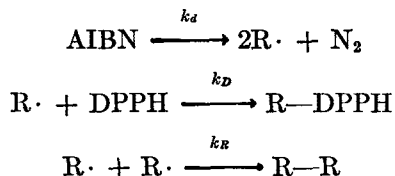
The method of measurement of the rate of thermal decomposition of 2,2-azobisisobutyronitrile in organic solvents, which is used as a polymerization initiator, by using a 2,2-diphenylpicrylhydrazyl, has been studied by Bawn and Mellish<sup>1</sup> and other investigators.<sup>2,3</sup> Bawn and Mellish used more than twentyfold as much AIBN as DPPH and reported that the result was just as they had expected. Walling<sup>4</sup> expressed as the efficiency of initiators the difference between the rate constant measured by nitrogen evolved and that by DPPH fading. What causes this efficiency has been explained as the effect of the "cage" reaction.

A study of polymerization by ultrasonic waves led to some doubts about the investigation method that had been in use. It is natural from the standpoint of physical chemistry that plenty of scavenger must be used to make all the free radicals formed to react completely.

### THEORY

When AIBN undergoes thermal decomposition in organic solvents, it evolves  $\text{N}_2$  and forms 2,3-dicyano-2,3-dimethylbutane. On reacting with DPPH, AIBN forms 1-cyanoisopropyl-2,2-diphenyl-1,1-picryl hydrazine. In either reaction AIBN first causes free radicals of cyano-isopropyl. This

formation of radicals is considered to be a first-order reaction, no matter what the product may be. Then it is considered that when thermal decomposition takes place in DPPH solution, there are produced a compound of diradical and a compound of radical and DPPH, though there may be a quantitative difference, depending on the conditions; that is:



where  $k_d$ ,  $k_D$ , and  $k_R$  are the rate constants of respective reaction.

Therefore the rate of loss of DPPH may be written as:

$$\frac{-d[\text{DPPH}]}{dt} = \frac{-k_D[\text{DPPH}][\text{R}\cdot]}{k_D[\text{DPPH}][\text{R}\cdot] + k_R[\text{R}\cdot]^2} \frac{d[\text{R}\cdot]}{dt} \quad (1)$$

where  $d[\text{R}\cdot]/dt$  is the rate of radical formation. In this reaction each product may be made in quantities corresponding to the concentration of DPPH and free radicals formed.

Suppose the following conditions be put into eq. (1):

(A)  $[\text{DPPH}] \gg [\text{R}\cdot]$ , i.e., the concentration of DPPH is much higher than that of free radicals formed; (B)  $[\text{DPPH}] \ll [\text{R}\cdot]$ , i.e., the concentration of DPPH is extremely low compared with that of radicals; (C) generally ordinary concentrations.

Under condition A, the denominator of the right-hand term of eq. (1) will be considered as

$$k_D[\text{DPPH}][\text{R}\cdot] + k_R[\text{R}\cdot]^2 \doteq k_D[\text{DPPH}][\text{R}\cdot]$$

Therefore

$$-d[\text{DPPH}]/dt = -d[\text{R}\cdot]/dt \quad (2)$$

The quantity of radicals, which reacted with DPPH, is equal to that formed by thermal decomposition,

$$\left| -\frac{d[\text{R}\cdot]}{dt} \right| = \left| \frac{d[\text{R}\cdot]}{dt} \right|$$

and there are the following relations between initiator and radical when the radical is formed by thermal decomposition,

$$-2d[\text{AIBN}] = d[\text{R}\cdot]$$

when radical is consumed in the reaction with DPPH,

$$-2d[\text{AIBN}] = -d[\text{R}\cdot]$$

and the initiator is a latent radical

$$2[\text{AIBN}] = [\text{R}\cdot] \quad (3)$$

From the supposition that the decomposition of initiator is a first-order reaction,

$$1/2 d[\text{R}\cdot]/dt = d[\text{AIBN}]/dt = k_d[\text{AIBN}] \quad (4)$$

or

$$\ln [\text{AIBN}]_0/[\text{AIBN}] = k_d t \quad (5)$$

where  $[\text{AIBN}]_0$  and  $[\text{AIBN}]$  are the concentration of AIBN at zero time and time  $t$ . Though the concentration of DPPH has no relation with eq. (4) or (5), the initial concentration of AIBN and the changing quantity of DPPH, through which the changing quantity of AIBN is indirectly measured, are important. Therefore, so long as the extinction coefficient of DPPH is accurate, impurities give no optical effect and the concentration of DPPH does not matter theoretically. To obtain the value  $k_d$  we should experiment under condition A.

Under condition B, which has been considered necessary to obtain the rate constant of thermal decomposition of AIBN, the denominator of the right hand term of eq. (1) will be

$$k_D[\text{DPPH}][\text{R}\cdot] + k_R[\text{R}\cdot]^2 \doteq k_R[\text{R}\cdot]^2$$

Therefore

$$-d[\text{DPPH}]/dt = -k_D[\text{DPPH}][\text{R}\cdot]d[\text{R}\cdot]/k_R[\text{R}\cdot]^2 dt \quad (6)$$

$$-d[\text{DPPH}]/[\text{DPPH}] = -k_D d[\text{R}\cdot]/k_R[\text{R}\cdot] \quad (7)$$

With eq. (3), we have  $-d[\text{DPPH}]/[\text{DPPH}] =$

$$-2k_D d[\text{AIBN}]/2k_R[\text{AIBN}]$$

Hence,

$$\ln ([\text{DPPH}]_0/[\text{DPPH}]) = k_D/k_R \ln ([\text{AIBN}]_0/[\text{AIBN}]) \quad (8)$$

$$= (k_D/k_R)/k_d t \quad (9)$$

The rate constant of DPPH loss indicated a pseudo first-order reaction when a large amount of AIBN was used. In this case, the reaction of AIBN indicated a pseudo first-order reaction also. Equation (8) shows that there is a proportional relation, by which  $\ln ([\text{AIBN}]_0/[\text{AIBN}])$ , when multiplied by  $k_D/k_R$ , becomes  $\ln ([\text{DPPH}]_0/[\text{DPPH}])$ .

Under condition C, when we resolve the differential eq. (1) as homogeneous, it follows that

$$\ln \frac{[\text{DPPH}]_0}{[\text{DPPH}]} = \left( \frac{1}{K} - 1 \right) \ln \frac{1 + 2[(1/K) - 1] [\text{AIBN}]_0/[\text{DPPH}]_0}{1 + 2[(1/K) - 1] [\text{AIBN}]/[\text{DPPH}]} \quad (10)$$

where  $K = k_D/k_R$ .

We can draw figures of eqs. (5) and (9), but cannot do so with eq. (10). We must give  $K$  a reasonable value and try to find some means to ascertain the validity of eq. (10).

## EXPERIMENTAL

Commercial AIBN and DPPH used in this experiment were purified by recrystallizing twice from ether. A color meter made by Tokyo-Koden Co. was used with which it was possible to estimate the concentration of 0–50 mg./l. of DPPH. The air was removed by bubbling  $N_2$  through a toluene solution containing a weighed amount of DPPH in a constant-temperature bath. We quickly poured a weighed amount of AIBN dissolved in toluene into the solution. The starting point of the reaction was taken as that time when we finished pouring. Aliquots were taken at regular intervals, and we measured the extinction of this DPPH solution. In accord with Lambert-Beer's law we obtained the change in concentration of DPPH, which could be converted in the concentration of AIBN.

## RESULTS

Figures 1 and 2 are graphs showing  $\ln [AIBN]_0/[AIBN]$  against time at 50 and 60°C., respectively. We changed only the concentration of AIBN

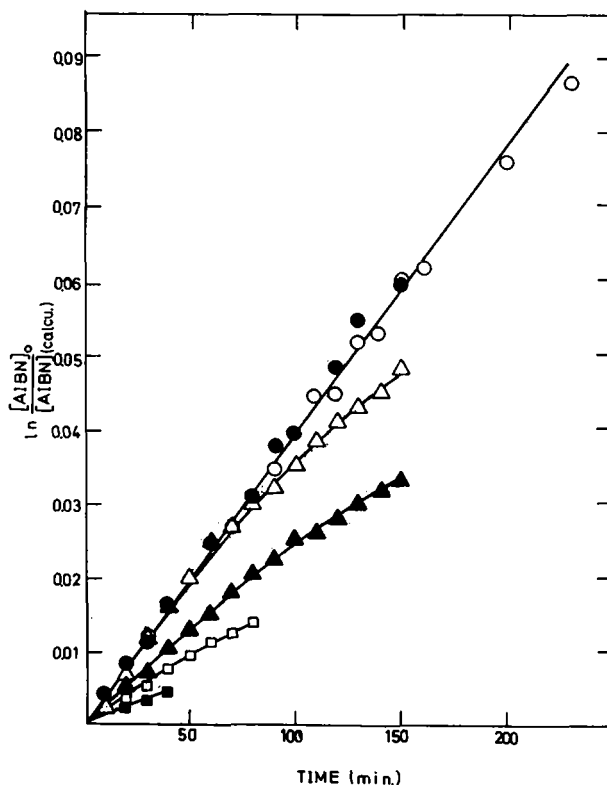


Fig. 1. Decomposition of AIBN in various concentrations in toluene at 50°C.: (■) [AIBN] = 1116 mg./l.; (□) [AIBN] = 558 mg./l.; (▲) [AIBN] = 250 mg./l.; (△) [AIBN] = 125 mg./l.; (●) [AIBN] = 63 mg./l.; (○) [AIBN] = 32 mg./l.

and kept the concentration of DPPH constant because of the limits of the photometer we used. As we increased the concentration of AIBN relative to DPPH (Figs. 1 and 2), the value of  $\tan \theta$ , the gradient of lines, became smaller. When the concentration of AIBN was as low as possible, the line became straight, but it began to curve as the concentration of AIBN became higher. In these cases the values of the rate constant, as first-order reaction, changed with time.

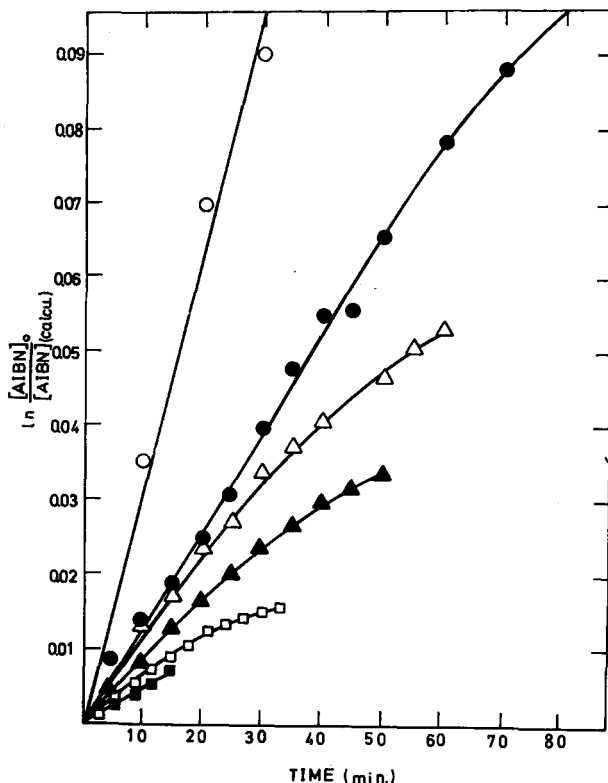


Fig. 2. Decomposition of AIBN in various concentrations in toluene at 60°C.: (■) [AIBN] = 1116 mg./l.; (□) [AIBN] = 558 mg./l.; (▲) [AIBN] = 250 mg./l.; (△) [AIBN] = 125 mg./l.; (●) [AIBN] = 63 mg./l.; (○) [AIBN] = 14 mg./l.

Figure 3 shows the relation between logarithm of the rate constant of decomposition of AIBN and the reciprocal absolute temperature, i.e., the relation of the Arrhenius equation. As seen in Figure 3, the values of the rate constant in our experiments are larger than those obtained by other experimenters. The activation energy we obtained by calculation on this basis is 32 kcal./mole.

Figures 4 and 5 show a graph of  $\ln ([\text{DPPH}]_0/[\text{DPPH}])$  against time at 60°C. Figures 5 and 6 show results calculated for the same experiment,

in which AIBN was used at a concentration 100 times that of DPPH. According to our theory [eq. (9)]; this value for the slope in Figure 5 is  $(k_D/k_R)k_d$ , that is, the rate constant of decomposition of AIBN multiplied by the ratio of the rate constant of reaction of radicals with DPPH, and that of recombination of radicals. We obtained  $3.65 \times 10^{-1} \text{ min.}^{-1}$  for the value  $k_D/k_R \cdot k_d$  at  $60^\circ \text{C}$ .

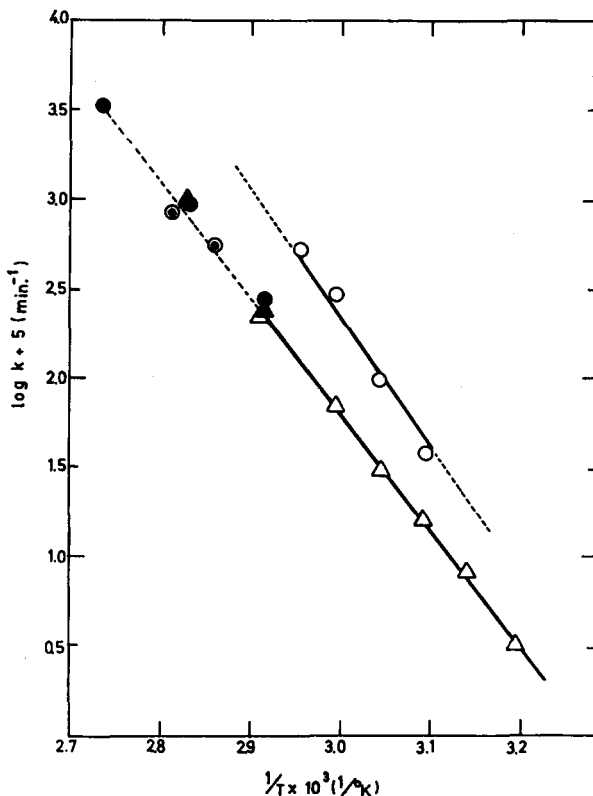


Fig. 3. Arrhenius plots for AIBN: (O) by DPPH, in toluene, present work; ( $\Delta$ ) by DPPH, in benzene, data of Bawn and Mellish;<sup>1</sup> ( $\bullet$ ) by  $\text{N}_2$  evolution, in xylene, data of Lewis and Matheson;<sup>5</sup> ( $\diamond$ ) by  $\text{N}_2$  evolution, in xylene, data of Arnett;<sup>6</sup> ( $\blacktriangle$ ) by  $\text{N}_2$  evolution, in toluene, data of Overberger et al.<sup>7</sup>

Figure 7 shows the results of the reaction between AIBN and DPPH in various concentrations, including the cases when AIBN or DPPH was used in excess, according to eq. (10). In calculation we used the value of  $k_d$  which was obtained from our experiment in making this graph. The value  $K$ , which is the ratio of  $k_D/k_R$ , was checked at every fifty over a range of 50–1000. The gradient,  $\tan \theta$ , is  $-1$  in each experiment, and  $K$  is a large value in this reaction as will be mentioned later; therefore theoretically  $1/(K - 1)$  nearly equals  $-1$ . It seems that this justifies eq. (1).

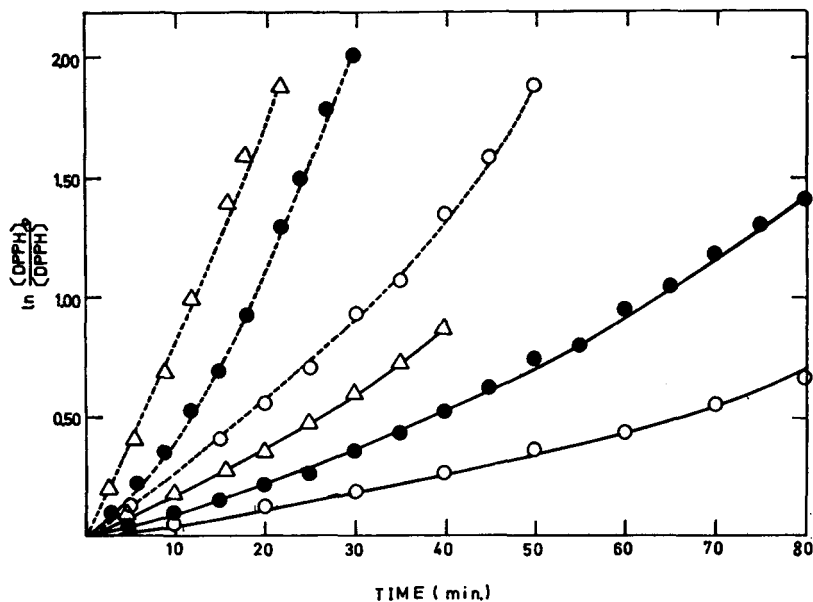


Fig. 4. Disappearance of DPPH (49.6 mg./l.) in toluene when AIBN was used in excess: (O) [AIBN] = 250 mg./l.; (●) [AIBN] = 558 mg./l.; (Δ) [AIBN] = 1116 mg./l.; (—) at 50°C.; (---) at 60°C.

TABLE I  
Rate Constants of AIBN

Experiment number	Temperature, °C.	AIBN concentration, mg./l.	DPPH concentration, mg./l.	$k_d$ (calcd.), min. <sup>-1</sup>
1	65.0	14.0	50.0	$5.20 \times 10^{-3}$
2	65.0	32.1	49.3	$1.95 \times 10^{-3}$
3	60.0	14.0	50.0	$3.15 \times 10^{-3}$
4	60.0	63.2	49.6	$1.28 \times 10^{-3}$
5	60.0	125.2	49.6	$9.37 \times 10^{-4}$
6	60.0	249.2	50.0	$7.58 \times 10^{-4}$
7	60.0	558.0	49.8	$6.08 \times 10^{-4}$
8	60.0	1115.6	49.7	$5.57 \times 10^{-4}$
9	60.0	2333.0	23.0	$4.52 \times 10^{-4}$
10	60.0	3008.0	31.6	$4.67 \times 10^{-4}$
11	55.0	32.0	49.6	$1.00 \times 10^{-3}$
12	55.0	558.0	49.8	$3.73 \times 10^{-4}$
13	50.0	32.2	49.4	$3.87 \times 10^{-4}$
14	50.0	62.4	49.6	$3.73 \times 10^{-4}$
15	50.0	124.8	49.6	$3.37 \times 10^{-4}$
16	50.0	250.0	50.4	$2.17 \times 10^{-4}$
17	50.0	558.0	49.4	$1.81 \times 10^{-4}$
18	50.0	1116.0	49.6	$1.30 \times 10^{-4}$

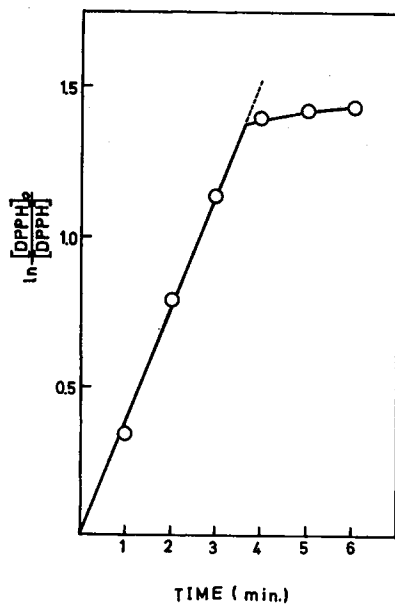


Fig. 5. Decomposition of AIBN in excess at 60°C.

In Table I are summarized the rate constants which were determined by method of least squares for the comparatively straight part of the line on the basis of Figures 1 and 2.

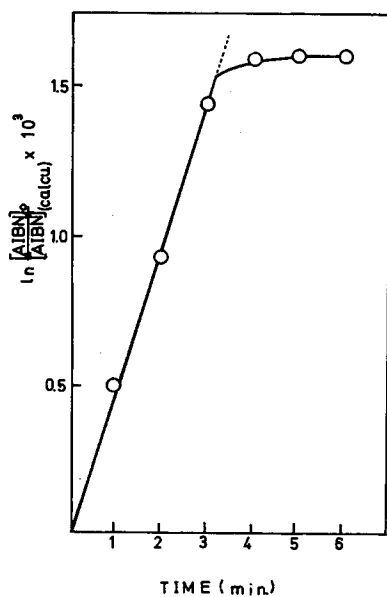


Fig. 6. Disappearance of DPPH at 60°C. when AIBN was used in excess.



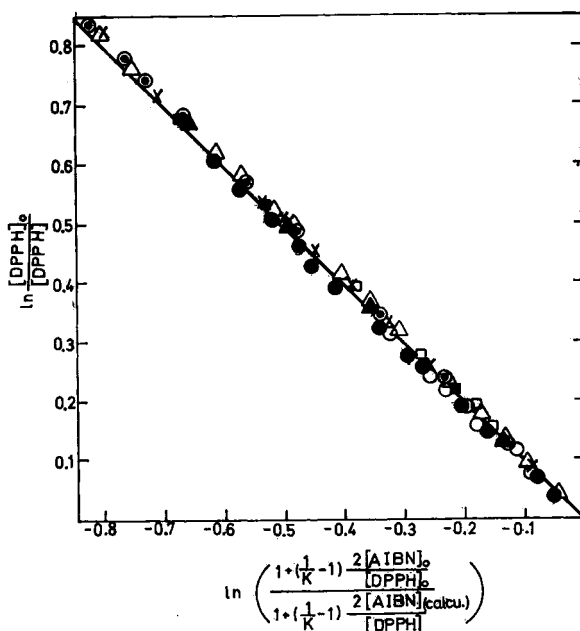


Fig. 7. Relations between the concentrations of AIBN and DPPH and  $K$  under various conditions: (O) expt. 13; (●) expt. 3; (□) expt. 8; (■) expt. 10; (△) expt. 17; (▲) expt. 7; (×) expt. 16; (⊙) expt. 12. Numbers refer to Table I.

## DISCUSSION

### Rate Constant of Thermal Decomposition

Estimating the reaction rate of AIBN with DPPH without giving any special conditions to their quantities, we obtained various kinds of values depending on the concentrations. It seems that, as the concentration of AIBN increased the rate constant gradually decreased. That difference was quite conspicuous. Some think that it is the effect of a "cage reaction" owing to the solution becoming dilute. The cage reaction, however, is a theory to explain the mechanism when the molecules diffuse in solvents. Therefore we believe that this effect is already included in the rate constant.

The thermal decomposition of AIBN in solvents evolves  $N_2$  gas at all times, where there is no DPPH. In order to ascertain whether the radicals have a short life or a long one after the evolution of  $N_2$  gas, we did decompose AIBN without adding DPPH, and  $1/2$  hr. later or 1 hr. later, we added DPPH to the sample. In both cases free radicals did not remain in the solution and so the rate of loss of DPPH was not accelerated. In our calculation we considered the concentration of AIBN to be initial at the time when DPPH was added into the solution. By this experiment we can explain the fact that the rate of recombination of radicals is much more rapid than the rate of decomposition of AIBN. The free radicals formed

by thermal decomposition of AIBN must be involved in two different kinds of reactions. Hence, comes eq. (1).

If free radicals react not only with DPPH but also with other free radicals, we must use a large quantity of DPPH in order to prevent the reaction of the latter. Accordingly, in estimating the thermal decomposition rate of AIBN, it is a mistake to use AIBN in excess relative to the quantity of DPPH. The results will not show the right decomposition rate. By eq. (9) we can fully explain why the rate of loss of DPPH becomes constant when AIBN is used in excess. When we consider that the rate of loss of DPPH is a pseudo first-order reaction, the slope of the line in Figure 5 will be expressed by  $(k_D/k_R) \cdot k_d$  in eq. (9). We can calculate the value of  $K$  as  $k_D/k_R$ , but we cannot know absolute values of  $k_D/k_R$  without another experiment. From this we can explain that the reactivity of free radicals with DPPH is much stronger than the reactivity of recombination of radicals. The reaction rate of the former is about 120 times as fast as the latter. This is quite in contradiction in the explanation of cage reaction. This coincides with the organic electronic theory that the free radicals which have an electrophilic character, react with the nucleophilic radical DPPH more easily than with an electrophilic radical of the same character. The slope of  $1/(K - 1) \doteq -1$  in Figure 7, which was made from a general eq. (10) by using the data obtained in ordinary experiments, is a straight line. It seems that the theory coincides well with experiments.

### Efficiency of Initiators

Free radicals formed by the decomposition of initiator react with DPPH or monomers of vinyl type and become stable compounds, while some radicals recombine with others and disappear. The ability of initiators to form stable radicals is what is referred to by the term efficiency. The explanation for the reaction mechanism of free radicals and DPPH has been incomplete to date.

We have supposed two kinds of loss of free radicals. One of them is a loss of radicals by recombination, called cage reaction. The other is a loss of radicals which cannot react with a scavenger or monomer. That supposition, however, is due to the incomplete combination mechanism of free radicals. Therefore, efficiency can be expressed by eq. (11):

$$\begin{aligned} \text{Efficiency} &= \frac{\int \frac{k_D[\text{DPPH}]}{k_D[\text{DPPH}] + k_R[\text{R}\cdot]} d[\text{R}\cdot]}{\int d[\text{R}\cdot]} \\ &= \frac{[\text{DPPH}]_0 - [\text{DPPH}]}{\int 2k_D[\text{AIBN}]_0 e^{-kt} dt} \end{aligned} \quad (11)$$

Accordingly, efficiency is changed by the kinds and concentrations of scavengers or monomer and the time of reaction, which becomes an important factor.

### CONCLUSION

For the determination of the rate constant of thermal decomposition of an initiator, we must use a large quantity of scavenger or a small quantity of initiator. According to our experiments the rate of decomposition in toluene was:

$$k = 4.0 \times 10^{16} e^{-32,000/RT}$$

When a large quantity of initiators was used, the ratio  $k_D/k_R$  was obtained. We also knew that the reactivity of radicals with DPPH was far greater than that of recombination of radicals, and that it was unnecessary to think of the mechanism of cage reaction.

We have come to the conclusion that the efficiency of initiators is a simple matter to be determined by the ratio of the quantity of reactions caused by the reactivity of radicals and DPPH to the reactivity of recombination of radicals.

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### Résumé

On a fait réagir avec le 2,2-diphénylpicrylhydrazyle (DPPH) des radicaux libres formés par décomposition thermique d'azobisisobutyronitrile (AIBN) dans divers solvants organiques; la vitesse de décomposition thermique de AIBN a été mesurée au départ de la vitesse de disparition de DPPH. On a douté de la relation quantitative entre AIBN et DPPH qui est requise pour obtenir une constante de vitesse de décomposition thermique d'AIBN. L'AIBN a été utilisé en excès. Les constantes de vitesse mesurées en utilisant le DPPH sont d'une valeur plus faible qu'elles devraient être. Dans nos expériences, les auteurs utilisent une quantité aussi faible que possible d'AIBN par rapport au DPPH et obtenaient une valeur de  $3.8 \times 10^{-4} \text{ min.}^{-1}$  à 50°C. comme constante de vitesse de la réaction de premier ordre, ce qui fournissait un graphique linéaire satisfaisant. Nous avons également obtenu 32 kcal./mole comme énergie d'activation. Nous avons également été capable de montrer la signification du résultat lorsque une quantité plus importante d'AIBN est utilisée.

### Zusammenfassung

Indem wir die durch thermische Zersetzung von Azobisisobutyronitril (AIBN) in organischen Lösungsmitteln gebildeten freien Radikale mit 2,2-Diphenylpicrylhydrazyl

(DPPH) zur Reaktion brachten, haben wir die Geschwindigkeit der thermischen Zersetzung von AIBN aus der Umsatzgeschwindigkeit von DPPH bestimmt. Es besteht eine zweifelhafte Anschauung über die quantitative Beziehung zwischen AIBN und DPPH, welche zur Gewinnung der Geschwindigkeitskonstanten der thermischen Zersetzung von AIBN erforderlich ist. AIBN wurde im Überschuss angewendet. Die bis jetzt mit DPPH gemessenen Geschwindigkeitskonstanten besitzen einen kleineren Wert als zu erwarten wäre. In den vorliegenden Versuchen verwendeten die Autoren so wenig als möglich AIBN im Verhältnis zu DPPH und erhielten den Wert  $3,8 \times 10^{-4} \text{ min.}^{-1}$  bei  $50^\circ\text{C}$ . als Geschwindigkeitskonstante erster Ordnung, die sich in befriedigender Weise aus der Linearität des Diagramms ergab. Als Aktivierungsenergie erhielten wir 32 kcal./Mol. Schliesslich konnte auch die Bedeutung der Ergebnisse bei Verwendung einer grossen Menge von AIBN klar gemacht werden.

Received February 1, 1967

Prod. No. 1591