

## Determination of Rates of Thermal Decomposition of Polymerization Initiators with a Differential Scanning Calorimeter

K. E. J. BARRETT, *Research Department, Paints Division, Imperial Chemical Industries Ltd., Slough, Bucks., England*

### Synopsis

A commercial differential scanning calorimeter has been used to determine thermal and kinetic data of some typical polymerization initiators. Since the rate of heat change due to decomposition is directly related to the rate of decomposition at a given temperature, suitable analysis of the differential thermal curve can yield the Arrhenius parameters of a reaction from a single run. In order to test the method, the well-established first-order decomposition of azobisisobutyronitrile was determined in di-*n*-butyl phthalate as solvent. Reproducible results were obtained which accorded with published data by orthodox determinations. The rates of thermal decomposition in solution of benzoyl peroxide and diisopropyl peroxydicarbonate were also determined. The method provides a rapid means for the direct determination of fast rates not possible with orthodox analytical determinations.

### INTRODUCTION

A differential thermal analyzer for obtaining kinetic data for reactions occurring in solution was described by Borchardt and Daniels.<sup>1</sup> Two stirred vessels, immersed in a heating bath, contained reactants and solvent, respectively. The differential output ( $\Delta T$ ) from copper/Constantan thermocouples, immersed in the reaction vessels heated at about 1°C./min. was amplified and recorded with respect to both reaction time and bath temperature. By a suitable analysis of the resultant differential thermal analysis curve the Arrhenius parameters of the first-order, thermal decomposition of benzene diazonium chloride in aqueous solution and the bimolecular reaction of *N,N*-dimethylaniline with ethyl iodide were determined. More recently the method of Borchardt and Daniels has been validated by Reed, Weber, and Gottfried<sup>2</sup> by a more rigorous mathematical treatment and a re-examination of the benzene diazonium chloride decomposition.

The present work was carried out with a commercial differential scanning calorimeter which has the advantage of measuring energy changes directly.<sup>3,4</sup> Very much smaller samples than could be examined by Borchardt and Daniels can be used and the quantities measured to derive rate data are easier to obtain. A typical differential enthalpic analysis

(DEA) curve obtained with the scanning calorimeter together with the quantities measured to evaluate the rate constants is given in Figure 1.

The heat change involved in a reaction can be measured directly with the differential scanning calorimeter. The rate of heat evolution ( $dH/dt$ , mcal./sec.) with respect to time (or temperature) is recorded directly.

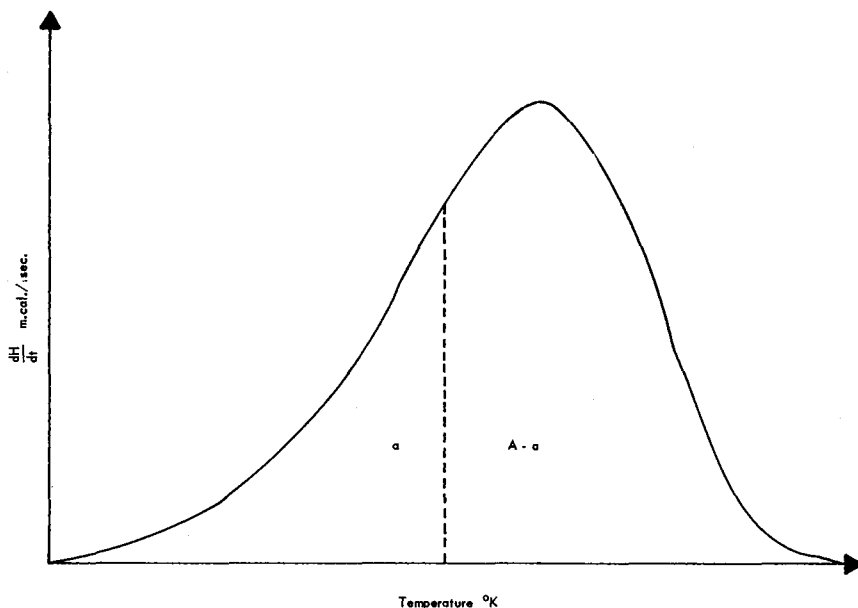


Fig. 1. Differential enthalpic analysis curve and quantities measured to evaluate rate constants.

The total area under the curve,  $A$  (mcal.), corresponds to the total heat of reaction,  $\Delta H$ , and the area  $a$  (mcal.), to the heat evolved up to any time  $t$ . If it is assumed that the amount of heat evolved is proportional to the number of moles reacted,  $n$

$$a/A = n/n_0$$

also,

$$- dn/dt = (-n_0/A) (dH/dt)$$

where  $n_0$  is the number of moles of reactant present initially. The amount of reactant present at any time is given by

$$n' = n_0 - (n_0 a/A)$$

leading to the expression for the rate constant

$$k = \frac{[(AV)/(n_0)]^{x-1} (dH/dt)}{(A - a)^x}$$

where  $V/n_0$  is the reciprocal of the initial concentration of reactants and  $x$  is the order of the reaction. For a first-order reaction,  $x = 1$ , the expression reduces to the following simple form

$$k = (dH/dt)/(A - a)$$

Since the temperature of the reactant solution was rising continuously, each run yielded a set of rate constants, each obtained by measurement of a value of  $dH/dt$  and of the corresponding area under the thermal curve. It was therefore possible to obtain a value of the activation energy by a plot of  $\log k$  against the reciprocal of the absolute temperature in the usual way.

## EXPERIMENTAL

### Materials

Azobisisobutyronitrile and benzoyl peroxide were recrystallized and stored at  $-10^\circ\text{C}$ . before use. Diisopropylperoxydicarbonate (Perkadox IPP, ex Novadel Ltd.) was used without further purification and stored in solid carbon dioxide before use. A suitably involatile solvent for the solution decomposition in the required temperature range was di-*n*-butylphthalate, b.p.  $340^\circ\text{C}$ ., which gave a steady base-line on the recorder trace up to  $150^\circ\text{C}$ .

### Method

A Perkin-Elmer differential scanning calorimeter, Model DSC-1, was used for the thermal determinations. The standard aluminum sample pans were used without lids. Due to some "solvent creep" at higher temperatures ( $80$ – $150^\circ\text{C}$ .) it was necessary to crimp the top of the aluminum container slightly to retain the initiator solution. Mixtures of initiator (2–3 mg.) and di-*n*-butylphthalate (25–30 mg.) or the corresponding solutions (5–10% by weight of initiator) were weighed directly into the aluminum pan. An aluminum sample pan containing the same weight of sol-

TABLE I  
Determination of Kinetic Temperatures of Reaction Mixtures  
at Various Heating Rates

Heating rate, $^\circ\text{C}/\text{min}$ .	Temperature of transition, $^\circ\text{C}$ .		
	Solid ammonium nitrate	Ammonium nitrate and solvent	Ammonium nitrate solvent and initiator
4	125	122(–3)	122(–3)
8	125	122(–3)	123(–2)
16	125	124(–1)	125(0)
32	125	127(+2)	127(+2)

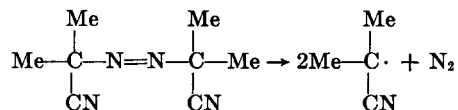
vent only was used as a reference. A slow current of nitrogen passed over the sample holders during the determination.

In order to ensure that correct kinetic temperatures were obtained at various heating rates, ammonium nitrate was used as an internal temperature standard in preliminary runs. The characteristic endothermic transition of ammonium nitrate at 398°K. due to a change from the rhombohedral to the cubic crystalline form<sup>3</sup> was superimposed as a sharp endothermic indentation on the exothermic reaction curve and enabled actual kinetic temperatures to be determined directly. The values, given in Table I, were used to correct temperatures over the range of heating rates used.

## RESULTS AND DISCUSSION

### Thermal Decomposition of Azobisisobutyronitrile in Di-*n*-butyl Phthalate

In order to test the method, the thermal decomposition of azobisisobutyronitrile



was examined. This is a clean, first-order reaction not complicated by induced decompositions and whose rate of decomposition is largely independent of the nature of the solvent. The results of a range of methods used to determine the decomposition rates have been critically reviewed by Van Hook and Tobolsky.<sup>5</sup> They also re-examined the decomposition in benzene and toluene over the temperature range 37–100°C. by an ultra-violet absorption technique with the following results.

Temp., °C.	$k_d$ , sec. <sup>-1</sup>
100	$1.52 \times 10^{-3}$
60	$9.15 \times 10^{-6}$
50	$2.16 \times 10^{-6}$
43	$7.35 \times 10^{-7}$
37	$2.83 \times 10^{-7}$

The best value obtained for the decomposition from a composite plot of all rate data was  $k_d = 1.58 \times 10^{15} \exp \{ -30.8 \text{ kcal.}/RT \}$ .

A typical differential enthalpy curve obtained for the decomposition of azobisisobutyronitrile (3 mg.) in di-*n*-butyl phthalate (30 mg.) at a heating rate of 16°C./min. and a range setting of 4 mcal./sec. is illustrated in Figure 2. A comparison of the curves for azobisisobutyronitrile, diisopropyl peroxydicarbonate, and benzoyl peroxide gives a direct qualitative illustration of the rate of reaction with respect to temperature. It is important for the method of kinetic analysis that no reaction is proceeding

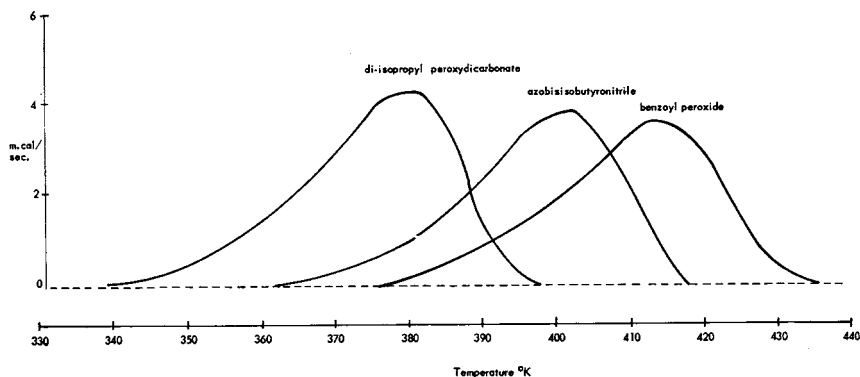


Fig. 2. Typical differential enthalpic curves obtained for the decomposition of polymerization initiators.

at the starting temperature and that the reaction should be complete at the final temperature. In the examples examined the return to base line at the completion of reaction was satisfactory. However, the kinetic method does not depend on measurements of the absolute value of the heat of reaction since ratios of heats evolved with respect to the total heat of reaction are measured.

The decomposition of azobisisobutyronitrile in di-*n*-butyl phthalate was carried out in duplicate at three heating rates (4, 8, 16°C./min.) and singly at the highest heating rate (32°C./min.). Using the method of kinetic analysis described, the first-order rate constants obtained for each run, are listed in Table II.

These results have been used together with those obtained by Van Hook and Tobolsky<sup>5</sup> to construct a composite plot of the Arrhenius parameter

TABLE II  
Determined Values of Rate Constants for the Decomposition  
of Azobisisobutyronitrile over a Range of Heating Rates

Heating rate 4°C./min.		Heating rate 8°C./min.	
Temp., °C.	$k_d$ , sec. <sup>-1</sup>	Temp., °C.	$k_d$ , sec. <sup>-1</sup>
80	$2.64 \times 10^{-4}$	89	$4.03 \times 10^{-4}$
90	7.21, $5.73 \times 10^{-4}$	99	1.26, $1.35 \times 10^{-3}$
100	1.82, $1.73 \times 10^{-3}$	109	4.03, $4.29 \times 10^{-3}$
110	4.96, $4.79 \times 10^{-3}$	119	1.22, $1.24 \times 10^{-3}$
120	1.21, $1.66 \times 10^{-2}$	129	2.63, $2.36 \times 10^{-2}$
Heating rate 16°C./min.		Heating rate 32°C./min.	
97	1.01, $0.924 \times 10^{-3}$	105	$2.10 \times 10^{-3}$
107	2.80, $3.02 \times 10^{-3}$	115	$6.67 \times 10^{-3}$
117	7.96, $9.23 \times 10^{-3}$	125	$1.98 \times 10^{-2}$
127	2.32, $2.65 \times 10^{-2}$	135	$5.70 \times 10^{-2}$
137	4.35, $6.51 \times 10^{-2}$	145	$1.24 \times 10^{-1}$

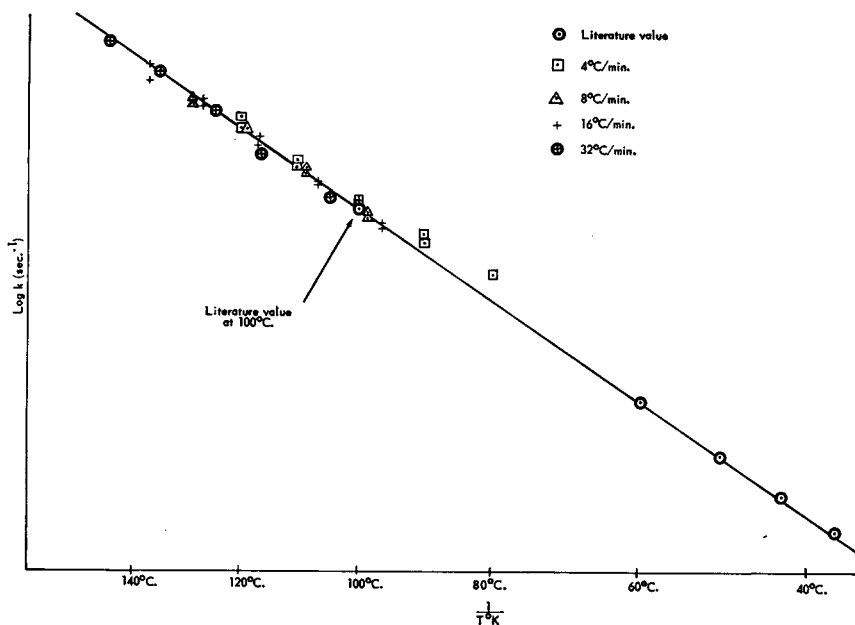


Fig. 3. Arrhenius plot for the decomposition of azobisisobutyronitrile at various heating rates together with literature values.

(Fig. 3). The linearity of the Arrhenius plot serves as a diagnosis for the order of the reaction. A plot of the data according to zero-, second-, and third-order kinetics gave curves. Good correspondence is observed between the extrapolated literature values and the values obtained by differential enthalpic analysis. The temperature range examined by thermal analysis is higher than that possible with orthodox analytical determinations and serves as a useful method for the direct determination of fast rates. The temperature range examined by thermal analysis can be varied by the appropriate choice of heating rate and sample size. Larger sample sizes would allow lower heating rates and consequently a lower temperature

TABLE III  
Thermal and Kinetic Quantities Determined for the Decomposition  
of Azobisisobutyronitrile at Different Heating Rates

Heating rate, °C./min.	Energy of activation, kcal./mole	Frequency factor, sec. <sup>-1</sup>	Heat of decomposition, kcal./mole
4	26.8, 31.6	$9.0 \times 10^{13}$ , $5.3 \times 10^{15}$	51.7, 50.9
8	31.3, 30.8	$2.8 \times 10^{15}$ , $1.6 \times 10^{15}$	46.4, 44.9
16	29.5, 32.0	$2.3 \times 10^{14}$ , $7.2 \times 10^{15}$	52.2, 45.5
32	32.9	$2.0 \times 10^{16}$	48.4

range to be examined. In the extreme case, provided the rate of heat production is large enough, reactions under isothermal conditions can be measured, although the advantage of obtaining Arrhenius data directly is lost.

The thermal and kinetic quantities obtained from individual runs of the decomposition of azobisisobutyronitrile are summarized in Table III.

### Thermal Decomposition of Benzoyl Peroxide in Di-*n*-butyl Phthalate

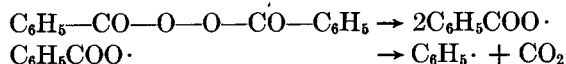


TABLE IV  
Determined Values of Rate Constants for the Decomposition of Benzoyl Peroxide by Nitrometry and Iodometry<sup>6</sup> and by Differential Enthalpic Analysis

Method, nitrometry and iodometry <sup>6</sup>		Method, differential enthalpic analysis (heating rate, 16°C./min.)	
Temp., °C.	$k_d$ , sec. <sup>-1</sup>	Temp., °C.	$k_d$ , sec. <sup>-1</sup>
55	$1.14 \times 10^{-6}$	117	2.72, $2.84 \times 10^{-3}$
60	$2.76 \times 10^{-6}$	127	7.54, $7.34 \times 10^{-3}$
70	$1.17 \times 10^{-5}$	137	1.72, $1.72 \times 10^{-2}$
75	$2.62 \times 10^{-5}$	147	4.03, $3.75 \times 10^{-2}$
80	$4.39 \times 10^{-5}$		

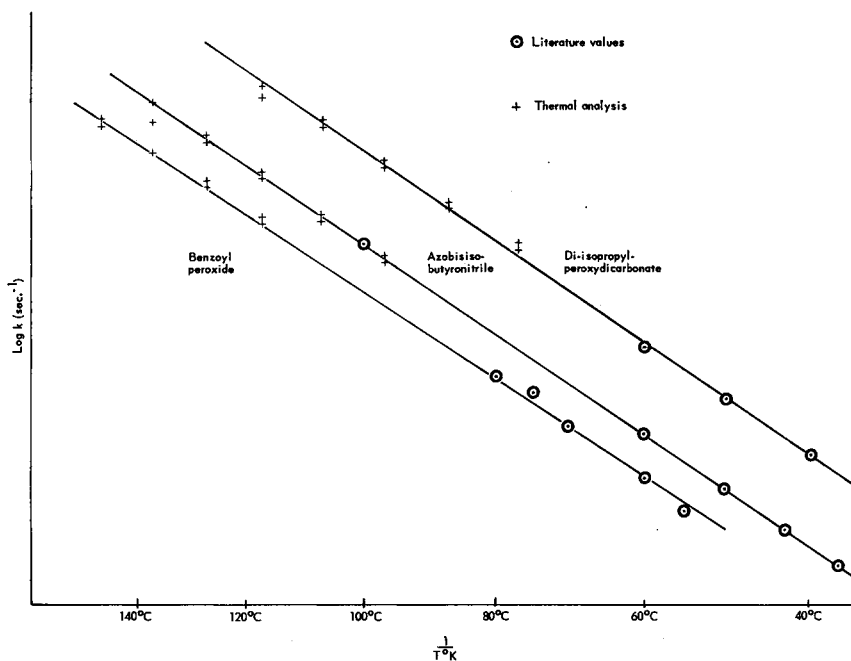
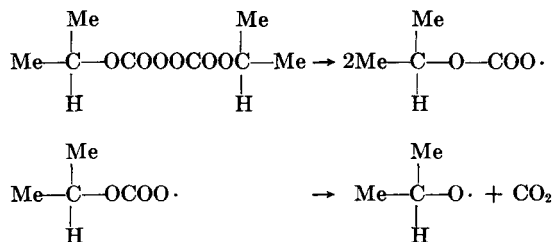


Fig. 4. Arrhenius plot for the decomposition of polymerization initiators at a constant heating rate (16°C./min.) together with literature values.

The rate of thermal decomposition of benzoyl peroxide varies with the nature of the solvent and is complicated by induced decompositions leading to a higher order of reaction than first order with increasing concentration. A typical result for benzoyl peroxide (25 mg. of a 5% solution by weight in di-*n*-butyl phthalate) by differential scanning calorimetry is shown in Figure 2. Duplicate determinations were carried out at a single heating rate (16°C./min.) and the first-order rate constants obtained are compared with those obtained by nitrometer<sup>6</sup> with benzene as solvent (Table IV).

These results have been used together to construct a composite Arrhenius plot (Fig. 4). A reasonable correspondence, for the rather less well-defined data, between values by the orthodox analytical determination and by differential enthalpic analysis was obtained. The slope obtained is compared with the corresponding slopes (obtained at a heating rate of 16°C./min.) for the decomposition of azobisisobutyronitrile and diisopropyl peroxydicarbonate.

#### Thermal Decomposition of Diisopropyl Peroxydicarbonate in Di-*n*-butyl Phthalate



The decomposition of diisopropyl peroxydicarbonate is also complicated by free-radical-induced reactions. Its rate of decomposition in toluene and 2,2'-oxydiethylene bis(allyl carbonate) has been followed by an iodometric method.<sup>7</sup> A typical differential enthalpic curve for the decomposition in di-*n*-butyl phthalate at a heating rate of 16°C./min. is given in Figure 2. Results obtained by the thermal method are listed together with the literature values in Table V.

TABLE V  
Determined Values of Rate Constants for the Decomposition of Diisopropyl Peroxydicarbonate by Iodometry<sup>7</sup> and by Differential Thermal Analysis

Method, iodometry <sup>7</sup>		Method, differential enthalpic analysis, (heating rate 16°C./min.)	
Temp., °C.	$k_d$ , sec. <sup>-1</sup>	Temp., °C.	$k_d$ , sec. <sup>-1</sup>
40	$6.39 \times 10^{-6}$	77	1.47, $1.30 \times 10^{-3}$
50	2.28, $3.03 \times 10^{-5}$	87	4.00, $4.18 \times 10^{-3}$
60	$9.45 \times 10^{-5}$	97	1.15, $1.35 \times 10^{-2}$
		107	3.16, $3.93 \times 10^{-2}$
		117	6.53, $9.42 \times 10^{-2}$



Both sets of results have been plotted (Fig. 4) to obtain the Arrhenius parameters. Again, a reasonable correspondence between the two sets of results was obtained. The kinetic and thermal results obtained, at a heating rate of 16°C./min., for the three initiators examined are summarized with the literature values in Table VI.

TABLE VI

Summary of Thermal and Kinetic Quantities Determined for the Decomposition of the Polymerization Initiators by Thermal Analysis at a Heating Rate of 16°C./min.\*

Radical generator	Energy of activation, kcal./mole	Frequency factor, sec. <sup>-1</sup>	Heat of decomposition, kcal./mole
Azobisisobutyronitrile	29.5, 32.0 (30.8)	$2.3 \times 10^{14}$ , $7.2 \times 10^{15}$ ( $1.6 \times 10^{15}$ )	52.2, 45.5
Benzoyl peroxide	29.1, 28.2 (~30)	$5.2 \times 10^{13}$ , $1.6 \times 10^{13}$ —	44.8, 42.5
Diisopropyl peroxydicarbonate	25.6, 28.8 (28.1)	$1.5 \times 10^{13}$ , $1.4 \times 10^{15}$ —	54.7, 55.4

\* Literature values given in brackets.

The differential enthalpic method of kinetic analysis, therefore, provides a rapid and useful method for a direct determination of the temperature coefficient of reaction rates. The method is particularly useful for the direct determination of rates too fast to be followed by orthodox methods of analysis.

The author wishes to thank N. R. Garrard for experimental assistance in the work described in this paper and Dr. R. A. W. Hill for kindly reading the manuscript.

### References

1. H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, **79**, 41 (1957).
2. R. L. Reed, L. Weber, and B. S. Gottfried, *Ind. Eng. Chem., Fundamentals*, **4**, 38 (1965).
3. E. S. Watson, M. J. O'Neill, J. Justin, and N. Brenner, *Anal. Chem.*, **36**, 1233 (1964).
4. M. J. O'Neill, *Anal. Chem.*, **36**, 1238 (1964).
5. J. P. Van Hook and A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 779 (1958).
6. B. Barnett and W. E. Vaughan, *J. Phys. Colloid Chem.*, **51**, 926 (1947).
7. F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens, and J. H. Langston, *J. Am. Chem. Soc.*, **72**, 1254 (1950).

### Résumé

Un calorimètre différentiel commercial a été utilisé pour déterminer les données thermiques et cinétiques de certains initiateurs typiques de polymérisation. Puisque la vitesse d'échange de chaleur due à la décomposition est directement liée à la vitesse de décomposition à une température déterminée, une analyse convenable de la courbe thermique différentielle permet d'obtenir les paramètres d'Arrhénius d'une réaction au départ d'une seule expérience. En vue d'essayer la méthode, la décomposition de premier ordre bien connue de l'azobisisobutyronitrile a été déterminée dans le phthalate de di-*n*-butyle comme solvant. Des résultats reproductibles ont été obtenus qui étaient

en accord avec les résultats publiés au moyen des déterminations orthodoxes. Les vitesses de décomposition thermique en solution dans du peroxyde de benzoyle et du peroxydicarbonate de di-isopropyle ont également été déterminées. La méthode fournit un moyen rapide de détermination directe de vitesses rapides es qui n'était pas possible par des déterminations analytiques.

### Zusammenfassung

Ein kommerzielles Differential-Scanning-Kalorimeter wurde zur Bestimmung thermischer und kinetischer Daten einiger typischer Polymerisationstarter benützt. Da die Geschwindigkeit der durch die Zersetzung bedingten Wärmeänderung in direkter Beziehung zur Zersetzungsgeschwindigkeit bei einer gegebenen Temperatur steht, kann eine geeignete Analyse der Differential-thermokurve die Arrheniusparameter einer Reaktion aus einem einzigen Versuchsablauf liefern. Zur Überprüfung der Methode wurde die gut bekannte Zersetzung erster Ordnung von Azobisisobutyronitril in Di-*n*-butylphthalat als Lösungsmittel gemessen. Es wurden reproduzierbare, mit den Literaturdaten übereinstimmende Ergebnisse erhalten. Auch die Geschwindigkeit der thermischen Zersetzung von Benzoylperoxyd und Di-isopropylperoxydikarbonat in Lösung wurde bestimmt. Die Methode liefert eine rasche Möglichkeit zur direkten Bestimmung hoher Geschwindigkeiten, wie sie mit orthodoxen analytischen Bestimmungen nicht möglich ist.

Received November 1, 1966

Revised January 6, 1967

Prod. No. 1555