Thermochimica Acta, 220 (1993) 103–115
Elsevier Science Publishers B.V., Amsterdam

Kinetic study by differential scanning calorimetry of the thermal decomposition of ethyl 2-*t*-butylperoxymethyl propenoate in hydrogen donor solvents

C. Navarro and B. Maillard *

Laboratoire de Chimie Organique et Organométallique, Associé au CNRS URA 35, Université Bordeaux 1, 351 Cours de la Libération, F-33405 Talence-Cédex (France)

(Received 1 October 1992; accepted 16 October 1992)

Abstract

A kinetic study of the thermal decomposition of ethyl 2-*t*-butylperoxymethyl propenoate in triisopropylbenzene using differential scanning calorimetry showed the existence of induced decompositions in addition to the expected homolysis of the peroxidic bond. The kinetic rate law for the disappearance of the peroxide was determined as being of the form $-\mathrm{d}C/\mathrm{d}t = k_1C + k_2C^2$. The study of the thermolysis of ethyl 2-*t*-butylperoxymethyl propenoate in octadecane using the same technique could not be used to determine the kinetic rate law.

INTRODUCTION

In a previous paper [1], a preliminary study of the decomposition of ethyl 2-*t*-butylperoxymethyl propenoate **1** in different solvents was made using differential scanning calorimetry (DSC) under dynamic conditions (linear temperature programming). The disappearance of an important proportion of the peroxide by induced decomposition was thought to explain the results, even at very low concentrations in octadecane and triisopropylbenzene. The identification of an epoxide in the reaction products in cyclohexane and cumene indicated an induced decomposition of the peroxide **1** through an addition–intramolecular homolytic substitution mechanism (Fig. 1) [2]. Such a reaction prohibited the direct determination of the kinetic parameters of its spontaneous decomposition by classical analysis of the thermogram [3].

Some ten years ago, in a study of the thermolysis of benzoyl peroxide in di-*n*-butylphthalate, we proposed [4] the use of DSC under dynamic conditions. This made possible the determination of the kinetic equation for the consumption of an initiator by the two competitive reactions: spontaneous decomposition and induced decomposition. Ethyl 2-*t*-butyl-

---

* Corresponding author.

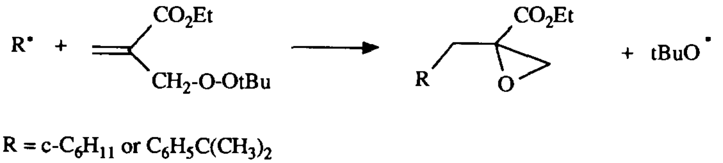


Fig. 1. Decomposition of **1** by addition–intramolecular homolytic substitution.

peroxymethyl propenoate has been analysed in the same way in order to assess its stability and reactivity in free radical reactions. This study also sought to confirm the mechanism proposed for the induced decomposition. Indeed, in recent years, we have focussed our interest on the induced decomposition of unsaturated peroxidic compounds through the addition of a radical to the double bond, followed by an intramolecular free radical attack on the O–O bond [5].

The use of DSC under dynamic conditions is based on a constant proportionality between the rate of heat evolution and the rate of the reaction in the temperature range of the study. This condition is met for a single reaction but in the case of competitive processes, it is necessary that they have similar enthalpies; this is generally the case for the spontaneous and induced decompositions of free radical initiators. The thermolyses of various solutions of the studied compound (generally 0.05, 0.1, 0.25, 0.5 and 1 M) performed in the cell of a DSC apparatus, provided thermograms (Fig. 2) whose analyses yielded sets of values [6] for temperature, the experimental parameter $z = h/(A - a)$ and the instantaneous concentration of the peroxide $C_t = C_0 a/A$.

The type of kinetic equation governing the consumption of the initiator can be determined from various plots of the parameters z and C at each temperature [4, 6, 7], e.g.

(a) $\ln z = f(\ln C)$. A straight line would indicate a kinetic law of the form $-\mathrm{d}C/\mathrm{d}t = kC^{x+1}$ (x being the slope of the line).

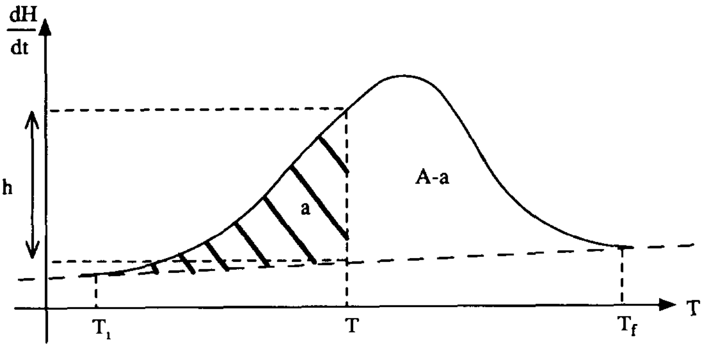


Fig. 2. Thermogram.

(b) $\ln(z - z') = f(\ln C)$ (z' being the value of z for the smaller concentration of initiator used in the study, generally 0.05 M). A straight line would indicate a kinetic law of the form $-\mathrm{d}C/\mathrm{d}t = k_1C + k_{x+1}C^{x+1}$ (x being the slope of the line).

The thermolysis of a free radical initiator generally yields the latter type of equation, the first term corresponding to the spontaneous decomposition of the compound and the second to the induced decomposition; i.e. $k_1 = k_d$ and $k_{x+1} = k_i$.

Whatever the plot, if no straight line or lines with different slopes at the various temperatures are obtained, the single conclusion of the study is that either the processes do not obey the previous kinetic laws, or the proportionality condition between the rates of heat evolution and of reaction is not met.

EXPERIMENTAL

A Mettler DSC 30 fitted with a TC10A processor was used. Aluminium caps of 160 μl capacity were filled with about 100 μl of peroxide solution. After crimping, no hole was made in the top of the cap thus preventing evaporation of low boiling products (a hole is recommended by the manufacturer to avoid the cap blowing off).

Triisopropylbenzene, cumene and octadecane, purchased from Aldrich, were filtered over silica, neat or in pentane solution for the solid compound, prior to distillation under argon.

The thermogram was analysed as previously described [4, 6]. The activation parameters of the reactions were determined from the rate constants using a program on a Hewlett-Packard 97 calculator [7].

The preparation and chemical analyses of the thermolysis products of peroxide **1** in cumene have been described in a previous work [1].

RESULTS AND DISCUSSION

Thermolyses of 1 in triisopropylbenzene

From the values of the various experimental parameters obtained in the analyses of the thermograms (Table 1), plots of $\ln z$ versus $\ln C_i$ were made. Straight lines were not observed, indicating that the kinetic rate law for the disappearance of the peroxide **1** thermolysed in triisopropylbenzene was not of the form $-\mathrm{d}C/\mathrm{d}t = k_xC^x$.

Conversely, the plots of $\ln(z - z_{0.05})$ versus C_i at each temperature gave straight lines with slopes in a relatively narrow range (1.05–1.2) which indicated that the kinetic law could be of the form $-\mathrm{d}C/\mathrm{d}t = k_1C + k_2C^2$.

TABLE 1

Values of $z(\times 10^4\,\mathrm{s}^{-1})$, $C\,(\mathrm{M}^{-1}\,\mathrm{l})$ and T (°C) in the thermolyses of **1** at various concentrations in triisopropylbenzene

T (°C)	C_t									
	0.05		0.11		0.25		0.5		1.0	
	z	C	z	C	z	C	z	C	z	C
127.5			2.45	0.0954	2.90	0.222	4.29	0.416	6.49	0.783
			2.23	0.0972	3.23	0.220	4.37	0.414	7.18	0.757
130			3.08	0.0932	3.83	0.216	5.43	0.403	8.64	0.742
			2.91	0.0944	3.96	0.216	5.73	0.398	9.30	0.715
132.5	2.41	0.0431	3.81	0.0914	4.95	0.22	6.97	0.387	11.3	0.703
	2.76	0.0426	3.56	0.0933	5.15	0.205	7.02	0.387	11.9	0.671
135	3.15	0.0422	4.74	0.0888	6.17	0.204	8.77	0.369	14.6	0.644
	3.49	0.0417	4.67	0.0906	6.38	0.199	9.02	0.364	15.3	0.613
137.5	3.93	0.0413	5.64	0.0862	7.55	0.196	10.9	0.349	18.0	0.590
	4.39	0.0405	5.82	0.0882	8.13	0.192	11.0	0.346	17.1	0.650
140	4.88	0.0402	6.73	0.0824	9.48	0.184	13.7	0.322	22.2	0.512
	5.48	0.0393	7.25	0.0844	9.96	0.182	13.8	0.319	22.0	0.577
142.5	5.80	0.0389	8.40	0.0787	11.8	0.173	16.7	0.295	26.1	0.452
	6.77	0.0379	8.91	0.0796	12.5	0.169	16.6	0.290	26.3	0.501
145	7.15	0.0375	10.4	0.0745	14.6	0.159	20.1	0.261	30.7	0.376
	8.38	0.0361	10.8	0.0752	15.5	0.156	19.7	0.262	31.3	0.415
147.5	8.78	0.0356	12.5	0.0696	17.7	0.145	23.5	0.232	35.4	0.311
	10.3	0.0342	13.2	0.0699	18.2	0.140	23.5	0.229	35.5	0.342
150	10.9	0.0334	15.8	0.0624	21.2	0.127	27.4	0.197	39.6	0.246
	12.6	0.0321	16.7	0.0684	22.0	0.124	27.5	0.194	39.8	0.271

The plots of $z = f(C_t)$ gave straight lines, confirming this result [4]. The measurement of the slope and the intercept provided, respectively, the values of k_2 and k_1, see Table 2. The representation of ln k_1 and ln k_2 versus $1/T$ indicated good Arrhenius relationships, which could be considered as corroborating the reality of these numbers as rate constants. Indeed, such an unfulfilled condition would have indicated that the linear relationship obtained on plotting of z against C at each temperature was an artefact.

According to Tobolski and Mesrobian [8], such a kinetic rate law for the disappearance of the peroxide **1** would indicate an induced decomposition of the peroxide by a radical deriving from the solvent, with two possible terminations between radicals issued from the solvent and peroxide, or from the solvent alone.

Taking into account these results one would attribute the first term of the

TABLE 2

Rate constants k_1 and k_2 determined for the thermolysis of **1** in triisopropylbenzene

T(°C)	$1/T \times 10^{-3}$	$k_1 \times 10^4$ (s^{-1})	$k_2 \times 10^4$ ($M^{-1} l s^{-1}$)
127.5	2.497	1.63	6.69
130	2.481	1.95	9.49
132.5	2.466	2.16	13.5
135	2.451	2.56	19.1
137.5	2.436	3.47	22.4
140	2.421	3.92	32.5
142.5	2.407	4.68	44.0
145	2.392	5.37	62.0
147.5	2.378	6.30	84.3
150	2.364	7.76	115.0

kinetic law k_1C to the spontaneous decomposition of **1** and the second k_2C^2 to the induced decomposition. A comparison of the values of k_1 and the corresponding k_d obtained during the thermolysis of **1** in the mixture diphenylmethane–triphenylmethane [1], through the activation parameters ($E_{ad} = 150$ kJ, $E_{a1} = 89$ kJ; $\ln Z_d = 35$, $\ln Z_1 = 20.7$) showed important discrepancies. This could not be attributed to the solvents because they are relatively similar. Nor was a difference in the enthalpies of reaction for the competitive induced (addition–elimination) and spontaneous processes the reason because their rough calculation [9] gave values of 299 and 342 kJ (Table 3). (These estimations seem reliable because the values measured in the various experiments were in the range 293–334 kJ.) Moreover, we have to stress that the existence of a factor m between the enthalpies of both processes would give a systematic error on the rate constant; $k_{\text{measured}} = mk$, which would make a difference between the measured and real frequency factors but not in the activation energies.

This led us to consider the presence of two different induced decompositions. The analysis of the decomposition products of **1** in various solvents [2] showed the formation of similar high-boiling products, whatever the solvent. The determination of the balance of the products formed from the peroxide and the NMR study of this residues indicated that they were essentially produced by an initial allylic attack on **1**, leading to highly polymerizable alkenes (Fig. 3). Such an induced decomposition of allylic peroxides had been suspected in the preliminary DSC study of the thermolysis of such compounds [1].

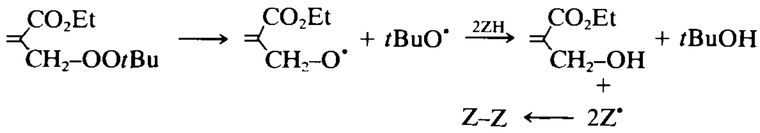
An estimation of the enthalpy of the second induced decomposition was performed to confirm that it is similar to those of the other processes (Table 3).

Assuming steady state concentrations of the radicals, a mathematical treatment similar to that of Tobolski and Mesrobian [8] (see Appendix) was

TABLE 3

Estimation of the enthalpies of the various decompositions of **1**

Spontaneous decomposition



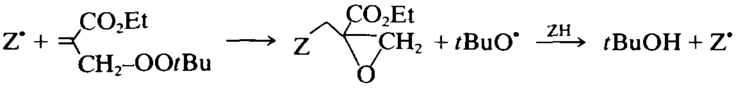
ZH = triisopropylbenzene

Broken bonds: O–O, 2C–H

Created bonds: 2O–H, C–C

$$\Delta H = 2E_{\text{O-H}} + E_{\text{C-C}} - E_{\text{O-O}} - 2E_{\text{C-H}}$$
$$= 2 \times 462.3 + 345.3 - 146.3 - 2 \times 412.5 = 299\ \text{kJ mol}^{-1}$$

Induced decomposition by addition–intramolecular homolytic substitution



Broken bonds: C=C, O–O, C–H

Created bonds: 2C–C, C–O, O–H

$$\Delta H = 2E_{\text{C-C}} + E_{\text{C-O}} + E_{\text{O-H}} - E_{\text{C=C}} - E_{\text{O-O}} - E_{\text{C-H}}$$
$$= 2 \times 345.3 + 357.4 + 462.3 - 609.4 - 146.3 - 412.5 = 342\ \text{kJ mol}^{-1}$$

carried out on the basis of the two induced decompositions addition–intramolecular homolytic substitution and allylic hydrogen abstraction–β-elimination, with the various hypotheses of termination (Fig. 4).

It can be seen that, among the various possible terminations, the single case where a kinetic rate law of the type $k = k_1C + k_2C^2$ could be obtained, corresponds to a cross-termination reaction between the radical issued from the solvent and the peroxide.

The analysis of the reaction products of the thermolysis of **1** (130°C, 12 hours) in cumene (0.5 M), as a model of triisopropylbenzene, indicated the formation of α-methylstyrene (5% yield relative to peroxide), which could

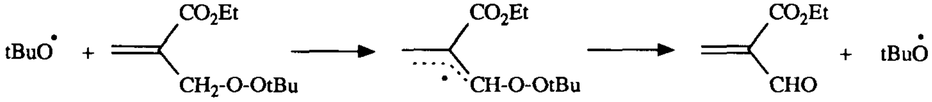


Fig. 3. Induced decomposition by allylic attack followed by β-elimination.

$$\begin{aligned}
&\mathrm{P} &&\xrightarrow{\mathrm{k_d}} && 2\,\mathrm{R}^{\bullet}\\
&\mathrm{R}^{\bullet} + \mathrm{P} &&\xrightarrow{\mathrm{k_a}} && \mathrm{R}^{\bullet} + \text{"High boiling products"}\\
&\mathrm{R}^{\bullet} + \mathrm{SH} &&\xrightarrow{\mathrm{k_H}} && \mathrm{RH} + \mathrm{S}^{\bullet}\\
&\mathrm{S}^{\bullet} + \mathrm{P} &&\xrightarrow{\mathrm{k_i}} && \mathrm{R}^{\bullet} + \text{Epoxide}\\
&\text{Radicals} &&\xrightarrow{\mathrm{k_t}} && \text{Products}
\end{aligned}$$

Fig. 4. Radical reactions of **1**.

be produced by disproportionation of cumyl and alcoxy radicals. A complementary experiment demonstrated the consumption of α-methylstyrene under the reaction conditions (heating a solution of 0.06 M of this alkene and 0.5 M of **1** in cumene at 130°C for 12 h showed that 80% of it disappeared). The dehydrodimer of cumene formed by the coupling of cumyl radicals was detected, but to a very low extent (yield of 3% relative to **1**). Two epoxides corresponding to the induced decomposition of **1** by the addition of cumyl and methyl radicals were formed with respective yields of 44% and 7%.

The formation of all these compounds was fitted with the mechanism proposed according to the kinetic analysis [9]. The second induced decomposition of **1** involving an allylic attack was difficult to prove. Nevertheless, assuming that the peroxide is disappearing by homolysis and the two induced decompositions, the balance of peroxide could be considered as an indirect piece of evidence, i.e.; spontaneous decomposition: $5\% \times 100/20 + 3\% = 28\%$ (the α-methylstyrene and dehydrodimer of cumene produced); induced decompositon by addition: $44\% + 7\% = 51\%$ (epoxides); induced decomposition by allylic attack: $100\% - 28\% - 51\%$ $=21\%$ [11].

A total products balance has been determined in the study of the induced decomposition of **1** initiated by *t*-butyl peracetate in benzene [2], confirming this approach.

The identification of the experimental and theoretical kinetic rate law has led to the equations

$$k_1 = k_d + \frac{2k_i k_H \mathrm{SH}}{k_t\left[1 + \sqrt{1 + \dfrac{4k_i k_H \mathrm{SH}}{k_d k_t}}\right]}$$

$$k_2 = \frac{k_a k_d}{2k_H \mathrm{SH}}\left[1 + \sqrt{1 + \frac{4k_i k_H \mathrm{SH}}{k_d k_t}}\right]$$

which suggests that it is surprising that the experimental values of k_1 and k_2

TABLE 4

Estimation of the rate constants of the elementary free-radical reactions at 130°C

$k_d = 5 \times 10^{-5}\ \mathrm{s^{-1}}$	
$k_t = 10^{10}\ \mathrm{M^{-1}\,l\,s^{-1}}$	Reaction controlled by molecular diffusion [12]
$k_i = 8 \times 10^{3}\ \mathrm{M^{-1}\,l\,s^{-1}}$	
	$k_{\mathrm{polym}}(\mathrm{styrene}) = 5 \times 10^{3}\ \mathrm{M^{-1}\,l\,s^{-1}}$ [13] $\dfrac{k_{\mathrm{polym}}(\mathrm{styrene})}{k_{\mathrm{copolym}}(\mathrm{styrene{-}EMA})} = 0.67$ [13] $k_{\mathrm{copolym}}(\mathrm{styrene{-}EMA}) = 8 \times 10^{3}\ \mathrm{M^{-1}\,l\,s^{-1}}$
$k_a = 1.6 \times 10^{7}\ \mathrm{M^{-1}\,l\,s^{-1}}$	allylic abstraction to cyclopentene [14]
$k_H = 5 \times 10^{6}\ \mathrm{M^{-1}\,l\,s^{-1}}$	estimated from toluene and cumene [15] toluene $\rightarrow 1.5 \times 10^{5}\ \mathrm{M^{-1}\,l\,s^{-1}}$ cumene: 10 times more reactive than toluene $\rightarrow 1.5 \times 10^{6}\ \mathrm{M^{-1}\,l\,s^{-1}}$ TIPB $\rightarrow$ 3 positions equivalent to cumene $\rightarrow 4.5 \times 10^{6}\ \mathrm{M^{-1}\,l\,s^{-1}}$
$[\mathrm{SH}] = 4\ \mathrm{mol\,l^{-1}}$	Molecular weight = 204; density ≈ 0.8

could satisfy Arrhenius relationships, unless several terms are neglectable. Using the estimated values of the rate constants of the elementary free-radical reactions at 130°C, provided in Table 4, approximated values of k_1 and k_2 can be obtained

$$k_1 \approx \sqrt{\frac{k_i k_H \mathrm{SH}}{k_t}}$$

$$k_2 \approx \sqrt{\frac{k_d k_i}{k_H k_t \mathrm{SH}}}$$

with estimated final values of $k_1 = 10^{-2}\ \mathrm{s^{-1}}$ and $k_2 = 2 \times 10^{-2}\ \mathrm{M^{-1}\,l\,s^{-1}}$. The experimental values obtained from DSC measurements were $k_1 = 2 \times 10^{-4}\ \mathrm{s^{-1}}$ and $k_2 = 10^{-3}\ \mathrm{M^{-1}\,l\,s^{-1}}$. Thus there is not a perfect agreement between the calculated and measured rate constants but, taking into account the rough estimation of the rate constants for the elementary free-radical reactions, this is not really surprising.

*Thermolyses of **1** in octadecane*

The values reported in Table 5 for the different sets of data (T, z, C_t) were used to represent the variations of $\ln z$ and $\ln(z - z')$ versus C_t at each temperature. The first did not yield straight lines whereas the second provided a set of lines with a slope varying in the range 0.7–1.3. These plots indicated that no kinetic exploitation of the DSC experiments for the thermolysis of **1** in octadecane was possible. The analysis of the reaction products [2] in cyclohexane, a simple model of octadecane because it bears

TABLE 5

Values of $z(\times 10^4\,s^{-1})$, $C\,(M^{-1}\,l)$ and T (°C) in the thermolyses of **1** at various concentrations in octadecane

T (°C)	C_i									
	0.061		0.1		0.25		0.51		1.08	
	z	C	z	C	z	C	z	C	z	C
117.5					3.60	0.211	3.45	0.448	5.21	0.992
					3.3	0.216	3.45	0.441	5.03	0.910
120			3.86	0.084	4.54	0.205	4.88	0.431	6.6	0.944
			3.38	0.090	4.57	0.210	4.71	0.425	6.48	0.872
122.5	3.59	0.054	4.75	0.083	6.00	0.200	6.50	0.419	8.65	0.849
	3.67	0.052	4.40	0.087	6.02	0.204	6.02	0.413	8.58	0.825
125	5.21	0.051	6.21	0.080	8.83	0.191	8.28	0.396	11.3	0.846
	5.31	0.048	6.11	0.085	7.86	0.195	8.09	0.393	11.1	0.786
127.5	6.68	0.05	8.12	0.076	9.80	0.181	10.6	0.380	15.1	0.781
	7.02	0.045	8.20	0.080	10.3	0.182	10.4	0.372	14.8	0.720
130	8.93	0.047	10.2	0.072	12.6	0.170	13.9	0.347	19.7	0.702
	9.12	0.044	10.8	0.075	12.8	0.171	14.1	0.344	14.5	0.653
132.5	11.2	0.045	13.2	0.067	16.1	0.155	17.8	0.320	26.9	0.611
	11.6	0.042	13.6	0.071	17.1	0.154	18.1	0.310	26.3	0.566
135	14.3	0.045	16.2	0.061	20.8	0.138	23.6	0.277	37.1	0.499
	14.5	0.040	17.5	0.064	20.6	0.141	23.8	0.272	35.9	0.467
137.5	17.6	0.038	20.1	0.054	27.2	0.119	30.1	0.240	49.9	0.393
	18.2	0.035	21.1	0.057	26.2	0.122	29.6	0.236	49.0	0.358
140	23.7	0.033	24.7	0.048	33.2	0.102	39.0	0.194	66.2	0.27
	23.8	0.031	26.6	0.049	32.9	0.103	39.0	0.186	64.4	0.259

similar aliphatic hydrogens, was then undertaken [2]. Two different induced decompositions take place in cyclohexane, as was the case for cumene. The difference in the thermolyses of **1** in cyclohexane (or octadecane) and cumene (or triisopropylbenzene) certainly came from the termination reactions which defined the steady state concentration of the radicals and, hence, on the type of kinetic law (see Appendix). This was in agreement with the identification of dicyclohexyle in the reaction products of the thermolysis of **1** in cyclohexane. Disproportionation of the cyclohexyl radical with alcoxyl radical was not so efficient as in the case of cumyl radical because the concentration of cyclohexyl radicals was certainly lower in the medium according to a more efficient addition to the unsaturated peroxide, and because this reaction was less favoured as it does not produce a conjugated double bond.

CONCLUSIONS

The kinetic study using DSC of the thermolysis of ethyl 2-*t*-butylperoxymethyl propenoate in triisopropylbenzene provided the kinetic rate law for the disappearance of this compound, $-\mathrm{d}C/\mathrm{d}t = k_1C + k_2C^2$, and confirmed the complex mechanism accounting for it. The analysis of the reaction products proved the existence of two induced decompositions of the peroxide by an addition–intramolecular homolytic process and an allylic hydrogen abstraction–β-elimination, in addition to the expected homolysis. Termination was found to occur by disproportionation of oxy radicals issued from the peroxide with radicals coming from the solvent. Assuming steady state concentrations of the radicals, the calculation of the theoretical kinetic rate law for consumption of the peroxide proved that the experimental kinetic law is only an approximation. A similar study performed on the thermolysis of the same compound in octadecane did not allow the kinetic rate law to be determined because it was too complicated and no approximation was possible.

ACKNOWLEDGEMENTS

The authors acknowledge Akzo Chemicals for a fellowship to one of us (C.N.), and Dr A.J. De Jong, Dr P. Hope, Dr J. Meijer (Akzo Chemicals Deventer) and Dr L. Vertommen (Akzo Corporate Research Arnhem) for very fruitful discussions during the course of this study. B.M. is grateful to the Conseil Régional d'Aquitaine for a specific grant of equipment on a project "Peroxides and Free Radicals".

REFERENCES AND NOTES

1 C. Navarro and B. Maillard, New J. Chem., 20 (1992) 987.
2 C. Navarro, A. Saux and B. Maillard, New J. Chem., 20 (1992) 993.
3 C. Filliatre, B. Maillard and J.J. Villenave, Thermochim. Acta, 30 (1979) 83.
J.J. Villenave, C. Filliatre and B. Maillard, Computer and Chemistry, 3 (1979) 95.
4 J.-P. Bop, C. Filliatre, B. Maillard and J.J. Villenave, Thermochim Acta, 43 (1981) 339.
5 E. Montaudon, X. Lubeigt and B. Maillard, J. Chem. Soc. Perkin Trans. 2, (1991) 1531 and previous papers in the series.
6 J.J. Villenave, J.-P. Bop, C. Filliatre and B. Maillard, Computer and Chemistry, 5 (1981) 117.
7 B. Maillard, J.J. Villenave and C. Filliatre, Computer and Chemistry, 3 (1979) 101.
8 A.V. Tobolski and R.B. Mesrobian, Organic Peroxides, Interscience, New York, 1954, p. 83.
9 The bond energy values (C–H, C–O, C=O, C–C, C=C, O–O and O–H) used in this calculation were taken as general values [10]. The particular characters of the benzylic C–H bond and of the methacrylic double bond are not taken into account but cannot make an important difference; we could agree with a factor of two between the enthalpies of reaction.
10 J.D. Roberts and M. Caserio, Chemie Organique Moderne, Ediscience, Paris, 1968, p. 70 (in French).

11 In addition to the main induced decompositions and termination reaction, two minor processes are apparent: the addition of a methyl radical and the coupling of cumyl radicals. A tentative determination (without the computer) of the kinetic rate law for the disappearance of the peroxide, accounting for all these processes, did not succeed because of the highly complex calculations.
12 K.U. Ingold, in J.K. Kochi (Ed.), Free Radicals, Vol. 1, Wiley, New York, 1973, p. 37.
13 J. Brandrup and E.H. Immergut, Polymers Handbook, 2nd edn., Wiley Interscience, New York, 1975, Chap. 2.
14 P.C. Wong, D. Griller and J.C. Scaiano, J. Am. Chem. Soc., 104 (1982) 5106.
15 K.U. Ingold, in J.K. Kochi (ed.), Free Radicals, Vol. 1, Wiley, New York, 1973, p. 73.

APPENDIX

1. Induced decomposition of **1** by radicals from solvent ($S^{\bullet}$) and peroxide ($R^{\bullet}$) with termination by coupling or disproportionation of radicals $R^{\bullet}$.

$$P \xrightarrow{k_d} 2R^{\bullet}$$

$$R^{\bullet} + P \xrightarrow{k_a} R^{\bullet} + \text{products}$$

$$R^{\bullet} + SH \xrightarrow{k_H} RH + S^{\bullet}$$

$$S^{\bullet} + P \xrightarrow{k_i} R^{\bullet} + \text{products}$$

$$R^{\bullet} + R^{\bullet} \xrightarrow{k_t} \text{products}$$

Steady state concentration $\Rightarrow \dfrac{d[S^{\bullet}]}{dt} = 0 = \dfrac{d[R^{\bullet}]}{dt}$

$$\frac{d[S]}{dt} = k_H(R^{\bullet}SH) - k_i(S^{\bullet}P) \Rightarrow k_H(R^{\bullet}SH) = k_i(S^{\bullet}P) \qquad \text{(A1)}$$

$$\frac{d[R]}{dt} = 2k_d(P) - k_H(R^{\bullet}SH) + k_i(S^{\bullet}P) - 2k_t(R^{\bullet})^2 \qquad \text{(A2)}$$

$$\text{(A1)} + \text{(A2)} \rightarrow k_d(P) = k_t(R^{\bullet})^2$$

$$R^{\bullet} = \sqrt{\frac{k_d}{k_t}} \cdot P^{1/2} \qquad S^{\bullet} = \frac{k_H SH}{k_i P} \qquad R^{\bullet} = \frac{k_H SHP^{1/2}}{k_i P} \sqrt{\frac{k_d}{k_t}}$$

$$-\frac{d[P]}{dt} = k_d P + k_a R^{\bullet}P + k_i S^{\bullet}P$$

$$-\frac{d[P]}{dt} = k_d P + k_a \sqrt{\frac{k_d}{k_t}} \cdot P^{3/2} + k_H \sqrt{\frac{k_d}{k_t}} SHP^{1/2}$$

2. Induced decomposition of **1** by radicals from solvent ($S^\bullet$) and peroxide ($R^\bullet$) with termination by coupling or disproportionation of radicals ($S^\bullet$).

$$P \xrightarrow{k_d} 2R^\bullet$$

$$R^\bullet + P \xrightarrow{k_a} R^\bullet + \text{products}$$

$$R^\bullet + SH \xrightarrow{k_H} RH + S^\bullet$$

$$S^\bullet + P \xrightarrow{k_i} R^\bullet + \text{products}$$

$$S^\bullet + S^\bullet \xrightarrow{k_t} \text{products}$$

$$\frac{d[R^\bullet]}{dt} = 2k_d(P) + k_a(R^\bullet P) - k_a(R^\bullet P) - k_H(R^\bullet SH) = 0 \qquad \text{(A3)}$$

$$\frac{d[S^\bullet]}{dt} = k_H(R^\bullet SH) - k_i(S^\bullet P) - 2k_t(S^\bullet)^2 = 0 \qquad \text{(A4)}$$

$$(A3) + (A4) \rightarrow S^\bullet = \sqrt{\frac{k_d}{k_t}}P^{1/2}$$

$$(A3 - A4) \rightarrow k_d(P) - k_H(SHR^\bullet) + k_i(S^\bullet P) + k_t(S^\bullet)^2 = 0$$

$$\Rightarrow R^\bullet = \frac{2k_dP}{k_HSH} + \frac{k_i}{k_HSH}\sqrt{\frac{k_d}{k_t}}P^{3/2}$$

$$-\frac{d[P]}{dt} = k_d(P) + k_a(R^\bullet P) + k_i(S^\bullet P)$$

$$= k_dP + k_aP\left[\frac{2k_dP}{k_HSH} + \frac{k_i}{k_HSH}\sqrt{\frac{k_d}{k_t}}P^{3/2}\right] + k_i\sqrt{\frac{k_d}{k_t}}P^{3/2}$$

$$-\frac{d[P]}{dt} = k_dP + k_i\sqrt{\frac{k_d}{k_t}}P^{3/2} + \frac{2k_ak_dP^2}{k_HSH} + \frac{k_ik_a}{k_HSH}\sqrt{\frac{k_d}{k_t}}P^{5/2}$$

3. Induced decomposition of **1** by radicals from the solvent ($S^\bullet$) and peroxide ($R^\bullet$) with termination by coupling or disproportionation of radicals $R^\bullet$ and $S^\bullet$.

$$P \xrightarrow{k_d} 2R^\bullet$$

$$R^\bullet + P \xrightarrow{k_a} R^\bullet + \text{product}$$

$$R^\bullet + SH \xrightarrow{k_H} RH + S^\bullet$$

$$\mathrm{S}^{\bullet} + \mathrm{P} \xrightarrow{k_i} \mathrm{R}^{\bullet} + \text{product}$$

$$\mathrm{S}^{\bullet} + \mathrm{R}^{\bullet} \xrightarrow{k_t} \text{products}$$

$$\frac{\mathrm{d}[\mathrm{R}^{\bullet}]}{\mathrm{d}t} = 2k_{\mathrm{d}}(\mathrm{P}) - k_{\mathrm{H}}(\mathrm{R}^{\bullet}\mathrm{SH}) + k_{\mathrm{i}}(\mathrm{S}^{\bullet}\mathrm{P})k_{\mathrm{t}}(\mathrm{R}^{\bullet}\mathrm{S}^{\bullet}) = 0 \qquad \text{(A5)}$$

$$\frac{\mathrm{d}[\mathrm{S}^{\bullet}]}{\mathrm{d}t} = -k_{\mathrm{i}}(\mathrm{S}^{\bullet}\mathrm{P}) + k_{\mathrm{H}}(\mathrm{R}^{\bullet}\mathrm{SH}) - k_{\mathrm{t}}(\mathrm{S}^{\bullet}\mathrm{R}^{\bullet}) = 0 \qquad \text{(A6)}$$

$$\text{(A5)} + \text{(A6)} \rightarrow 2k_{\mathrm{d}}(\mathrm{P}) = 2k_{\mathrm{t}}(\mathrm{S}^{\bullet}\mathrm{R}^{\bullet}) \Rightarrow \mathrm{S}^{\bullet} = \frac{k_{\mathrm{d}}\mathrm{P}}{k_{\mathrm{t}}\mathrm{R}^{\bullet}}$$

$$\text{(A5)} - \text{(A6)} \rightarrow k_{\mathrm{d}}(\mathrm{P}) + k_{\mathrm{i}}(\mathrm{S}^{\bullet}\mathrm{P}) - k_{\mathrm{H}}(\mathrm{R}^{\bullet}\mathrm{SH}) = 0$$

$$k_{\mathrm{d}}(\mathrm{P}) + \frac{k_{\mathrm{i}} + k_{\mathrm{d}}(\mathrm{P})^2}{k_{\mathrm{t}}(\mathrm{R}^{\bullet})} - k_{\mathrm{H}}(\mathrm{R}^{\bullet}\mathrm{SH}) = 0$$

$$k_{\mathrm{t}}k_{\mathrm{H}}(\mathrm{SHR}^{\bullet})^2 - k_{\mathrm{d}}k_{\mathrm{t}}(\mathrm{PR}^{\bullet}) - k_{\mathrm{i}}k_{\mathrm{d}}(\mathrm{P})^2 = 0$$

$$\mathrm{R}^{\bullet} = \frac{k_{\mathrm{d}}k_{\mathrm{t}}\mathrm{P} + \sqrt{k_{\mathrm{d}}^2k_{\mathrm{t}}^2\mathrm{P}^2 + 4k_{\mathrm{i}}k_{\mathrm{d}}\mathrm{P}^2k_{\mathrm{t}}k_{\mathrm{H}}\mathrm{SH}}}{2k_{\mathrm{t}}k_{\mathrm{H}}\mathrm{SH}}$$

$$\mathrm{R}^{\bullet} = \frac{k_{\mathrm{d}}\mathrm{P}}{2k_{\mathrm{H}}\mathrm{SH}}\left[1 + \sqrt{1 + \frac{4k_{\mathrm{i}}k_{\mathrm{H}}\mathrm{SH}}{k_{\mathrm{d}}k_{\mathrm{t}}}}\right]$$

$$\mathrm{S}^{\bullet} = \frac{k_{\mathrm{d}}\mathrm{P}}{k_{\mathrm{t}}\mathrm{R}^{\bullet}} = \frac{k_{\mathrm{d}}\mathrm{P}}{k_{\mathrm{t}}\dfrac{k_{\mathrm{d}}\mathrm{P}}{2k_{\mathrm{H}}\mathrm{SH}}\left[1 + \sqrt{1 + \dfrac{4k_{\mathrm{i}}k_{\mathrm{H}}\mathrm{SH}}{k_{\mathrm{d}}k_{\mathrm{t}}}}\right]} = \frac{2k_{\mathrm{H}}\mathrm{SH}}{k_{\mathrm{t}}\left[1 + \sqrt{1 + \dfrac{4k_{\mathrm{i}}k_{\mathrm{H}}\mathrm{SH}}{k_{\mathrm{d}}k_{\mathrm{t}}}}\right]}$$

$$-\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_{\mathrm{d}}\mathrm{P} + k_{\mathrm{a}}\mathrm{R}^{\bullet} + k_{\mathrm{i}}\mathrm{S}^{\bullet}\mathrm{P}$$

$$-\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_{\mathrm{d}}\mathrm{P} + \frac{k_{\mathrm{a}}k_{\mathrm{d}}\mathrm{P}}{2k_{\mathrm{H}}\mathrm{SH}}\left[1 + \sqrt{\frac{4k_{\mathrm{i}}k_{\mathrm{H}}\mathrm{SH}}{k_{\mathrm{d}}k_{\mathrm{t}}}}\right]\mathrm{P} + \frac{2k_{\mathrm{i}}k_{\mathrm{H}}\mathrm{SHP}}{k_{\mathrm{t}}\left[1 + \sqrt{1 + \dfrac{4k_{\mathrm{i}}k_{\mathrm{H}}\mathrm{SH}}{k_{\mathrm{d}}k_{\mathrm{t}}}}\right]}$$

$$-\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = \left[k_{\mathrm{d}} + \frac{2k_{\mathrm{i}}k_{\mathrm{H}}\mathrm{SH}}{k_{\mathrm{t}}\left[1 + \sqrt{1 + \dfrac{4k_{\mathrm{i}}k_{\mathrm{H}}\mathrm{SH}}{k_{\mathrm{d}}k_{\mathrm{t}}}}\right]}\right]\mathrm{P} + \frac{k_{\mathrm{a}}k_{\mathrm{d}}}{2k_{\mathrm{H}}\mathrm{SH}}\left[1 + \sqrt{\frac{4k_{\mathrm{i}}k_{\mathrm{H}}\mathrm{SH}}{k_{\mathrm{d}}k_{\mathrm{t}}}}\right]\mathrm{P}^2$$