JOURNAL OF APPLIED POLYMER SCIENCE VOL. 14, PP. 329–333 (1970)

Determination of Isopropyl Peroxydicarbonate Decomposition Rate Constant Using EPR

P. P. RATHKE, *Owens-Illinois, General Offices, Toledo, Ohio 43601*

Synopsis

The decomposition rate constant, k_d, of isopropyl peroxydicarbonate in toluene at 23.3°C was determined using electron paramagnetic resonance techniques (EPR). Diphenylpicrylhydrazyl (DPPH) was used to monitor the formation of radicals. Because DPPH has a strong absorption spectrum on the EPR, the accuracy of measuring small changes in the indicator concentration should be greater than measuring small concentrations of primary radicals. A value for k_d of 4.5×10^{-7} sec^{-1} was obtained. This is in good agreement with previously published values.

INTRODUCTION

The study of the free-radical polymerization of vinyl monomers requires knowledge of the rate of initiation. This rate is a function of the decomposition rate of the initiator, the initiator concentration, and the initiator efficiency according to the equation

$$R_i = 2k_d f[\mathrm{I}] = -\frac{d[R\cdot]}{dt}, \tag{1}$$

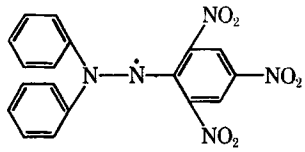
where R_i is the rate of initiation, k_d is the initiator decomposition rate constant, f is the initiator efficiency, [I] is the initiator concentration [R·] is the concentration of radicals, and t is time.

Experimental determination of initiator decomposition rate constants have been done in a number of ways. If initiator efficiency is high, end-group analysis of a polymer provides a measure of the number of initiator fragments which initiate polymer chains. A comparison can be made between the number of fragments and the unreacted initiator concentration. Disagreement between the amount lost and the fragments found would be a measure of the initiator efficiency.[1]

Another method used for the determination of both k_d and/or efficiency involves the addition of an inhibitor. The number of moles of radicals produced during the inhibition period should be equal to twice the number of moles of inhibitor present if the inhibitor reacts stoichiometrically with radicals.[2] However, if the radical generated by the inhibitor can disappear by disproportionating, then one inhibitor molecule could conceivably stop two radicals and the 1:1 stoichiometry is not valid.[3]

© 1970 by John Wiley & Sons, Inc.

A third method, and perhaps the most straightforward, for determining the decomposition rate of initiators is to react the initiator in the presence of an inhibitor whose concentration can be monitored. Such an inhibitor is α,α-diphenyl-β-picrylhydrazyl (DPPH). This inhibitor is a free radical which owes its stability to a delocalized unpaired electron.



The product of a reaction with an initiator radical will pair the single electron, producing a stable molecule which should be incapable of further reaction.[4] DPPH has a characteristic absorption spectrum in organic solvents, and the purple color fades as it reacts with radicals, thus providing a means of monitoring initiator decomposition.[5] Although the 1:1 stoichiometry between DPPH and radicals has been questioned for certain initiator–solvent systems,[6–8] confirmation of the 1:1 stoichiometry has been obtained by independent means[9,10] and the technique is still used.[11]

Sasaki and Nagayama[11] have studied the reactions of azobisisobutryonitrile (AIBN) and DPPH and have evaluated the effect of their relative concentrations on the decomposition rate constant of AIBN. Their results suggest that DPPH must be used in excess in order to obtain reliable data. On this basis then, the only reactions occurring are

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}\cdot \qquad \text{formation of radicals} \tag{2}$$

and

$$\mathrm{DPPH} + \mathrm{R}\cdot \xrightarrow{k} \mathrm{DPPHR} \qquad \text{formation of inactive specie} \tag{3}$$

where $[\mathrm{DPPH}] > [\mathrm{R}\cdot]$.

These authors[11] used the colorimetric method of measuring the concentration changes in DPPH. This paper concerns the determination of a decomposition rate constant, k_d, using electron paramagnetic resonance (EPR) techniques to monitor the DPPH concentration. The use of EPR for measuring radical concentration is not new.[9,12–17] However, the measurement of a decreasing EPR signal from a good indicating source is felt to be more accurate than trying to measure the concentration of the primary radicals, on the order of 10^{-8} moles/l. DPPH has a strong characteristic signal whose integrated intensity is directly proportional to its concentration.

EXPERIMENTAL

A DPPH control solution was prepared by dissolving the inhibitor in toluene at a concentration of 0.001 mole/l. The EPR spectrum of this solution was obtained using a Varian V-4500 system incorporating a 12-in.

magnet, 100 kc/sec field modulation, and a Varian V-4531 rectangular cavity operating in the TE_{102} mode. The spectrum was scanned over a 50-gauss range, and the control curve was cut out and the paper weighed. The standard solution produced 1.26×10^{18} spins per gram of DPPH. This calibration was used to determine the decomposition rate constant of diisopropyl peroxydicarbonate (IPP).

Commercial IPP was used for this determination as received. A 1 wt-% solution (0.0425 mole/l) was prepared in toluene and stored at Dry Ice temperature until used to prevent premature decomposition. As the IPP is crystallized from solution at these temperatures, it was allowed to warm up until the IPP was dissolved just prior to use. The quartz EPR sample holder, with a test volume of 0.162 cc, was filled with the IPP solution. DPPH was then added to an equivalent concentration of that used in the control. The EPR readings were taken over a 6-hr period, each time running over the 50-gauss range. The test curves were then cut out and weighed.

RESULTS AND DISCUSSION

The intensity of the EPR signal decreased with time in the presence of the IPP. At the same time, the expected color change in the DPPH–IPP solution was observed. Based on the weighed curves, the spins per gram of DPPH could be directly calculated.

The relationship between the loss of DPPH and the loss of IPP is based on a 1:1 stoichiometry. From eqs. (2) and (3), the rate expressions can be written as

$$-\frac{d[\text{IPP}]}{dt} = k_d[\text{IPP}] \qquad \text{loss of initiator} \tag{4}$$

$$-\frac{d[\text{DPPH}]}{dt} = k[\text{DPPH}][\text{R}\cdot] \qquad \text{loss of DPPH.} \tag{5}$$

The change in radical concentration is thus

$$\frac{d[\text{R}\cdot]}{dt} = 2\frac{d[\text{IPP}]}{dt} - \frac{d[\text{DPPH}]}{dt} \tag{6}$$

where the factor 2 enters because two radicals are formed from each molecule of IPP.

If the steady state form is used, which says that the change in radical concentration is negligible compared with the change in initiator concentration or the change in DPPH concentration, then

$$2\frac{d[\text{IPP}]}{dt} = +\frac{d[\text{DPPH}]}{dt}. \tag{7}$$

This equation suggests that the 1:1 stoichiometry holds between a radical and a DPPH molecule. However, as Sasaki and Nagayama[11] point out,

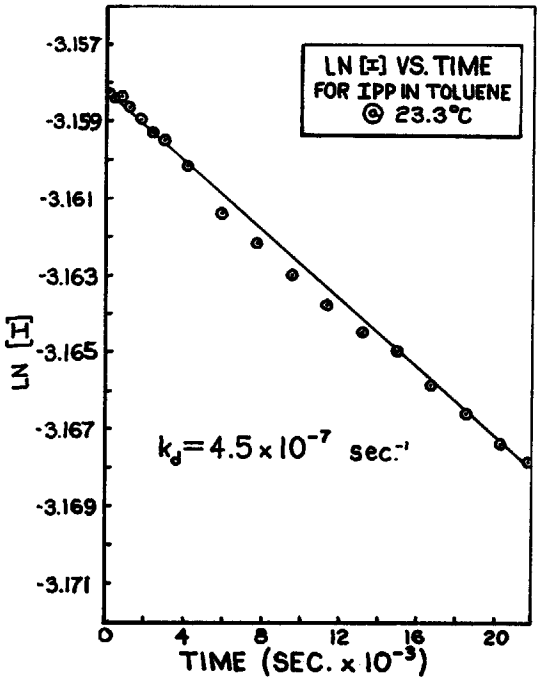


Fig. 1. Plot of ln[I] versus time for IPP in toluene at 23.3°C.

when $[R\cdot] > [DPPH]$, recombination of radicals can occur, not necessarily producing the original initiator, and the 1:1 relationship is not valid.

Solving eq. (4) with the usual boundary conditions of $[IPP] = [IPP]_0$ at $t = 0$, the desired form is obtained, as follows:

$$[IPP] = [IPP]_0 \exp\{-k_d t\} \tag{8}$$

Plotting ln [IPP] versus time should give ln $[IPP]_0$ as the intercept and k_d as the slope, as shown in Figure 1. A "best fit" line was obtained from a regression analysis of the data.

A k_d for IPP at 23.3°C in toluene of 4.5×10^{-7} ($\pm 1 \times 10^{-7}$) sec^{-1} was obtained. This agrees well with k_d values obtained from the literature in toluene at other temperatures (Table I).

TABLE I
k_d Values for IPP in Toluene

k_d	Temperature, °C	Source
4.5×10^{-7} [a]	23.3	this work
7.3×10^{-6} [b]	35	Strong[18]
3.03×10^{-5} [c]	50	Strain et al.[19]

[a] At a concentration of 0.0425 m/l.

[b] At a concentration of 45% which produces a more rapid reaction owing to deviation from first order r × n.[18]

[c] At a concentration of 0.144 m/l.

On the basis of this single determination, use of EPR for measuring the rate of radical generation from a free-radical initator by monitoring the decrease in DPPH concentration appears to be a very practical method.

I would like to express thanks to Mr. I. Siegel and Mr. J. A. Lorenc who generated the EPR data, and to Owens-Illinois, Inc., for permission to publish.

References

1. M. G. Evans, *J. Chem. Soc.*, **266** (1947).
2. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 119.
3. F. W. Billmeyer, *Textbook of Polymer Science*, Interscience, New York, 1962, p. 268.
4. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 162.
5. C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).
6. G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Amer. Chem. Soc.*, **77**, 3244 (1955).
7. J. C. Bevington, *J. Chem. Soc.*, 1127 (1956).
8. P. J. Proll and L. H. Sutcliffe, *Trans. Faraday Soc.*, **59**, 2090 (1963).
9. C. H. Bamford and A. D. Jenkins, *Proc. Roy. Soc., Ser. A*, **228**, 220 (1955).
10. C. H. Bamford, D. J. E. Ingram, A. D. Jenkins, and M. C. R. Symons, *Nature*, **175**, 894 (1955).
11. H. Sasaki and M. Nagayama, *J. Appl. Polym. Sci.*, **11**, 2097 (1967).
12. M. Bersohn and J. R. Thomas, *J. Amer. Chem. Soc.*, **86**, 959 (1964).
13. W. T. Dixon and R. O. C. Norman, *Nature*, **196**, 891 (1962).
14. W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).
15. K. Takakwa and B. Ranby, *J. Polym. Sci. B*, **5**, 83 (1967).
16. H. Fischer, *Proc. Roy. Soc. Ser. A*, **302**, 321 (1968).
17. L. A. Tikhomiron and N. Y. Buben, *Vysokomol. Soedin.*, **8**, 1181 (1966).
18. W. A. Strong, *Ind. Eng. Chem.*, **56** (**No. 12**), 33 (1964).
19. F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens, and J. H. Langston, *J. Amer. Chem. Soc.*, **72**, 1254 (1950).

Received September 9, 1969