794. *The Rates of Decomposition of Free-radical Polymerisation-catalysts: Measurements of Short Half-lives by a Thermal Method.*

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The rates of decomposition of a number of free-radical polymerisation-initiators have been measured by a thermal method over temperature ranges in which the half-lives were of the order of ten seconds. Dilute solutions were used and the method of measurement was such that the concentration of the initiator need not be known.

Compounds which decompose to yield free radicals are widely used as polymerisation-initiators. In this connection it is essential to know the rates at which they decompose at elevated temperatures; the rates of decomposition of di-t-butyl peroxide,[1] diethyl peroxide,[2] diacetyl peroxide, dipropionyl peroxide, and dibutyryl peroxide [3] have been measured by flow methods, the half-lives being less than one minute. All these compounds are volatile, however, and no measurements have been reported of fast decompositions of non-volatile compounds which yield free radicals when heated. Such measurements have now been made by a thermal method similar to that described by Bell and Clunie.[4]

In this work half-lives of the order of ten seconds were to be measured and it was therefore necessary to use a method which did not involve measuring the concentration of the compounds studied and could be used with dilute solutions. The method adopted depends on observation of the temperature changes which result from adding a small sample of the compound to a comparatively large volume of hot solvent with rapid mixing, under conditions such that the heat of reaction is continuously lost to surroundings at constant temperature. By using dilute solutions the total temperature change may be

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[1] Murawski, Roberts, and Swarcz, *J. Chem. Phys.*, 1951, **19**, 698; Lossing and Tickner, *ibid.*, 1952, **20**, 907.

[2] Rebbert and Laidler, *J. Chem. Phys.*, 1952, **20**, 574.

[3] Rembaum and Swarcz, *J. Amer. Chem. Soc.*, 1954, **76**, 5975; *J. Chem. Phys.*, 1955, **23**, 909.

[4] Bell and Clunie, *Proc. Roy. Soc.*, 1952, *A*, **212**, 16.

kept below 0·5°, so that the rate of decomposition is measured under approximately isothermal conditions.

Although the first step in the decomposition of the compounds studied is endothermic, the subsequent reactions of the radicals produced are exothermic and a temperature rise is observed. The method is valid because the radical reactions are very much faster than the initial dissociation into radicals.

When the cold sample is first added to the system there is a momentary fall in temperature; then as the decomposition proceeds, the temperature rises above its original value to a maximum, and finally falls again (Fig. 2, p. 4025). For first-order reactions the time taken to reach the maximum temperature after the system has recovered from the introduction of the cold sample, that is, after the temperature has returned to its original value, is determined by the ratio of the reaction velocity constant to the cooling rate constant and is independent of the concentration of reagent.

If the first-order reaction constant is k_1 and heat loss from the system is governed by a first-order rate constant k_2, then after the initial disturbance the rate of change of temperature is given by

$$\mathrm{d}\theta/\mathrm{d}t = (Q/H)/k_1 x \mathrm{e}^{-k_1 t} - k_2\theta$$

where θ is the temperature at any time t, x is the amount of the reacting substance remaining when the temperature returns to its original value after the initial disturbance, Q is the heat of decomposition of the substance, and H is the water equivalent of the system.

It can be shown [4] that the time (T) taken to reach the maximum temperature after the initial disturbance is given by

$$T = \frac{1}{k_1 - k_2} \log_e \frac{k_1}{k_2}$$

which is independent of x, Q, and H.

The precision with which T can be measured depends upon the sharpness of the maximum in the temperature change. Errors in measuring T will have least effect on the result when $\mathrm{d}T/\mathrm{d}k_1$ is as large as possible; since

$$\frac{\mathrm{d}T}{\mathrm{d}k_1} = \frac{1}{k_1 - k_2}\left(\frac{1}{k_1} - T\right)$$

it follows that $\mathrm{d}T/\mathrm{d}k_1$ becomes infinitely large when $k_1 = k_2$, and errors in measuring T will therefore have least effect on the value of k_1 in the range where k_1 is nearly equal to k_2. The apparatus was therefore designed with a heat-transfer coefficient such that the half-time of cooling was about equal to the half-life times to be measured; in practice it was found to be rather more convenient to use when k_1 was slightly greater than k_2. It can be shown that the value of k_2T tends to unity as k_1 approaches k_2, so that T is approximately equal to $1/k_2$ in the best working range of the method. Evidently it is important to determine the apparatus constant, k_2, as accurately as possible.

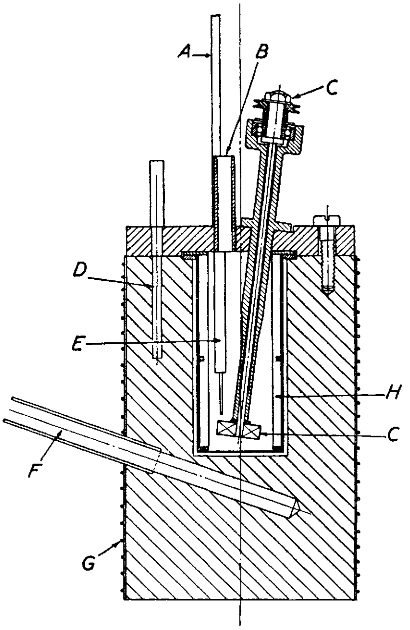
EXPERIMENTAL AND RESULTS

Apparatus.—This was a cylindrical block of aluminium 10 cm. in diameter and 15 cm. high, the centre of which was bored out to provide a reaction vessel of 100 ml. capacity (Fig. 1). The vessel was provided with four vertical baffles, a high-speed stirrer running in ball bearings in the lid of the vessel, and one junction of a copper–constantan thermocouple made from 36 S.W.G. wire. The reference junction was housed in a small hole near the periphery of the aluminium block, and the apparatus was heated to a constant temperature by an electric winding on the outside, controlled by a bimetallic thermoregulator inserted in the side of the block. The removable lid of the reaction vessel was ground to fit the upper face of the aluminium block to ensure good thermal contact, and the whole apparatus was embedded in coarsely powdered insulating firebrick (Johns-Manville Co. Ltd.) contained in a polished tin, 18 cm. in diameter.

The thermocouple was connected to a D.C. amplifier with a voltage gain of $2{\cdot}5 \times 10^5$, and the output from this was connected to one pair of vertical deflection plates of a double-beam oscillograph. The second pair of plates was connected to a 1·5 v dry cell through a clock-driven contactor which interrupted the circuit every 0·5 sec., so that the second beam was displaced periodically through a short vertical distance. The oscillograph time base was not used; the vertical movements of the two beams were recorded on a 35 mm. strip of sensitive paper drawn continuously through a camera at nominal speeds of from 0·2 to 10 cm./sec. The sensitivity of the temperature measurement was such that a change of 0·3° produced 1 cm. deflection of the image on the sensitive paper; time intervals were measured to the nearest 0·05 sec. by interpolation of the square wave marked by the second beam.

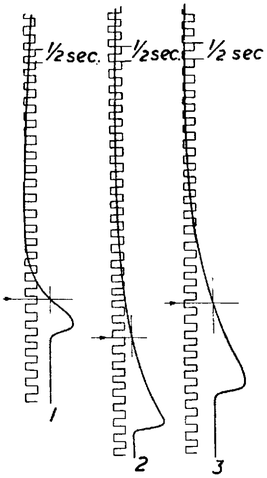
Determination of Cooling Rate Constant.—The output from the D.C. amplifier was temporarily connected to a high-speed pen-recorder giving full-scale deflection for 0·5° change in temperature; the chart speed was 12 inches/min. Liquid paraffin (B.P.; 50 ml.) was put into the reaction vessel, the apparatus was brought to the required temperature, and a small platinum resistance heater was inserted into the liquid. When the temperature had been raised about 0·5° the heater was withdrawn and a cooling curve recorded. This was used to calculate the half-time of cooling and the cooling rate constant. In preliminary experiments, determinations were made over a range of stirring speeds (Table 1), and all subsequent measurements were made with the stirrer rotating at 4500 r.p.m. at least. The cooling rate constant was measured over a temperature range from 80° to 230°, six determinations being made at each temperature; the results are given in Table 2.

FIG. 1. *Apparatus for measuring decomposition rates.*



A, Thermometer. B, Tube for injecting catalyst. C, Stirrer. D, Socket for reference junction. E, Thermocouple. F, Socket for thermo-regulator. G, Heater winding. H, Baffles.

FIG. 2. *Typical temperature–time recordings.*



The arrows mark t = 0.

TABLE 1. *Effect of stirring speed on cooling rate at* 130°.

Stirring speed (r.p.m.)	1600	3800	4000	4800	6000
Half-time of cooling (sec.)	12·0	8·7	8·4	8·4	8·4
Cooling rate constant (sec.$^{-1}$)	0·058	0·080	0·082	0·082	0·082

Catalysts.—Lauroyl peroxide was crystallised from benzene, and benzoyl peroxide from 50% methanol. t-Butyl perbenzoate and n-octanoyl peroxide were purified by fractional freezing; dimethyl 2,2′-azobis(isobutyrate) was crystallised from methanol, and isopropyl peroxydicarbonate from pentane. Di-t-butyl peroxalate was prepared from t-butyl hydroperoxide and oxalyl chloride [5] and crystallised from ether. Di-(γ-carboxypropionyl) peroxide was prepared as described by Clover and Houghton.[6] Dibenzyl hyponitrite was prepared according to directions of Partington and Shah [7] and recrystallised from carbon disulphide by chilling a solution prepared at room temperature.

TABLE 2. *Cooling rate constants from* 80° *to* 230°.

Temp.	Half-time of cooling (sec.)	Cooling rate constant (sec.$^{-1}$)	Temp.	Half-time of cooling (sec.)	Cooling rate constant (sec.$^{-1}$)
80°	10·93 ± 0·10	0·0634 ± 0·0006	151°	7·52 ± 0·03	0·0922 ± 0·0004
105	9·08 ± 0·14	0·0763 ± 0·0013	168	7·42 ± 0·06	0·0934 ± 0·0008
120	8·61 ± 0·04	0·0805 ± 0·0004	216	7·12 ± 0·11	0·0973 ± 0·0016
135	8·44 ± 0·09	0·0821 ± 0·0009	230	6·67 ± 0·06	0·1040 ± 0·0009
143	8·01 ± 0·03	0·0865 ± 0·0004			

Compounds that were liquid or could be melted without serious decomposition were used in a pure state; benzoyl peroxide and lauroyl peroxide were made into a paste with an approximately equal weight of liquid paraffin; di-t-butyl peroxalate was dissolved in diethyl oxalate.

Measurement of Decomposition Rates.—Liquid paraffin (B.P.; 50 ml.) was put into the reaction vessel and the apparatus was brought to the required temperature. The camera motor was started, and a small sample (*ca.* 5 × 10^{-4} mole) of the pure catalyst or an equivalent amount of paste or solution was rapidly injected into the reaction vessel through the tube in the lid from a hypodermic syringe. After a suitable interval the injection was repeated, and up to six determinations were made at each temperature.

The photographic record was developed and the position of the temperature maximum was located (Fig. 2); a convenient method of doing this has been described by Hartree.[8] The time interval between the maximum and the point at which the temperature regained its original value after the initial cooling was determined by comparison with the time scale marked by the second beam of the oscillograph; the mean of each set of measurements was then used to calculate the first-order reaction constant and the corresponding half-life time. The results are collected in Table 3.

TABLE 3. *Decomposition rates and half-lives.*

Compound	Temp.	k (10^{-2} sec.)	Half-life (sec.)	Compound	Temp.	k (10^{-2} sec.)	Half-life (sec.)
t-Butyl perbenzoate	164°	3·7	19	Isopropyl peroxydicarbonate	121°	6·9	10
					135	46	1·5
Benzoyl peroxide	143	4·6	15		143	72	1·0
	150·5	8·2	8·5				
	166	45	1·5	Di-t-butyl peroxalate	95	7·9	8·8
					105	27	2·6
Lauroyl peroxide	135	6·1	11				
	145	17·9	3·9	Dibenzyl hyponitrite	89	5·4	13
	161	51	1·4		100	10·0	6·9
					112	21	3·2
n-Octanoyl peroxide	135	8·9	7·8		123	33	2·1
	151	29	2·4				
				Di-(γ-carboxypropionyl) peroxide	134	3·0	23
Dimethyl 2,2′-azobis(isobutyrate)	126	1·25	55				
	135	2·8	25				
	143	9·0	7·7				
	151	19·4	3·6				
	166	52	1·3				

Effect of Concentration.—The rate of decomposition of isopropyl peroxydicarbonate was

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[5] Pajaczkowski and I.C.I., B.P. Appl. 15,443/1958.

[6] Clover and Houghton, *Amer. Chem. J.*, 1904, **32**, 43.

[7] Partington and Shah, *J.*, 1932, 2589.

[8] Hartree, " Numerical Analysis," Clarendon Press, Oxford, 1952, p. 120.

measured several times at constant temperature, solutions of the compound in kerosene as well as the pure substance being used. The following results were obtained:

Temp.	Concn. of solution (% w/v)	Half-life (sec.)
120°	10	10·5
120	30	11·2
120	45	9·6
120	Pure substance	10·0

DISCUSSION

Experimental Errors.—The apparatus had a half-time of cooling ranging from 7 to 11 seconds depending on the temperature, and it was used to measure half-lives between 1 and 30 seconds. Within this range it was estimated that the experimental error did not exceed 10% of the half-life; the chief sources of error were as follows.

Measurement of T. In a series of determinations at constant temperature each of which was repeated six times the standard error of the half-lives was nearly constant at 2%.

Cooling rate constant. The cooling rate constant was measured at several temperatures, with six determinations at each temperature; the average standard error of the corresponding half-life times was about 1% (Table 2). After the experimental work was finished some further determinations of the cooling rate constant gave results which agreed closely with the original values.

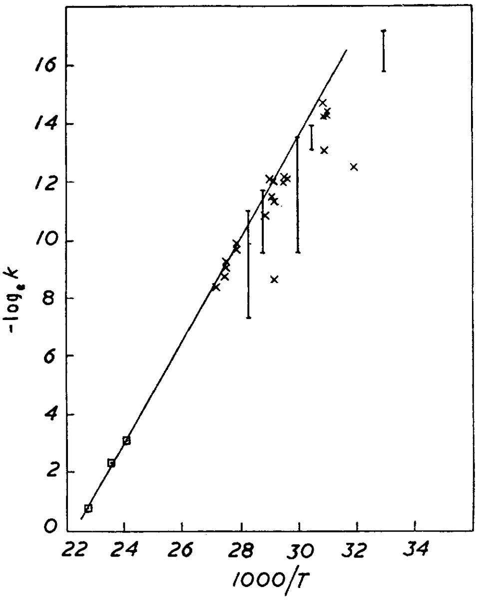

FIG. 3. *Rate of decomposition of benzoyl peroxide.*

□ *these results.*
× *previous work.*

Temperature measurement. The temperature of each experiment was measured with a mercury thermometer calibrated in degrees and a correction was applied for the emergent stem; it is estimated that the observed temperature was correct to 0·5°. During an experiment the temperature change was also about 0·5°; the temperature at which each half-life was measured could therefore be in error by as much as 1°, and this would cause an error of up to 5% in the half-life in a typical case.

Loss of heat by evaporation. Loss of heat by evaporation of a volatile compound during a determination would cause a serious error because it would alter the rate of cooling. For this reason it was impossible to obtain valid results with di-t-butyl peroxide, for instance, which does not decompose rapidly below its boiling point. Results on compounds which evolve a gas on decomposition are unlikely to be much in error from this cause because the amount of heat lost is quite small.

Comparison with Previous Results.—In Fig. 3 the results obtained with benzoyl peroxide between 143° and 166° are compared with previously published values at lower temperatures collected from twelve papers.[9] Vertical lines have been used to represent the range when there were too many results at one temperature to show separate points, and the line drawn somewhat arbitrarily through the present results indicates reasonably good agreement with most of the previous work.

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[9] Bamford and White, *J.*, 1959, 1860; Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216; Bartlett and Vaughan, *J. Phys. Colloid Chem.*, 1947, **51**, 942; Blomquist and Buselli, *J. Amer. Chem. Soc.*, 1951, **73**, 3883; Bailey and Godin, *Trans. Faraday Soc.*, 1956, **52**, 68; Cass, *J. Amer. Chem. Soc.*, 1946, **68**, 1976; Cohen, *ibid.*, 1945, **67**, 17; Ewald, *Discuss. Faraday Soc.*, 1956, **22**, 146; Hartmann, Sellers, and Turnbull, *J. Amer. Chem. Soc.*, 1947, **69**, 2416; Nicholson and Norrish, *Discuss. Faraday Soc.*, 1956, **22**, 97; Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; Swain, Stockmeyer, and Clarke, *ibid.*, 1950, **72**, 5426.