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A simple technique for gas kinetic studies in organosilicon chemistry

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Abstract

A batch stirred-flow technique, although simple and inexpensive to build and operate, is shown to be capable of yielding useful kinetic data, even from pyrolyses of considerable mechanistic complexity. Details are given in the hope of encouraging organosilicon chemists to make wider use of kinetics in elucidating reaction mechanism.

Introduction

Although a great deal of information about the mechanism of reactions of organosilicon molecules and intermediates may be obtained from the product analysis of well-conceived pyrolysis experiments using methods such as flash vacuum or sealed-tube pyrolysis, much more may be obtained if these pyrolysis studies are extended to include kinetic measurements over a range of temperature, thus enabling order of reaction, rate constants, and Arrhenius parameters to be calculated. The following three examples illustrate the point. The first evidence for the existence of dimethylsilene, $Me_2Si{=}CH_2$, and the first quantitative information about its stability and reactions, came from the gas kinetic studies of the pyrolysis of 1,1-dimethyl-1-silacyclobutane by Flowers and Gusel'nikov [1]. Gas kinetic experiments led to a quantitative model to account for the different course of the pyrolysis of hexamethyldisilane under high [2] and low [3] pressure conditions [4–6], and to a reliable value for the silicon–silicon bond dissociation energy [5]. Problems with the relative importance of homolysis and a retroene reaction as primary processes in the pyrolysis of allyltrimethylsilane, and with the mechanism of formation of vinyltrimethylsilane in that pyrolysis, were resolved by gas kinetic measurements [7].

Much of our gas kinetic work has been done with a variant of the stirred-flow technique. Many detailed accounts of the principles and operation of stirred-flow reactors have appeared in the literature of physical chemistry and chemical en-

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gineering, but Herndon's review is particularly clear and straightforward [8]. Our version [9] is simpler, easier to use, and more economical than conventional methods. In the hope of stimulating wider interest in the application of kinetic methods, this paper describes recent refinements of this technique, extending its scope to complex reactions without prejudicing its simplicity and low cost in apparatus and materials.

Results and discussion

1. Basic principles

In a conventional flow experiment, reactant continuously flows into the pyrolysis reaction vessel while pyrolysis products and undecomposed reactant continuously flow out. The flow is generally sustained by an inert carrier gas, while the extent of pyrolysis depends not only on the temperature but on the "residence time", i.e. the ratio of the volume of the reaction vessel to the volumetric flow rate. If it is desired to study a reaction in its early stages, short reaction times can easily be achieved without the need for expensive detection equipment with high time-resolution. This advantage is, of course, exploited in flash vacuum pyrolysis experiments. A further important advantage of the flow method for the kineticist is that very simple kinetic equations may be derived by considering the mass balance in a continuous flow reactor [8].

For example, in a first order reaction, A → B (1) with rate constant k_1, we consider the mass balance for the product B:

Formation $-$ Loss $= 0$

$k_1 v[\mathrm{A}] - u[\mathrm{B}] = 0$ where $v =$ volume of reactor;

$u =$ volumetric flow rate; and [ ] = molar conc. in reactor.

Hence, $k_1 = u[\mathrm{B}]/v[\mathrm{A}]$

$k_1 = [\mathrm{B}]/[\mathrm{A}] \cdot \tau$ (i) where $v/u = \tau$, the "residence time"

If there is a parallel reaction, A → C (2) with rate constant k_2,

$k_2 = [\mathrm{C}]/[\mathrm{A}] \cdot \tau$ (ii), by exact analogy with (i).

Consequently, rate constants for the formation of any pyrolysis product can be calculated from straightforward equations like (i) and (ii) provided that v, u, and the concentrations of the reactant and products are known. In practice, problems may arise with measuring concentrations in the reactor, with maintaining a uniform flow of reactant during the experiment, and with the rather substantial waste of reactant in a continuous flow experiment. We overcame all of these problems by changing from continuous to batch flow.

2. Original batch flow method

In its original form [9], our apparatus just consisted of a standard gas chromatograph with gas sampling valve, but with the electrically-heated stirred-flow reactor [10] inserted in the carrier gas line between the sampling valve and the gas chromatograph; a vacuum line attached to the sampling valve enabled low pressures of reactant vapour to be injected into the carrier gas, which was dried, de-oxygenated, and flow-controlled. Instead of a continuous flow of reactant, a single small analytical-sized sample was injected into the carrier gas with the sampling valve; this sample was carried into the reactor, mixed by stirred flow [10], and partially pyrolysed; the resulting mixture of products and unpyrolysed reactant was swept into the gas chromatograph where the components were separated and individual peak areas measured. Because sweeping out the contents of the reactor by the carrier gas is an exponential decay, it is analogous to a first order kinetic process with rate constant $= 1/\tau$. If the pyrolysis proceeds by first order reactions like (1) or (2), then exact equations for rate constants may be derived having the same form as equations (i) and (ii), with [A], [B], [C] replaced by the respective molar quantities detected by the gas chromatograph [9]. Once the gas chromatograph has been calibrated for reactant and products, rate constants for formation of each product can thus be measured from one injection, and a full kinetic investigation covering a range of initial concentration and temperature would only require about 10 micromoles of reactant. Reaction orders other than one can be determined, and the corresponding rate constants measured, provided the major process taking place is first order [9]. As the sweeping out of the sample from the reactor is invariably a first order process, that proviso can always be met irrespective of the complexity of a pyrolysis, simply by keeping the extent of pyrolysis small, so that "sweeping out" is the major process.

Under these conditions [9], for a reaction $A \rightarrow B$ of order n and rate constant k, $[B] = [A]^n\{k\tau/nv^{(n-1)}\}$. All of the terms in the brackets being constant, a plot of log [B] against log [A] gives a straight line through the origin of slope n, enabling the order to be measured by varying the size of the initial samples of A.

Kinetics of the reaction of an intermediate with a trapping agent may be measured by injecting mixtures of the trapping agent and the precursor to the intermediate.

3. *Refinements of original method*

Reversible reactions

The extension of the basic method to more complex pyrolysis is well illustrated by a recent study of a *cis–trans* isomerisation in which the *cis*-isomer, but not the *trans*-, was thermally unstable under the isomerisation conditions and each isomer was initially contaminated by small amounts of the other [11].

We denote the *cis–trans* isomerisation by $C \rightleftharpoons T$, with first-order rate constants k_f and k_r for *cis*- to *trans*- and *trans*- to *cis*-, respectively; and we denote the decomposition by $C \rightarrow P$, with first-order rate constant k_d. The simplest way to proceed in such a case is stepwise. At each stage, a rate expression may be derived by considering the material balance for a species that is formed by a chemical reaction, just as we did with reaction (1) above.

(a) Isomerisation without decomposition, starting from pure C. Apply mass balance to T:

$$k_f v[C] - k_r v[T] - u[T] = 0$$

$$k_f v[C] = \{k_r v + u\}[T]$$

$$k_f[C] = \{k_r + 1/\tau\}[T]$$

$$[T]/[C] = k_f/\{k_r + 1/\tau\} \qquad \text{(iii)}$$

Eq. iii simplifies to an expression like eq. i only if $k_r \ll 1/\tau$; i.e. if $k_r \leqslant 10^{-3}\ \mathrm{s}^{-1}$, since typically $1/\tau \simeq 10^{-1}\ \mathrm{s}^{-1}$. Before showing how to measure k_f and k_r experimentally, let us consider the more general case in which C and T are impure.

(b) As in (a), but C contaminated with some T. Apply mass balance to T; the *total* concentration of T is denoted by [T] and the initial impurity by [T′], giving an extra input of $\mathrm{T} = u[\mathrm{T}']$:

$$u[\mathrm{T}'] + k_f v[\mathrm{C}] - k_r v[\mathrm{T}] - u[\mathrm{T}] = 0$$

$$k_f v[\mathrm{C}] - k_r v[\mathrm{T}] - u\{[\mathrm{T}] - [\mathrm{T}']\} = 0$$

$$k_f[\mathrm{C}] = \{k_r + 1/\tau\}[\mathrm{T}] - [\mathrm{T}']/\tau$$

$$k_f = \{k_r + 1/\tau\}[\mathrm{T}]/[\mathrm{C}] - [\mathrm{T}']/[\mathrm{C}]\tau \qquad \text{(iv)}$$

Experimentally, we measure [T]/[C] as if the reaction were a simple irreversible first-order process, to get an apparent rate constant, $k_f' = [\mathrm{T}]/[\mathrm{C}] \cdot \tau$, as in eq. (i). Substitution in eq. (iv) then gives:

$$k_f = \{k_r + 1/\tau\}k_f'\tau - k_f'[\mathrm{T}']/[\mathrm{T}]$$

i.e. $k_f = k_f'\{1 + k_r\tau - [\mathrm{T}']/[\mathrm{T}]\}$ (v)

The same treatment applied to experiments starting from T initially contaminated with C would give eq. (vi), exactly analogous to eq. (v):

$$k_r = k_r'\{1 + k_f\tau - [\mathrm{C}']/[\mathrm{C}]\} \qquad \text{(vi)}$$

Knowing [C′] and [T′] from experiments below pyrolysis temperature, and τ, k_f' and k_r', we can then evaluate k_f and k_r from the simultaneous equations (v) and (vi). If only one isomer is available, both k_f and k_r can still be calculated from the appropriate equation (v) or (vi) and the value of k_f/k_r deduced from the equilibrium concentrations of T and C; the latter may be measured in separate sealed-tube experiments.

If pure isomers are used, eqs. (v) and (vi) simplify to the simultaneous eqs. (vii) and (viii) respectively:

$$k_f = k_f'\{1 + k_r\tau\} \qquad \text{(vii)}$$

$$k_r = k_r'\{1 + k_f\tau\} \qquad \text{(viii)}$$

(c) Isomerisation as in (b) accompanied by decomposition of C. Applying mass balance to C for experiments starting from T contaminated with C gives:

$$u[\mathrm{C}'] + k_r v[\mathrm{T}] - k_f v[\mathrm{C}] - k_d v[\mathrm{C}] - u[\mathrm{C}] = 0$$

hence $k_r = \{k_f + k_d + 1/\tau\}[\mathrm{C}]/[\mathrm{T}] - [\mathrm{C}']/[\mathrm{T}]\tau$ (ix)

and $k_r = k_r'\{1 + (k_f + k_d)\tau - [\mathrm{C}']/[\mathrm{C}]\}$ (x)

as in the derivation of eqs. (iv) and (v).

Substitution for k_r from eq. (x) in eq. (v) then gives:

$$k_f = \frac{k_f'\{1 + k'{}_r\tau + k_r'k_d\tau^2 - k_r'\tau[\mathrm{C}']/[\mathrm{C}] - [\mathrm{T}']/[\mathrm{T}]\}}{\{1 - k_f'k_r'\tau^2\}} \qquad \text{(xi)}$$

Similarly, substitution for k_f from eq. (v) in eq. (x) gives:

$$k_r = \frac{k_r'\{1 + k_f'\tau + k_d\tau - k_f'\tau[\mathrm{T}']/[\mathrm{T}] - [\mathrm{C}']/[\mathrm{C}]\}}{\{1 - k_f'k_r'\tau^2\}} \qquad \text{(xii)}$$

Once k_d has been measured (vide infra), eqs. (xi) and (xii) may be used to evaluate k_f and k_r from experimentally measured quantities, but the complexity of these equations clearly introduces additional errors compared to eqs. (vii) and (viii).

(d) Determination of k_d. If decomposition of C as in (c) above gives product P, then application of mass balance to P gives:

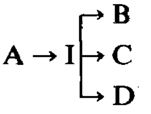
$$k_d v[C] - u[P] = 0$$

$$k_d = u[P]/v[C] = [P]/[C] \cdot \tau \qquad \text{(xiii)}$$

It is important to note that eq. (xiii) is valid *irrespective of whether C or T is the starting point*, and irrespective of whether the initial isomer is contaminated with the other or not, because k_d simply depends on the value of [P]/[C] regardless of the source of C. On the other hand, there is obviously not a simple relationship between [P]/[T] and k_d.

Parallel reactions

The treatment of independent parallel reactions was covered in "Basic Principles" above. A variant often found in practice is that several products result from a common intermediate, formation of which is rate-determining with rate constant k, as in the following example of three products B–D with common intermediate I:



$$A \rightarrow I \begin{cases} \rightarrow B & (1) \\ \rightarrow C & (2) \\ \rightarrow D & (3) \end{cases}$$

Experimentally, we can measure apparent rate constants k_1, k_2 and k_3 for formation of B, C, and D respectively from A.

e.g. for B, $k_1 = [B]/[A] \cdot \tau$ (i); and similarly for C and D.

Since $k_1/k_2/k_2 = [B]/[C]/[D]$, these apparent rate constants give a direct measure of the relative importance of pathways (1), (2), and (3). Each is related to the rate-determining rate constant k: $k_1 = f_1 k$, $k_2 = f_2 k$, and $k_3 = f_3 k$, where f_1, f_2, f_3 are "pathway factors". $f_1 = k_1/(k_1 + k_2 + k_3)$, etc., i.e. $\Sigma f_n = 1$. Hence, $k = k_1/f_1 = k_2/f_2 = k_3/f_3$. Obviously, the major pathway gives the most reliable measure of k.

Kinetic experiments will therefore give some evidence for or against such a mechanism. If the activation energies $E_1 - E_3$ derived from the three apparent rate constants are found to be equal, then the above type of mechanism may well be operating. If they are not, the different products must be formed by independent pathways with no rate-determining step in common.

Varying the flow rate

The simplest way to apply eq. (i) and the more elaborate equations derived from it above is to do a series of experiments at fixed flow rate, and hence at constant τ, and to calculate a rate constant from each individual experiment. We have obtained quite satisfactory kinetic data with this procedure, but is is better in principle not to depend on just one experiment, but to calculate each rate constant from a plot of several data points obtained from a number of individual experiments at each temperature. This can be done by varying the flow rate. Taking eq. (i) as an

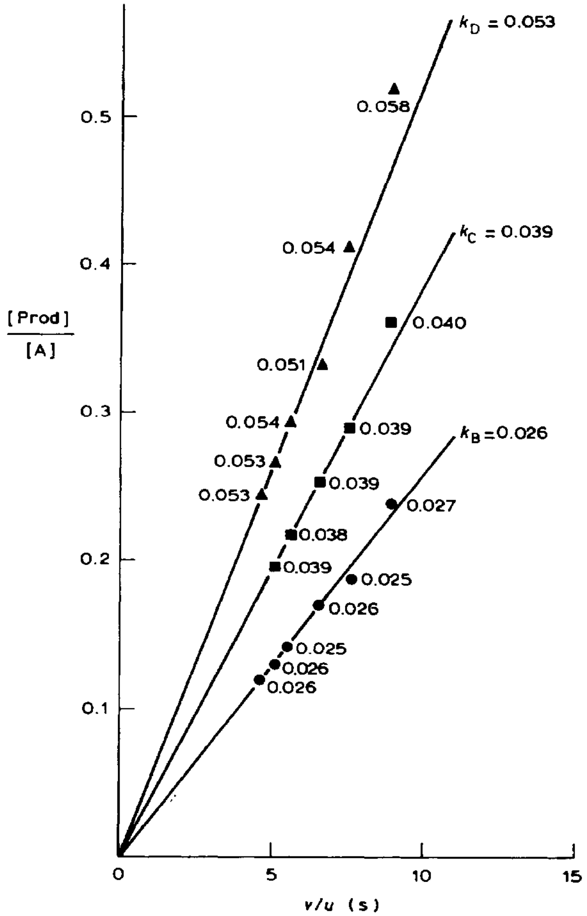


Fig. 1. Variable flow-rate pyrolyses at 527° C.

example, $k_1\tau = [B]/[A]$ and a plot of $[B]/[A]$ against τ would be a straight line through the origin of slope k.

To use this approach, we modified the apparatus by installing a simple flow splitter between the pyrolysis reactor and the gas chromatograph to allow higher flow rates through the reactor while maintaining the same flow rate through the gas chromatograph. Typical results obtained by varying the flow rate through the reactor between 50 and 100 cm^3 min^{-1} with a constant flow rate through the gas chromatograph of 50 cm^3 min^{-1} are shown in Fig. 1 for the formation of products B–D from reactant A. Rate constants were calculated from the slopes of the lines by least-squares analysis; for comparison, the rate constant obtained directly from eq. (i) is given beside each data point. It follows from the good agreement, especially at low conversion, that the discrimination between different compounds inevitably introduced by a splitter was insufficient to affect the results adversely.

The evidence from Fig. 1 that the flow rate can be varied without affecting the measured rate constant can be exploited to reduce problems caused by secondary reactions in complex pyrolyses. Low percentage decomposition, so that secondary reactions are of minor importance, can be maintained over a range of pyrolysis temperatures by increasing the flow rate (i.e. reducing the "residence time") as the temperature is increased, thus greatly improving the reliability of kinetic measurements for the primary reactions. This is therefore a substantial improvement on the original technique, considerably extending its applicability.

4. Use of capillary gas chromatography

When a sample enters the pyrolysis reactor it is dispersed throughout the reactor by stirred-flow mixing then swept out into the gas chromatograph. The time required for 99% of the sample to leave the reactor $\simeq 5\tau$, and products with gas chromatographic retention times $< 5\tau$ give unacceptably broad peaks; retention times should be at least 10τ for good peak shape and resolution [9]. This criterion has been easily satisfied in our work so far with packed gas chromatography columns and a reactor volume $\simeq 10$ cm^3, giving values of τ from 5 to 10 s, but a time-scale of 50–100 s is too long for capillary columns. In order to benefit from the considerable advantages that they confer, we have recently modified the technique by interposing a trap between the outlet of the pyrolysis reactor and the gas chromatograph; during the pyrolysis the trap is cooled in liquid nitrogen, then heated rapidly to evaporate the pyrolysis mixture quickly on to the column [12]. This procedure, which is not original [9], is satisfactory for products other than those which are not fully condensible in liquid nitrogen, e.g. methane. A versatile non-discriminating splitter is, of course, essential to reconcile the range of high flow rates through the pyrolysis reactor with the low column flow rate required by capillary gas chromatography.

Experimental

A block diagram of the modified apparatus based on a gas chromatograph with packed columns is in Fig. 2. The gas chromatograph and gas sampling valve were standard unmodified commercial models (Pye Unicam); the carrier gas was nitrogen, purified by passage through a molecular sieve column and an "Oxytrap". The

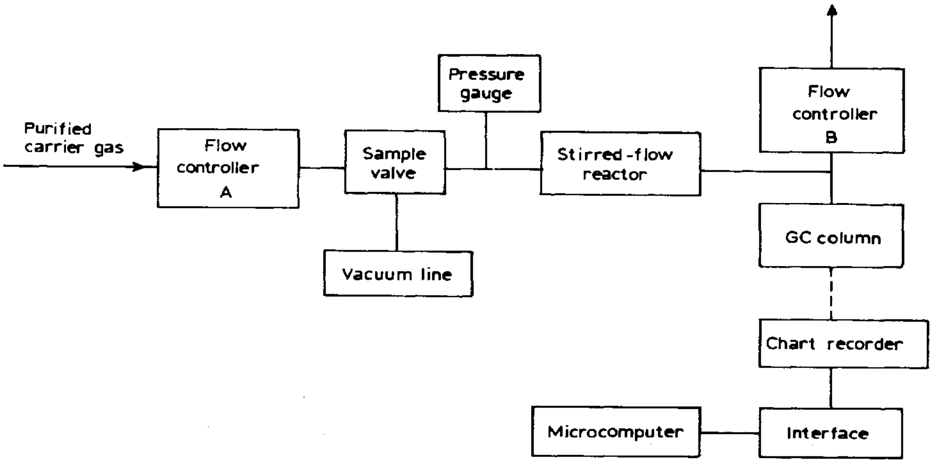


Fig. 2. Stirred-flow apparatus.

flow controllers were solid-state with digital readout of flow rate (ASM); in the variable flow rate experiments the flow rate through the pyrolysis reactor was set by controller A, while the flow rate through the gas chromatography column was the difference between the settings of controllers A and B. The pressure gauge monitored the pressure of carrier gas at the reactor [9]. The output from the flame ionization detector of the gas chromatograph was fed to a potentiometric chart recorder and to a microcomputer (RML 380Z) through an interface built in-house. The microcomputer both logged and processed data; if necessary, details of the BASIC programs are available from the authors, but most laboratories now have microcomputers with software suitable for the simple operations involved.

Originally [9], the quartz stirred-flow reactors were made to the design of Mulcahy and Williams [10], but with a volume of 10 cm^3. These are quite difficult to make because the inlet tube terminates at the center of the reactor in a small perforated bulb, but we have found that a much simpler jet inlet is satisfactory, as are reaction vessels made of stainless steel. We have also found that the technique tolerates considerable variations in the volume of the reactor and of the sample loop. The vacuum line was of conventional design, with pressure measurement by a "Baratron" pressure gauge. Greaseless stopcocks (Youngs) were used throughout.

The version of the apparatus suitable for capillary columns was attached to a Hewlett-Packard HP5995C gc/mass spectrometer. The layout was similar to that in Fig. 1, but with a cold trap between the reactor and the gas chromatograph and without flow controller B, which was unnecessary because the HP5995C has its own splitter system. The recorder, interface and microcomputer were also redundant because these are integral features of the HP5995C, as they are of other modern microprocessor-controlled gas chromatographs. The HP software was readily adapted to calculate rate constants from peak areas and calibration data.

Conclusions

The apparatus described above requires little more than a standard gas chromatograph and a basic vacuum line, not much more complex than would be required for flash vacuum pyrolysis experiments, yet it is capable of producing kinetic data for primary reactions quickly from small quantities of reactants, even if the pyrolysis mechanism is quite complex. The methods of doing so described in this paper are straightforward, and are readily extended to other mechanisms besides the examples used here, especially as the way to deal with any complex mechanism is to treat it experimentally as if it were a simple, one-step reaction, then relate the apparent rate constant thus obtained to the true rate constants for the mechanism in question. In view of the considerable additional mechanistic information about the reactions of organosilicon molecules and intermediates that is revealed by kinetic measurements, we hope that this demonstration of the versatility and simplicity of our version of the stirred-flow technique will encourage its wider adoption. We shall be pleased to provide more details of any aspect of it.

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