

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Oxygen-18 Tracer Studies of Alkylperoxy Radicals. II. Kinetic Technique with Mass Spectrometry

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The method is described by which kinetic studies have been made involving a record of changes in concentration of nitrogen, carbon dioxide and the three oxygen species $O^{16}O^{16}$, $O^{16}O^{18}$ and $O^{18}O^{18}$, during initiated autoxidations and other reactions involving the $RO_2\cdot$ radical. Experimental results and conclusions are presented in accompanying papers of this series.

Introduction

Accompanying papers of this series² present kinetic studies of reactions in which various alkylperoxy radicals $RO_2\cdot$ are generated, usually during autoxidations initiated by azobis-isobutyronitrile or by di-*tert*-butyl diperoxyoxalate. The former initiator evolves nitrogen as it decomposes, the second evolves carbon dioxide. In the course of their interaction, pairs of $RO_2\cdot$ radicals produce oxygen molecules whose isotopic composition betrays their origin when the original oxygen fed to the reaction is high in $O^{18}O^{18}$ and low in $O^{16}O^{18}$, compared to the statistical distribution. For use in such systems we have developed a mass spectrometric kinetic method which affords an accurate running record of the concentrations of the isotopic species of oxygen and of the gas produced by the initiator.

This method involves the measurement of gases evolved in a constant volume apparatus by comparing mass spectrometer peak heights with those of a standard gas (argon) which is not used or produced in the reaction. From the measured amount of argon, one can determine the amounts of various gases and isotopic species present at the time of sampling, thus determining the rates of reactions involving these gases. It is also possible to measure isotopic effects in some cases.

Experimental

Oxygen-Argon Mixtures.—A large metal tank equipped with pressure gage and vacuum stopcock was evacuated and filled to 50–70 mm. pressure with argon and then to one atmosphere with Airco oxygen. This tank was used to fill the source bulb.

Oxygen Source Bulb.—The bulb A in Fig. 1 was prepared by attaching the 10-ml. bulb of pure O_2^{36} (1 atm.)³ to a 300-ml. round-bottom flask containing a glass-covered 0.25 in. \times 1 in. iron rod and equipped with a 2-mm. vacuum stopcock. The bulb was evacuated, flamed and closed. After breaking the seal to the O_2^{36} with the iron bar the source bulb was attached to the oxygen-argon tank through a T-form stopcock. All intervening tubing was evacuated and the tank then connected to stopcock B. This stopcock was opened for about 1 sec. to fill the bulb but prevent back diffusion of the O_2^{36} . The closed bulb then had the composition 5–10% argon, 3–4% O_2^{36} , 0.4% O_2^{34} , 85–95% O_2^{32} and was ready for use.

General Kinetic Procedure.—The reaction flask shown in Fig. 1 consists of a 100-ml. round-bottom flask C equipped with a 4-mm. angle vacuum stopcock D to which is attached a 3-way 2-mm. stopcock E and two joints F and G. The volume of the reactor containing a small Teflon-covered magnetic stirring bar was determined by weighing while completely filled with water to and including stopcock D but not the sampling lock H. In all these runs the total volume was 121.9 ml.

Solution.—If the initiator did not decompose rapidly at room temperature the solutions of substrate and initiator were made up in volumetric flasks and pipetted into the reactor. Otherwise, the substrate and solvent were pipetted into the reactor and cooled below 0° before adding a weighed amount of initiator. The stopcock D was then inserted and clamped (Apiezon T stopcock grease was used on all stopcocks). The flask was cooled in Dry Ice-acetone and pumped at 1 to 5 μ for 15 min. Stopcock D was closed and the solution warmed until it was liquid, cooled again in Dry Ice-acetone and pumped another 30

min. The evacuation was carried out by attaching the vacuum system at F.

Gas Filling and Measurement.—After evacuating the system, the oxygen source bulb shown in Fig. 1 was attached at G and the intervening tubing evacuated. With the reactor still at about -80° , the system was closed off from the vacuum line and the oxygen source bulb was opened to reactor C. After 10–15 sec. the reactor and source bulb were closed and the latter removed. A 3-mm. bore open U-form manometer was connected through a short length of pressure tubing and a 10/30 joint to G and, by turning stopcock E very slowly, evacuated so that the manometer could be used for the subsequent pressure measurement at 25°.

Kinetic Measurements.—When the kinetic runs were made at 25°, the charged flask was first warmed to 0°, then placed in the 25° thermostat above the submerged magnetic stirrer (Fig. 1) and stirred vigorously for 5 min. to allow attainment of thermal equilibrium.

The stirrer was made by attaching a 6-oz. magnet (Sears Roebuck No. 9G40336) to a 3 ft. flexible drive shaft (Radio Shack Corp.). A pressure measurement was made after 4 min. by carefully opening first E and then D to the manometer. Both stopcocks were then closed and the manometer quickly replaced by a sampling bulb. After quickly pumping out the space between D and the pre-evacuated sampling bulb, a zero time sample was taken after 5 min. total time in the bath.

If higher temperatures were employed the pressure measurement was made as above at 25° and a gas sample taken at this temperature. The reactor was then stirred 5 min. in the thermostat and a zero time gas sample taken. These two samples did not differ appreciably in most cases.

Samples for mass spectrometer analyses were taken by attaching bulbs such as J to joint G as described above and shown in Fig. 1. The bulb, all the tubing, and the sampling lock, which is the 0.66-ml. space between the stopcocks D and E, were evacuated to about 1 μ . The vacuum line was then connected to the bulb through stopcock E, thus closing the sampling lock H. Stopcock D was then opened for about 3 seconds, closed, the time recorded, and the lock connected to the sampling bulb by turning stopcock E. (The only time when D was open was during the 3-sec. sampling when stopcock E was closed to the sampling lock.) The stopcock E and that on the sampling bulb were closed and the bulb removed and cooled in Dry Ice-acetone.

The bulbs were kept in Dry Ice-acetone during analysis on the Consolidated Engineering Corp. 21-103C mass spectrometer. This minimizes errors due to organic impurities. Analyses were generally performed at 70 v. and 20 μ amp. at a pressure of 0.1 mm. in the expansion reservoir. Masses 28 to 44 were scanned at rate 3. Checks for organic impurities were made by rapidly scanning to mass 80. All samples in one run were analyzed at one time and background scans taken (usually negligible).

The use of ionization type vacuum pumps on the spectrometer rather than diffusion pumps is not advisable because the former are very easily saturated with argon regardless of their rated capacity!

Treatment of Data

The rates and other data are given for the amounts of material in each run and must be divided by the volume of solution (V_{soln}) to obtain initiation or oxidation rate constants in moles/l./sec.

Definitions of R_i , b , C_w , G_w , y , z , w , e , β , f_y , M_y and α are given in part I as are the equations used to arrive at values of these expressions.

The mass spectra are converted to rate data as follows:

I. The observed peak heights are transformed into numbers (N_i) proportional to pressure or number of molecules by eq. 1.

$$N_i = H_i S_i \quad (1)$$

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(2) See also (a) P. D. Bartlett and T. G. Traylor, *Tetrahedron Letters*, **24**, 30 (1960); (b) *J. Am. Chem. Soc.*, **85**, 2407 (1963).

(3) Obtained from the Isotope Department, Weizmann Institute of Science, Rehovoth, Israel.

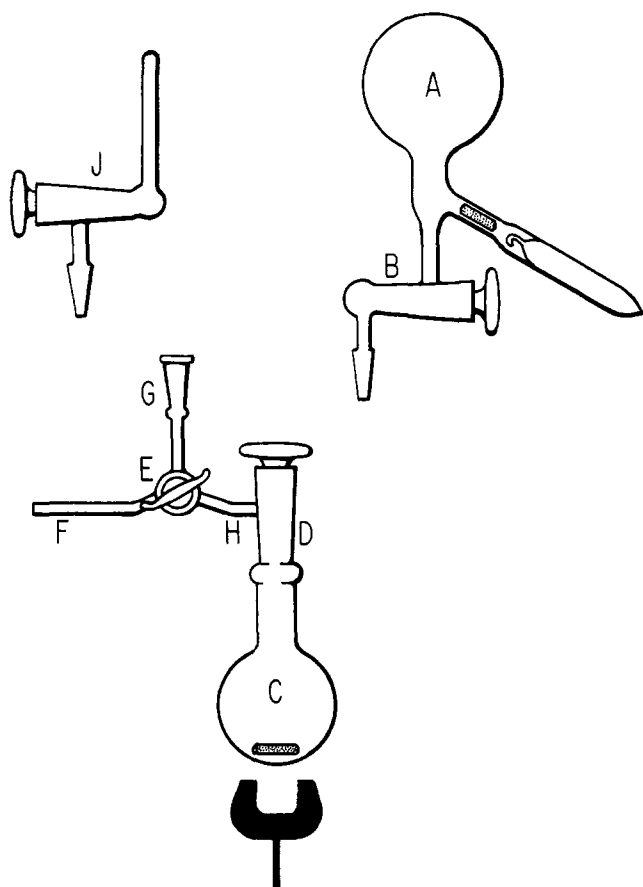


Fig. 1.—Apparatus used for kinetic studies of autoxidation by mass spectrometry.

where H_i is the observed peak height and S_i the "sensitivity," *i.e.*, ratio of the amounts of molecule *i* and of argon required to produce the same peak height. The sensitivities of gases recorded in the API tabulation⁴ are converted to S_i by the equation

$$S_i = (S_{\text{butane}}^{\text{API}}/S_i^{\text{API}}) \times (S_{\text{argon}}^{\text{API}}/S_{\text{butane}}^{\text{API}}) \quad (2)$$

where the S -values in one set of parentheses are determined in one laboratory⁴ (American Petroleum Institute Spectra 1592, 1594–6). Values thus obtained are $S_{\text{Ar}} = 1$, $S_{\text{O}_2} = 1.72$, $S_{\text{N}_2} = 1.426$, $S_{\text{CO}_2} = 1.219$. It is assumed that sensitivities of all isotopic combinations of O_2 are equal.

II. Internal Argon Standard.—The total number of moles of gas in the vapor phase in the beginning of a run is given by

$$N_T = P(V_{\text{reactor}} - V_{\text{soln.}})/RT \quad (3)$$

in which the pressure P has been corrected for vapor pressure of solvent (72 mm. in the case of benzene at 25°). The amount of argon in this gas in moles is

$$N_{\text{Ar}} = \left(\frac{H_{\text{Ar}}}{H_{\text{Ar}} + H_{\text{N}_2}S_{\text{N}_2} + \Sigma H_{\text{O}_2}S_{\text{O}_2} + H_{\text{CO}_2}S_{\text{CO}_2}} \right) N_T \quad (4)$$

Solubility of argon need not enter into the calculations as a result of the small (0.66 ml. from 82 ml.) samples of gas taken and consequently the constancy of N_{Ar} .

III.—The number of moles of any gas (N_i) at any subsequent time in the run can be calculated by using the total number of moles of argon and the equation

$$N_i = H_i S_i N_{\text{Ar}} / H_{\text{Ar}} \quad (5)$$

for all gases except O_2^{36} . In the latter case, $0.00334H_{\text{Ar}}^{40}$ must be subtracted from $H_{\text{O}_2^{36}}$ to correct for Ar^{36} . The

(4) American Petroleum Institute, Research Project 44, Index of Mass Spectral Data, Vol. 6, Chem. & Pet. Res. Lab., Carnegie Institute of Technology, Pittsburgh 13, Penna.

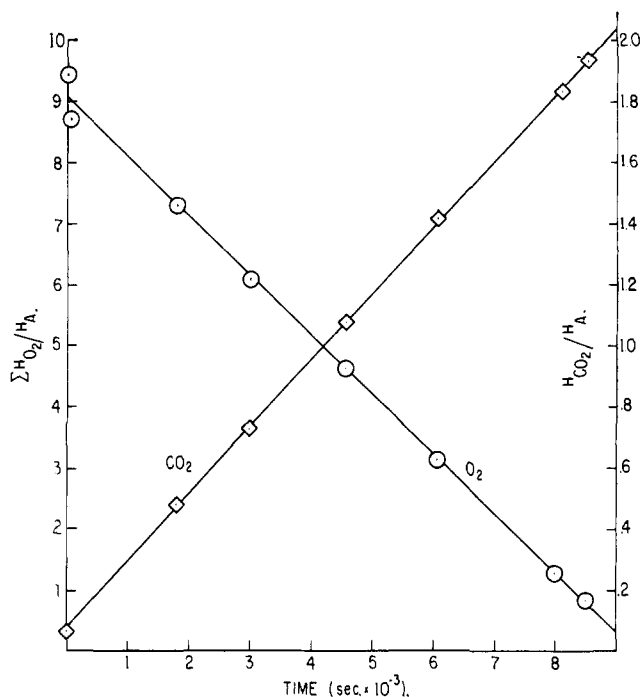


Fig. 2.—Plots of the peak height ratios $(H_{32} + H_{34} + H_{36})/H_{40}$ and H_{44}/H_{40} vs. time during the autoxidation of tetralin shown in Table I.

abundance, 0.00334, of Ar^{36} was determined in this work and agrees with other recent observations.

IV. Effect of Gas Solubilities.—In the high temperature runs the solubilities of nitrogen and oxygen are low enough to be neglected. However, at 19° the solubility of oxygen, α_{O_2} , equals 0.163 ml. of gas/ml. of benzene at 1 atm. oxygen pressure. The solubility of carbon dioxide at 25° and 1 atm. is 2.222 ml. of gas/ml. of benzene. Then the actual volume of gas in the reactor is

$$N_i = N_i^{\text{vapor}} \left(\frac{V_{\text{vapor}} + \alpha_i V_{\text{soln.}}}{V_{\text{vapor}}} \right) \quad (6)$$

This is a 7% correction on oxygen, hence on $d\text{O}_2/dt$, and a 109% correction on carbon dioxide or on $d(\text{CO}_2)/dt$. Thus, the amount of any gas N_i is given by

$$N_i = \frac{H_i S_i N_{\text{Ar}}}{H_{\text{Ar}}} \left[\frac{V_{\text{vapor}} + \alpha_i V_{\text{soln.}}}{V_{\text{vapor}}} \right] \quad (7)$$

It follows from constancy of all these quantities except H_i and H_{Ar} that

$$\frac{dN_i}{dt} = S_i N_{\text{Ar}} \left[\frac{V_{\text{vapor}} + \alpha_i V_{\text{soln.}}}{V_{\text{vapor}}} \right] \frac{d(H_i/H_{\text{Ar}})}{dt} \quad (8)$$

Therefore, H_i/H_{Ar} can be plotted directly against time and

$$\frac{dN_i}{dt} = \text{slope} \times S_i N_{\text{Ar}} \left[\frac{V_{\text{vapor}} + \alpha_i V_{\text{soln.}}}{V_{\text{vapor}}} \right] \quad (9)$$

Similarly the equations used to get G_w and C_w (part I) can be expressed as

$$\log(f_y - M_y) = \frac{G_w}{b} \log w = \frac{G_w}{b} \log \left(\frac{\Sigma H_{\text{O}_2}}{H_{\text{Ar}}} \right) + \frac{G_w}{b} \log S_i N_{\text{Ar}} \left[\frac{V_{\text{vapor}} + \alpha_i V_{\text{soln.}}}{V_{\text{vapor}}} \right] \quad (10)$$

Thus

$$\frac{d \log(f_y - M_y)}{d \log(\Sigma H_{\text{O}_2}/H_{\text{Ar}})} = \frac{G_w}{b} \quad (11)$$

and for C_w

$$\log z = \frac{C_w}{b} \log w, \text{ or} \\ \frac{d \log(H_{\text{O}_2^{36}}/H_{\text{Ar}})}{d \log(\Sigma H_{\text{O}_2^{32}}/H_{\text{Ar}})} = \frac{C_w}{b} \quad (12)$$

TABLE I
 AUTOXIDATION OF TETRALIN (TRITIUM LABELED)^a

Run 125: concn. of di-*tert*-butyl diperoxyoxalate, 0.0952 *M*; concn. of tetralin, 2.203 *M* (15.00 ml. in 30.00 ml. of benzene); vol. reactor, 121.9 ml.; solution, 45.0 ml.; temp., 24.90°; obsd. press. at 0 time 834.4 mm.; pressure – vapor pressure, ^b 762.4; amount of gas (N_T) = 3.150×10^{-3} mole; amount of argon (N_{Ar}) = 1.770×10^{-4} mole

Time, sec.	Mass spectrometer peak heights								H_{44}/H_{40}	H_{O_2}/H_{40}
	28	32	34	36	40	44	78			
0	363	8780	37.6	144.6, 141.4 ^c	951	61.7	8	0.0649	9.43	
600	275	8810	39.3	144.6, 141.2	1032	233.4	15.6	.2261	8.72 ^c	
1800	398	6410	31.6	105.0, 102	897	434	71	.484	7.30	
3000	385	7190	40.3	117.3, 113.3	1209	876	60	.725	6.080	
4553	441	6560	43.0	104.7, 99.9	1449	1560	20	1.077	4.630	
6064	654	5700	44.2	93.0, 86.8	1866	2640	206	1.414	3.145	
8100	1104	3800	38.9	62.1, 52.1	3000	5500	138	1.832	1.298	
8520	1113	2460	27.9	43.5, 33.8	2900	5610	165	1.935	.869	

^a Experiments to be described in a subsequent paper of this series. ^b Taken as the vapor pressure of benzene at 25.9° times its mole fraction. ^c This column is corrected for Ar³⁶.

A typical set of kinetic data, on the autoxidation of tetralin, is shown in Table I and plotted in Fig. 2 as suggested by eq. 8 and 9. Plots of eq. 11 and 12 are shown in ref. 2a.

In some cases the total amount of calculating is minimized by calculating the final slopes and other quantities without the use of sensitivity and solubility corrections, then correcting them by the formulas below. Log-log plots require no corrections because all multiplicative constants drop out.

Moles of argon (N_{Ar}) without corrections

$$N'_{Ar} = \left(\frac{H_{Ar}}{H_{Ar} + \Sigma H_{O_2} + H_{N_2}} \right) (\text{total moles of gas}) \quad (13)$$

$$\text{Moles of } i, N_i' = (H_i/H_{Ar})N_{Ar}' \quad (14)$$

$$\text{Corrected } N_{Ar} = \left[\frac{H_{Ar}}{H_{Ar} + \Sigma H_{O_2}S_{O_2} + H_{N_2}S_{N_2}} \right] \times (\text{total moles of gas})$$

$$N_i = (H_i S_i / H_{Ar}) N_{Ar}$$

Corrected $dN_i/dt = b$ or R_i is obtained from 15

$$\frac{dN_i}{dt} = \frac{dN_i'}{dt} \frac{S_i N_{Ar}}{N'_{Ar}} \left[\frac{V_{gas} + \alpha_i V_{soln.}}{V_{gas}} \right] \quad (15)$$

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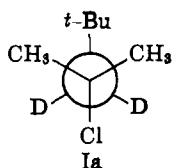
The Effects of Deuterium Substitution on the Rates of Organic Reactions. VIII. The Solvolysis of *t*-Butyl-*d*₁, -*d*₂, -*d*₃, -*d*₆ and -*d*₉ Chlorides¹

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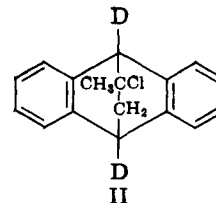
The solvolysis rate retardations caused by substitution of 1, 2 and 3 deuterium atoms in one methyl group of *t*-butyl chloride are not quite cumulative; the isotope effect per deuterium increases slightly as the number of deuterium atoms increases. The previously proposed conformational dependence of the β -deuterium isotope effect quantitatively predicts just such a trend. The retardations caused by complete deuteration of 1, 2 and 3 methyl groups are more nearly cumulative.

The unusually small isotope effect observed in the solvolysis of 2,4,4-trimethyl-2-chloropentane (I) was originally attributed to a conformational dependence



of the isotope effect together with a sterically controlled transition state conformation, related to Ia, in which the deuterium atoms are situated *gauche* to the leaving group.⁴ It was suggested that the larger isotope effects caused by β -deuterium substitution in related systems⁵ were characteristic of a deuterium situated *trans* to the solvolytic leaving group in the transition state. This

conformational dependence of the β -deuterium secondary isotope effect in carbonium ion reactions was further confirmed by the observation of an insignificantly small isotope effect in the solvolysis of the bridgehead deuterated bicyclooctane derivative II,⁶ where the C–D bond is oriented perpendicular to the developing vacant orbital at the adjacent solvolysis center.



This strong conformational dependence of the isotope effect leads to the prediction that the rate retardations caused by successive replacements of the hydrogens of a methyl group adjacent to a solvolyzing center will not be precisely cumulative. For example, if the solvolysis rate with a deuterium *trans* to the leaving group is relatively slower, then the transition state with an

(1) (a) Taken in part from the thesis submitted by B. L. Murr to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree. (b) Supported in part by Grants G 5062 and G 16831 from the National Science Foundation, Washington, D. C.

(2) Alfred P. Sloan Research Fellow, 1957–1961.

(3) Dow Fellow, 1958–1959.

(4) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **78**, 2653 (1956); **83**, 240 (1961).

(5) For a review see V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959).

(6) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **82**, 2655 (1960).