

# Effects of Self-heating During the Thermal Decomposition of di-*t*-Butyl Peroxide

Anomalous Reaction Orders and Activation Energies, and their Correction

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Self-heating accompanying an exothermic reaction that has a positive activation energy enhances the reaction rate. This means that measured reaction orders and rate constants (and hence the effective activation energy) are no longer the true, isothermal values. Theories have been formulated to assess the magnitude of the discrepancies and the way in which they are controlled by conditions. Now it is possible to write down an approximate, but very precise, algebraic expression for the proportionate errors ( $\Delta E/E$  and  $\Delta n/n$ ) in terms of the measured, centre-temperature excesses that are generated within a spherically shaped reacting mass. This is an important development because the sphere has only recently yielded to satisfactory analytical interpretations of self-heating and criticality, yet its finite dimensions make it the shape, amongst class A geometries, that is an archetype for most practical cases.

The objective in the present study is thus to show whether or not the theoretical predictions for anomalous orders and activation energies are quantitatively satisfactory.

The subject for experimental investigation is di-*t*-butyl peroxide. Its thermal decomposition is studied over the temperature range 420-510 K at low pressures of the pure vapour ( $< 10$  Torr) in a spherical vessel (1 dm<sup>3</sup>). Pressure increases are monitored continuously by transducer and internal temperature changes measured by a very fine thermocouple.

At the lowest temperature, decomposition remains virtually isothermal; we observe a first-order dependence of initial rate on initial pressure, and we measure an overall isothermal activation energy consistent with reported values. At higher temperatures, approaching but still below those at which ignition occurs ( $T_a < 460$  K), self-heating accompanies reaction and centre-temperature excesses of up to 15 K are measured. They are quasi-steady maxima, achieved within 2 s of entry of reactant to the vessel; there is a subsequent decline, and from *ca.* 20 s on the reaction is virtually isothermal. Reaction times, characterized by successive 'quarter-lives', are considerably shorter during the first interval than the subsequent isothermal periods. Where self-heating occurs, enhanced reaction orders are measured, rising as  $(\Delta T_0)_{\max}$  increases, and in carefully chosen circumstances curvature of a  $\log(dp/dt)_0$  against  $\log p_0$  plot is seen. The same is true for effective activation energies, and we show a curved Arrhenius plot ( $\ln k$  against  $1/T_a$ ). The measured activation energy can easily exceed the isothermal value by 50% because of self-heating. The anomalous reaction orders and activation energies predicted from theory are in very good agreement with the experimental values. We show that retrospective correction of kinetic data, influenced by self-heating, can be very successful.

When an exothermic reaction proceeds, it is accompanied by self-heating, although swift rates may be necessary for the temperature rise to be substantial. Rate constants, and through them reaction rates, are strongly temperature-dependent and so they increase as the reactant temperature rises. Modest temperature changes (several K) are influential and this means that measured Arrhenius parameters ( $E$ ,  $A$ ) and effective reaction orders are enhanced. If the reactant temperature is being measured routinely then the experimentalist is made aware of the influences being imposed on his results, and he can take steps to correct them. Except in the case of combustion

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studies it is not common to find continuous monitoring of reactant temperature during 'isothermal' kinetic studies. Thus significant errors may be introduced.

Theoretical approaches have been made to yield expressions that assess the size of these effects and their dependence on conditions.<sup>1</sup> Interpretations follow the steady-state analysis for thermal explosions and criticality. The first treatments were able to provide solutions only in terms of spatially averaged temperatures. The next development was to predict the effects of distributed temperatures in systems for which simple analytical solutions were available—the infinite cylinder or the infinite slab. From a practical point of view, finite vessels are more important: the sphere is the shape that can yield to theoretical treatments and in which experimental studies can be made with precision. Numerical solutions to the classical, steady-state equations have been known for many years,<sup>2-4</sup> and recently analytical approaches have been devised.<sup>5</sup> The virtue of an analytical interpretation is that we can see explicitly what factors are influential.

There are already experiments<sup>6,7</sup> which show that anomalous  $k$  values can arise through self-heating, and what is now required are tests to show whether or not the theoretical predictions are quantitatively satisfactory. The subject for the most convenient investigation needs to be a well-behaved, simple, exothermic, gaseous reaction that is capable of ignition at low pressures. Di-*t*-butyl peroxide (DTBP) decomposition appears to be a satisfactory example; it has long been used as a thermal source of methyl radicals<sup>8</sup> and the need for controlled rates of generation has prompted more than ten independent determinations of the kinetic and Arrhenius parameters. Overall, wide ranges of temperature (360–626 K), pressure (5–500 Torr) and extents of dilution with inert gases have been investigated.<sup>9</sup> Although a critical appraisal of the results leads to recommended 'best' values for  $E = 157.9 \pm 1.3$  kJ mol<sup>-1</sup> and  $\log(A/s^{-1}) = 15.80 \pm 0.13$ , in fact the margins of discrepancies between different determinations are wider. Activation energies span the range 138–167 kJ mol<sup>-1</sup>, and accordingly  $\log(A/s^{-1})$  varies between 14 and 17.4. The exothermicity for decomposition<sup>10</sup>  $\Delta H_{298} = -180$  kJ mol<sup>-1</sup> ( $\Delta U_{460} \approx -196$  kJ mol<sup>-1</sup>). Decomposition is first-order and it does not appear to be susceptible to unimolecular fall-off even at pressures as low as 1 Torr.<sup>11</sup> The extent of decomposition can be followed by pressure change in a closed vessel.

We investigate the decomposition of DTBP throughout the isothermal regime from 420 K, through non-isothermal decomposition up to 500 K, and in conditions where ignition occurs. The  $p_0$ – $T_a$  ignition boundary is located for the first time; our vessel is spherical (1.1 dm<sup>3</sup>). Decomposition is followed by monitoring pressure changes, and in all experiments the temperature change is measured using a very fine thermocouple. From these measurements, quasi-steady temperature excesses which accompany decomposition are mapped throughout the  $p_0$ – $T_a$  region. Conditions at which non-isothermal reaction is accompanied by convection are avoided.

The temperature measurements provide the main route to assessing how and when self-heating influences the measured reaction order and activation energy. We also show that even without knowledge of temperature change, retrospective correction of a rate constant to that for isothermal reaction is viable from data obtained in non-isothermal circumstances.

In what follows the symbols to be used are:

$p/\text{Torr}$	total pressure
$p_0/\text{Torr}$	initial reactant pressure
$c_0$	initial concentration
$c$	reactant concentration

$x/a$	fraction of DTBP decomposed
$\gamma = (1 - x/a)$	fraction of DTBP remaining
$t/s$	time
$t_1/s$	quarter-life for the decomposition of DTBP
$T/K$	reactant temperature
$T_a/K$	vessel temperature
$\Delta T/K = (T - T_a)$	temperature rise
$R/J \text{ mol}^{-1} \text{ K}^{-1}$	gas constant
$E/J \text{ mol}^{-1}$	overall activation energy [ $d \ln k / d(1/T_a)$ ]
$q/J \text{ mol}^{-1}$	exothermicity
$k/s^{-1}$	first-order rate constant
$A/s$	pre-exponential factor
$\kappa/W \text{ m}^{-1} \text{ K}^{-1}$	thermal conductivity
$r/m$	vessel radius
$n$	reaction order
$f$	rate correction factor
$\delta$	Frank–Kamenetskii dimensionless heat-release rate

$$\left( = \frac{qr^2 A E c_0 \exp(-E/RT_a)}{\kappa R T_a^2} \right)$$

$\psi$	Semenov dimensionless heat-release rate
$\theta$	dimensionless temperature rise ( $= \Delta T E / R T_a^2$ )
$\theta_0$	central dimensionless temperature rise
$\bar{\theta}$	spatially-averaged dimensionless temperature rise
$j$	geometric factor.

## THEORETICAL BACKGROUND

The correction of kinetic rate data for non-isothermal conditions and negligible reactant consumption has been considered by Boddington and Gray.<sup>1</sup> They show how errors in activation energy  $E$  and in reaction order  $n$  may be expressed in terms of the same dimensionless group as is already used to discuss the critical boundary between stable and unstable behaviour from the point of view of thermal explosion theory. For non-uniform heating resulting from purely conductive control of heat transport, this is the Frank–Kamenetskii  $\delta$ ; for uniform internal heating it is the Semenov number  $\psi$ . Although either of the terms  $\delta$  or  $\psi$  is sufficient to determine the errors, they are more conveniently set out in other ways. In particular, if the rate correction-factor  $f$  is used, where

$$f = \frac{\text{ideal rate (all reactant at } T_a)}{\text{observed rate}} = \frac{V(\text{isothermal})}{V(\text{observed})}$$

then

$$\frac{\Delta E}{E} \approx \frac{\Delta n}{n} = -\frac{d \ln f}{d \ln \delta} \quad \text{or} \quad -\frac{d \ln f}{d \ln \psi} \quad (\text{Semenov conditions}).$$

To proceed further, we need to know  $f$  and  $\delta$  or  $f$  and  $\psi$  in terms of some suitable quantity such as reactant temperature  $\theta$ . Under Semenov conditions this is easy. In terms of the dimensionless, average excess temperature  $\bar{\theta}$  we have

$$\frac{\Delta E}{E} \approx \frac{\Delta n}{n} \approx \frac{\bar{\theta}}{1 - \bar{\theta}}.$$

For distributed temperatures the solution depends on the shape. For the simplest shapes analytical solutions exist: in parametric form for the infinite slab and in explicit form for the infinite cylinder. For the sphere progress has hitherto had to be guided by numerical solutions tabulated by Chandrasekhar and Wares.<sup>2</sup> Proceeding from these, Boddington *et al.*<sup>12</sup> argued that, although the dependence of  $f$  upon  $\delta$  might not be identical in the cylinder and the sphere, differences between the two quotients  $(1-f)/(1-f_{\text{crit.}})$  would be negligible. Subsequently, Archer and Tyler<sup>6</sup> generated numerical solutions for  $f(\theta_0)$  and hence for  $\text{dln } f/\text{dln } \delta$ .

Recently Boddington *et al.*<sup>5</sup> have provided two new, analytical solutions for the sphere. They use a reversion of the known, infinite-series solution for the exponential approximation to the Arrhenius rate law. Although not exact, errors are around only 1%, so the precision is very satisfactory. In terms of centre temperature they write

$$\delta = \frac{8}{3}[1 + 9 \exp(-\theta_0/2)][1 - \exp(-\theta_0/2)],$$

$$f = \frac{4}{3} \exp(-\theta_0/2) + \frac{1}{3}$$

and

$$\Delta E/E \cong \Delta n/n = 2[\exp(\theta_0/2) - 1][9 + \exp(\theta_0/2)]/[4 + \exp(\theta_0/2)][9 - 4\exp(\theta_0/2)].$$

The solution is applicable right up to criticality and (just as in the Semenov case) errors grow without limit as  $\theta_0$  approaches its critical value. The value  $\delta_{\text{crit.}} = 10/3$  is in error only by 1 part in 300. (They extend this treatment to generalised boundary conditions so that all cases between Frank-Kamenetskii and Semenov extremes are now soluble algebraically.)

When  $\delta$  is small, errors for the slab, cylinder and sphere ( $j = 0, 1, 2$ , respectively) may be put in common form:

$$\lim_{\delta \rightarrow 0} \frac{\Delta E}{E} = \lim_{\delta \rightarrow 0} \frac{\Delta n}{n} = \frac{\delta}{(j+1)(j+3)} = \frac{2\theta_0}{j+3}.$$

For the sphere, the limiting fractional errors are thus  $(\delta/15)$  or  $(2\theta_0/5)$ . These limiting forms are excellent rough guides, being only 10% in error for  $\delta$  as large as 1.5.

## EXPERIMENTAL

The reaction vessel (Pyrex glass, spherical, volume 1.1 dm<sup>3</sup>) was located in an electrically heated furnace which had a spherical cavity in order to maintain a uniform temperature ( $\pm 0.8$  K) over the vessel surface. The furnace was thermostatted over long periods to  $\pm 1$  K; stability over short intervals was better than this. The temperature was measured with a chromel-alumel thermocouple fixed to the outer surface of the reactor. A reference junction was placed in ice at 0 °C and the e.m.f. developed between them was measured using a potentiometer (sensitivity  $\pm 0.01$  mV).

The reaction vessel was connected to a conventional, glass vacuum line. DTBP vapour was admitted to the vessel from a roughly equal sharing volume *via* an electromagnetic valve (Leybold-Heraeus). The valve could be opened for short, reproducible time intervals (0.1-1 s). Initial reactant pressures and pressure changes were measured using a pressure transducer (SE labs SE42, sensitivity 19.09 Torr mV<sup>-1</sup>). Its signal was recorded using a potentiometric chart recorder (Smiths Servoscribe, maximum sensitivity 0.5 mV f.s.d.). The transducer was mounted externally but as close as possible to the furnace by a side-arm to the vessel. The total dead volume (including that to the entry valve) was less than 1% of the reactor volume.

Measurement of temperature rises accompanying reaction were made using a very fine thermocouple (Pt-Pt/13% Rh, 25  $\mu$ m wire) mounted at the tip of a probe which was inserted concentrically through the gas-entry arm to the vessel. Measurements in the present study were made with the junction located at the centre. A reference junction was attached to the outer

vessel surface and the signal between the two was amplified and recorded on an oscilloscope (Tektronix 564B). The highest sensitivity compatible with low noise was  $10 \text{ K cm}^{-1}$  displacement. Temperature changes were measured to  $\pm 0.5 \text{ K}$  from these records.

DTBP (Fluka AG, 99.9%) was further purified by trap-to-trap distillation and its vapour stored at s.v.p. in reservoirs ( $2 \times 5 \text{ dm}^3$ ) on the vacuum line. The storage volumes were painted black to prevent photochemical change. The decomposition of DTBP in the reaction vessel was investigated in the pressure range 0.5–10 Torr at temperatures in the range 420–503 K.

## RESULTS

### $p_0$ – $T_a$ IGNITION DIAGRAM

Fig. 1 displays a  $p_0$ – $T_a$  ignition diagram for the spontaneous decomposition of DTBP in a  $1.1 \text{ dm}^3$  spherical vessel. With the exception of that for methyl nitrate<sup>7, 13</sup> the present diagram is more comprehensive than those usually found in the literature. Not only do we locate the ignition boundary, but also we show the position of isotherms which join points where equal extents of self-heating are measured during

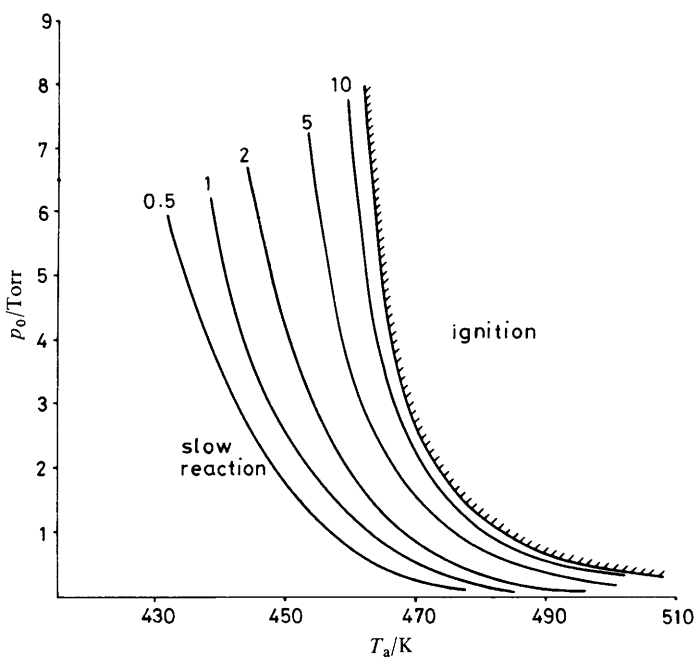


FIG. 1.— $p_0$ – $T_a$  ignition diagram for DTBP decomposition in a spherical vessel ( $1.1 \text{ dm}^3$ ). The solid lines join experimental conditions at which the same quasi-steady, central-temperature excess is reached.

decomposition (see below). The lines in fig. 1 relate to quasi-steady temperature rises of 0.5, 1, 2, 5 and 10 K; these data are important because they show (i) the extent of non-isothermal decomposition within the subcritical region and (ii) the magnitude of self-heating achieved and the way it is controlled by the initial ( $p_0$ – $T_a$ ) conditions. The principal purpose of measuring quasi-steady centre-temperature excesses is to be able to compare predicted deviations of reaction orders and activation energies due to non-isothermal reaction with experimentally measured anomalies.

However, the  $p_0$ – $T_a$  location of the ignition boundary determines the pressure and

temperature ranges to be investigated, and the locations of the isotherms show us where heating effects are expected to influence the measured kinetic parameters. When  $T_a < 435$  K, reaction is virtually isothermal throughout the entire pressure range studied (0-10 Torr). Between 435 and 462 K a similar range of pressures may still be investigated, but now the non-isothermal regime is invaded and quasi-steady temperature excesses increase as the initial pressure is raised. At higher vessel temperatures (462-480 K) the accessible pressure range becomes limited by the location of the ignition boundary. Moreover, the non-isothermal regime of decomposition extends to lower reactant pressures, and this means that at all initial pressures above *ca.* 1 Torr self-heating accompanies the early stages of reaction (see below).

#### NON-EXPLOSIVE DECOMPOSITION: TEMPERATURE-TIME RECORDS AND QUASI-STEADY TEMPERATURE EXCESSES

An initial cooling is first registered as cold reactant enters the vessel [fig. 2(a)]. In circumstances where non-isothermal decomposition follows, the temperature then rises through ambient, and continues upward to approach a low, quasi-steady

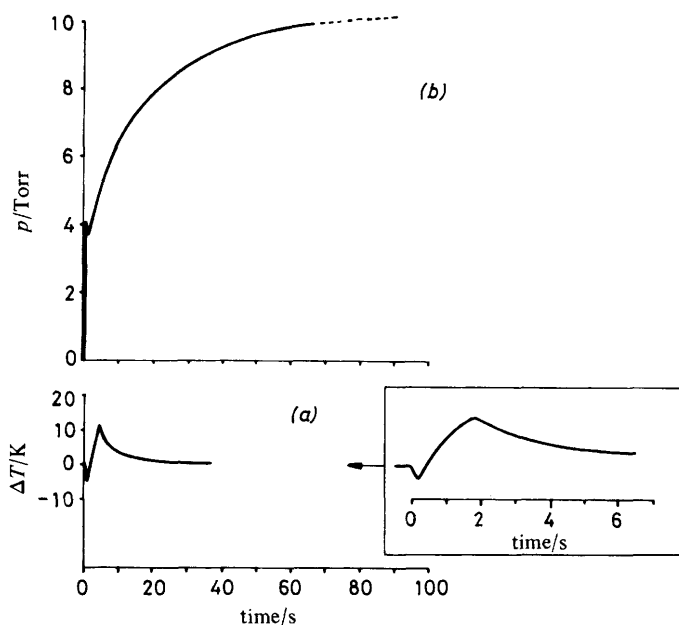


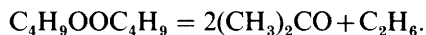
FIG. 2.—Typical pressure and temperature histories during the non-isothermal decomposition of DTBP,  $p_0 = 3.8$  Torr,  $T_a = 466$  K. The maximum temperature change is reached very early during decomposition. During much of the later period, reaction is isothermal.

maximum before decaying to ambient. The maximum temperature is always achieved within a very brief interval after admission to the vessel ( $< 4$  s), and the system is restored to virtually isothermal conditions in less than *ca.* 20 s. In the present study all temperature measurements ( $> 100$  experiments) were obtained at the centre of the vessel; accordingly the isotherms of fig. 1. are unique to the centrally measured temperature rises.

# NON-EXPLOSIVE DECOMPOSITION: PRESSURE-TIME RECORDS, OVERALL STOICHIOMETRY AND EXTENTS OF DECOMPOSITION

The pressure record always shows an initial jump as the gas enters the vessel. It is followed by a further rise due to thermal decomposition of DTBP. At sub-critical conditions the pressure increases smoothly to its final value. To measure  $p_{\infty}$ , reaction is allowed to continue for more than 6 half-lives, when decomposition is virtually complete. A typical record is shown in fig. 2(b); the conditions chosen here are close to criticality, but even so, more than 60 s elapses before  $p$  ceases to rise perceptibly. This distinction from the early rise and fall of  $T$  is important because it means that the bulk of reaction is occurring when reaction is isothermal. When  $T_a < 460$  K,  $t_{\frac{1}{2}}$  (isothermal)  $> 70$  s.

In gas-phase studies under closed-vessel conditions, pressure-time records are potentially a more precise and certainly a more convenient route to extents of reaction than are direct concentration measurements. Provided that the overall stoichiometry does not vary during reaction, the isothermal pressure change is proportional to the measurements. The ratio of the final pressure to initial reactant pressure, measured at many points throughout the slow-decomposition region, is  $2.98 \pm 0.02$ . This is the value to be expected on the basis of the stoichiometry



The fraction of reactant remaining at any time  $t$  is thus given by the relationship

$$c/c_0 = (2.98 p_0 - p)/1.98 p_0.$$

In principle the measured pressure must be corrected for the effect of internal temperature rise. A useful relationship is

$$p(\text{isothermal}) = p(\text{measured}) T_a / (T_a + 0.4 \Delta T_0)$$

in which  $0.4 \Delta T_0$  assumes that the average temperature rise is  $\frac{2}{5}$  of that measured at the centre.<sup>6</sup> This correction is always  $< 1\%$ . Extents of decomposition and velocity constants were derived from pressure changes in the present study.

## REACTION ORDER FROM INITIAL RATES

The pressure-time records obtained enable  $dp/dt$  at  $t = 0$  to be deduced. Thus the sensitivity of rate to concentration is determined appropriately from the variation of initial reaction rate with initial concentration:  $\log(dp/dt)_{t=0}$  against  $\log p_0$  at constant temperature leads to reaction order from its gradient. The initial rates of pressure change for various initial pressures determined at different vessel temperatures are given in tables 1 and 2 and displayed in fig. 3. The enhanced gradients of lines drawn through points that represent data at vessel temperatures in excess of 450 K is to be attributed to non-isothermal effects. The solid lines in fig. 3 are not arbitrarily selected: they are derived from a theoretical interpretation. This point is taken up in the Discussion.

## VELOCITY CONSTANTS

The decomposition of DTBP is implicitly first-order and the gradient of the isothermal graph in fig. 3 shows this. Moreover,  $\log(c/c_0)$  plotted against time is expected to be linear, and in isothermal circumstances [e.g. fig. 4(a)] this is found to be so. The isothermal rate constant is obtained from the gradient. Provided that reactant pressures are in excess of those at which unimolecular fall-off in rate is



TABLE 1.—INITIAL RATES, QUARTER-LIVES AND ISOTHERMAL RATE CONSTANTS

$T_a/K$	$p_0/\text{Torr}$	$(dp/dt)_0$ / $10^3 \text{ Torr s}^{-1}$	$t_i/s$	$k/10^4 \text{ s}^{-1}$
423	2.54	—	965	2.98
	4.18	—	1069	2.69
	4.54	—	937	3.07
	4.96	—	1049	2.74
	6.45	—	1183	2.43
	6.9	—	1329	2.18
	7.3	—	1183	2.43
423		mean values	$1100 \pm 130$	$2.6 \pm 0.3$
427	2.86	—	720	3.99
	3.86	—	648	4.44
	4.05	—	612	4.70
	4.77	—	810	3.55
	5.15	—	594	4.84
	6.11	—	690	4.16
	6.29	—	630	4.56
	6.5	—	780	3.69
	6.68	—	738	3.89
	8.4	—	708	4.06
427		mean values	$690 \pm 60$	$4.2 \pm 0.4$
430	1.53	1.59	512	5.62
	1.74	1.58	562	5.12
	2.77	2.41	600	4.79
	3.9	3.56	540	5.33
	4.6	4.67	510	5.64
	6.32	6.26	600	4.79
	8.4	8.74	521	5.52
	10.9	11.1	510	5.64
430		mean values	$544 \pm 36$	$5.3 \pm 0.3$

observed, the first-order dependence should also be reflected by rate constants that are independent of initial reactant pressures (constant  $T_a$ ). This is confirmed in table 1 at three vessel temperatures, in which are included rate constants obtained from (i) the gradient of the least-mean-squares line of the respective  $\log(c/c_0)$  against time graph and (ii) the time to 25% decomposition of DTBP. The scatter ( $\pm 10\%$ ) of these values is not pressure-dependent; it reflects variations of vessel temperature ( $\pm 1 \text{ K}$ ) between successive experiments when the duration of reaction is very long ( $> 1 \text{ h}$ ).

At vessel temperatures  $> 450 \text{ K}$  and at sufficiently high pressures for substantial self-heating to occur, first-order plots [ $\log(c/c_0)$  against  $t$ ] show a distinct curvature [e.g. fig. 4(b)]. The interval over which curvature is found (*i.e.* up to *ca.* 30% reaction) corresponds to the time during which a temperature rise accompanies decomposition. At constant vessel temperature the time to 25% decomposition of DTBP now diminishes consistently as reactant pressure is raised, and the rate constant is enhanced accordingly (table 2). In circumstances when the quasi-steady temperature excess is found to increase substantially (e.g. at  $T_a = 460$  and  $466 \text{ K}$ , where  $p_0$  can be varied over a wide range) the characteristic reaction time ( $t_i$ , 100-75% DTBP) is almost



TABLE 2.—TEMPERATURE RISES, QUARTER-LIVES AND NON-ISOTHERMAL RATE CONSTANTS

$T_a/K$	$p/\text{Torr}$	$\Delta T_{ss}/K$	$(dp/dt)_0$ / $10^2 \text{ Torr s}^{-1}$	$t_i/s$	$k/10^4 \text{ s}^{-1}$
460	isothermal prediction			32	90.6
	0.8	0.5	1.35	31	92.8
	1.0	1	1.97	27	106.5
	1.9	2	4.41	23.5	122.4
	3.6	5	8.61	21	137.0
	4.0	5	1.17	22	130.7
	5.4	6	1.59	19.5	143.8
466	isothermal prediction			19.0	151.2
	1.72	3	6.68	17.5	164.4
	1.78	2.5	4.99	17.8	161.6
	2.29	4	5.06	15.7	183.2
	2.48	4	5.95	14.8	194.3
	3.02	5.5	9.60	15	191.8
	4.77	10	11.32	11.5	250.1
480	isothermal prediction			9.5	302
	0.94	6.5	10.7	5.2	553.2
	1.00	6	10.7	5.3	542.7
	1.10	7	12.7	5.3	542.7
	1.13	9	12.1	4.6	625.3
	1.29	10.5	14.8	5.0	575.3

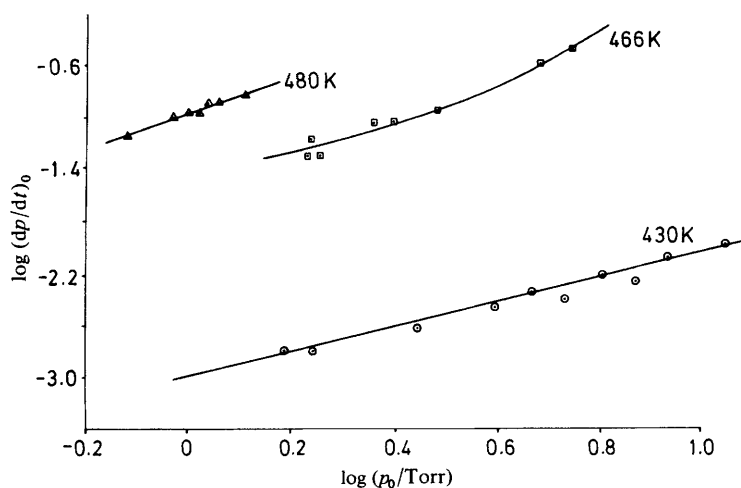


FIG. 3.—Determination of reaction order from the dependence of initial rate of pressure change on the initial pressure. Enhanced reaction orders are measured when self-heating is substantial. The points are determined experimentally. The solid lines are obtained from theoretical interpretation.  $\circ$ , 430;  $\square$ , 466 and  $\triangle$ , 480 K.

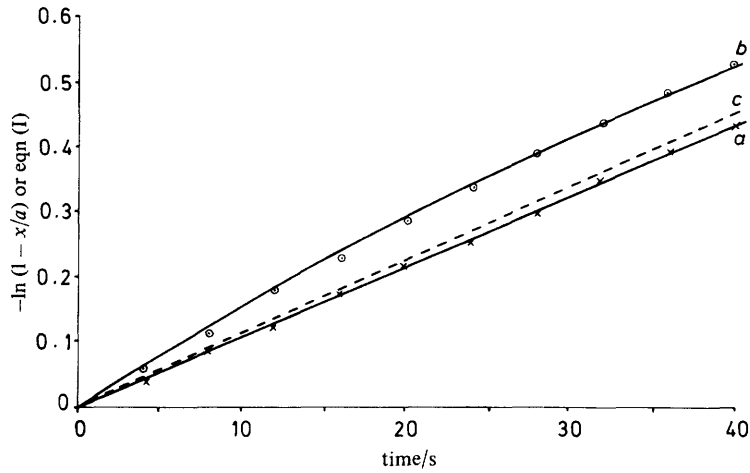


FIG. 4.—Function plots for the first order decomposition of DTBP at  $T_a = 460$  K. (a)  $p_0 = 1.0$  Torr;  $\ln(1 - x/a)$  against time; (b)  $p_0 = 7.7$  Torr;  $\ln(1 - x/a)$  against time; (c)  $p_0 = 7.7$  Torr; eqn (I) against time.

TABLE 3.—CONSECUTIVE QUARTER-LIVES DURING NON-ISOTHERMAL REACTION

$T_a/K$	$p_0/\text{Torr}$	$(\Delta T_0)_{ss}/K$	time intervals/s for change of concentration of DTBP			$t_1/s$ (isothermal)
			100-75%	75-56%	56-42%	
460	1.9	2	23.5	34	—	32
	4.0	5	22	34	—	32
	7.7	8	19.5	32	—	32
466	1.75	3	17	19	21	19
	4.77	10.5	11.5	15.5	19	19
	5.54	14.5	10	14	16	19
473	1.28	4	9	11	10	11.5
	1.72	8	7	9	9.5	11.5
480	1.0	6	5.5	6.5	9	9.5
	1.13	9	5	5	7	9.5
	1.29	10.5	5	6.5	9	9.5

halved and the rate constant derived from it increases nearly two-fold. However, the shorter characteristic times are not maintained throughout reaction; the second and third 'quarter-lives' representing the change in concentration of DTBP 75-56% and 56-42%, respectively, revert to that broadly characteristic of the isothermal reaction (table 3).

## DISCUSSION

## CORRECTION OF RATE DATA FOR THE INFLUENCE OF SELF-HEATING

Boddington *et al.*<sup>12</sup> have discussed three approaches to counter non-isothermal effects. The first is *avoidance*, and it requires a criterion for the maximum acceptable error due to self-heating. We might regard values for  $f$  in the range 0.95–1.00 to be tolerable; this means that for spherical geometries

$$\theta_0 \leq 0.1290 \quad \text{and} \quad \delta \leq 0.7078.$$

Thus if the isothermal rate is 5% less than the observed rate, the error in the activation energy is

$$\lim_{\delta \rightarrow 0} \frac{\Delta E}{E} = \frac{2\theta_0}{(j+3)} = \frac{2 \times 0.1290}{5} = 0.052.$$

For DTBP decomposition a typical temperature rise would be *ca.* 1.5 K and sufficient to generate an error in  $E$  of 7.5 kJ mol<sup>-1</sup>.

Method two is *allowance*, in which observed rate constants are corrected to their isothermal values on the basis of  $f(\theta_0)$ ;  $\theta_0$  is derived from measured internal temperature rises. Archer and Tyler<sup>6</sup> utilize this approach to correct rate data for the decomposition of 3-methyl-3-chlorodiazimine. Here we exploit the converse, namely to predict non-isothermal rate constants from  $k(T_a)$  and to compare them with measured values (see below).

Method three is *retrospective correction*: it is suggested that a function plot [*e.g.*  $\log(1 - a/x)$  against  $t$ ] influenced by heating effects may be corrected, even without knowledge of the temperature changes involved. The procedure has yet to be tested, and so we investigate the consequences here, taking the data of fig. 4(b) as an example in which non-isothermal effects are prominent.

The corrected function obtained by integration of the rate equation

$$dx/dt = [k(T_a)/f] (a-x)^n$$

is, for a first-order reaction,<sup>12</sup>

$$k(T_a)t = -f_c \ln \gamma + (1-f_c) \left[ 2(1-d)^{\frac{1}{2}} - 2(1-\gamma d)^{\frac{1}{2}} + \ln \left( \frac{[1-(1-d)]^{\frac{1}{2}}}{1+(1-d)^{\frac{1}{2}}} \right) - \ln \left( \frac{[1-(1-\gamma d)]^{\frac{1}{2}}}{1+(1-\gamma d)^{\frac{1}{2}}} \right) \right] \quad (I)$$

where  $\gamma = 1 - x/a$  and  $d = \delta/\delta_{\text{crit.}}$ . For spherical geometry  $\delta_{\text{crit.}} = 3.32$ , and  $\delta$  can be calculated, although the enthalpy of reaction and the thermal conductivity of reactant are required. Here  $d$  is evaluated most conveniently from

$$d = T_{\text{crit.}}^3 \exp(-E/RT_a)/T_a^3 \exp(-E/RT_{\text{crit.}})$$

where  $T_{\text{crit.}}$  is the vessel temperature for ignition at a corresponding pressure to that for decomposition at  $T_a$ .  $f_c = \frac{5}{9}$  for a spherical reacting mass at criticality. A valid assumption<sup>6</sup> in this analysis is that for a first-order reaction at the quasi-steady state

$$f = [V(\text{isothermal})/V(\text{observed})] = [k(\text{isothermal})/k(\text{observed})].$$

Representative values for eqn (I), applied to the kinetic data which yield fig. 4(b) ( $p_0 = 7.7$  Torr,  $T_a = 460$  K) are given in table 4. These revised data are plotted in fig. 4(c). A linear relationship exists where previously a curve was found, and its

TABLE 4.—RETROSPECTIVE CORRECTION OF DATA

$t/s$	$\gamma$	$-\ln \gamma$	eqn (I)
0	1	0	0
4	0.941	0.0608	0.0471
8	0.889	0.1176	0.09215
12	0.833	0.1827	0.1448
16	0.793	0.2319	0.1854
20	0.749	0.2890	0.2331
24	0.712	0.3397	0.2523
28	0.674	0.3827	0.3229
32	0.642	0.4432	0.3651
36	0.613	0.4894	0.4054
40	0.586	0.5344	0.4450

gradient,  $k(T_a)$ , corresponds to that for isothermal reaction at 460 K [fig. 4(a)]. The retrospective correction of a first-order function plot thus offers a very satisfactory route to isothermal rate constants.

#### ANOMALOUS REACTION ORDERS

The quasi-steady temperature increases that accompany the decomposition of DTBP are the closest realization of idealized steady-state conditions. They are the route to  $\theta_0$  and  $f$  via the relation  $f = \frac{1}{3} \exp(-\theta_0/2) + \frac{1}{3}$  and thence predicted dependences for the initial rate of pressure change on initial reactant pressure, viz.

$$(dp/dt)_0 = 2[k(T_a)/f]p_0.$$

Typical values for  $f$  are given in table 5 based on our experimental values for  $\Delta T_0$  when  $T_a = 460, 466$  and  $480$  K. We see that when  $\Delta T = 5$  K, the isothermal rate constant is at least 15% less than that measured. The discrepancy is still 6.5% when  $\Delta T_0$  is only 2 K, and it is noteworthy that these conditions can prevail when  $T_a = 20$  K or more below the critical vessel temperature.

We may derive  $\log(dp/dt)_0$  against  $\log p_0$  in graphical form and these are the solid lines drawn in fig. 3. There is excellent agreement between the predicted and

TABLE 5.—RELATIONSHIPS BETWEEN ISOTHERMAL AND NON-ISOTHERMAL RATE CONSTANTS

$T_a/K$	$(\Delta T_0)_{ss}/K$	$\theta_0$	$f$	$k(T_a)/10^{-3} \text{ s}^{-1}$	$k(T)/10^{-3} \text{ s}^{-1}$
460	2	0.1728	0.9338	9.06	9.70
	5	0.4320	0.8446	—	10.71
	8	0.6912	0.7662	—	11.82
466	2.5	0.2105	0.9201	15.12	16.52
	10.5	0.8840	0.7142	—	21.17
	14.5	1.2207	0.6345	—	23.83
480	6	0.4761	0.8324	30.2	36.28
	9	0.7141	0.7598	—	39.75
	10.5	0.8331	0.7275	—	41.51

experimental relationships. At  $T_a = 430$  K reaction is isothermal throughout the pressure range and thus a straight line, gradient ( $n$ ) = 1, is found. As  $\theta_0$  rises  $\Delta n/n$  increases and so an enhanced gradient, giving curvature for  $\log (dp/dt)_0$  against  $\log p_0$ , is to be expected. This is a distinct feature when  $T_a = 466$  K and it matches our experimental observations: the gradient at low pressure is 1, rising to *ca.* 2.3 when  $p_0$  exceeds 5 Torr.

At  $T_a = 480$  K, only a very restricted pressure range (0.75-1.3 Torr) is accessible and in it  $\Delta T_0$  varies from 6 to 10.5 K. It is extremely difficult to interpret curvature over these limited ranges: the overall order appears to be 1.43. Even here the predicted enhancement of reaction order as a result of self-heating is supported by experimental observations; one would not normally assess reaction order over such a limited pressure range.

#### ACTIVATION ENERGY AND THE ERRORS IN IT ARISING FROM SELF-HEATING

The overall activation energy for decomposition of DTBP is of course derived from the dependence of the measured rate constant on vessel temperature *via* the gradient of an Arrhenius plot ( $\ln k$  against  $1/T_a$ ).  $k$  is independent of initial pressure when reaction is isothermal and a mean value can be assigned at each vessel temperature. An average value is not appropriate to reaction in the non-isothermal decomposition region since measured values for  $k$  are now dependent on initial pressures (see table 2). The graph of  $\ln k$  against  $1/T_a$  shown in fig. 5 corresponds to data obtained at the initial pressure  $4.5 \pm 0.5$  Torr.

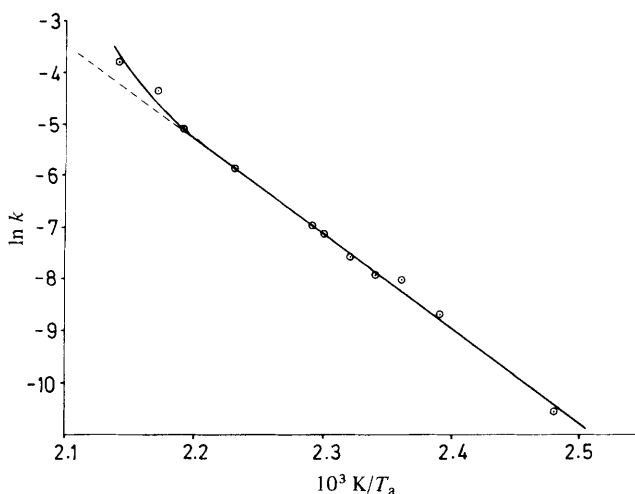


FIG. 5.—Arrhenius activation energy plot for the decomposition of DTBP over the temperature range  $T_a = 403$ -470 K. The points are experimental values for  $\ln k$ . The linear portion of the solid line and the extrapolated dashed line are obtained from a least-mean-squares analysis of isothermal rate data. The curved part of the solid line is obtained by correction for non-isothermal effects *via f*.

Over a range of vessel temperatures where self-heating during decomposition does not rise beyond 1 K (*i.e.*  $T_a = 403$ -445 K), the graph is linear and its gradient from a least-mean-squares analysis corresponds to  $152 \pm 0.6$  kJ mol<sup>-1</sup>, and  $\log (A/s^{-1}) = 15.3 \pm 0.3$ , broadly consistent with accepted values.<sup>9</sup>

On the basis of these Arrhenius parameters we may now calculate isothermal rate

constants for higher vessel temperatures: the extrapolation of the linear portion of fig. 5 (dashed line) represents these values. Non-isothermal values for  $k(T) = k(T_a)/f(T)$  are thus accessible and the solid line in fig. 5 represents them. The experimental data are remarkably consistent with it throughout the temperature range ( $T_a = 403$ – $470$  K). The graph is, of course, linear in the isothermal regime where  $f = 1$ . The major implication for the apparent activation energy in non-isothermal circumstances is the substantial over-estimation of  $E$ . When  $\delta$  is not small, the error in  $E$ , expressed in the terms of  $x(\theta)$  used by Boddington *et al.*,<sup>5</sup> is given by

$$\frac{\Delta E}{E} = \frac{4x/5(1+x/10)}{(1+x/5)(1-4x/5)}$$

but this can be rationalized in terms of  $f$  as

$$\frac{\Delta E}{E} = \frac{E(\text{observed}) - E(\text{isothermal})}{E(\text{isothermal})} = \frac{\frac{5}{9}(1-f)(9f-1)}{10f(f-\frac{5}{9})}.$$

The limiting conditions are explicit. When  $f = 1$ ,  $E(\text{observed}) = E(\text{isothermal})$ . When  $f = \frac{5}{9}$  (i.e. at  $\delta_{\text{crit.}}$ ), the error is infinite. Some values of  $f$  for decomposition of DTBP at 4.5 Torr through a range of temperatures are given in table 6, and the errors due to them are calculated.

TABLE 6.—QUASI-STEADY TEMPERATURE RISES,  $f$  AND ERRORS IN  $E$  AT 4.5 Torr

$T_a/\text{K}$	$(\Delta T_0)_{ss}/\text{K}$	$\theta_0$	$f$	$\Delta E/E$
448	1.5	0.1366	0.9472	0.06
456	3	0.2637	0.9012	0.12
460	5.5	0.4752	0.8308	0.26
466	10	0.8206	0.7307	0.62

These errors are not strictly those measured experimentally because they represent tangents to the  $\ln k$  against  $1/T_a$  curve. Nonetheless, the apparent activation energy can be substantially greater than the isothermal value. For example, the gradient from  $\ln k$  against  $1/T_a$  in the temperature range  $T_a = 446$ – $466$  K is equivalent to an activation energy of *ca.* 240 kJ mol<sup>-1</sup>, an error of nearly 50%.

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