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THE THERMOKINETIC PERFORMANCE OF AN ACCELERATING RATE CALORIMETER

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ABSTRACT

The Arrhenius parameters of the thermal decomposition of pure di-*t*-butyl peroxide in toluene were measured to be $E = 37.8 \pm 1.1$ kcal mole^{-1} and $\log A$ (sec^{-1}) $= 16.15 \pm 0.61$ from a series of accelerating rate calorimetric experiments covering a broad range of thermal inertia, from 3.1 to 17. The values are comparable to $E = 37.78 \pm 0.06$ kcal mole^{-1} and $\log A$ (sec^{-1}) $= 15.80 \pm 0.03$ recommended by Shaw and Pritchard from a least-squares treatment of 177 data points obtained by various workers with different techniques. The highest self-heat rates that the calorimeter can follow without deviation from the expected self-heat rate curve were found to be dependent on the types of the sample bombs and the nature of the sample. They are ~70°C min^{-1} for the Ti bombs (~9 g), ~20°C min^{-1} for the light-weight Hastelloy C bombs (~19 g) and only about ~2°C min^{-1} for the heavy-weight Hastelloy C bombs (~70 g) for the reaction system studied.

INTRODUCTION

An accelerating rate calorimeter (ARC) was recently developed for kinetic evaluation of thermal hazards [1]. The instrument provides time (t)—temperature (T)—pressure (P) data for thermally initiated chemical reactions taking place under adiabatic conditions. The initial evaluation [1] based on the study of the thermal decomposition reaction of di-*t*-butyl peroxide from 16 experiments indicates that the relative precision in the determination of adiabatic temperature rise, ΔT_{AB}, the Arrhenius parameters, the frequency factor, A, and the activation energy, E, and the reaction order are ±7.7%, ±2.9%, ±2.3% and ±9.5%, respectively. The accuracy of the Arrhenius parameters was only estimated, but not critically evaluated. A question has been raised about the accuracy of the data obtained under various ARC operating conditions. Theoretically speaking, the Arrhenius parameters obtained should be the kinetic representation of a chemical reaction under investigation, but not dependent on the experimental procedure.

One of the most extensively studied kinetic systems is the thermal decomposition of di-*t*-butyl peroxide. Shaw and Pritchard [2] have critically reviewed the subject and reanalyzed 272 kinetic data points obtained by various workers, including their own, with different techniques, with and without the presence of diluent, in the temperature range 90—350°C. A remarkably good Arrhenius plot was obtained. A least-squares treatment gave $E = 37.90 \pm 0.14$ kcal mole^{-1} and $\log A$ (sec^{-1}) $= 15.80 \pm 0.07$, and $E = 37.78 \pm 0.06$ kcal mole^{-1} and $\log A$ (sec^{-1}) $= 15.80 \pm 0.03$ if three deviating data sets were excluded from the calculation. The variation in the values of E and A from one study to another is mainly attributed to small systematic errors associated with the experiments. One of the kinetic data sets which deviated from the bulk was reported by Murawski et al. [3]. The kinetic rates were based on the pressure measurements. The recalculated values [2] for E and $\log A$ (sec^{-1}) are 36.17 ± 0.39 and 15.05 ± 0.17, respectively. In the above study, it was found that the rate of the reaction was not influenced by the presence of toluene or by the toluene/peroxide ratio. The rate remained the same even in the absence of toluene or when benzene was used instead of toluene, indicating that the solvent effect is not significant. Lewis [4] has also studied the gas phase thermal decomposition of di-*t*-butyl peroxide with the use of a single pulse shock tube and extended the temperature range of the kinetic measurements up to 404°C. The Arrhenius parameters obtained, $E = 36.40 \pm 1.40$ kcal mole^{-1} and $\log A$ (sec^{-1}) $= 15.33 \pm 0.50$, are in agreement with the values recommended by Shaw and Pritchard [2]. An earlier study by Raley et al. [5] reveals that even in such diverse solvents as cumene, *t*-butyl benzene and tri-*n*-butyl amine, the rate of decomposition of di-*t*-butyl peroxide is nearly equal to the rate in the vapor phase. The activation energies obtained from the above solvent systems are 37.5, 38.0, 37.0 kcal mole^{-1}, respectively. However, the effects of solvent in the unimolecular decomposition of di-*t*-butyl peroxide were also reported. Walling and Bristol [6] have investigated the thermal decomposition reaction of di-*t*-butyl peroxide in acetonitrile and cyclohexane and the activation energies were calculated to be 34.2 and 38.4 kcal mole^{-1}, respectively. Huyser and Van Scoy [7] have also studied the solvent effects on the decomposition kinetics of di-*t*-butyl peroxide in various solvents and found activation energies ranging from 31.0 to 40.8 kcal mole^{-1}. An isokinetic relationship was obtained and the isokinetic temperature was calculated to be 437 K. The observed effect was attributed to the interaction of the solvent molecules with the oxygens of the peroxide linkage in the activated state, in which the molecules exhibit considerable free *t*-butoxy radical character.

Even though the complication of the solvent effect was involved in the thermal decomposition of di-*t*-butyl peroxide, all the experimental data indicate that the simple dissociation of the peroxy-oxygen linkage is the rate determining step. However, the product distribution will be strongly governed by the mechanism of the subsequent reactions [4, 5, 7].

Based on the above studies, the thermal decomposition reactions of pure di-*t*-butyl peroxide and di-*t*-butyl peroxide in toluene were chosen for evaluating the kinetic performance of an accelerating rate calorimeter. Di-*t*-butyl peroxide is easy to handle and does not show significant solvent effect on the thermal decomposition kinetics [3]. Hopefully, the results obtained will reveal not only the kinetic performance of the calorimeter and a better understanding of various experimental conditions, but also the significance of the deviation of the data set published by Murawski et al. [3] from the bulk data sets evaluated by Shaw and Pritchard [2].

EXPERIMENTAL

The thermokinetic performance of a microprocessor controlled accelerating rate calorimeter, manufactured by Columbia Scientific Industries of Austin, Texas, under an abbreviated name CSI-ARC™, was investigated in the present study. The detailed description of the ARC principle can be found elsewhere [1, 8].

The key to the operation of the ARC is the ability to maintain the adiabaticity of the sample bomb. Since conduction, convection, and radiation modes of heat transfer along with temperature measurement errors can cause drift in a calorimeter, the ARC employs an operational drift correction routine to achieve high adiabaticity. The ARC calculates the temperature drift at a previously designated temperature and then applies an offset bias voltage in microvolts to the thermocouple output proportional to the observed drift rate. The instrument then checks to see how well this offset corrects the calorimeter drift. It continues to estimate offset voltages and check drifts until an acceptable drift rate is achieved. When the drift is acceptable, as determined by the operator prior to the experiment, it automatically heats to a new temperature and repeats the drift correction process. The drift corrections are performed normally every 50°C for the entire temperature range while the corrections at any other temperature are obtained by interpolation. With these corrections or calibrations, the system will maintain its adiabaticity with respect to the sample bomb at any temperature.

In the CSI-ARC™, the bomb Nisil/Nicrosil thermocouple sheathed in a high-temperature insulating sleeve was pressed on the bomb body with a clip, of which one end was welded onto the bomb body, while the jacket thermocouple was cemented on the inside surface of the jacket at a point one-quarter the distance between the two cartridge heaters. The placement of the bomb thermocouple has to be repeated in every experiment. In normal operation, without extreme care, it was suspected that the thermal contact was not very reproducible, causing a highly undesirable random scattering of the calibration curves. The jacket offset voltage was found to deviate as much as 50 μV. This is demonstrated in Fig. 1. Because of this poor reproducibility, loss of adiabaticity was anticipated. In order to correct this uncertainty, a silver plate of 1.5 × 2.5 cm was folded around the insulated thermocouple and the entire assembly was pressed flat to insure good thermal contact. Because of its rigidity, the thermocouple assembly can be easily attached to the bomb body. With this modification, the reproducibility of the calibration was dramatically improved, as shown in Fig. 2, with the maximum jacket offset voltage deviation less than 10 μV. Also demonstrated in Fig. 2 is the bias voltage of two pairs of thermocouples relative to the same jacket thermocouple. Recent changes in thermocouple manufacture and use have improved thermocouple-to-thermocouple reliability in this laboratory.

Three types of sample bombs with a total volume of about 9 cc were used in the present study. They are the sample bomb made of titanium (~9 g), the light-weight (~19 g) Hastelloy C sample bomb, and the heavy-weight (~70 g) Hastelloy C sample bomb. With the above sample bombs of different weight, the thermal inertias [1], i.e.

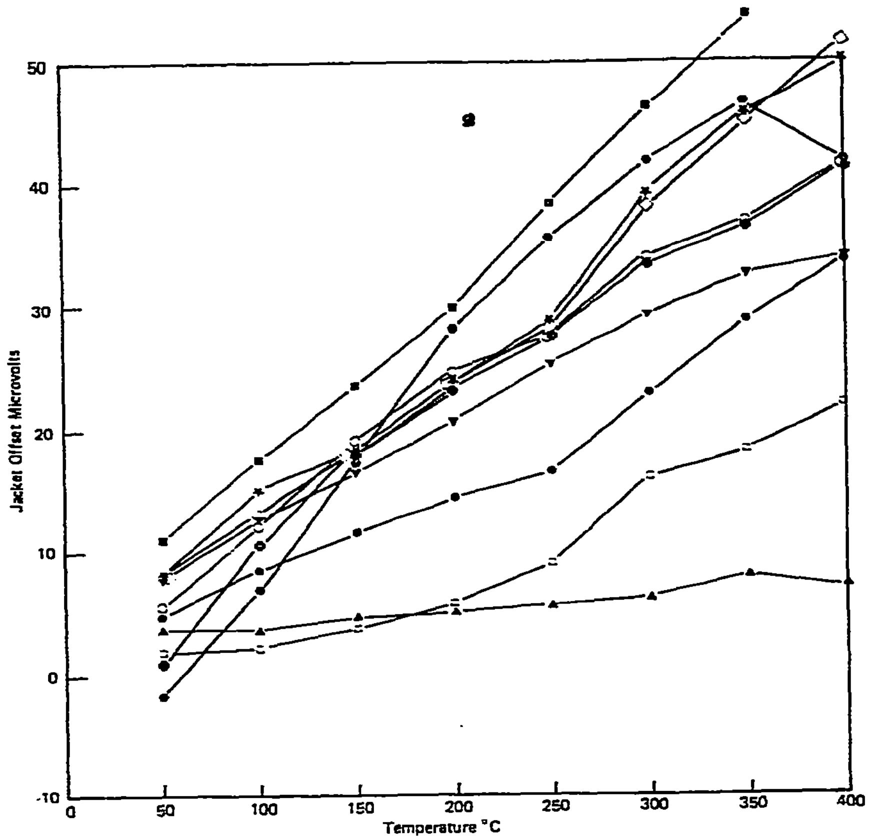

Fig. 1. ARC calibration runs before the modification.

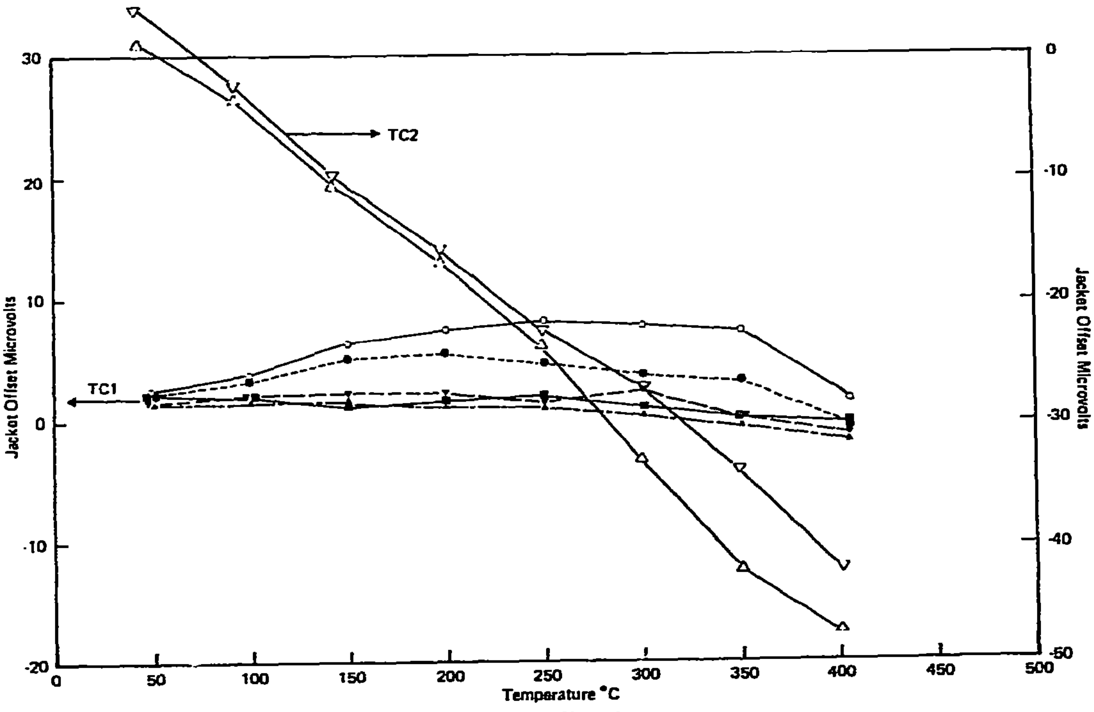

Fig. 2. ARC calibration runs after the modification.

$$\phi = 1 + M_b\bar{C}_{v,b}/M\bar{C}_v \tag{1}$$

where M_b and M are the masses of the bomb and the sample and $\bar{C}_{v,b}$ and C_v are their average heat capacities, respectively, are calculated to be ~1.5, ~1.8 and ~3.8, respectively, with a normal sample loading of ~5 g, assuming the heat capacities of the sample, Ti and Hastelloy C as 0.5, 0.13 and 0.1 cal $°C^{-1}$ g^{-1}, respectively, and assuming that they are constant with temperature. The di-*t*-butyl peroxide used in the experiments was purchased from Pennwalt Corporation, Buffalo, NY. Solutions of 10%, 20%, 30% and 60% by weight of di-*t*-butyl peroxide in toluene were prepared and stored in a refrigerator before use. Toluene is known to be an inert solvent in the decomposition of di-*t*-butyl peroxide [3] and can, therefore, be treated as part of the sample bomb if the thermal inertia based on the pure compound is calculated. This allows us to investigate the thermokinetic performance of the ARC with a wide range of thermal inertias, from 3.1 to 17, based on the pure compound.

The effect of different amounts of sample loading on the thermokinetic performance of the ARC was also studied with 1.7, 2.6, 3.6, 4.3 g of 60% solution loaded in the heavy-weight Hastelloy C bombs, giving thermal inertias of 16, 11, 8.3 and 7.2, respectively, calculated based on the pure compound.

The starting temperature and the calorimetric detection sensitivity were set at 70°C and 0.02°C min^{-1}, respectively. After the calorimeter reached 70°C, a 5°C heat—15 min wait—search sequential operation was carrried out automatically by the microprocessor control until a rate greater than 0.02°C min^{-1} was detected. The calorimeter was then maintained adiabatic until the completion of the reaction. The heat generated from the decomposition of di-*t*-butyl peroxide, ΔH, was determined by

$$\Delta H = \phi M\bar{C}_v \; \Delta T_{AB,s} \tag{2}$$

where ϕ is the thermal inertia calculated based on di-*t*-butyl peroxide only and $\Delta T_{AB,s}$ is the experimental adiabatic temperature rise.

The molar heat of reactions, ΔH_r, can be simply evaluated from

$$\Delta H_r = \frac{\Delta H}{M} \text{ (molecular weight)} \tag{3}$$

It should be noted that the heat determined by ARC is not the enthalpy of reaction since the experiment is carried out at constant volume, not constant pressure.

For comparison with the ARC data on ΔH_r, the heat of decomposition of each solution was also determined with a modified sealed glass ampoule microreactor [9] utilizing a DuPont DSC 910 unit driven by a DuPont 990 programmer. The temperature scanning rate was 20°C min^{-1} with nitrogen flow at a rate of 50 cc min^{-1}. The relative precision, $2\sigma/\bar{x}$, of the method was found to be ±14%, where σ is the standard deviation, and $\bar{x}$ is the average value of a series of determinations.

All the calculations based on the equations derived previously [1] were done on a Hewlett-Packard 9825 A calculator with 9872 A plotter. The equation for computing the time to maximum rate was numerically integrated.

RESULTS AND DISCUSSION

With the improved bomb thermocouple assembly as described in the experimental section, the isothermal stability or the drift of the ARC unit was investigated at several temperatures. The results are shown in Fig. 3. Generally speaking, the average temperature drifts were found to be less than 0.005°C $\min^{-1}$ at temperatures below 300°C. The average drift at 350°C was calculated to be 0.012°C $\min^{-1}$. The thermokinetic performance of the ARC unit was examined under these conditions.

Shown in Figs. 4 and 5 are T vs. t and dT/dt (or $m_{T,s}$) vs. $1/T$ curves of the thermal decomposition reaction of 10%, 20%, 30% and 60% solutions of di-*t*-butyl peroxide in toluene in a light-weight Hastelloy C bomb. The experimental time to maximum rate (TMR), $\theta_{m,s}$, is shown in Fig. 6. Summarized in Table 1 are the initial temperature, $T_{0,s}$, initial rate, $m_{0,s}$, temperature at maximum rate, $T_{m,s}$, maximum rate, $m_{m,s}$, experimental TMR, $\theta_{m0,s}$, and TMR calculated for the pure compound, θ_{m0}. Both of the two latter quantities are evaluated from where the reaction was initially detected at $T_{0,s}$ of each experiment.

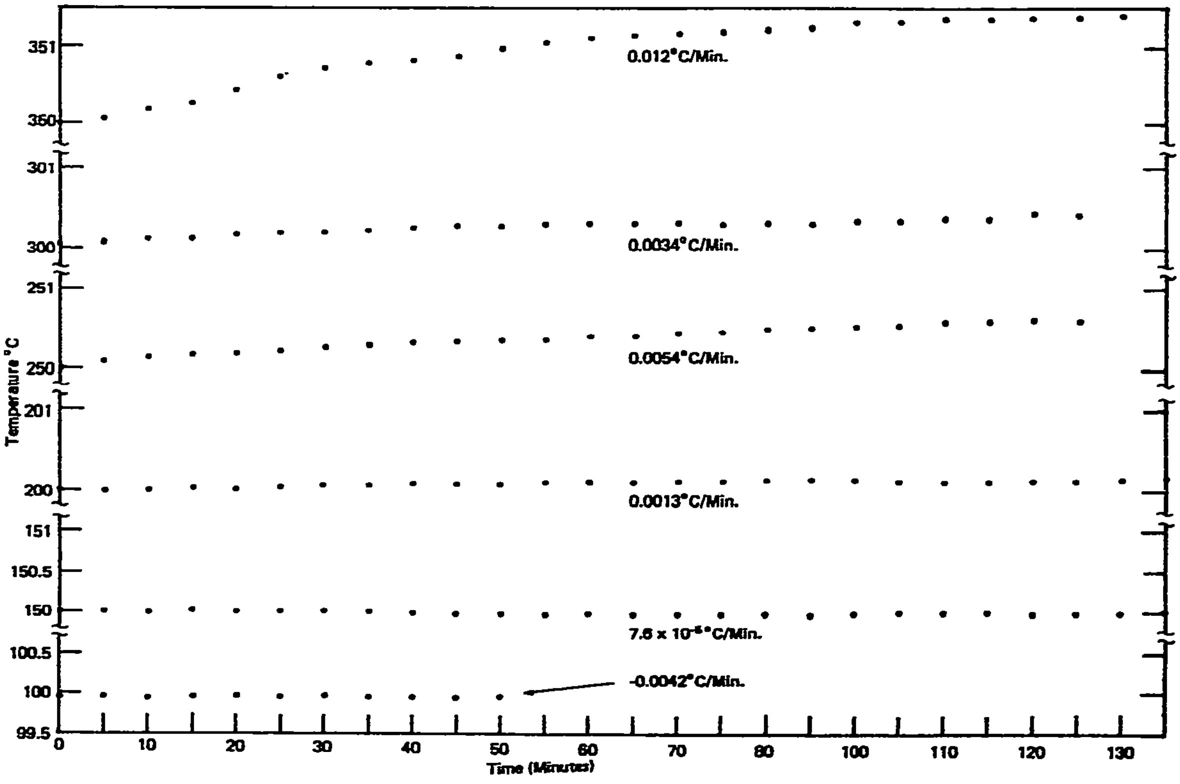

Fig. 3. The isothermal stability of the ARC.

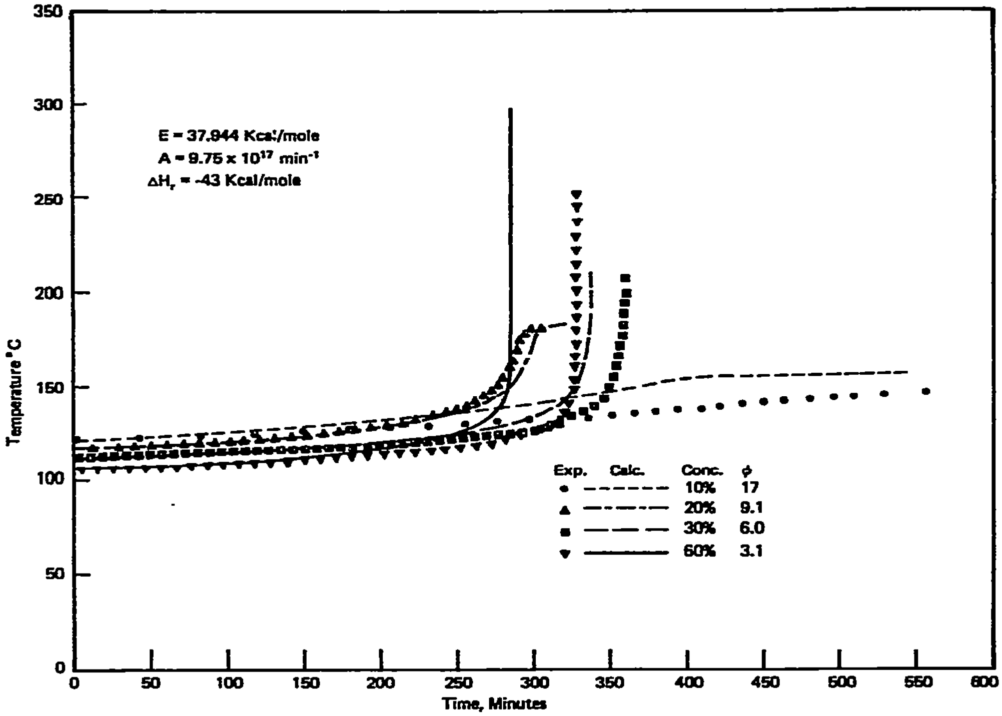

Fig. 4. The experimental and calculated T vs. t curves of the thermal decomposition reaction of di-t-butyl peroxide in toluene in a light-weight Hastelloy C bomb.

The pseudo zero-order rate constant [1], k^*, which equals the rate constant, k, for the present first order reaction, was calculated from the observed self-heat rate, $m_{T,s}$ at T and the experimental final temperature, $T_{f,s}$ [1]

$$k^* = \frac{m_{T,s}}{T_{f,s} - T} = k \tag{4}$$

This can be equated to

$$\log k^* = \log A - \frac{E}{2.303R}\frac{1}{T} \tag{5}$$

where A is the frequency factor, E is the activation energy, and R is the gas constant, assuming Arrhenius type temperature dependence of the rate constant.

The plot of log k^* vs. $1/T$ is, therefore, expected to be a straight line, providing the order of reaction is correctly chosen [1]. The results are shown in Fig. 7 for the above four experiments, covering the range of the thermal inertias, ϕ, from 3.1 to 17 calculated based on the pure compound. A reasonably linear curve was obtained, from which E and A were calculated to be 37.944 kcal mole^{-1} and 9.75×10^{17} min^{-1} [or log A (sec^{-1}) = 16.21], respectively, for the experiment of $\phi = 6.0$. Shown in Table 2 are the heats of reaction and the kinetic parameters computed for each experiment. These ARC results of the heat of reaction are compared to those from the DSC measurements. A very good agreement was obtained between the two techniques for

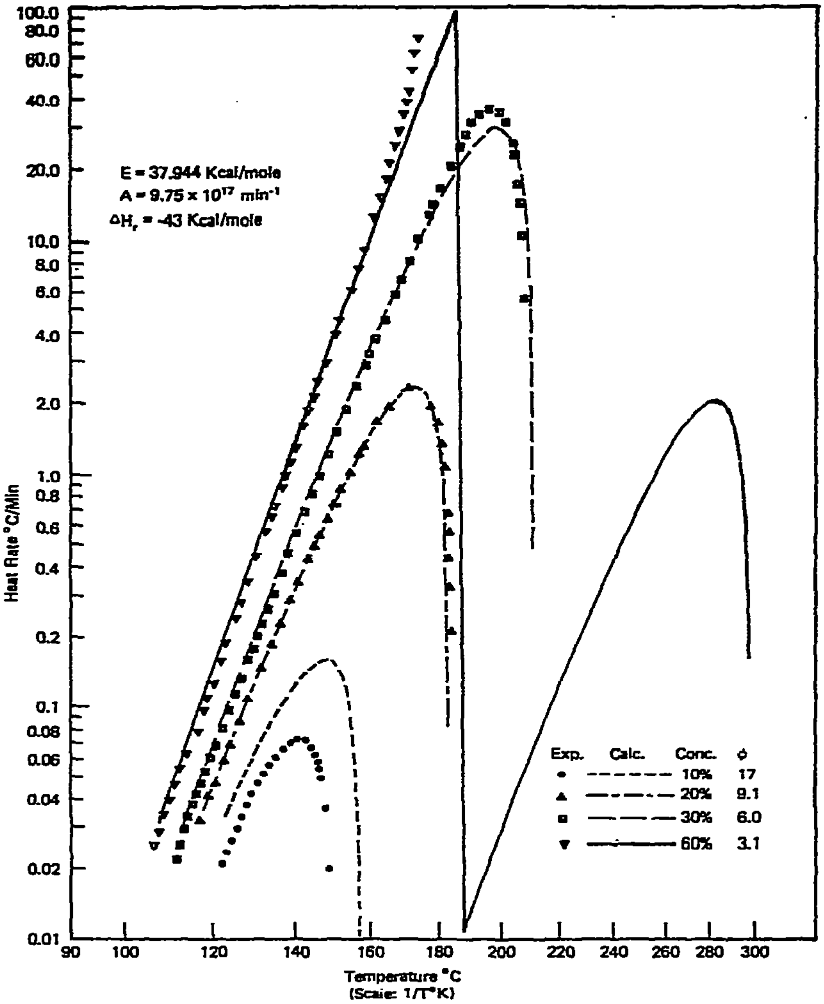

Fig. 5. The experimental and calculated dT/dt vs. 1/T curves of the thermal decomposition reaction of di-t-butyl peroxide in toluene in a light-weight Hastelloy C bomb.

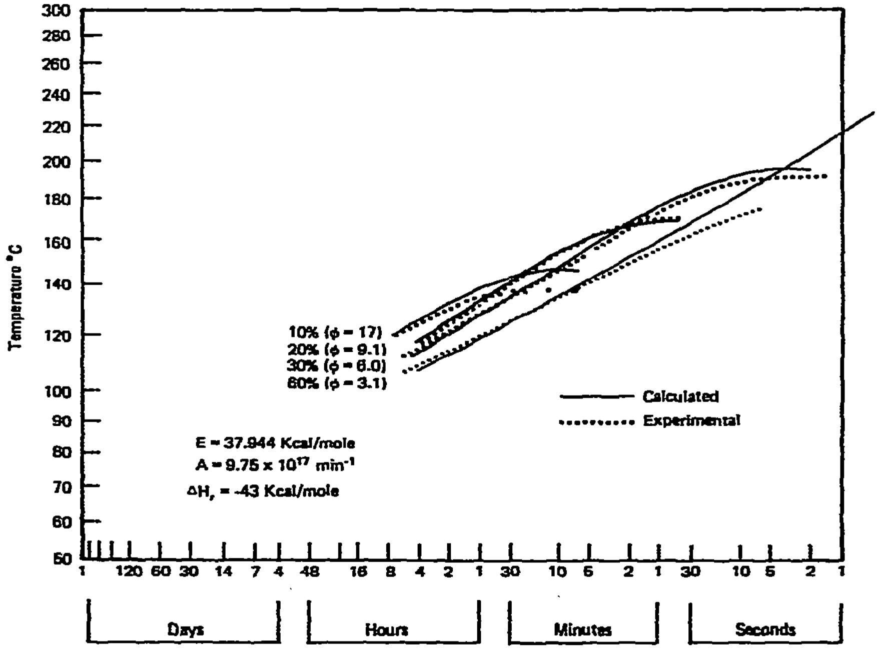

Fig. 6. The experimental and calculated TMR, $\theta_{m,s}$, of the thermal decomposition reaction of di-t-butyl peroxide in toluene in a light-weight Hastelloy C bomb.

TABLE 1

The $T_{0,s}$, $m_{0,s}$, $T_{m,s}$, $m_{m,s}$, $\theta_{m_0,s}$ and θ_{m_0} of the thermal decomposition reaction of di-*t*-butyl peroxide in toluene and in its pure form

Bomb type	Concn.	ϕ [a]		$T_{0,s}$ (°C)	$m_{0,s}$ (°C min^{-1})		$T_{m,s}$ (°C)		$m_{m,s}$ (°C min^{-1})		$\theta_{m_0,s}$(min)		θ_{m_0}(min)	
		Solution	Pure		Exp.	Calcd. [b]	Exp.	Calcd. [b]	Exp.	Calcd. [b]	Exp.	Calcd. [b]	Exp.	Calcd. [b]
Light-weight Hastelloy C	10%	1.8	17	121.5	0.021	0.031	141	148	0.073	0.16	439	355	26	21
	20%	1.8	9.0	116.6	0.033	0.033	173	172	2.4	2.3	291	295	32	33
	30%	1.8	6.0	111.5	0.022	0.027	196	198	37	30	286	247	48	41
	60%	1.8	3.1	106.5	0.025	0.029	226	282	460	2000	329	295	108	95
Ti	30%	1.7	5.6	106.3	0.018	0.016	194	199	27	34	562	551	100	98
	30%	1.6	5.4	111.4	0.025	0.027	200	209	60	69	326	330	61	61
Heavy-weight Hastelloy C	Pure		8.3	111.6	0.016	0.018	163	171	1.2	1.8	428	640	52	77
	Pure		7.9	111.3	0.033	0.015	170	176	2.9	3.2	352	520	45	66
Heavy-weight Hastelloy C	60%	9.4	16	116.5	0.025	0.019	151	145	0.23	0.12	446	595	29	37
	60%	6.4	11	111.4	0.019	0.014	163	157	0.98	0.42	523	745	49	68
	60%	5.0	8.3	111.4	0.024	0.019	177	172	7.3	2.1	406	545	49	66
	60%	4.3	7.2	111.4	0.026	0.022	184	183	39	5.8	360	463	50	73

[a] $\overline{C}_{v,b}$ = 0.1 cal °C^{-1} g^{-1} for Hastelloy C and 0.13 cal °C^{-1} g^{-1} for Ti, $\overline{C}_v$ = 0.5 cal °C^{-1} g^{-1}.

[b] E = 37.944 kcal $mole^{-1}$, $A = 9.75 \times 10^{17}$ min^{-1}, ΔH_r = −43 kcal $mole^{-1}$.

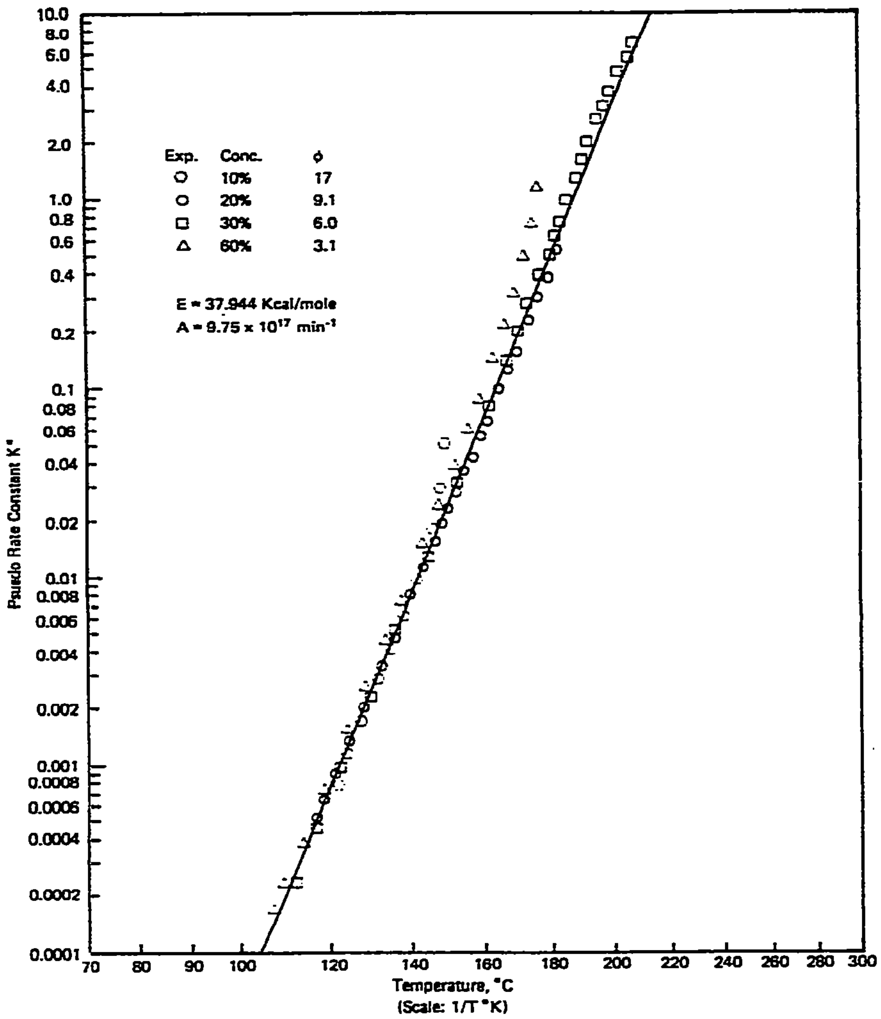

Fig. 7. The log k^* vs. $1/T$ plot of the thermal decomposition reaction of di-*t*-butyl peroxide in toluene in a light-weight Hastelloy C bomb with ΔH_r determined from each individual experiment.

the cases of 20% and 30% solutions. However, much lower values were obtained from the ARC for the cases of 10% and 60% solutions, where the maximum rates were found to be 0.073°C min^{-1} and 467°C min^{-1}, respectively, as shown in Table 1. This discrepancy is believed to be due to self-heat rates either too slow or too fast to be measured accurately. If the rates are very slow, minor calorimetric instability will affect the accuracy of measurements in both rates and the adiabatic temperature rise. If the rates are too fast for the calorimeter to follow, loss of adiabaticity in the calorimeter is expected, resulting in a loss of the reaction heat distributed in the sample bomb to its surroundings. Therefore the experimental self-heat rate and the heat of reaction will be less than those obtained under more adiabatic conditions.

Shown in Fig. 8 is the plot of log k^* vs. $1/T$, where k^* is calculated from the heat of reaction, —43 kcal mole^{-1}, obtained for 20% solution and the

TABLE 2

The Arrhenius parameters, E and A, and the heat of reaction of di-*t*-butyl peroxide in toluene and in its pure form

Bomb type	Concn.	ϕ [a]		E (kcal mole^{-1})	A (min^{-1})	log A (sec^{-1})	ΔH_r (kcal mole^{-1})	
		Solution	Pure				ARC	DSC
Light-weight Hastelloy C	10%	1.8	17	40.916	3.86×10^{19}	17.81	—33	—38
	20%	1.8	9.1	37.338	4.64×10^{17}	15.89	—43	—42
	30%	1.8	6.0	37.944	9.75×10^{17}	16.21	—41	—42
	60%	1.8	3.1	38.485	2.46×10^{18}	16.61	—33	—41
Ti	30%	1.7	5.6	37.682	6.87×10^{17}	16.28	—41	—42
	30%	1.6	5.4	37.337	4.63×10^{17}	15.89	—42	
Heavy-weight Hastelloy C	Pure		8.3	37.330	5.61×10^{17}	15.97	—37	—38
	Pure		7.9	37.852	1.13×10^{18}	16.27	—41	
Heavy-weight Hastelloy C	60%	9.4	16	35.867	7.872×10^{16}	15.12	—49	—41
	60%	6.4	11	36.788	2.71×10^{17}	15.66	—48	
	60%	5.0	8.3	37.855	9.26×10^{17}	16.19	—46	
	60%	4.3	7.2	37.724	7.77×10^{17}	16.11	—45	
Average				37.80 ± 1.1 [b]	8.48×10^{17}	16.15 ± 0.61 [b]		

[a] $\overline{C}_{v,b} = 0.1$ cal °C^{-1} g^{-1} for Hastelloy C and 0.13 cal °C^{-1} g^{-1} for Ti, and $\overline{C}_v = 0.5$ cal °C^{-1} g^{-1}.

[b] Precision is based on 1σ value.

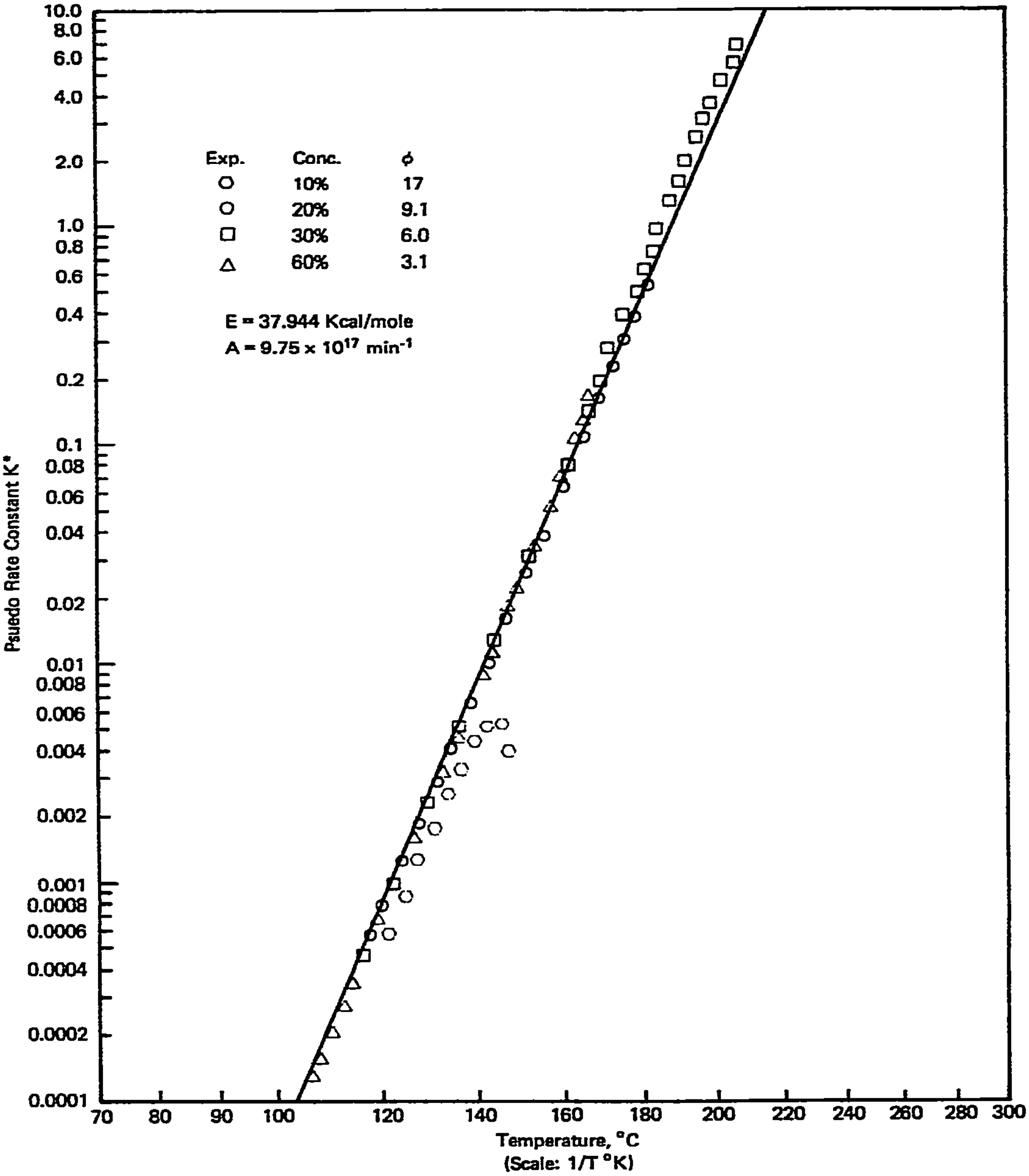

Fig. 8. The log k^* vs. $1/T$ plot of the thermal decomposition reaction of di-*t*-butyl peroxide in toluene in a light-weight Hastelloy C bomb with $\Delta H_r = -43$ kcal mole^{-1}.

experimental self-heat rates of the individual solutions. The maximum self-heat rate obtained from the 20% solution is believed to be well within the capability of the calorimeter and therefore the heat of reaction should be close to the true value. This is also evident from the DSC experiment. The activation energy and the frequency factor from this linear plot are almost indistinguishable from those shown in Fig. 7. Based on the kinetic parameters, $E = 37.944$ kcal mole^{-1} and $A = 9.75 \times 10^{17}$ min^{-1}, and the heat of reaction, —43 kcal mole^{-1}, the T vs. t, dT/dt (or $m_{T,s}$) vs. $1/T$ and TMR, $\theta_{m,s}$

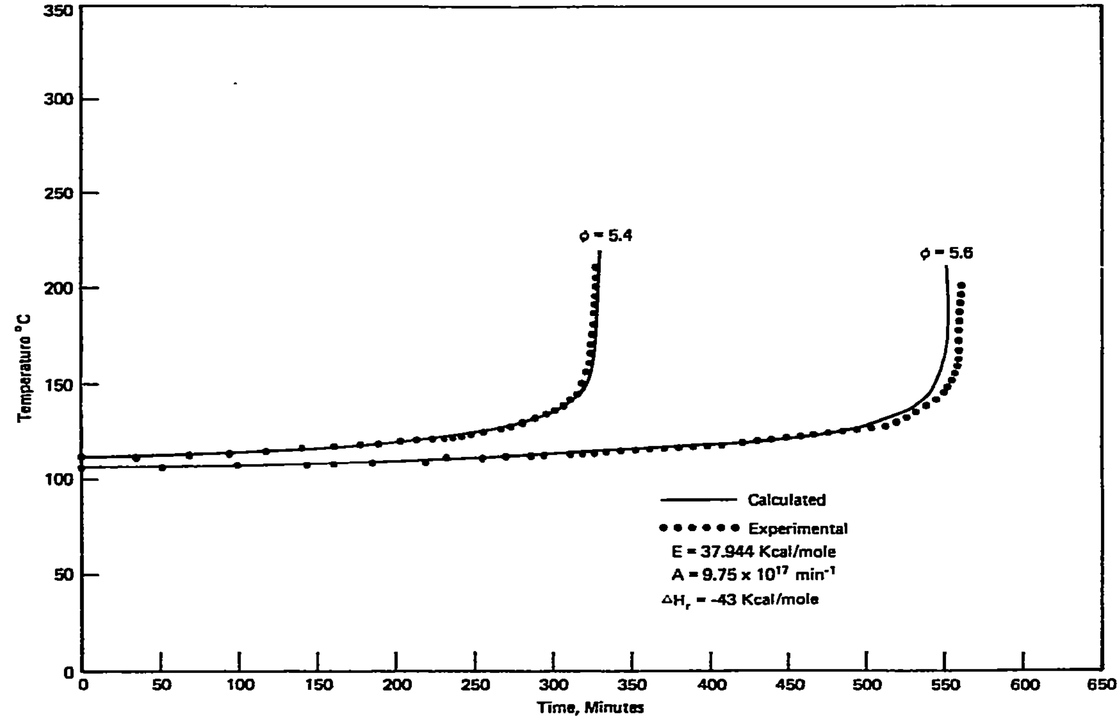

Fig. 9. The experimental and calculated T vs. t curves of the thermal decomposition reaction of 30% di-*t*-butyl peroxide in toluene in a Ti bomb.

for the above four experiments were calculated according to the equation derived previously [1]. The calculated curves and the selected numerical values are also presented in Figs. 4—6 and Table 1 along with the experimental ones for a direct comparison.

Similarly, the calculated and experimental curves are shown in Figs. 9—12, 13—16, and 17—20 for three other sets of experiments involving a 30% solution in a Ti bomb, pure di-*t*-butyl peroxide in a Hastelloy C bomb, and various amounts of a 60% solution in a heavy-weight Hastelloy C bomb, respectively. The numerical values of the calculated and experimental ARC quantities are summarized in Table 1 for easy comparison. The calculations are based on the same set of Arrhenius parameters and the heat of reaction as described previously.

The activation energy and the frequency factor are calculated from the log k^* vs. $1/T$ plots shown in Figs. 12, 16 and 20 for each experiment. The heat of reaction is evaluated according to eqn. (3) for each case from the observed adiabatic temperature rises shown in Figs. 10, 14 and 18. The results are summarized in Table 2.

As shown in Table 2, the average activation energy and log A (sec^{-1}) of the 12 different experiments were calculated to be 37.8 ± 1.1 kcal mole^{-1} and 16.15 ± 0.61 (or the geometric average frequency factor 8.48×10^{17} min^{-1}), which are in good agreement with the values 37.78 ± 0.06 kcal mole^{-1} and 15.80 ± 0.03 recommended by Shaw and Pritchard [2] from the least-squares treatment of 177 data points. However, the above values are

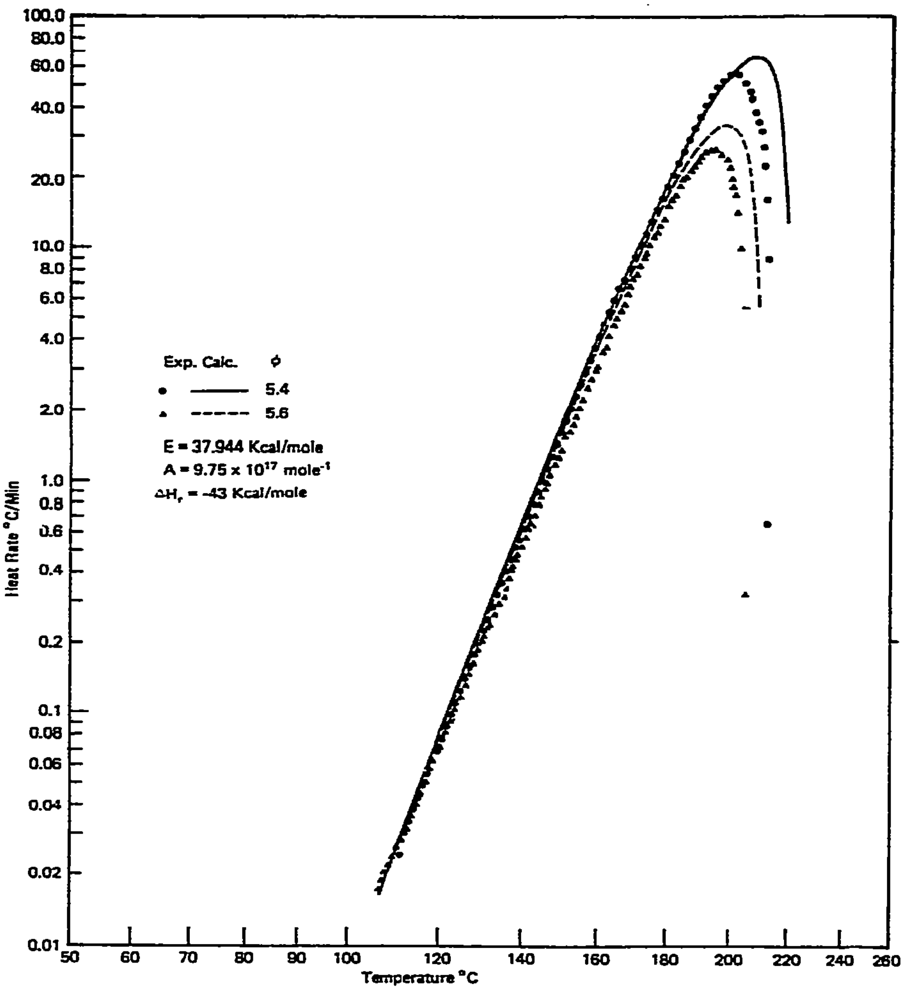

Fig. 10. The experimental and calculated dT/dt vs. $1/T$ curves of the thermal decomposition reaction of 30% di-*t*-butyl peroxide in toluene in a Ti bomb.

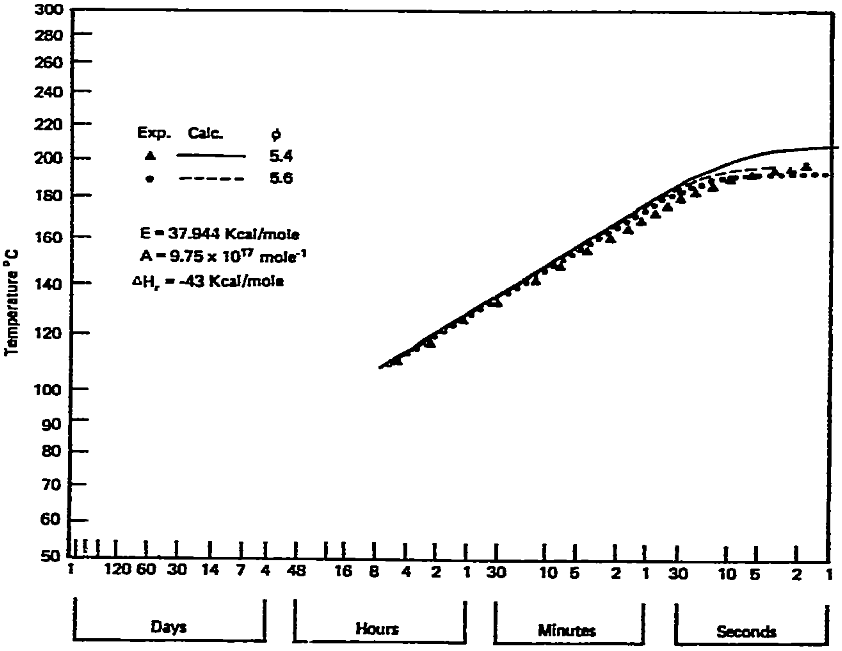

Fig. 11. The experimental and calculated TMR, $\theta_{m,s}$, of the thermal decomposition reaction of 30% di-*t*-butyl peroxide in toluene in a Ti bomb.

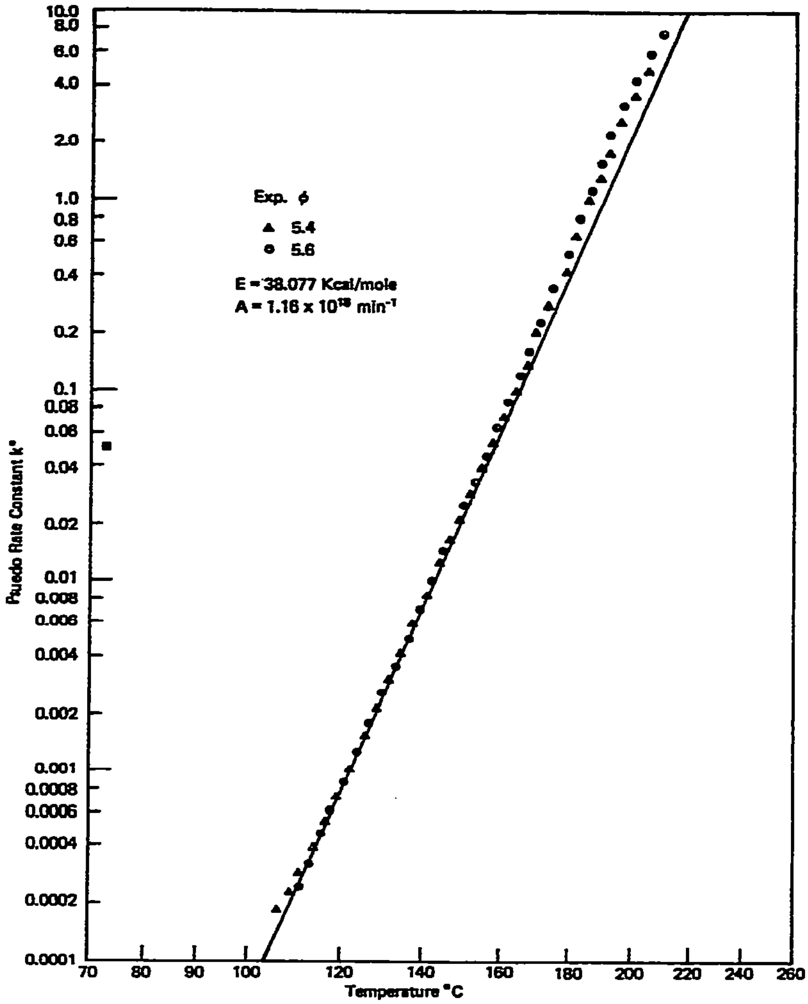

Fig. 12. The log k^* vs. $1/T$ plot of the thermal decomposition reaction of 30% di-*t*-butyl peroxide in toluene in a Ti bomb with ΔH_r determined from each individual experiment.

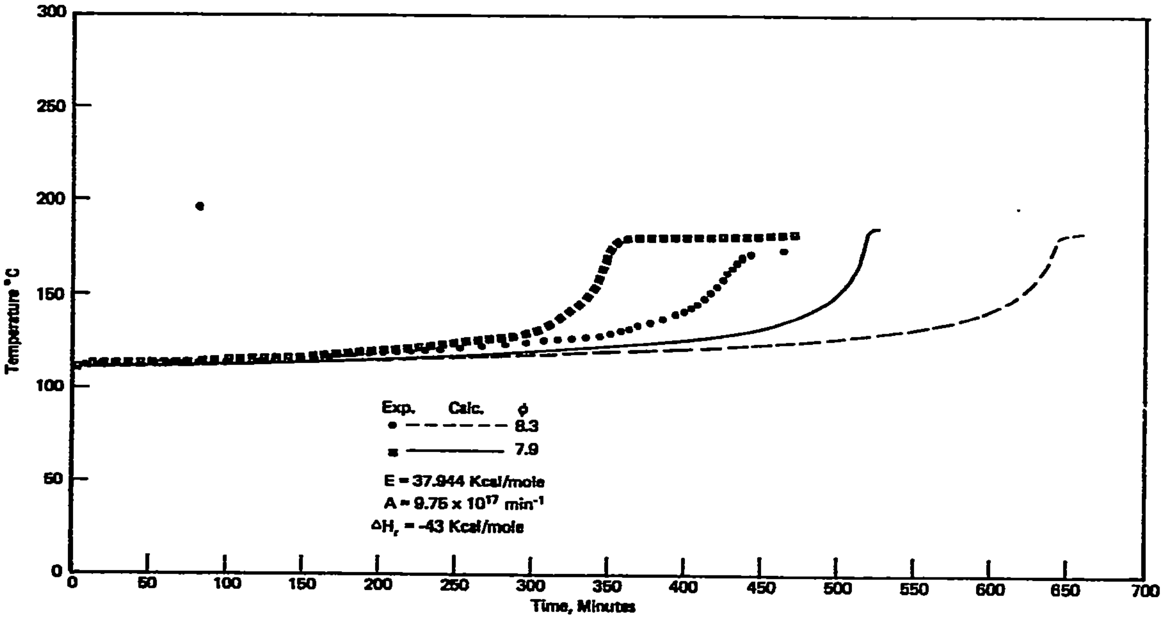

Fig. 13. The experimental and calculated T vs. t curves of the thermal decomposition reaction of pure di-*t*-butyl peroxide in a heavy-weight Hastelloy C bomb.

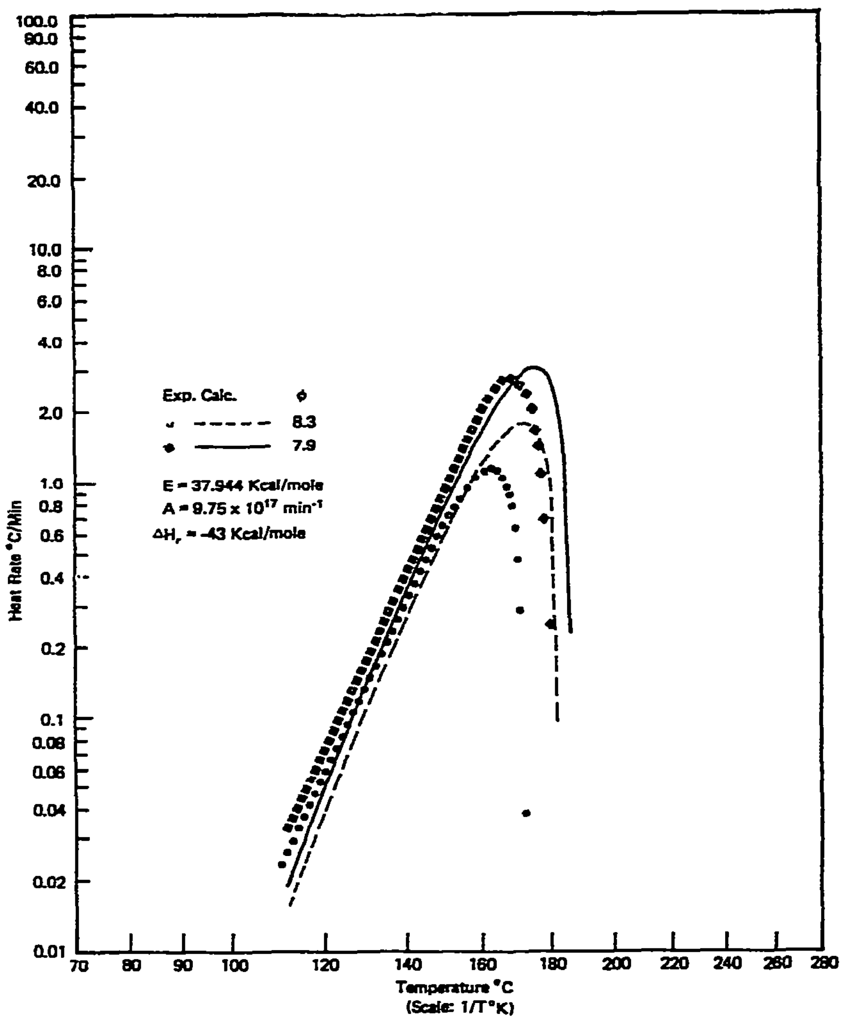

Fig. 14. The experimental and calculated dT/dt vs. $1/T$ curves of the thermal decomposition reaction of pure di-*t*-butyl peroxide in a heavy-weight Hastelloy C bomb.

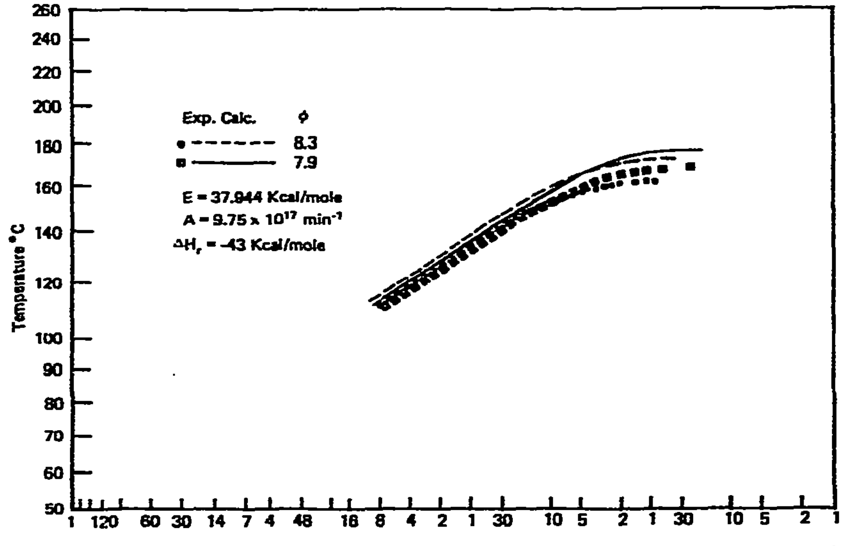

Fig. 15. The experimental and calculated TMR, $\theta_{m,s}$, of the thermal decomposition reaction of pure di-*t*-butyl peroxide in a heavy-weight Hastelloy C bomb.

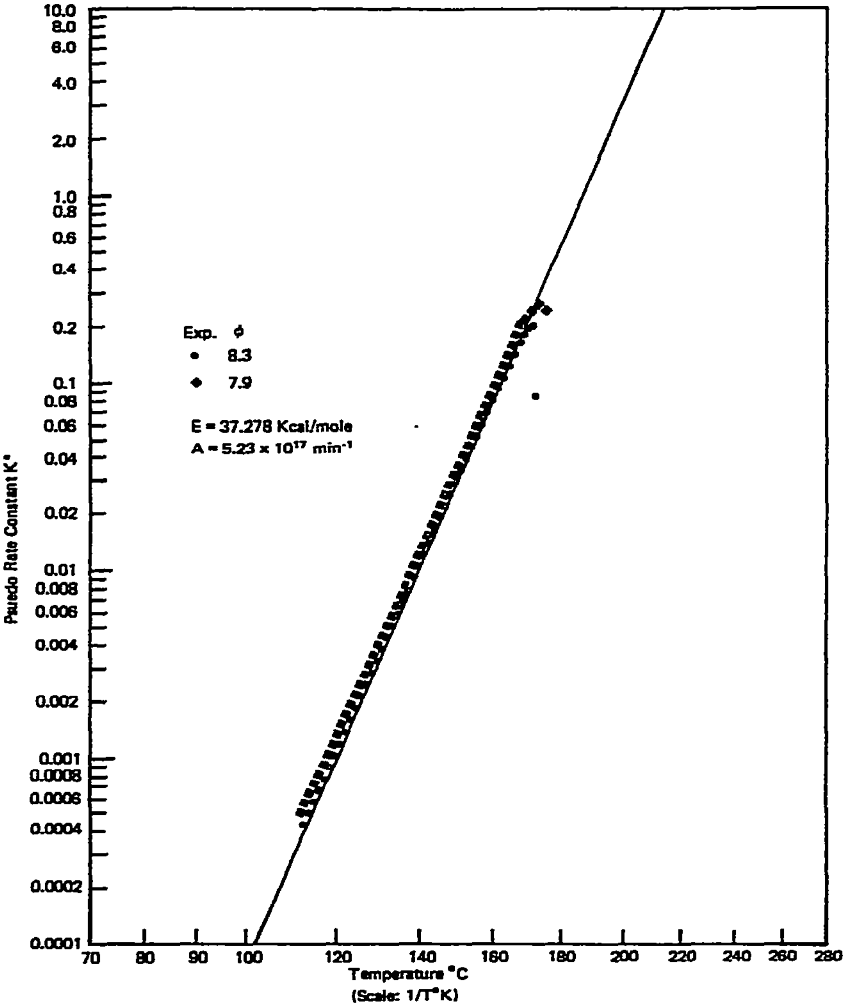

Fig. 16. The log k^* vs. $1/T$ plot of the thermal decomposition reaction of pure di-*t*-butyl peroxide in a heavy-weight Hastelloy C bomb with ΔH_r determined from each individual experiment.

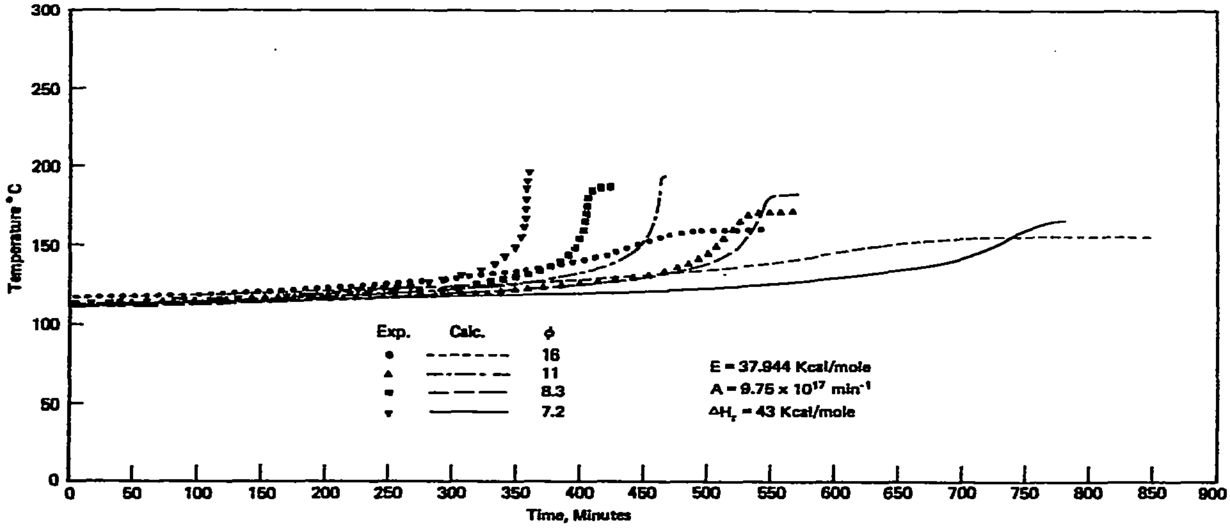

Fig. 17. The experimental and calculated T vs. t curves of the thermal decomposition reaction of 60% di-*t*-butyl peroxide in toluene in a heavy-weight Hastelloy C bomb.

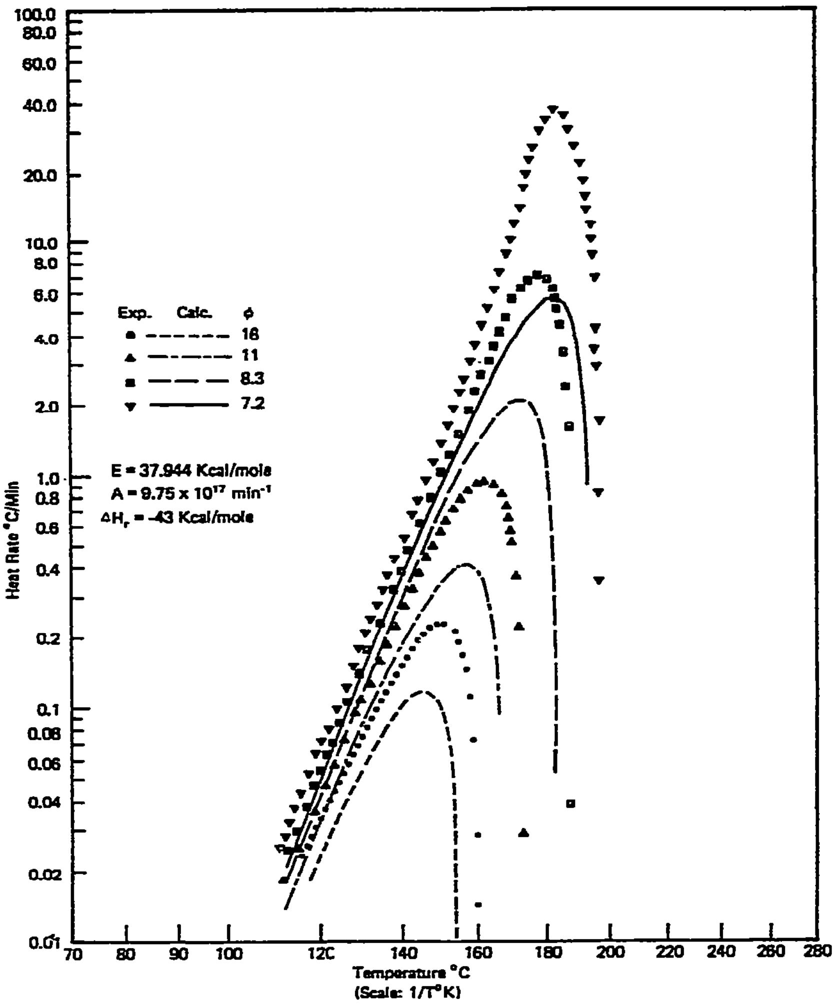

Fig. 18. The experimental and calculated dT/dt vs. $1/T$ curves of the thermal decomposition reaction of 60% di-*t*-butyl peroxide in toluene in a heavy-weight Hastelloy C bomb.

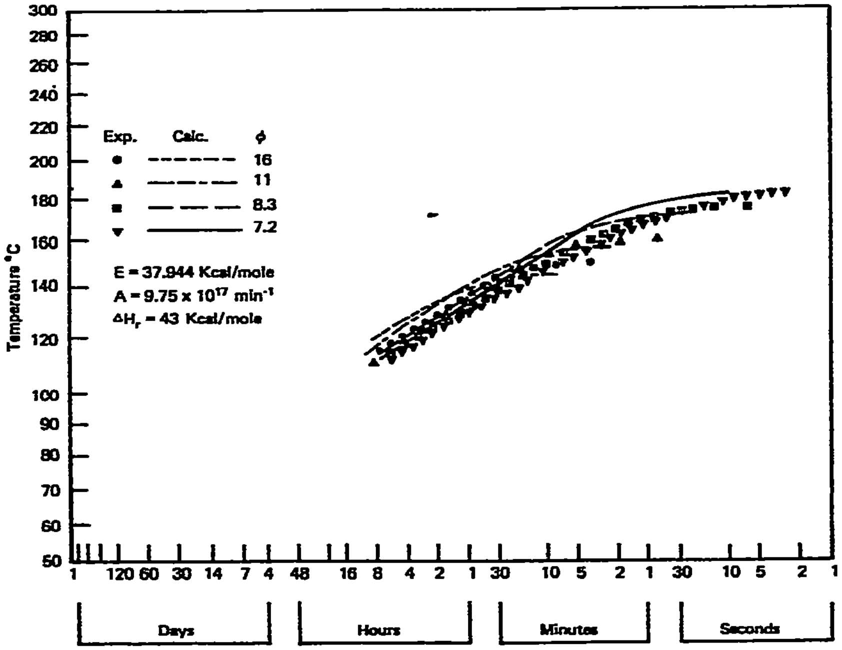

Fig. 19. The experimental and calculated TMR, $\theta_{m,s}$, of the thermal decomposition reaction of 60% di-*t*-butyl peroxide in toluene in a heavy-weight Hastelloy C bomb.

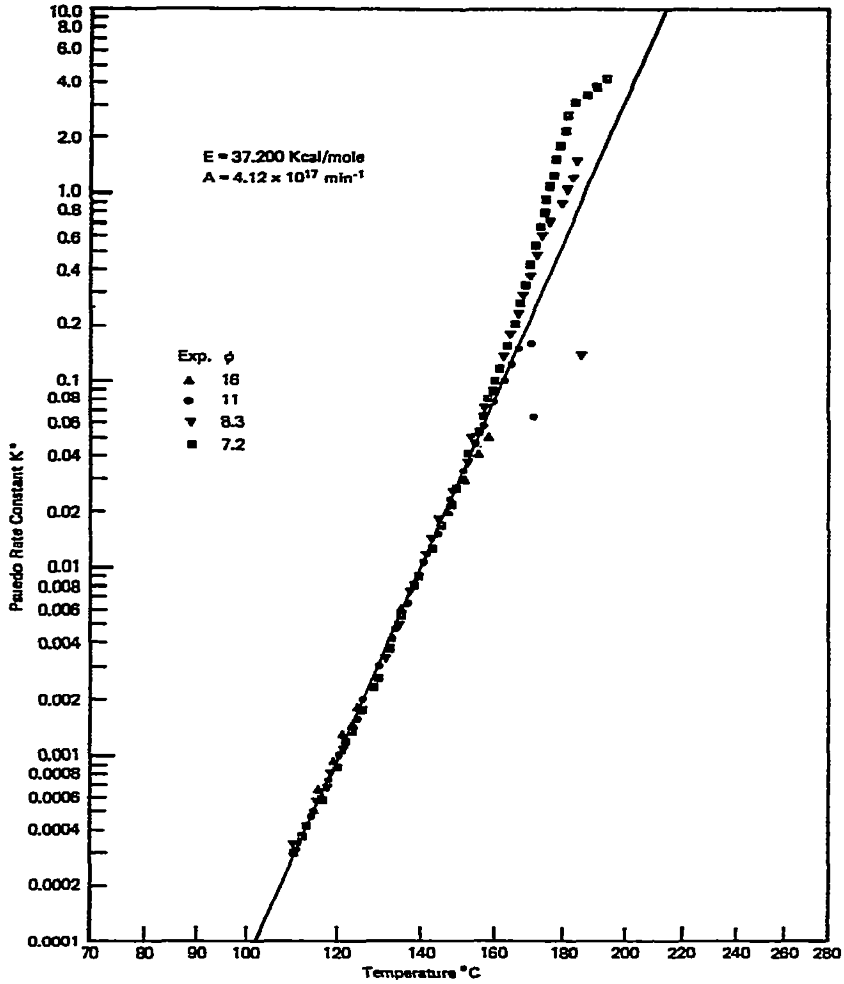

Fig. 20. The log k^* vs. $1/T$ plot of the thermal decomposition reaction of 60% di-*t*-butyl peroxide in toluene in a heavy-weight Hastelloy C bomb with ΔH_r determined from each individual experiment.

slightly different from 36.17 ± 0.39 kcal mole^{-1} and 15.05 ± 0.17 based on the pressure measurement experiment by Murawski et al. [2,3]. The above comparison leads one to believe that the pressure measurement experiments may involve small systematic errors. This was also suggested by Shaw and Pritchard [2].

An examination of the dT/dt (or $m_{T,s}$) vs. $1/T$ plots shown in Figs. 5, 10, 14 and 18 involving various sample bombs shows that the shape of experimental curves can deviate significantly from that of the calculated ones in the high self-heat rate range. These deviations in the upward direction of the self-heat rate are observed at ~70° C min^{-1} for the Ti bomb (Fig. 10), ~20° C min^{-1} for the light-weight Hastelloy C bomb (Fig. 5) and only ~2° C min^{-1} for the heavy-weight Hastelloy C bombs (Figs. 14 and 18).

This phenomenon is due to the temperature measurement lag of the detection system. Since the thermocouple element is located on the outside of the sample bomb, the temperature response of the measurement system is dependent on how quickly the sample and bomb together respond to a change in temperature. The speed with which the sample/bomb system responds, or the measurement time constant, is dependent on the mass of the bomb, the specific heat of the bomb, the liquid contact area in the bomb, and the interfacial heat transfer coefficient for the materials of interest. In order to graphically illustrate this measurement problem at high self-heat rates, a thermo-

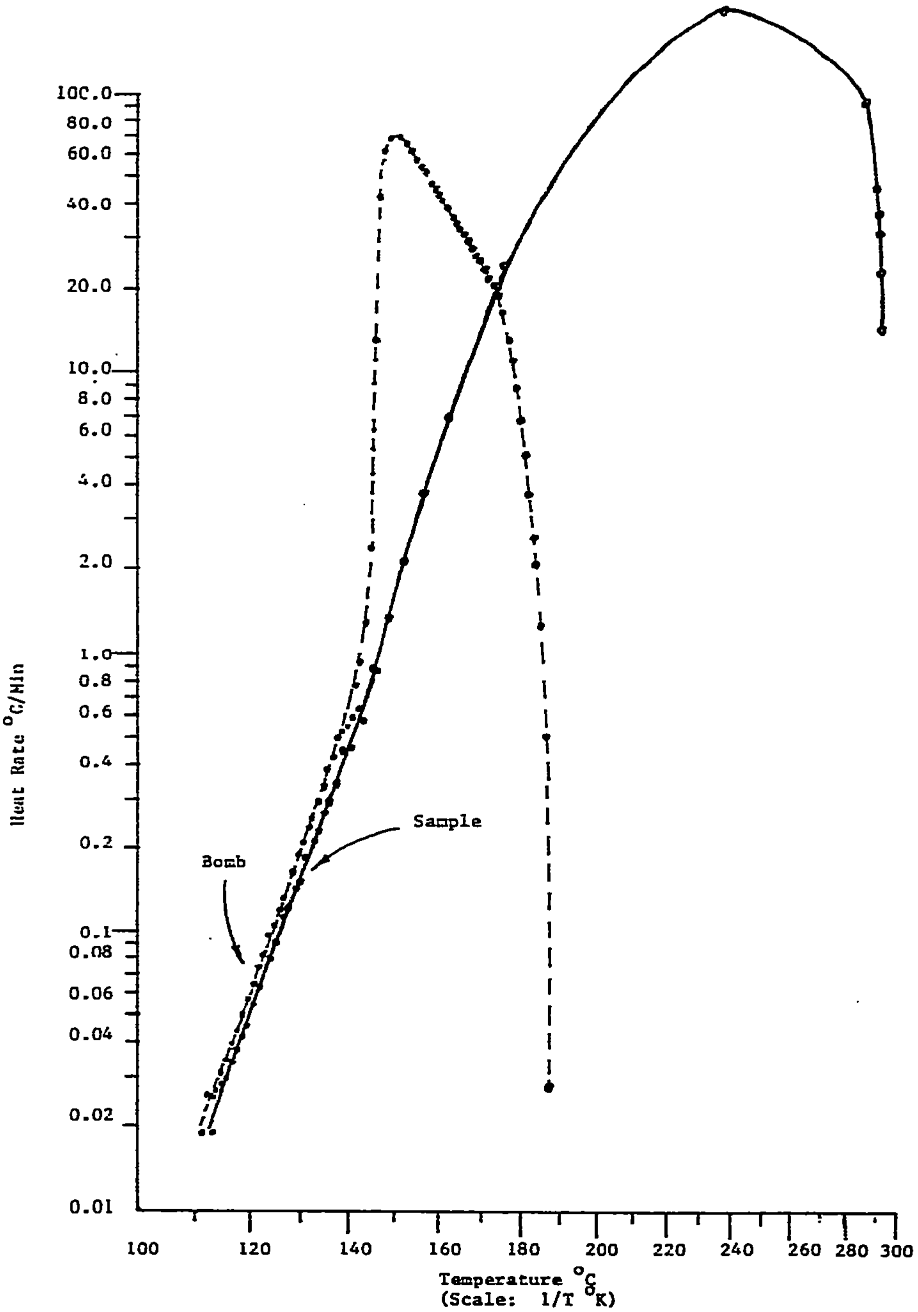

Fig. 21. Demonstration of measurement lag in experimental dT/dt vs. 1/T curves using a thermocouple in the liquid for comparison with the bomb thermocouple data on 60% di-*t*-butyl peroxide in a viscous silicone oil.

couple was placed directly in contact with the liquid mixture of 60% DTBP in a viscous, 500 centipoise, silicone oil, in a heavy-weight Hastelloy C bomb. Due to its high viscosity, heat transfer in this sample is expected to be poor and thus accentuate the measurement lag. Figure 21 shows the results of that experiment. As can be seen, a sharp upward deviation in the self-heat rate curve is evident at slightly below 1°C min^{-1} for the bomb thermocouple, the normal detection system. However, the thermocouple placed directly in the liquid showed very little upward deviation in the self-heat rate plot. In addition, one may note that the self-heat rates in the liquid are nearly an order of magnitude higher than those detected by the bomb thermocouple. Since evaluation of rate data at high self-heat rates is complex due to measurement lags in the normal detection system, only data in the low self-heat rate region were used in the kinetic analyses of this study. Work is currently underway in this laboratory to further characterize this measurement lag and to analyze its effect on kinetic determinations using the ARC.

Shown in Table 1 are the experimental and calculated ARC quantities of $T_{0,s}$, $m_{0,s}$, $T_{m,s}$, $m_{m,s}$, $\theta_{m_0,s}$ and θ_{m_0}. Generally speaking, the agreement between the experimental and calculated values is satisfactory except for the experiments with the heavy-weight Hastelloy C bombs loaded with different amounts of 60% solution. In the latter cases, the log k^* vs. $1/T$ plot, shown in Fig. 20, deviates from the expected linear line over one-third of the temperature range. Severe disagreement between the calculated and experimental self-heat rate curves was also observed in Fig. 18 and Table 1. The exact reason for such disagreement is not known as yet. However, if one uses the observed ΔT_{AB} from each experiment rather than that calculated from $\Delta H_r = -43$ kcal mole^{-1}, then the agreement is greatly improved between the experimental and the calculated self-heat rate data. Apparently, eqns. (2) and (3) are not accurate representations in relating ΔT_{AB} to ΔH_r for the sets of data obtained in the heavy-weight Hastelloy C bombs loaded with varying amounts of 60% di-*t*-butyl peroxide solution.

Based on the above experiments, the limitations of the various ARC procedures have been defined. It was also demonstrated that one set of Arrhenius parameters and heat of reaction could satisfactorily predict the kinetic behavior of the thermal decomposition of di-*t*-butyl peroxide, observed under different experimental conditions covering wide ranges of the thermal inertias from 3.1 to 17. The agreement between the experimental and calculated data also provides an appraisal of the accuracy of the kinetic performance of an accelerating rate calorimeter.

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