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Kinetics and Mechanism of Gas-Phase Thermolysis Using Headspace-Gas Chromatographic Analysis

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Abstract

Headspace gas chromatography is employed in order to study the thermal decomposition reaction of gaseous di-*tert*-butyl peroxide (DTBP) in the 130°C to 160°C temperature range and in the presence of *n*-hexane as the internal standard and nitrogen as the carrier gas. The reaction exclusively yields acetone and ethane as products. First-order kinetics are observed, including when the surface-to-volume ratio (S/V) of the Pyrex 20-mL vial employed as the reactor is increased by packing it with silanized glass wool. However, a small increase in the rate constant values is observed at each temperature, which supports a heterogeneous surface process in DTBP decomposition. The rate constant's dependence on the homogeneous unimolecular decomposition reaction corresponds to the O–O bond rupture of the DTBP molecule in a stepwise three-stage mechanism. Thus, the relevant question of the participation of a surface catalytic effect in the DTBP gas-phase thermolysis can easily be assessed through the procedure described in this work. In general, this is advantageous for the rapid investigation of the reaction kinetics of volatile compounds at different temperatures.

Introduction

Headspace (HS) gas chromatography (GC) is a preferred method for the analysis of volatiles in matrices that cannot be injected directly into a GC. Furthermore, there are advantages to using headspace methods, even for analytical samples that can be injected directly. Although numerous articles have been published using this technique to measure equilibrium constants, only a few are found on reaction kinetics and HS sampling (1). Thus, the application of HS-GC instrumentation to measure the rate of gaseous reactions is so far not sufficiently developed. The main purpose of this study is to establish the reliability of this simple analytical method in comparison with other more-complex procedures for studying the kinetics of gaseous reactions.

An automated and rapid method for the determination of the rate of di-*tert*-butyl peroxide (DTBP) thermolysis in the gas phase is described. Although this is a well-known dialkyl peroxide sufficiently investigated by conventional methods, this study demonstrates the value of using the HS-GC technique to obtain relevant kinetic data. The application also allows for the identification of the corresponding reaction products by connecting the GC to a quadrupole mass-selective detector.

Experimental

Materials

DTBP was freed from the usual acetone and *tert*-butyl alcohol impurities by several washings with distilled water and then dried on anhydrous potassium carbonate and further distilled under reduced pressure (> 99.4% purity by GC). Analytical-grade *n*-hexane was employed as the GC internal standard.

Sample preparation and automated sampler operation

A 20-mL HS vial was oven-dried and sealed hermetically with a high-temperature silicone rubber septum. After placement in a Hewlett-Packard (Palo Alto, CA) Model 7694 E HS sampler connected to a Model 8000 PerkinElmer (Norwalk, CT) GC, the vial was flushed several times at approximately 165°C with the purified carrier gas. After cooling the vial at room temperature, 0.5 and 100 µL of a 1:1 mixture of DTBP–*n*-hexane (depending on the DTBP partial pressure required into the vial) was injected by syringe through the septum. In order to perform the DTBP thermolysis and identify the reaction products, the HS module followed a programmed sequence with its operational conditions held constant.

In standby mode, a 1-mL stainless steel sampling loop was purged by the carrier gas (i.e., nitrogen) from the GC. The thermostatted oven temperature was chosen depending upon the kinetic run that was to be performed. The valve/loop and transfer-line temperatures were set at 102°C and 100°C, respectively. The carrier gas was N_2, and the pressure was set at 1190

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torr (8.7 psi overpressure). The vial pressurization was set at 1447 torr (13.9 psi overpressure). The pressurization, venting, and injection times were 0.2, 0.01, and 0.2 min, respectively. After these operational conditions were selected in the keyboard of the HS sampler for performing the reaction, the vial was automatically introduced into the oven.

Then, at previously selected reaction times used to obtain suitable DTBP conversions for a reliable chromatographic analysis, the vial was pressurized with the carrier gas. After filling the sample loop, its contents (i.e., unreacted DTBP, *n*-hexane, nitrogen, and the reaction products) were quickly swept into the GC injection port. A fused-silica capillary column (25-m × 0.25-mm i.d., 1.2-µm film thickness, crosslinked 5% phenylmethyl silicone stationary phase) was used; it was obtained from Hewlett-Packard. The oven temperature program was initially set at 40°C for 5 min, increased at 15°C/min to 200°C, and then held at 200°C for 5 min. The carrier gas was N_2 with a 30-cm/s linear gas velocity (split ratio of 64:1). A GC flame ionization detector was used, and its temperature was set at 250°C. The injector port temperature was 120°C. Finally, after a selected chromatographic run time, the system was returned to the standby mode ready to start another kinetic run at the same temperature and reaction time. In order to perform a new measurement either at the same or another temperature, the HS oven temperature and the reaction time would be selected again in the sampler keyboard. The checks of temperature uniformity and accuracy inside the HS oven were satisfactory (± 0.1°C) to perform reliable kinetic experiments.

Kinetic calculations

The corresponding rate constant values (k_{obs}) for the peroxide thermolysis were determined from the slope of a least-squares data treatment plotting the natural log of the DTBP/*n*-hexane peak-area ratio versus the reaction time in each run (Figure 1).This is in consideration of the well-known first-order behavior of the kinetics of decomposition of that substance in the gas phase:

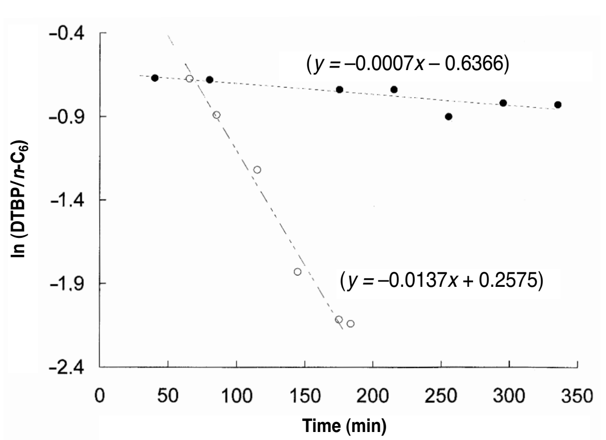


Figure 1. Representation through first-order kinetic plots of typical data for DTBP gas-phase thermolysis at different temperatures using the HS-GC technique: (o) values in runs performed at 160°C in nonpacked single vials (S/V = 2.3 cm^{-1}; r = 0.9925) and (•) in packed single vials at 130°C (S/V = 12.3 cm^{-1}; r = 0.8527).

$$\ln C_o/C = k_{obs}(t) \qquad \text{Eq. 1}$$

The initial partial pressures of DTBP (developed in the vial after its thermostatted heating) were calculated using the ideal gas law. The surface-to-volume (S/V) ratio of the vials that were used as the reactors were worked out by the measurement of their internal geometrical area. In the case of the vials packed with silanized Pyrex glass wool, the specific surface of this material was calculated by using the average diameter of the glass fibers, estimating its total length, and considering its density. The pre-exponential A factor and the energy of activation (E_a) of the DTBP thermolysis were obtained by the application of the linear Arrhenius equation method to the k_{obs} values and the corresponding error limits determined from a least-squares data treatment:

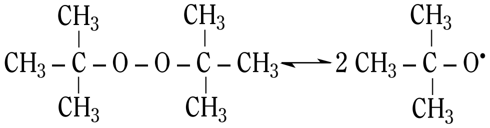
$$\ln k = \ln A - E_a/RT \qquad \text{Eq. 2}$$

Identification of the reaction products

Acetone and other expected products of DTBP thermolysis were investigated using authentic samples or by a GC–mass spectrometry (MS) library search using helium as the carrier gas with a Q-Mass 910 quadrupole detector (PerkinElmer) at 180°C interfaced to the GC.

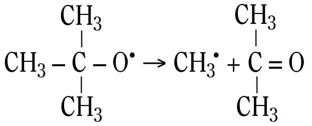
Results and Discussion

The products of a DTBP thermal decomposition reaction in the 130°C to 160°C temperature range and the 0.7- to 350-torr initial partial-pressure range are acetone and ethane. Their appearance can be interpreted by the well-established scheme:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \rightarrow 2\,CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\bullet} \qquad \text{Eq. 3}$$

The *tert*-butoxyl free radicals thermally decompose giving acetone and methyl radicals:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\bullet} \rightarrow CH_3^{\bullet} + \underset{CH_3}{\overset{CH_3}{C}}=O \qquad \text{Eq. 4}$$

Under the previously mentioned experimental conditions, the methyl free radicals yield ethane:

$$2\,CH_3^{\bullet} \rightarrow C_2H_6 \qquad \text{Eq. 5}$$

In this study, *tert*-butyl alcohol and isobutylene oxide were not detected as reaction products (excluding hydrogen abstraction reactions by *tert*-butoxyl free radicals and the eventual attack on the DTBP molecule by other reactive species). This fact precludes an S_H2-type induced decomposition reaction, which might accelerate the DTBP decomposition. However, these reactions have been known to occur in DTBP liquid-phase thermolysis, which has already been investigated by conventional kinetic methods (2,3).

Rate measurements of the DTBP thermal decomposition reactions (Table I) indicate that the thermolysis follows first-order kinetic laws up to at least a 5% conversion at 130°C and 41% at 160°C (Figure 1).

A similar kinetic behavior was observed when the vial used as the reaction vessel was filled with silanized glass wool to increase its S/V ratio from 2.3 cm^{-1} (i.e., nonpacked vial) to 12.3 or 40.2 cm^{-1} values. This demonstrates that the S/V ratio of the vials does not have influence on the kinetic order of the whole reaction. The experiments performed in individual nonpacked vials (each charged with the same initial DTBP partial pressure) gave results that were similar to those obtained using a single vial as the reactor, either sealed with high-temperature silicone or Teflon-lined septa (Table I). This shows that the products of previous reactions or the silicone polymer of the septa did not influence the kinetics of the DTBP thermolysis.

The temperature effects on the DTBP thermal decomposition reactions in the presence of nitrogen showed Arrhenius plots (Figure 2) that were reasonably linear in the usually investigated temperature interval of 30°C. Therefore, the similar Arrhenius equation parameters (A and E_a values) for the DTBP thermolysis (Table II) obtained in the nonpacked reactors (S/V = 2.3 cm^{-1}) support the claim that those values belong to a simple reaction, which is the unimolecular homolytic cleavage of the DTBP molecule (equation 3).

Table I. First-Order Rate Constant Values* for the Thermal Decomposition Reactions of Gaseous DTBP in the Presence of Nitrogen (Total Pressure Approximately 760 torr)

Temperature (°C)	Partial pressure of DTBP (torr)	$10^{-5}k_{obs}$ of DTBP (s^{-1})
130	35	0.61
130	3.5	0.83
130†	3.5	1.1
130§	3.5	0.83
130§,**	3.5	0.67
135§	26	1.2
135†	26	2.1
140†	2.5	3.6
140	150	2.9
150	350	6.2
150†	14	12.8
150**	6.5	6.1
155	7.0	9.3
160†	0.7	25.0
160	70	22.8
160‡	7.0	22.1
160**	7.0	17.5

* In the corresponding plots, the correlation coefficient values were in the range of 0.8527 to 0.9999.

† Apparent rate constant values obtained in packed single vials (S/V = 12.3 cm^{-1}).

‡ Runs performed in a packed single vial (S/V = 40.2 cm^{-1}).

§ Runs performed in nonpacked single vials (S/V = 2.3 cm^{-1}) capped with Teflon-lined septa.

** Runs performed using different nonpacked vials (S/V = 2.3 cm^{-1}) charged with the same initial partial pressure of DTBP but capped with Teflon-lined septa.

The Arrhenius equation parameters (Table II) for the unimolecular initial step of the radical initiated mechanism of thermolyses as indicated previously (equations 3–5) were similar to the already recommended values for the DTBP homogeneous reaction in the gas phase (5). In the study of Raley et al. (4), the rate constant values reported for the DTBP thermolysis showed to be slightly affected (an approximate 6% increase at 147.2°C) by a Pyrex rod packing that produced an eleven-fold change in its S/V ratio. Thus, those parameters (Table II) were invalidated by thermal gradients installed in the spherical reaction vessel (500-mL capacity) employed (5). However, the almost coincidental k_{obs} values obtained at the maximum temperature of 160°C with different S/V values (Figure 2) suggest the onset of other secondary reactions apart from the homolytic unimolecular decomposition (equation 3) that starts to contribute to DTBP thermolysis.

Because the temperature dependence of the reactions in the packed vials can also be described by an Arrhenius equation with normal parameter values, the rate determining step in this case is the thermal decomposition of the DTBP molecule. Although the rate constant values observed (Table I) corresponded to the rupture of the O–O bond of the DTBP molecule, a small lowering in the pre-exponential A factor and the corresponding E_a value could be observed in the packed vial reaction (Figure 2, Table II). However, it is not sufficiently certain that this catalytic effect is statistically significant given the experimental data available. In reality, the activation energy found in the packed vial experiments was a composite value. During the Langmuir–Hinshelwood treatment of catalytic effects (6) at the points in which it is assumed that a surface reaction at relatively high pressures is rate controlling, the corresponding activation

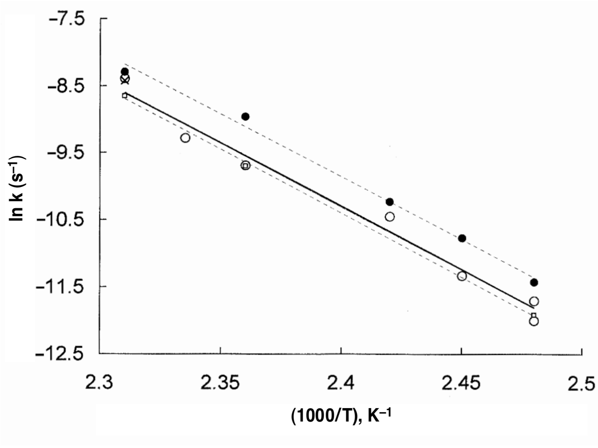


Figure 2. Arrhenius equation plots for the thermolysis of DTBP in the gas phase using the HS-GC technique: (o) values in runs performed in nonpacked single vials (S/V = 2.3 cm^{-1}), (•) in packed single vials (S/V = 12.3 cm^{-1}), (x) the same but in a vial (S/V = 40.2 cm^{-1}), and (□) values in runs performed using nonpacked vials (S/V = 2.3 cm^{-1}) charged with the same DTBP initial partial pressure but capped with Teflon-lined septa.

Table II. Arrhenius Equation Parameters for the Thermolysis of Gaseous DTBP

S/V (cm^{-1})	E_a (kcal/mol)	ln A (s^{-1})	r[*]	Reference
0.61	39.1	38.0		4
MSRV[†]	37.4 ± 0.5	35.9		5
2.3	37.9 ± 1.5[‡]	35.5 ± 0.5[‡]	0.9912	the present study
2.3	37.8 ± 0.2[‡,§]	35.3 ± 0.3[‡,§]	0.9995	the present study
12.3	37.1 ± 2.0[‡]	34.9 ± 0.8[‡]	0.9969	the present study

[*] Correlation coefficient values in the corresponding Arrhenius equation plots.

[†] Multisurface reaction vessel (as named in the corresponding reference) that was used to eliminate thermal gradients during DTBP thermolysis.

[‡] Error limits calculated by a least-squares data treatment.

[§] Values obtained in runs performed using several nonpacked vials (S/V = 2.3 cm^{-1}) charged with the same initial partial pressure of DTBP and capped with Teflon-lined septa.

energy values were regarded as a function of the activation energy of the surface step (E_s), the heats of absorption of the reactant (q), and sometimes the nature of the reaction products. At relatively high pressures and with the surface well-covered by the reactant molecules, the values of E_a and E_s can be nearly equal (6), as was actually observed in this study (Table II). Thus, this action on the kinetics of the reaction (employed here as the standard) depends on the adsorption of the DTBP molecules on the internal surface of the vessels and their packing. Besides, it is not very common for catalyzed reactions to show only variations of the apparent energy of activation with the pre-exponential A factor or variations of A with E_a constant. Generally, both vary—and in some cases, a compensation effect on the Arrhenius equation parameters is noted, as suggested by the results of the numerous studies on DTBP thermolysis mentioned in Table II.

Conclusion

The automated HS technique is useful for the rapid determination of the rate parameters of unimolecular gas-phase reactions. In this study, the validity of the procedure was checked using the sufficiently investigated DTBP thermolysis, because its kinetics and stoichiometry are well-established. The Arrhenius equation parameters obtained were similar to those reported using more sophisticated instrumentation and handling. Furthermore, by this technique a small catalytic effect of the surface of the reaction vessel on the DTBP thermolysis may be evident—a fact already reported using conventional kinetic methods (5). Therefore, the present application may improve the accuracy of reaction kinetic data for the thermolysis of volatile organic compounds and eliminate more sophisticated instrumentation and several time-consuming stages that involve inherent experimental errors.

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