Note

Kinetic investigation of the thermal decomposition of organic peroxides by pulse chromatography

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Gas chromatography (GC) has been widely used to study the kinetics of the thermal and catalytic decomposition of organic peroxides. The important feature is the possibility of studying the kinetics of complex chemical reactions with small degrees of conversion (under the so-called "pure conditions" where the influence of the reaction products on the kinetics is negligible)[1,2]. However, GC cannot be used with fast reactions, because by the time a sample has been taken from the reaction mixture and subsequently analysed, the chemical process being studied is further advanced.

Some new possibilities for studying the kinetics of chemical reactions have arisen from the development of pulse chromatographic methods, in which the chemical reaction and analysis are combined into the single process. The pulse method was first proposed and applied by Kokes *et al.* for studying catalytic processes[3].

Bassett and Habgood[4] were the first to point out the possibility of using the pulse method for reaction rate determinations. They studied first-order reaction kinetics at the catalyst surface (isomerization of cyclopropane to propylene using molecular sieve 13 ×) by the pulse method under chromatographic elution conditions.

Major contributions to the kinetic study of chemical reactions in the chromatographic reactor-column was made by Roginsky and co-workers[5–13]. They showed that kinetic reactions in chromatographic reactors are so unusual that it is necessary to consider a specific reaction chromatographic regime which is significantly different from both the statistical and dynamic regimes. Many papers on the processes that occur in a chromatographic reactor have been published[14–27].

Phillips *et al.*[28] have proposed a stop-flow method for the pulse kinetic study of catalytic reactions in chromatographic reactor in which the carrier gas flow passing through the reactor-column is periodically stopped for a certain time Δt, then turned on again. The products formed during the time Δt appear as sharp peaks on the chromatogram and are superimposed on the broad peaks of the products, formed while the carrier gas flows through the reactor-column.

Schindlbauer *et al.*[29] proposed a chromatographic method for the rapid determination of kinetic parameters, using as the reactor the thermostatic device, heated to a high temperature, for sample introduction. The volatile reagent mixture was introduced into this device, serving for the introduction of the sample, and the products formed in the sample introduction device (the reactor) were separated in the

column. They pointed out the following advantages of the method: (1) the products and reagents are separated in the column and are recorded quantitatively by the detector; (2) the amount of reagent required is very small (micro method); (3) the temperature, reaction duration, correlation of reagents and the nature and amount of the catalyst can easily be changed (4) the device is simple; and (5) no reactions occur in the chromatographic column.

We have studied the thermal decomposition kinetics of the high-boiling, thermally unstable 1,1-diphenylethyl hydroperoxide by a pulse chromatographic method.

EXPERIMENTAL AND RESULTS

The chromatographic column was packed with a sorbent, the part of the column inserted into the evaporator operating as a microreactor and the other part operating as a separating column. The hydroperoxide solution was introduced directly into the microreactor with a microsyringe, the carrier gas flow was turned off, the sample was kept inside the microreactor for a definite time (from 0.5 to 15 min), then the carrier gas was passed again and the sample was transported into the separation part of the column. A blank test had previously established that no thermal decomposition of the hydroperoxide occurred in the separation part of the column. The temperature in the microreactor for the investigation of the thermal decomposition ranged from 90 to 150°C and that in the separation part of the column was kept constant at 90°C.

The analysis was carried out on a gas chromatograph of the Tsvet-100 type (Model 104) equipped with a flame-ionization detector. The size of the glass column was 27 × 0.1 cm I.D. The sorbent was Chromaton N AW HMDS + 5% PMS-100 and the carrier gas was nitrogen. The concentration of 1,1-diphenylethyl hydroperoxide in the solvent (analytical-reagent grade chlorobenzene) was 0.1 mol/l.

The chromatograms obtained are shown in Fig. 1 and the kinetic curves for the consumption of 1,1-diphenylethyl hydroperoxide and for the accumulation of its main decomposition products in the range 110–150°C (acetophenone, phenol, benzophenol and diphenylmethylcarbinol) in Fig. 2.

As the thermal decomposition of the hydroperoxide in the PMS-100 (poly-
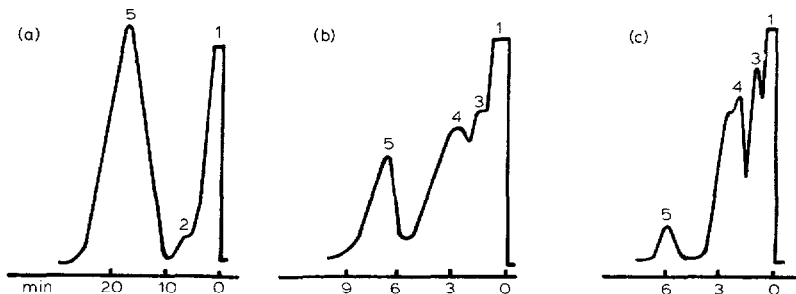

Fig. 1. Chromatograms of the thermal decomposition of 1,1-diphenylethyl hydroperoxide in the chromatographic regime at reactor temperatures of (a) 90, (b) 130 and (c) 150°C. Reaction time: (a) 10; (b) 2.5; (c) 1.5 min. Peaks 1 = chlorobenzene; 2 = acetophenone + phenol + benzophenone + diphenylethyl carbinol; 3 = acetophenone + phenol; 4 = benzophenone + diphenylmethyl carbinol; 5 = 1,1-diphenylethyl hydroperoxide.
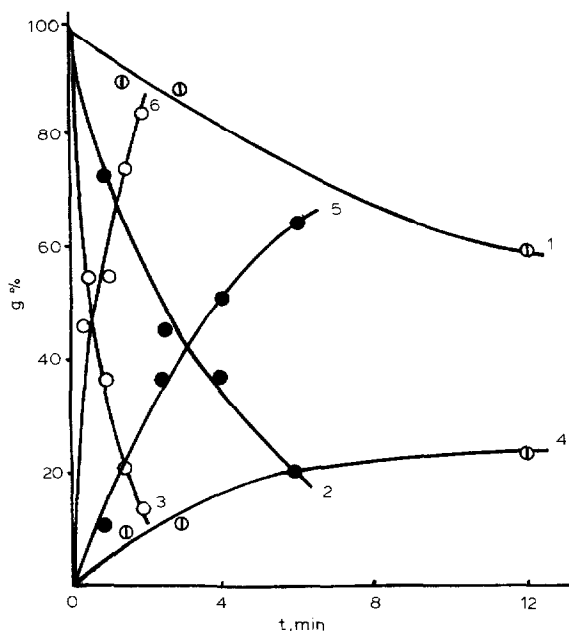
Fig. 2. Kinetic curves for 1,1-diphenylethyl hydroperoxide consumption (1–3) and accumulation of its main decomposition products (4–6) during thermal decomposition of the hydroperoxide in the chromatographic regime. Temperature: 1 and 4, 110°C; 2 and 5, 130°C; 3 and 6, 150°C.

methylsiloxane liquid) stationary phase is a first-order reaction, the rate constant was determined from the equation:

$$\log\left(\frac{1}{1-\alpha}\right) = \frac{kK}{2.303} \cdot t \tag{1}$$

where k is the true rate constant, K is the partition coefficient and t is the reaction time. Also

$$\frac{1}{1-\alpha} = \frac{S_0}{S_t} \tag{2}$$

where α is the degree of transformation, S_0 is the peak area of the hydroperoxide at time $t = 0$ and S_t at time t.

The validity of eqn. 2 was demonstrated[30] because the degree of transformation for first-order reactions does not depend on the pulse shape. The apparent reaction rate constant kK was determined from the gradient of the graph of $\log[1/(1-\alpha)]$ *versus* t, the partition coefficient, K, of 1,1-diphenylethyl hydroperoxide in PMS-100 was determined chromatographically[31] and the true rate constant was determined from the equation

$$k = \frac{2.303 \log \varphi}{K} \tag{3}$$

TABLE I

KINETIC CHARACTERISTICS OF THE THERMAL DECOMPOSITION OF 1,1-DIPHENYL-ETHYL HYDROPEROXIDE IN THE PULSE CHROMATOGRAPHIC REGIME

E_{true} = 105.4 kJ/mol; log A = 8.14 (A = pre-exponential factor in the Arrenius equation).

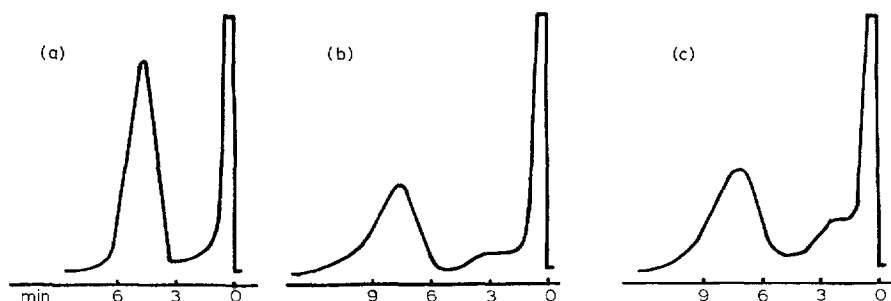| Temperature (°C)	$kK \cdot 10^4$ (sec^{-1})	$K \cdot 10^{-3}$	$k \cdot 10^7$ (sec^{-1})	$\tau_{1/2} \cdot 10^{-2}$ (sec)
90	1.13	123	0.020	61.10
110	3.12	100	10.071	22.10
130	14.79	85	10.339	4.66
150	71.04	73	12.234	0.97

Fig. 3. Chromatograms of 1,1-diphenylethyl hydroperoxide obtained on different sorbents: (a) Chromaton N AW HMDS + 5% PMS-100; (b) Chromaton N AW + 5% PMS-100; (c) Celite 535 + 5% PMS-100.

TABLE II

EFFECT OF THE NATURE OF THE SOLID SUPPORT ON THE RESULTS OF THE CHRO-MATOGRAPHIC ANALYSIS OF 1,1-DIPHENYLETHYL HYDROPEROXIDE

V_R = retention volume; $\Delta l_{1/2}$ = peak width at half-height; H = height equivalent to a theoretical plate.

Support	V_R (ml)	$\Delta l_{1/2}$ (cm)	H (cm)
Chromaton N AW HMDS	236.5	1.8	0.43
Chromaton N AW	313.4	2.9	0.66
Celite 535	274.9	2.3	0.54

The true activation energy was determined from the temperature dependence of the true rate constant. The hydroperoxide half-life period was calculated from

$$\tau = \frac{0.69}{kK} \tag{4}$$

The results are given in the Table I.

As the thermal decomposition of the hydroperoxide occurs in the sorbent-packed microreactor, the course of the reaction may be affected by chromatographic parameters such as the solid support and the stationary phase. The effect of the nature of the solid support on the results of the chromatographic analysis and the
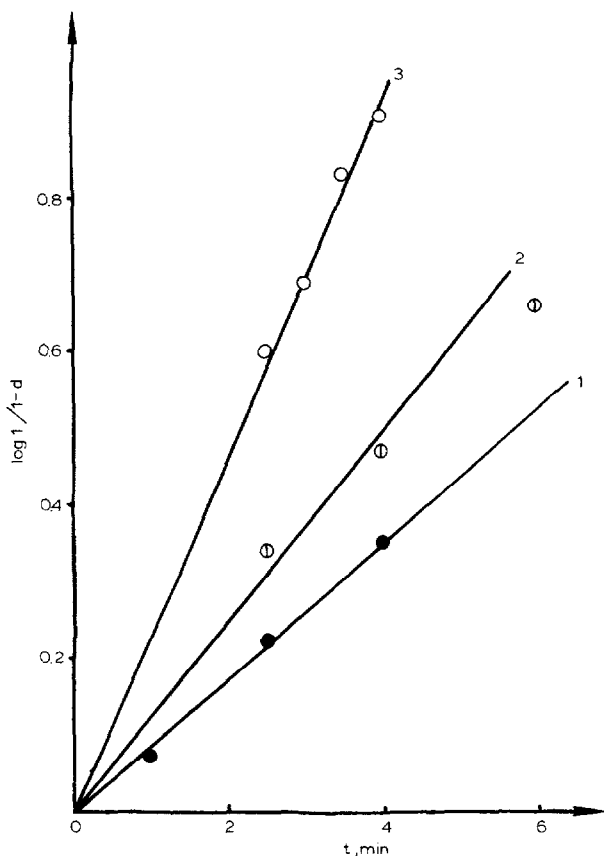
Fig. 4. Kinetics curves of the thermal decomposition of 1,1-diphenylethyl hydroperoxide in the chromatographic regime using different supports. Reactor temperature: 130°C. 1, Chromaton N AW HMDS; 2, Chromaton N AW; 3, Celite 535.

decomposition kinetics of 1,1-diphenylethyl hydroperoxide was investigated using supports such as Chromaton N AW and N AW HMDS and Celite 535. The polymethylsiloxane liquid PMS-100 (5% of the support weight) was used as the liquid stationary phase. Fig. 3 shows chromatograms of 1,1-diphenylethyl hydroperoxide

TABLE III

EFFECT OF THE NATURE OF THE SOLID SUPPORT ON THE THERMAL DECOMPOSITION KINETICS OF 1,1-DIPHENYLETHYL HYDROPEROXIDE

Support	$kK \cdot 10^4$ (sec^{-1})	$K \cdot 10^{-3}$	$k \cdot 10^7$ (sec^{-1})	$\tau_{1/2} \cdot 10^{-2}$ (sec)
Chromaton N AW HMDS	14.79	85	0.399	4.66
Chromaton N AW	20.80	98	0.480	3.31
Celite 535	39.24	147	0.616	1.78

obtained on the various supports and the effect of the nature of the solid support on the chromatographic analysis is shown in Table II.

Kinetic curves for the thermal decomposition of 1,1-diphenylethyl hydroperoxide on semi-logarithmic coordinates were constructed from the chromatographic results (Fig. 4), and the effect of the nature of the solid support is shown in Table III. According to the data obtained (Table III), the largest thermal decomposition rate is observed on Celite 535, indicating its catalytic activity.

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