

8. Gas-Phase Kinetics

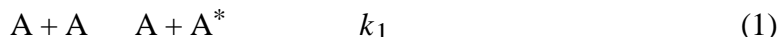
The unimolecular decomposition of gaseous di-*tert*-butyl peroxide is studied by monitoring the increase in the total pressure that results from the formation of three moles of gaseous products for each mole of reactant. The reaction is studied as a function of initial pressure, in the range 30-80 torr, and at two temperatures — $\sim 150^\circ\text{C}$ and $\sim 165^\circ\text{C}$.

General Reading

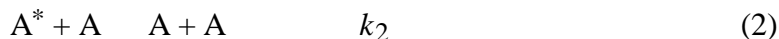
1. Oxtoby, Nachtrieb, and Freeman, *Chemistry: Science of Change* (2nd edit.); Sections 15.1-15.3 and 15.5-15.6.
2. Shoemaker, Garland, and Nibler, *Experiments in Physical Chemistry* (6th edit.); pp. 280-290 (Experiment 24); pp. 630-631 (manometers). [See also especially ref. 15 listed on p. 290.]
3. Levine, *Physical Chemistry* (4th edit.); Section 17.10 (unimolecular reaction theory).

Theory

Gas-phase decomposition reactions often exhibit first-order kinetics. Yet it is now understood that the mechanisms for these reactions are actually bimolecular in nature. The reaction is initiated by collisional activation (bimolecular) to an energy that is high enough to undergo decomposition,



where A^* represents the activated molecule. The observed first-order behavior is a consequence of a competition between the reverse of this process (collisional deactivation),



and the decay of A^* to products,



When the rate of Process (2) is much greater than that of (3), the concentration of A^* is maintained essentially at its equilibrium level. Then Process (3) becomes the rate-determining step, and the reaction exhibits first-order kinetics.

This qualitative description can also be reached more quantitatively by employing the steady-state approximation, whereby the rates of change for reaction intermediates are set equal to zero. In the present case the intermediate is the activated species A^* , and this approximation becomes

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_2[A][A^*] - k_A[A^*] = 0 \quad (4)$$

By solving this equation for $[A^*]$ and substituting into the rate law for loss of A, one obtains

$$-\frac{d[A]}{dt} = \frac{k_1 k_A [A]^2}{k_A + k_2 [A]} \quad (5)$$

This equation [Eq. (6) in SGN] predicts the observed first-order kinetics in the high pressure limit, where $k_2[A] \gg k_A$. It also reveals that at sufficiently low P (where $k_2[A] \ll k_A$), the reaction should exhibit kinetics second-order in $[A]$.

The latter case is difficult to treat in general, however, because the reaction products can also contribute to the activation step, so that the effective dependence may not be simply second order in $[A]$. One way to study this dependence is to work at very low $[A]$ and add an inert activating gas M whose pressure can be controlled (see indicated pages in Levine). The reaction then becomes pseudo-first-order, with effective rate constant proportional to $[M]$. Accordingly the effective rate constant should decrease with decreasing $[M]$. This falloff has indeed been observed in a number of cases.

The reaction to be studied here is the decomposition of di-*tert*-butyl peroxide, which occurs mainly via the process,



At the temperatures of the reaction vessel, all components are gases, so that the pressure should rise during the course of the reaction, from P_0 initially to $3 P_0$ at completion. From first-order kinetics the pressure should thus change exponentially in time,

$$P(t) = a e^{-kt} + b , \quad (7)$$

where a and b are constants that can be related to the initial and final pressures, P_0 and P .

Experimental

The instructor in charge of the experiment will explain the operation of the vacuum system. The oil bath will have been turned on several hours prior to the scheduled work, to ensure that the system is thermally equilibrated at a temperature near 165°C . Also, a sample of di-*tert*-butyl peroxide will be in place on the vacuum manifold; and a Dewar containing liquid N_2 will be placed on the trap. (This cold trap collects all product and unreacted reactant gases during the course of the experiment and is important for the protection of the vacuum pump. Do not proceed if it is not in place.)

At the outset of the experiment, the reaction vessel and mercury manometer are evacuated by turning on the pump with valves **A** and **B** (Fig. 2, p. 285 in SGN) both open. (Check with the instructor to make sure that this is done properly; mistakes here can result in catastrophic failure of the experiment, with the mercury from the manometer ending up either in the trap or in the reaction vessel!) Prior to the start of measurements, the sample bulb should be cooled with ice water. At this temperature the vapor pressure of di-*tert*-butyl peroxide is about 2 torr. With the reaction vessel evacuated, the valve to the pump (**B**) is closed and valve **C** to the sample bulb is opened carefully. Watch the manometer to observe the effects of the increased pressure. Then shut valve **C** and open **B** again to pump the reactant gas out of the vessel. Repeat this procedure several times, until the pressure rise is only ~ 2 torr. This will ensure that all air has been removed from the vacuum system.

A run is initiated by admitting reactant gas from the sample bulb by opening valve **C**, with **B** closed (and **A** open). To get a P_0 around 30 torr, immerse the sample bulb in hot water from the tap ($\sim 45^\circ\text{C}$) for one or two minutes before opening valve **C**. To obtain ~ 60 torr, it will be necessary to immerse the bulb in water at $70\text{--}80^\circ\text{C}$. Start the timer a few seconds after opening valve **C**, and leave the valve open for 10-20 s to get a full "charge" of reactant gas in the reaction vessel. Then shut **C** and begin recording manometer readings as a function of time. Record at short time intervals (~ 30 s) initially. As the reaction proceeds, the rate of change will decrease, and recordings at longer time intervals (1-4 minutes) will suffice. [Note: It is not necessary to record at specific times, as you will analyze the data using nonlinear least-squares; of course it is necessary to record both time and manometer level carefully.]

Conduct two runs at the initial bath temperature ($\sim 165^\circ\text{C}$), following the reaction for at least 30 minutes in each case, and 45 minutes or longer in one case, if time permits. One of these should be at low P_0 (~ 30 torr) and the other at higher (60 torr or more). Then drop the bath setting by $\sim 15\text{K}$. When the bath has stabilized at the new T , do one more run at $P_0 = 60$ torr. (It will take 30 min. or more for the bath to cool and stabilize at the lower T .)

After each run, open valve **B** and pump the reaction vessel back down to prepare for the next run.

Notes:

(1) Tap both arms of the Hg manometer gently for several seconds prior to each reading. The mercury tends to "stick" to the walls and you will obtain incorrect readings if you do not do this.

(2) Read just the left side of the manometer, and estimate its value to the nearest 0.1 mm. (Use a ruler to line up with the top of the Hg in the tube.) You will need to know the reading of the right arm also, since the pressure is the difference between these levels. However, this should be done separately (see below), to avoid systematic error from slight changes during the 10-20s time needed to measure the two levels.

(3) During the course of the measurements, record the thermometer temperature as a function of time. The bath T will fluctuate over a range of 1.5-2.0 K. You will need to know the time-averaged T to determine the activation energy from your data at the two different bath temperatures.

(4) At convenient times, when the pressure is not changing rapidly, record the levels on both sides of the manometer. These data will be used to produce a plot of P vs. h_l (the reading of the left arm). Since the pressure on the right arm (which is opened to the pump) is essentially zero, the pressure (in torr) in the reaction vessel is approximately $(h_r - h_l)$ (in mm).

(5) Be sure to measure the Hg levels of both arms of the manometer when the vessel is fully evacuated. You should observe a slight difference in the levels. (Why?) It will be necessary to take this into account to obtain accurate relative pressures from your measurements. (See Study Problems. On the other hand, since we need only relative pressures here, it will not be necessary to include any of the temperature corrections described on p. 630 of SGN.)

(6) The period when the bath is cooling is a good time to complete the collection of h_r vs. h_l data for the manometer. Shut valve **A** and open valve **B**; then open the vent valve to admit air to the apparatus to the desired pressure.

(7) After the first ~10 minutes of each run, there is a fair amount of "dead time" in this experiment. You could make use of this time by having one member of your team start entering and analyzing your data on one of the laboratory computers.

(8) Goggles are a must while working around a glass vacuum system. Also, it should be obvious that the bath is HOT. This includes especially the metal overflow rim, which will burn you quickly if you accidentally come into contact with it. BE CAREFUL!

Shutdown and Cleanup

At the end of the day the vacuum system should be left with the sample bulb under vacuum but the rest of the system at atmospheric pressure. With the assistance of the instructor, open valves **A** and **B** and turn off the pump. Then carefully open the vent valve and admit air to the apparatus. When the system is up to atmospheric P , remove the cold trap and place a beaker under the open tube to catch any "meltoff." Discard in the sink any liquid collected here or from the trap, and place the trap in the hood.

Data Analysis

(1) Use your h_r vs. h_l manometer data to obtain a plot of P vs. h_l . Devise a correction of these P s for the effect of thermal expansion of Hg. (See Study Problems below.) Then carry out a least-squares fit of the corrected P s as a function of h_l to obtain a calibration function that can be used for your kinetics data. Use this function to convert your h_l data to P for each kinetics run.

(2) Analyze the data for each run by nonlinear least squares, using the "General" routine in KaleidaGraph in the same manner as used to analyze the acetal hydrolysis data in Problem Set 4. In this you should consider (a) treating a and b in Eq. (7) as independent, and (b) taking into account the stoichiometry implied by Eq. (6).

(3) On occasion we have observed a very slow leak in this apparatus, probably due to melting of the grease on the heated ball joint. You may want to consider in your data analysis the inclusion of a

term for this effect. It should give an increase in P that is linear in t . If a test for inclusion of such a term shows that it is statistically significant, it may be justified in your analysis.

- (4) Do your results for different P_0 at a fixed T indicate any dependence of k on P_0 ?
- (5) Use a weighted fit of your k values to determine the activation energy E_a for the reaction.

Study Problems

1. Be sure that you can use the steady-state approximation to obtain Eq. (5) from Eqs. (1-3).
2. Express a and b in Eq. (7) in terms of P_0 .
3. Why is the level of Hg in the left arm higher than that in the right arm at zero pressure? Devise a correction for this effect on your measured pressures.
4. Assuming there is a leak in the apparatus that yields an increase in P that is proportional to the time t , how should Eq. (7) be modified to include this effect?
5. Suppose you choose to analyze your data in terms of a logarithmic plot as described in SGN. How should your individual data values be weighted?
6. The lab text (SGN) discusses analyzing the data in terms of $t_{1/3}$ and $t_{1/2}$. Express both of these in terms of k .
7. Suppose that measurements at 150.0°C and 165.0°C yield k values of 0.0100 ± 0.0007 and $0.0300 \pm 0.0010 \text{ min}^{-1}$. Calculate E_a and its uncertainty.
8. Now suppose that in addition the two temperatures are both uncertain by 0.7 K. What is the uncertainty in E_a now?