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A THERMOKINETIC METHOD FOR THE DETERMINATION OF HEATS OF REACTION OF GAS PHASE PROCESSES

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ABSTRACT

A novel method is presented for the determination of heats of reaction for gas phase processes by simultaneous measurement of the reaction rate and the internal temperature rise at the centre of a spherical vessel. The reaction stoichiometry must be known, and it is necessary to choose reaction conditions giving temperature rises of between 0.5 °C and 5 °C. The method makes use of well established relationships from self heating theory. The only additional essential datum is the thermal conductivity of the mixture; our experiments use mixtures with a high proportion of argon, typically 90 mol%, to ensure that this can be estimated to good accuracy.

The method is demonstrated by measurements on the decomposition reaction of di-*t*-butyl peroxide and the isomerisation reaction of methyl isocyanide. It is applied to the determination of heats of reaction for the decomposition reactions of 1,1,2,2-tetrafluoroethyltrifluorosilane and 1,1,2,2-tetrafluoroethyltrimethylsilane and for the reaction of trichloromethyltrichlorosilane with *trans*-but-2-ene. From this last reaction system, the heat of formation of dichlorocarbene is obtained as $\Delta H^{\ominus}_{f,298}(CCl_2) = 230$ kJ mol^{-1} with an uncertainty of the order of 12 kJ mol^{-1}. The most recent previous values for this quantity are 163 ± 12 kJ mol^{-1}, derived from measurements of gas phase proton transfer processes, and 230 ± 35 kJ mol^{-1} from the appearance potentials of ions from the dissociative photodissociation of CF_2CCl_2.

INTRODUCTION

In any exothermic gas phase reaction there will be an increase in the reactant temperature above that of its surroundings as the system seeks to balance the rate of heat production with heat loss. Often a stable steady state is reached, although other, more complex conditions may result. The theory of self heating is well developed [1], covering uniform temperature conditions (Semenov model) and distributed temperatures (Frank–Kame-

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netskii model) for pseudo zero-order steady state processes. These basic treatments have been extended to non-stationary systems [2], including some allowance for reactant consumption, and a fuller numerical treatment has been made [3]. With the development of fine wire, fast response thermocouples to measure gas temperatures within reacting systems, there have been many studies to confirm and develop these theoretical treatments, covering both stirred [4] and unstirred [5,6] systems. As well as confirming the predicted features of thermal ignitions, these studies show that, away from the ignition boundary in unstirred systems, there is rapid establishment of a steady state temperature profile within the reactants, and that this profile decays as reactant is consumed. There have also been experimental studies of other features of practical systems, including entry heating [6] and natural convection [5,7]. Thus there exists a good understanding of the self heating process, based on a well developed theory for exothermic processes, which has been extensively tested and supported by detailed experimental work.

This paper reports a novel method for the determination of heats of reaction, based on this understanding, by the simultaneous measurement of the rate and the temperature rise in a reacting system. The decomposition reaction of di-*t*-butyl peroxide and the isomerisation of methyl isocyanide have been used to evaluate and prove the method. The heats of reaction for the decompositions of 1,1,2,2-tetrafluoroethyltrifluorosilane and of 1,1,2,2-tetrafluoroethyltrimethylsilane and for the reaction of trichloromethyltrichlorosilane with *trans*-but-2-ene are then determined using the method.

THEORY

Our interest lies in distributed temperatures during a reaction within an unstirred, closed spherical vessel. If reactant consumption and convection can be ignored then a steady state profile is expected, provided that a dimensionless parameter, ∂, lies below a critical value [1], $\partial_{cr} = 3.32$. The temperature profile can be calculated for any $\partial \leqslant \partial_{cr}$ and can be expressed in terms of a dimensionless parameter, θ. With efficient heat transfer at the vessel walls, as normally applies in gas phase systems, a symmetrical temperature distribution results along any vessel diameter, rising from $\theta = 0$ at the vessel walls to a maximum value, θ_m, at the vessel centre. Precise values of θ_m are known as a function of ∂. Thus from the definitions of θ_m and ∂, i.e.

$$\partial = QEr^2(\text{rate})_{T_a}/(\lambda R T_a^2)$$

$$\theta_m = (T_m - T_a)E/(RT_a^2)$$

it is clear that, by measurement of $(T_m - T_a)$, it is possible to derive θ_m and thence the corresponding value for ∂. If the reaction rate is also known, then the reaction exothermicity, Q, can be derived, provided that the thermal conductivity, λ, and the activation energy, E, are also known. This is the basis of our method.

In practice there are a number of complications, partly due to experimental problems, and partly to the assumptions inherent in the theoretical analysis outlined above. The principal problems are as follows.

(i) There may be an initial temperature pulse as the gases are admitted to the vessel—the entry heating effect—due to the first gas to enter being compressed and adiabatically heated by the continuing inflow.

(ii) There may be significant reactant consumption before the steady state temperature profile is reached.

(iii) The effects of natural convection may not be negligible.

(iv) Measured reaction rates cannot be simply attributed to T_a, but must be corrected for the internal temperature rise due to self heating.

(v) For many systems of interest the thermal conductivity has not been determined at the reaction temperature (if at all).

These problems and our treatment of them are discussed below.

(i) A detailed study [6] of entry heating effects of cold gas into an evacuated heated reaction vessel showed that significant temperature rises could occur due to the compressive heating of the gas first admitted by the continuing inflow. Rises of several tens of degrees are easily generated. The effects depend on the actual configuration of the entry system, but increase with increasing pressure and are greatest for the gases of high specific heat ratio, C_p/C_v. The effects died away within 1–2 s of closure of the admission valve. Thus, provided that a spurious ignition is not induced, the temperatures observed a second or two after completion of the entry process should be unaffected by these entry effects. We confirmed that this was so for our system by direct experimental checks using mixtures of comparable thermal properties to our reactants. Our analyses were then based on temperatures measured after entry heating had died away.

(ii) We have used two different methods to allow for the effects of reactant consumption. The first method is to employ the simple self heating model, which ignores consumption, and to estimate the central temperature rise under conditions where this model applies, i.e. to extrapolate the observed temperature time trace back to the initial conditions. Our experimental conditions were chosen to have reaction half-lives of $\geqslant 60$ s, and we used entry times of $\leqslant 5$ s. Where there was no entry heating, the maximum temperature rise due to self heating occurred between 5 and 10 s; where entry heating occurred, the temperature fell to the steadily declining value we would associate with reactant consumption within 1 or 2 s of closing the entry valve. Thus, in either case, an extrapolation over a small fraction of a half-life is required and could be done with no obvious difficulty.

The second method uses an improved theoretical model to allow for reactant consumption. This has been done in numerical calculations [3,8] which provide, inter alia, values of θ_m as a function of ∂ for various reaction orders and exothermicities, and so allow a direct interpretation of the experimental measurements of θ_m. This method can only be used where there is no excess temperature rise due to entry heating.

Both methods have been applied, as convenient, in our analyses and as indicated in the Results section.

(iii) Experimental studies of natural convection in self heating systems show an unsymmetrical temperature profile occurs on the vertical diameter in the vessel, with the highest temperature occurring at a point above centre. In a system containing only one central thermocouple, the effect of convection is to reduce the measured temperature below that expected in a conduction only situation. In a parallel plate system without internal heating, convection only occurs once a critical value of the Rayleigh number has been reached. Similar behaviour is predicted [9] for a parallel plate system with internal reactive heating. The early studies of convection in spherical vessels due to reactive heating sought a similar critical Rayleigh number, Ra, for the onset of convective effects; a value of Ra $\approx$ 600 was first suggested [5]. However, Jones [9], in his analysis of convection in self heating systems, points out that convection within a spherical vessel is qualitatively different from the parallel plate case because, in consequence of the spherical symmetry, the temperature profile in the absence of convection is the same along any radius. Thus there will always be temperature gradients which are not parallel to the gravity vector, and so a fluid equilibrium is not possible. This implies that there will not be a critical value of Ra for the onset of convection but that convective effects can be expected whenever self heating occurs.

In his calculations on the effects of convection on the critical condition for thermal explosion (∂_{cr}) in a cylinder [10], Jones predicts that the value of ∂_{cr} will rise steadily with increasing Rayleigh number. The initial increase of ∂_{cr} is almost linear with Ra, approximately doubling in value between Ra = 0 and Ra = 4000. We have found in analysing our data, which cover the very wide range of Rayleigh numbers from 0.4 to 10^3, that the value of the reaction exothermicity, Q, as derived from a single experiment depends on the value of the Rayleigh number for that experiment, and that within each set there is an apparent upward trend in Q with decreasing Ra (see Figs. 2–6 below). Such a trend is consistent with the central temperature rise increasingly deviating from that expected in the absence of convection.

When the data are plotted as a function of $\log_{10}$(Ra), linear correlations result. We have used this observation to derive from each data set a value of the heat of reaction under conditions when convective effects will be trivial: this we have taken to be at Ra = 1, i.e. close to the lowest experimental value we achieved. Our choice is guided by several reasons. Firstly it must be recognised that the condition Ra = 0 is not attainable in a practical system, since some temperature rise will always occur in an exothermic reaction and, of course, it is not possible to extrapolate a semi-logarithmic plot to Ra = 0. Secondly, given the necessary conditions for experimentation (and in particular that we needed half-lives in excess of 60 s and a temperature rise of at least 0.5 °C) it is very difficult to work with $Ra < 1$ without introducing unacceptably large errors. Finally, we note that previous measurements [7,8] have shown that obvious asymmetry within the profile does not occur until $Ra \geqslant 1000$. Thus at $Ra = 1$ the profile should closely resemble the idealised conductive profile, which is very flat in its central portion and should lead to measured central values which are very close to ideal. These aspects of heat transfer by convection in reacting systems will be discussed more fully elsewhere [11].

(iv) Because of self heating, the average temperature of the reactants lies slightly above the temperature of the vessel, T_a. As the reaction rate at T_a is required in ∂ a correction must be made. If the rate constant has been calculated using the function plot method then a simple correction factor can be applied to get the rate constant at T_a; values of this factor, which depends upon the order of the reaction and its extent, are available [12]. Another method, used for two of the systems studied here, is to attribute the measured rate to the volume average temperature of the reactants and then to make a small correction using independently measured values of E. A good approximation to this average temperature is $T_a + 0.4(T_0 - T_a)$. The value of T_0 was taken as the average value of the experimental temperature rise over the time period used in the kinetic measurement.

(v) The consequences of using estimated values of thermal conductivities when direct experimental values are unavailable were minimised by working with mixtures of the reactant diluted with argon, typically with a tenfold excess of the inert gas. In these conditions we estimate (see Discussion) that a 10% uncertainty in the thermal conductivity of the reactant causes only a 1% uncertainty in the thermal conductivity of the mixture.

EXPERIMENTAL

Apparatus

A conventional glass vacuum system was used, with greaseless taps in the reaction, mixture preparation and storage sections. Reaction vessel pressures were measured using a pressure transducer (SE Labs, SE180) linked to a pen recorder; the maximum sensitivity was ±0.02 Torr. The spherical reaction vessel of 1107 cm^3 volume had a centrally mounted thermocouple for determining the temperature rise in the reacting mixtures. This thermocouple was made from 25 μm diameter wires of Pt and Pt–13%Rh and was coated with silica to avoid catalytic effects. The thermocouple output was

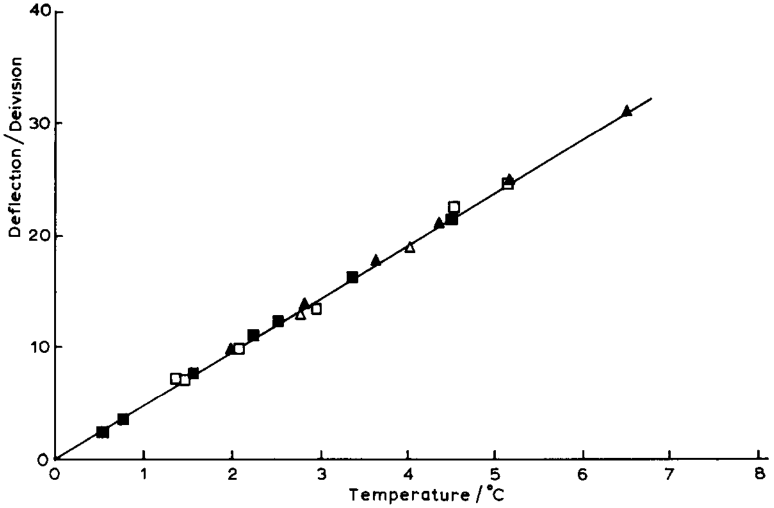


Fig. 1. Comparison of calibration methods for centre thermocouple. Thermocouple signal (in arbitrary units) vs. temperature (°C). □, Conventional static method; dynamic methods: △, H_2; ▲, N_2; ■, SF_6.

amplified using a Hewlett–Packard 419A DC null voltmeter and recorded on a potentiometric recorder. This arrangement gave a maximum sensitivity of 20 mm K^{-1}, allowing temperature changes as small as 0.05 K to be detected. Temperature calibrations were carried out using the method [5] of adiabatic expansion of nitrogen, hydrogen and sulphur hexafluoride from the reaction vessel at the working temperatures. Figure 1 shows a comparison of the calibration obtained by this method at room temperature with that obtained by a conventional method with temperatures measured to within 0.01 °C by a Beckmann thermometer. The two methods give indistinguishable results, an important conclusion given the need to measure accurately small temperature changes in the reaction mixtures.

The reaction vessel was held inside a close fitting, 2.5 cm thick aluminium block inside a forced circulation air thermostat. The temperature distribution around the vessel was examined using five chromel–alumel thermocouples placed first in a horizontal semicircle and then in a vertical semicircle; in the latter case the thermocouple assembly was rotated to provide measurements in different vertical planes. After optimisation of the furnace baffles, these tests showed that at 300 °C the temperature variation at any point did not exceed 0.1 °C over a 30 min period and that the variations around the vessel at any one time did not exceed 0.2 °C. Thus the temperature was satisfactorily constant during each experiment and the variation around the vessel surface could not distort the central temperature rise in a reacting gas by more than 0.1 °C. The reaction vessel dead space was determined [13] as 13.3 cm^3 at 300 °C.

Materials

The reactants were prepared by established routes (CH_3NC [14], $CHF_2CF_2SiF_3$ [15], $CHF_2CF_2Si(CH_3)_3$ [16], CCl_3SiF_3 [17]) or commercial samples were used (di-*t*-butyl peroxide from K&K Laboratories, *trans*-but-2-ene from BDH). All were purified before use either by trap-to-trap distillation followed by fractional distillation or by preparative GC. Purities were confirmed at > 99% by molecular weight determinations, IR spectroscopy, GC and ^1H NMR. The materials used for confirmation of product peaks on GC traces were direct commercial samples with the exception of 1,1-dichloro-*trans*-2,3-dimethylcyclopropane, which was prepared by the decomposition of CCl_3SiF_3 in the presence of an excess of trans-*but*-2-ene. Cylinder argon (BOC Ltd.) was used directly after drying.

Reactant mixtures were prepared in the usual way in a mixing vessel at the calculated delivery pressure, and then admitted to the hot, evacuated reaction vessel, allowing a few seconds ($\leqslant 5$) for equilibration. Pure reactants were also measured out into this vessel and the same admission procedure followed. In all runs an experimentally measured initial pressure was determined from the pressure–time trace.

RESULTS

Di-t-butyl peroxide (DTBP)

Runs were carried out at 453 K and 470 K using DTBP in mixtures with argon at total pressures up to 50 Torr, with $P_{DTBP} \leqslant 4$ Torr and P_{Ar}/P_{DTBP} of at least 5 and usually > 9 Torr. The reaction stoichiometry was determined as $(P_\infty - P_i)/P_i = 3.01 \pm 0.05$ (after making a dead space correction), in excellent agreement with literature values of 2.9 [18] and 3.0 [19]. Analysis of 14 completed runs by GC showed that acetone and ethane were the dominant products, produced in the ratio of $CH_3COCH_3 : C_2H_6$ of 1.97 ± 0.05, whilst methane, a minor product, was always < 3% of the ethane. These results are in accord with previous investigations which showed the major decomposition reaction to be

$$(CH_3)_3COOC(CH_3)_3 = 2CH_3COCH_3 + C_2H_6 \qquad (1)$$

with a minor contribution described by

$$(CH_3)_3COOC(CH_3)_3 = CH_3COCH_3 + CH_3COC_2H_5 + CH_4 \qquad (2)$$

A first order rate constant was calculated for each run. Firstly the observed pressures were corrected for the effects of the internal temperature rise using the measured centre temperature. These corrections were very small, typically < 0.2% of the total pressure. Then a first order rate constant was

TABLE 1

Temperature, K	Number of runs	Rate constant, 10^3k (s^{-1})	Lit. value [21,22] 10^3k (s^{-1})
453	25	3.82±0.11	3.76
470	24	17.8 ±1.5	16.4

calculated using Robinson's method [20], which allows for the vessel dead space. This value was finally corrected for the effects due to self heating using the function plot correction factor [12]; these corrections were in the ranges 2–6% at 453 K and 5–16% at 470 K. The values obtained are given in Table 1 and are in satisfactory agreement with literature values. Each run was used to derive an estimate of the reaction exothermicity, Q, using the observed maximum central temperature rise to obtain a value for θ_m from which a corresponding value of ∂ was derived using the theoretical relationship between these two parameters. This relationship depends on the value of the dimensionless adiabatic temperature rise, B, and on e $(= RT/E)$. For DTBP the best estimates of B and e are 48 and 0.024 respectively; the computed relationship between θ_m and ∂ for values of 50 and 0.020 was used in this analysis. Having obtained a value for ∂, the value of Q was derived using the known [23] values of E, T_a, thermal conductivity and

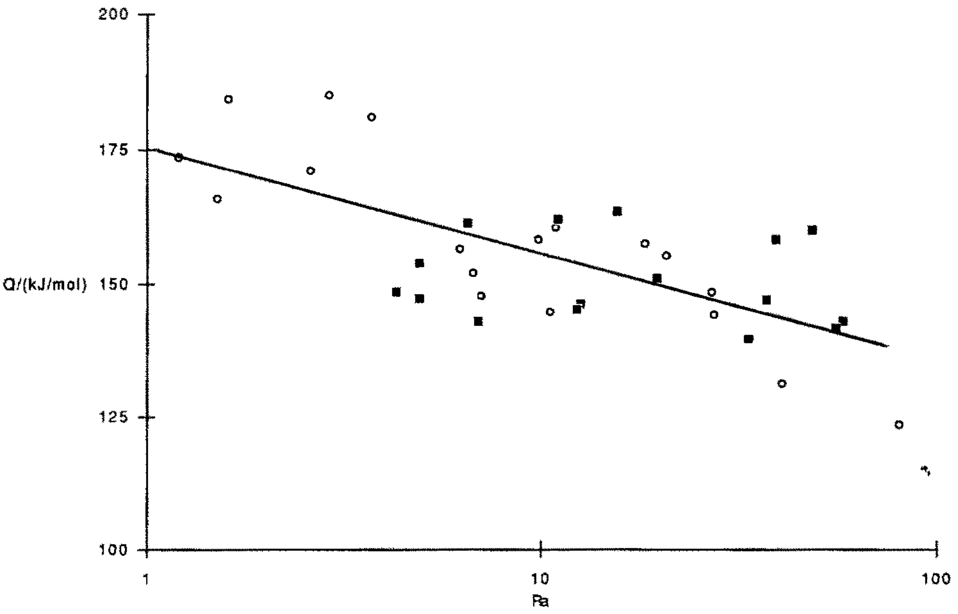


Fig. 2. Semi-logarithmic plot of exothermicity values (Q) against Rayleigh number (Ra) for di-t-butyl peroxide/argon mixtures. ○, 453 K; ■, 470 K. The line shows the least-squares fit.

reaction rate at T_a. The last-named value was taken from the measured initial pressure and the rate constant determined for the individual run. Figure 2 shows the values of Q plotted as a function of the logarithm of the Rayleigh number. The data show a good correlation, the individual values of Q falling as the value of the Rayleigh number increases. By using a least squares fit to the data and extrapolating to Ra = 1, a value of $Q = 183.8 \pm 9.6$ kJ mol^{-1} is obtained. This corresponds to the heat of reaction in a constant volume system, i.e. $\Delta U_{r,460} = -183.8 \pm 9.6$ kJ mol^{-1}. This converts to $\Delta H_{r,460} = -176.2 \pm 9.6$ kJ mol^{-1}, which can be corrected to $\Delta H_{r,298} = -171.3 \pm 9.6$ kJ mol^{-1}. The errors quoted here are standard deviations based on the difference between the experimental and least squares values of Q, a method which, in effect, attributes zero uncertainty of the slope of the line. This was adopted as we are taking as our best estimate of Q a value from one extreme of the measurement range but wish to assign to it an uncertainty which is typical of the bulk of the data. In the Discussion we consider other possible contributions to errors.

Methyl isocyanide

The isomerisation reaction of methyl isocyanide

$$CH_3NC = CH_3CN \tag{3}$$

at 561 K was used as a second test of the method, although its kinetics are more complicated than those of DTBP since, at the temperatures and pressures used here, this reaction is in the fall-off region. Thus the first order rate constant is dependent on both the pressure of the reactant and the nature and pressure of the inert gas. However, there have been several studies of this reaction and much kinetic data have been accumulated [24]. In the experiments used to measure Q, mixtures with a large excess of Ar were used to ensure that the thermal conductivity of the system could be reliably assigned. As the experimental rate constant cannot be determined by a simple method such as overall pressure change, it was necessary to use a calculated value. The procedure adopted was to carry out a set of reactions using pure CH_3NC to obtain a rate constant, and then to use this as the basis for calculation of the rate constant when mixtures with argon were used, taking the literature values for inert gas efficiency (0.137 for Ar : CH_3NC [25]) and Arrhenius parameters [24], and using the second order region expression for mixtures given by Fletcher et al. [26].

Some initial work was done using CH_3NC alone. Ten kinetics runs were performed with reactant pressures from 5.8 to 17.1 Torr. Each run was terminated at about one half-life by opening the reaction to an evacuated, liquid nitrogen-cooled vessel, in which the entire reaction vessel contents were quickly condensed. After evaporation and mixing, the ratio of CH_3NC to CH_3CN was measured by GC analysis [23] and then corrected for the dead space to give the percentage conversion within the reaction vessel. A first order rate constant was then calculated from the reaction time at this percentage conversion, and corrected by the average temperature method. The pressure dependent rate constants ranged from 4.51×10^{-3}–10.1×10^{-3} s^{-1}. Compared to the literature values [24] these showed a parallel dependence on the reactant pressure, but were consistently 20% lower. As the adjacent CH_3NC and CH_3CN peaks in the GC analysis were more clearly separated in our work than in previous work [24] we have preferred to rely on our own rate measurements. Hence for the thermochemical studies the rate constants calculated from the literature (see above) were reduced by 20%.

Twenty-three experiments were done at 561 K with Ar : CH_3NC ratios of between 8 and 14 and total pressures between 21 and 92 Torr, and 11 experiments with ratios between 2.5 and 5 and total pressures of 5–30 Torr. For all of these experiments there was a substantial entry heating effect as the premixed gases were admitted to the reaction vessel. Blank experiments, in which the CH_3NC was replaced by CH_3CN, showed that this decayed to less than 0.1° C within 5 s. Therefore the procedure adopted was to extrapolate the temperature–time trace over this period to give an estimate of the initial temperature rise corresponding to the initial pressure of CH_3NC. The rate constant, and hence the initial rate of reaction, were calculated for this pressure and a value of Q was then calculated for each run. The results are shown in Fig. 3.

Again, for each set of results, there is a trend of falling values of Q as Ra increases, and the relationship between Q and $\log_{10}(\mathrm{Ra})$ is satisfactorily linear, although the two data sets do not appear to be common, the lower ratio runs showing lower values and greater scatter. We are not able to suggest a satisfactory explanation for the difference, but note that there is greater uncertainty in the low ratio set since the thermal conductivity cannot be specified so precisely and since smaller temperature rises were generated (0.2–2.8° C as against 0.6–4.9° C). Thus we have used only the higher ratio set in estimating a value for Q. A least-squares fit to the 23 points in this set gives a value at $\mathrm{Ra} = 1$ of $Q = 88.1 \pm 5.3$ kJ mol^{-1}, which converts to $\Delta H_{r,298} = -88.1 \pm 5.3$ kJ mol^{-1}.

1,1,2,2-Tetrafluoroethyltrifluorosilane (TFETFS)

The overall reaction in the decomposition of TFETFS is [27,28]

$$CHF_2CF_2SiF_3 = SiF_4 + CHF{=}CF_2 \qquad (4)$$

although the mechanism involves two steps, the first involving the formation of the carbene CHF_2CF:, which then rearranges to $CHF{=}CF_2$. Alternative reactions of the carbene may occur as the concentration of $CHF{=}CF_2$ rises, but it has been shown [29] that at temperatures above 450 K these side

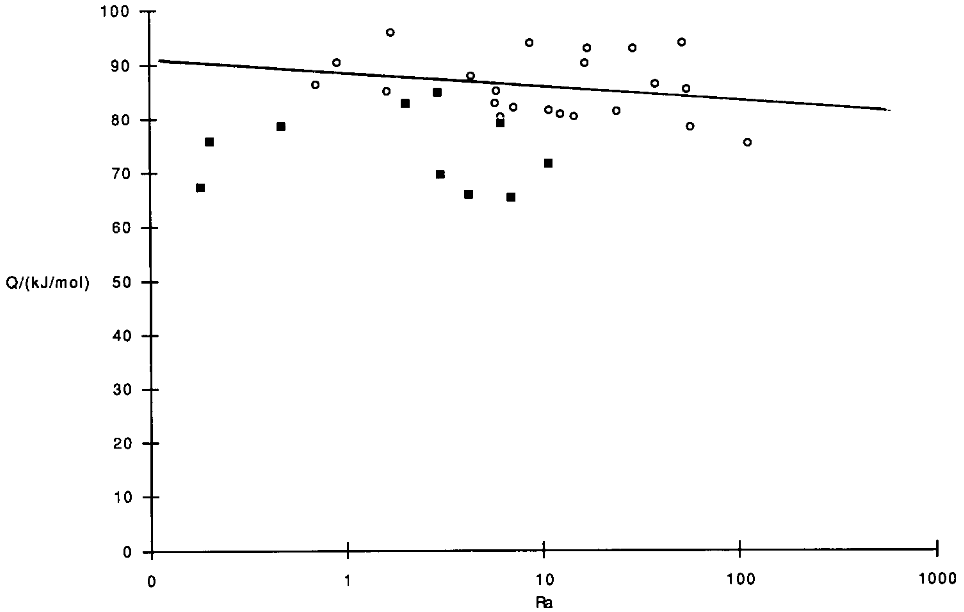


Fig. 3. Semi-logarithmic plot of exothermicity values (Q) against Rayleigh number (Ra) for methyl isocyanide–argon mixtures at 561 K. ○, $Ar/CH_3NC > 8:1$; ■, $Ar/CH_3NC < 5:1$. The line shows the least-squares fit to $Ar/CH_3NC > 8:1$ points.

reactions are not significant for the first 30% of the decomposition, and within this limit satisfactory first order function plots are obtained. We operated at 470 K with initial reactant pressures of between 1 and 11 Torr, deriving first order rate constants based on 20–30% reaction using the dead space corrected function plot followed by correction for self heating. Ten experiments using pure TFETFS gave k (in s^{-1}) $= (6.75 \pm 0.20) \times 10^{-3}$, whilst 18 experiments with argon present at a ratio of at least 8:1 gave $(6.71 \pm 0.21) \times 10^{-3}$; these values compare well with the literature value [28] of 6.33×10^{-3}. As with the DTBP analysis, the maximum observed temperature rise was used to estimate θ and then ∂. The measured rate constant for the run was used with the initial pressure to get the initial rate of reaction, and then Q was calculated. Again, a good correlation was found between Q and $\log_{10}(\text{Ra})$, as shown in Fig. 4, from which we derive, at $\text{Ra} = 1$, $Q = 71.9 \pm 3.1$ kJ mol^{-1}, leading to $\Delta H_{r,298} = -69.4 \pm 3.1$ kJ mol^{-1}.

1,1,2,2-Tetrafluoroethyltrimethylsilane (TFETMS)

Previous work [30] has shown this to decompose in a similar manner to TFETFS, although with a higher activation energy, with first order kinetics and an experimentally observed stoichiometry of 2.0 corresponding to the reaction

$$CHF_2CF_2Si(CH_3)_3 = CHF{=}CF_2 + (CH_3)_3SiF \qquad (5)$$

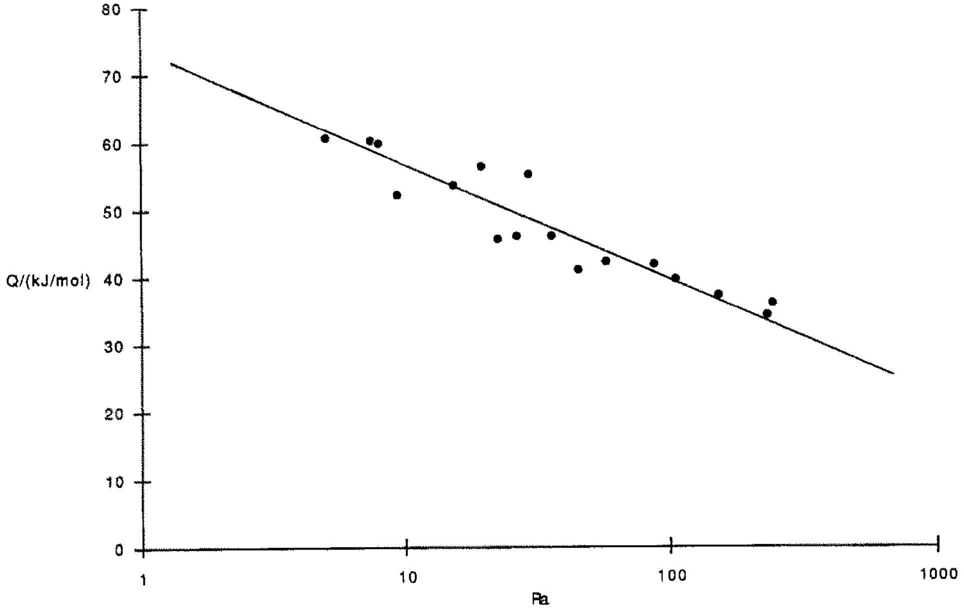


Fig. 4. Semi-logarithmic plot of exothermicity values (Q) against Rayleigh number (Ra) for $CHF_2CF_2SiF_3$–argon mixtures at 470 K. The line shows the least-squares fit.

The condition chosen for the thermokinetic work was a temperature of 653 K, at which the half-life was around 60 s. The reaction stoichiometry was confirmed and rate constants were determined from the pressure–time plots followed to 50% reaction, with corrections made as with TFETFS. Seventeen kinetic runs with pure TFETMS at 2–32 Torr gave a value of $(14.8 \pm 0.55) \times 10^{-3}\ s^{-1}$, whilst the 12 thermokinetic runs with Ar at $\geqslant 10:1$ and total pressures of 15–50 Torr gave $(14.6 \pm 0.7) \times 10^{-3}\ s^{-1}$; the value derived from the Arrhenius expression in the previous work [30] is $13.1 \times 10^{-3}\ s^{-1}$, in good agreement. The values of Q derived from the runs with argon present are plotted in Fig. 5; they give a value of Q, taken at Ra = 1, of 53.2 ± 8.4 kJ mol^{-1}, which leads to $\Delta H_{r,298} = -46.8 \pm 8.4$ kJ mol^{-1}.

Trichloromethyltrifluorosilane (TCMTFS)

It has been conclusively demonstrated [17,31] that TCMTFS decomposes to give dichlorocarbene in a first order step

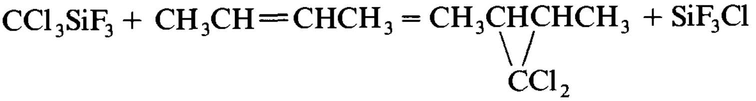
$$CCl_3SiF_3 = CCl_2 + SiF_3Cl \tag{6}$$

which is rate controlling when a reactive alkene is present to give a further reaction for the carbene, e.g. with *t*-but-2-ene.


(7)

$$CCl_2 + CH_3CH{=}CHCH_3 = CH_3\underset{\diagdown\diagup \atop CCl_2}{CHCH}CH_3$$

The stoichiometry of the overall reaction is then



$$CCl_3SiF_3 + CH_3CH{=}CHCH_3 = CH_3\underset{\overset{\diagdown\,\diagup}{CCl_2}}{CHCH}CH_3 + SiF_3Cl \qquad (8)$$

Again, the procedure adopted was to measure a rate constant for each run at the chosen working temperatures and to use that value in calculating Q, rather than rely on the literature values for the rate constant. As with CH_3NC, the rate constants were based upon a single analysis of the reaction mixture after about one half-life, measuring the concentration of the cyclopropane adduct by gas chromatography; the usual corrections were made to the data to yield a rate constant at the vessel temperature. Two sets of experiments, each of 16 runs, were done at 433 and 443 K using mixtures of TCMTFS and *t*-but-2-ene in the ratio 1 : 2 and with argon added to at least a tenfold excess. The total mixture pressure ranged from 23–170 Torr with partial pressures of TCMTFS of 0.8 to 5 Torr; these conditions gave central temperature rises between 0.4 and 2.8 °C. The averaged rate constants were $(283 \pm 15) \times 10^{-5}\ s^{-1}$ at 433 K and $(692 \pm 32) \times 10^{-5}\ s^{-1}$ at 443 K. The literature values [31] taken from the Arrhenius expression based on data in the range 373–433 K are $395 \times 10^{-5}\ s^{-1}$ and $870 \times 10^{-5}\ s^{-1}$ respectively. However, that work mainly involved an unusually small reaction vessel of only 3.7 cm^3 volume with a surface to volume ratio (S/V) of

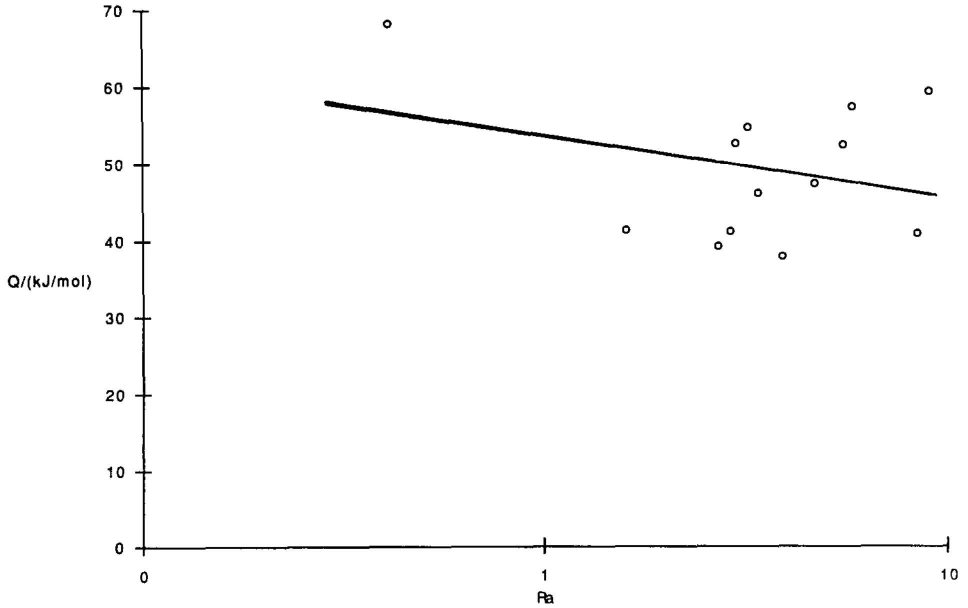


Fig. 5. Semi-logarithmic plot of exothermicity values (Q) against Rayleigh number (Ra) for $CHF_2CF_2Si(CH_3)_3$–argon mixtures at 653 K. The line shows the least-squares fit.

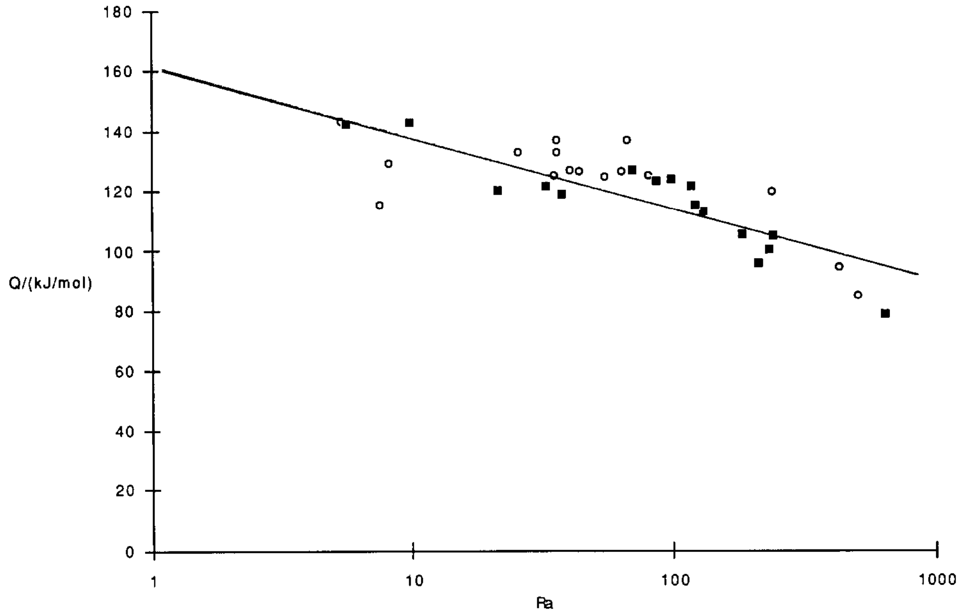


Fig. 6. Semi-logarithmic plot of exothermicity values (Q) against Rayleigh number (Ra) for CCl_3SiF_3-but-2-ene-argon mixtures. ○, 433 K; ■, 443 K. The line shows the least-squares fit.

7.8 cm^{-1} in contrast to our vessel of 1107 cm^3 and S/V of 0.47 cm^{-1}. In view of the differences in vessels and in the temperature ranges used, we have preferred to use our directly determined experimental values in the thermochemical calculations.

The higher total pressures used resulted in higher values of Rayleigh number than in any of the previous cases, but the same general pattern of variation of Q with Ra was observed, as shown in Fig. 6. The combined data for the two temperatures given $Q = 160.9 \pm 9.4$ kJ mol^{-1} at Ra = 1, which leads to $\Delta H_{r,298} = -161.6 \pm 9.4$ kJ mol^{-1}.

DISCUSSION

Evaluation of the method

Di-*t*-butyl peroxide and CH_3NC were selected for investigation, since their kinetics and mechanisms of reaction have been investigated in detail and there are data available from which their heats of reaction can be derived. Thus the results for these two reactions can be used to evaluate our method.

For DTBP, the observed heat of reaction will correspond to a weighted average for the two reactions that comprise the overall process, i.e. reactions

(1) and (2). Literature values [32] for $\Delta H_{r,298}$ for reactions (1) and (2) are -170.0 ± 5.0 kJ mol^{-1} and -191.3 ± 5.3 kJ mol^{-1} respectively, giving a weighted average for the reaction observed here [with 3% via reaction (2)] of $\Delta H_{r,298} = -170.6 \pm 5.0$ kJ mol^{-1}. Thus the value determined by our method, $\Delta H_{r,298} = -171.3 \pm 9.6$ kJ mol^{-1}, is in excellent agreement and provides strong support for the concept underlying our approach.

Methyl isocyanide is a more difficult test case, since not only are the kinetics more complex, as discussed in the results section, but there is some uncertainty about its heat of reaction. The most recent value [33], obtained by direct calorimetry of the isomerisation reaction, is $\Delta H_{r,298} = -99.2 \pm 0.6$ kJ mol^{-1}, a marked contrast to the previous value [34], based on the difference of heats of combustion, of -61 ± 23 kJ mol^{-1}. Our value of $\Delta H_{r,298} = -88.1 \pm 5.3$ kJ mol^{-1} lies about two standard deviations from the more recent (and more direct) value of -99.2 ± 0.6 kJ mol^{-1}, and we consider it gives support both to this value of $\Delta H_{r,298}$ for reaction (3) and to our method.

It must be emphasised that the errors quoted with our results are standard deviations due to the random variations in the primary determination of Q. These values, ranging up to ± 10 kJ mol^{-1}, probably represent the best that can be achieved. There could be, in addition, some possible systematic errors associated with the determinations, and these are considered below.

Errors due to uncertainty in the activation energy, which affect the calculation of θ and hence of ∂, are not important provided that the temperature rises are small since both θ and ∂ are proportional to E, and at low values of ∂ the relationship is nearly linear.

A greater uncertainty could be in the thermal conductivity of the mixture, an uncertainty we minimise by using a large excess of argon. The thermal conductivity of argon is accurately known [35], whilst the thermal conductivity of mixtures can be calculated using the well known Wassiljewa expression [36] as modified by Lindsay and Bromley [37]. This has been extensively tested [38–42] and shown to reproduce experimental values with errors that are usually less than 2% and rarely exceed 5%. Thus a reasonable assumption is that systematic error from this source is up to 2%, plus errors associated with the individual thermal conductivity values. For our materials, direct experimental values could be used without extrapolation for CH_3NC and after extrapolation for TCMTFS and *t*-but-2-ene. For the other materials, estimates were made [23] based on measured values for hydrocarbons of similar complexity, with allowances for the effects of the presence of oxygen, silicon or fluorine atoms in the structures. A cautious estimate would be to assume a 1% uncertainty in the thermal conductivity of Ar, 5% in other directly measured values and 10% in extrapolated or estimated values. Our mixtures were typically 90 mol% argon, and the effect of a 10% uncertainty in the thermal conductivity of the minor component results in the prediction for the mixture by the Wassiljewa formula being uncertain by no more than 1%. Thus we estimate the error arising from uncertainties in thermal conductivity values as up to 3%. Combined with the 2% error possible when calculating for mixtures, the maximum possible error in mixture thermal conductivities is 5%, although this will only occur when all the sources combine detrimentally. Since each derived value of Q is directly dependent on thermal conductivity, this is also the maximum likely additional error in Q above the random errors quoted with each result.

The overall conclusion is that our method, for suitable reactions, allows a direct determination of the heat of reaction, typically to ± 10 kJ mol^{-1}, with possible systematic errors up to 5%. This precision is acceptable for many purposes; indeed it is better than may result from indirect methods such as determination of the heats of combustion of reactants and products, where the heat of reaction is derived as a small difference of two large values. In this circumstance small errors in the original values represent a large uncertainty in the difference. Suitable reactions to which the method might be applied are those where other thermochemical methods are not easily applied and the stoichiometry, kinetics and mechanism of the reaction are known.

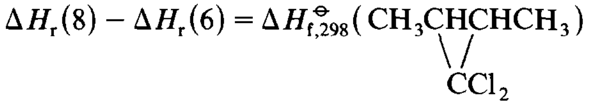
The applications

From $\Delta H_{r,298} = -69.4 \pm 3.1$ kJ mol^{-1} for the decomposition of $CHF_2CF_2SiF_3$, reaction (4), it is possible to derive a value for $\Delta H^{\ominus}_{f,298}(CHF_2CF_2SiF_3) = -2042 \pm 3$ kJ mol^{-1} by using the known values of $\Delta H^{\ominus}_{f,298}(SiF_4)$ and $\Delta H^{\ominus}_{f,298}(CHF{=}CF_2)$. Only the random errors in our determination of $\Delta H_{r,298}$ have been quoted. We are not aware of any previous determination of this heat of formation. For comparison, an estimate can be made using the suggested value [43] for $CHF_2CH_2SiF_3$ with correction based on the group contribution method for the difference in structure. This gives $\Delta H^{\ominus}_{f,298}(\mathrm{TFETFS}) = -2085$ kJ mol^{-1}.

Our data show that the mechanistically similar decomposition of 1,1,2,2-tetrafluoroethyltrimethylsilane, reaction (5), is slightly less exothermic than reaction (4), having $\Delta H_{r,298} = -46.8 \pm 8.4$ kJ mol^{-1}. It is not possible to estimate a value for the heat of formation of the reactant molecule, since there is no reported value for the heat of formation of $FSi(CH_3)_3$.

The result for reaction (8), $\Delta H_{r,298} = -161.6 \pm 9.4$ kJ mol^{-1}, corresponds to the overall reaction of trichloromethyltrifluorosilane with but-2-ene and, besides representing the first reported data for this system, provides a route to the heat of formation of the free carbene, CCl_2. This is of particular interest, since there are wide divergences in existing measurements.

Thus, when the heats of reaction for steps (6) and (8) are written in terms of the heats of formation of the reactants and products and combined, we get



$$\Delta H_r(8) - \Delta H_r(6) = \Delta H^{\ominus}_{f,298}(\underset{\displaystyle \backslash / \atop \displaystyle CCl_2}{CH_3CHCHCH_3}) - \Delta H^{\ominus}_{f,298}(CH_3CH{=}CHCH_3) - \Delta H^{\ominus}_{f,298}(CCl_2)$$

Of these, $\Delta H_r(8)$ has been determined here, and the first two heats of formation are known or can be estimated [23] as -11.2 kJ mol^{-1} and -53.6 kJ mol^{-1}. For $\Delta H_r(6)$ we can write

$$\Delta H_r(6) = E_6 - E_{-6} + RT$$

Previous kinetic work [31] has given $E_6 = 130 \pm 2.5$ kJ mol^{-1}, and a value of $E_{-6} = 22$ kJ mol^{-1} has been determined from a kinetic study [44] of chemically activated dicyclopropanes formed by the reaction of CCl_2 derived from reaction (6). These values lead to an estimate of $\Delta H^{\ominus}_{f,298}(CCl_2) = 230$ kJ mol^{-1}; the uncertainty in this value is of the order of ± 12 kJ mol^{-1}. The several previous measurements have given values for $\Delta H^{\ominus}_{f,298}(CCl_2)$ in the range 125–250 kJ mol^{-1}. Most recently reported values are 163 ± 12 kJ mol^{-1}, derived from measurements of gas phase proton transfer processes [45], and 230 ± 35 kJ mol^{-1} from the appearance potentials of ions from the dissociative photodissociation of CF_2CCl_2 [46]. Our value strongly supports the second of these and, unlike these determinations, relies solely on measurements involving only neutral species.

CONCLUSIONS

(i) Our results with di-*t*-butyl peroxide and methyl isocyanide have demonstrated that combined rate and temperature rise measurements can, under appropriate, carefully chosen conditions, be used to derive a heat of reaction of useful accuracy. We consider that this technique can be of value for reactions of materials where conventional thermochemical methods cannot be easily applied.

(ii) Application to the decompositions of 1,1,2,2-tetrafluoroethyltrifluorosilane and 1,1,2,2-tetrafluoroethyltrimethylsilane gives values of $\Delta H_{r,298} = -69.4 \pm 3.1$ kJ mol^{-1} and -46.8 ± 8.4 kJ mol^{-1} respectively.

(iii) Application to the decomposition of trichloromethyltrifluorosilane gives $\Delta H_{r,298} = -161.6 \pm 9.4$ kJ mol^{-1}, from which we derive for dichlorocarbene $\Delta H^{\ominus}_{f,298}(CCl_2) = 230$ kJ mol^{-1}, with an uncertainty of the order of 12 kJ mol^{-1}.

SYMBOLS

C_p	heat capacity at constant pressure
C_v	heat capacity at constant volume

g	gravitational acceleration
E	activation energy
ΔH	change in enthalpy
k	rate constant
K	thermometric conductivity
P	pressure
Q	exothermicity of reaction
R	gas constant
Ra	Rayleigh number, $\mathrm{Ra} = gr^3(T_\mathrm{m} - T)/T_\mathrm{a}KV$
r	vessel radius
T	temperature
ΔU	change of internal energy
V	kinematic viscosity

Greek letters

∂	$QEr^2\ (\mathrm{rate})_{T_\mathrm{a}}/(\lambda RT_\mathrm{a}^2)$
λ	thermal conductivity
θ	$(T - T_\mathrm{a})E/(RT_\mathrm{a}^2)$

Subscripts

a	vessel surface
cr	critical value
f	of formation
i	initial
m	maximum
o	at vessel centre
r	of reaction
∞	final

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