globulins are precipitated directly from the blood serum for such later purification or separation into sub-fractions as may be desired. The important differences in conditions of separation are the immediate adjustment of the serum to *p*H 7.7 and the use of a considerably greater dilution of the serum as fractionation begins. The new conditions serve several very useful purposes. The sharpness of cleavage between β- and γ-globulins is markedly increased. The removal of the gamma globulin is simple and direct. Tendencies toward denaturation are reduced. Actual yields of γ-globulin are now in excess of 85%.

As a result of the work described in this report and in the companion article[5] it may be predicted that practical and economical ethanol fractionation methods for the removal of antibody from hyperimmune sera will be soon in operation.

Acknowledgments.—The authors wish to thank Dr. J. W. Williams and Dr. Gerson Kegeles for their many helpful suggestions during the course of this work. It is a pleasure as well to thank Mr. E. M. Hanson and Mrs. Alice McGilvery for their technical assistance.

Summary

A procedure for the fractionation of bovine serum, which recovers approximately 85% of the gamma globulins in normal serum, has been outlined. These γ-globulins can be further separated into fractions with varying electrophoretic mobilities. The γ_1 and γ_2 sub-fractions are essentially monodisperse as regards molecular kinetic behavior, but there are marked indications of electrophoretic inhomogeneity.

Madison, Wisconsin Received November 12, 1946

[Contribution from the Emeryville Laboratories of Shell Development Company]

Decompositions of Di-*t*-Alkyl Peroxides. I. Kinetics

By John H. Raley, Frederick F. Rust and William E. Vaughan

The di-*t*-alkyl peroxides have been reported, almost simultaneously by Milas and Surgenor[1] and George and Walsh,[2] to undergo clean-cut decompositions in the vapor phase to ketone and hydrocarbon which, for the di-*t*-butyl compound, can be represented by

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{k_1} 2(CH_3)_3CO \qquad (1)$$

$$(CH_3)_3CO \longrightarrow (CH_3)_2CO + CH_3 \qquad (2)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (3)$$

During the past few years we have investigated the preparation and properties of these compounds in some detail,[3] and in this paper we present the results of a kinetic study of the pyrolyses of the di-*t*-butyl and di-*t*-amyl derivatives. The reactions of the free radicals produced in these decompositions with various compounds are reported in a following paper.[4]

In the studies of Milas and co-workers the vaporous peroxides were decomposed in the presence of a large amount of glass surface. Under such conditions, reactions of the alkyl radicals are essentially limited to combinations with one another and, in the case of di-*t*-butyl peroxide, ethane and acetone are the sole products. However, if the decompositions are carried out in a large diameter, unpacked vessel, interaction of the alkyl radicals and the ketone becomes important. Thus, methyl, ethyl and higher ketones and methane can also be formed

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2 \qquad (4)$$

$$CH_3 + CH_3COCH_2 \longrightarrow CH_3COCH_2CH_3 \qquad (5)$$

In the kinetic experiments to be described the fraction of released methyl radicals which reacts substitutively (5–10%) is dependent on the acetone concentration as well as the surface. Somewhat higher values (20%) are observed if the decomposition proceeds to completion or if acetone is added.

The reality of the *t*-butoxy radical is demonstrated by the formation of *t*-butyl alcohol when the decomposition is carried out in isopropylbenzene solution. The solvent is converted to 2,3-dimethyl-2,3-diphenylbutane.[5]

Experimental

1. **Materials.**—The di-*t*-butyl peroxide[3] ($n^{20}D$ 1.3890), redistilled under high vacuum, assayed at least 98% (reduction by hydriodic acid[3]) and gave negative tests for *t*-butyl alcohol and hydroperoxide. Steam-distilled di-*t*-amyl peroxide[3] was treated with bromine and vacuum distilled to remove olefin. The resultant material ($n^{20}D$ 1.4086) was also redistilled on the high vacuum line. The nitrogen, oxygen and propylene were taken directly from commercial cylinders and the carbon dioxide sublimed from Dry Ice. Nitric oxide was prepared according to the method of Noyes.[6]

2. **Rate Measurements.**—The apparatus used for all rate measurements is shown in Figs. 1 and 2. The temperature of the oil-bath was measured by a thermometer which was calibrated in position by comparison with a platinum resistance thermometer. The accuracy of the temperature readings is estimated as 0.04°. The quartz spiral gage[7] and leads from the reaction vessel were heated electrically to prevent condensation. The degassed liquid

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(1) Milas and Surgenor, This Journal, **68**, 205, 643 (1946).

(2) George and Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946); based on data supplied by Asiatic Petroleum Company.

(3) Vaughan and Rust, U. S. 2,403,771, July 9, 1946; *cf.* also earlier patents.

(4) Rust, Seubold and Vaughan, This Journal, **70**, 95 (1948).

(5) Kharasch, McBay and Urry (*J. Org. Chem.*, **10**, 401 (1945)) have previously demonstrated this free radical coupling reaction using acetyl peroxide.

(6) Noyes, This Journal, **47**, 2170 (1925).

(7) Vaughan, *Rev. Sci. Instruments*, **18**, 192 (1947).

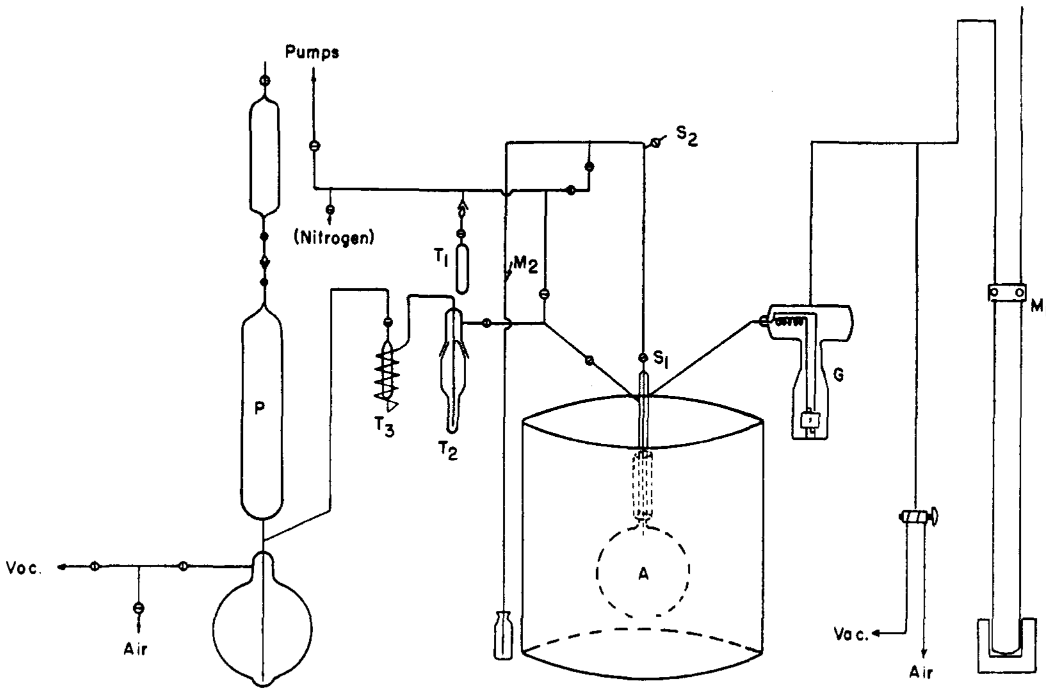

Fig. 1.—Apparatus for peroxide decompositions. Legend (see text): A, reaction vessel; G, quartz spiral pressure gage; M_1, gage manometer (equipped with vernier); M_2, input manometer; P, Toepler pump; S_1, input stopcock for peroxide and nitrogen; S_2, stopcock for admitting di-*t*-amyl peroxide; T_1, storage trap for di-*t*-butyl peroxide; T_2, T_3 product condensing traps.

peroxide was admitted to the capillary above S_1 (either by distillation or through S_2) and nitrogen added, the pressure of which was registered by M_2. The nitrogen served to force the peroxide into the reaction vessel when S_1 was opened. The pressure increase during the decomposition was followed by using the gage as a null point instrument in conjunction with M_1. The reaction was halted by freezing the vapors into T_2 and pumping the residual gases into a sample bulb for analysis with a mass spectrometer. Ketone was determined by adding an excess of hydroxylamine hydrochloride solution to the contents of T_2 and titrating the liberated acid.

3. **Flow Experiments.**—The technique for these experiments is described in the following paper.[4] In the subsequent paragraphs "cc./min." refers to cc. of vapor (N.T.P.) per minute.

Ketone Products of Di-*t*-butyl Peroxide.—Di-*t*-butyl peroxide (165 cc./min.) and nitrogen (25 cc./min.) were passed through the unpacked Pyrex tube at 225°. The liquid product was collected in a Dry Ice-cooled trap and fractionated. The distillation cuts obtained were (1) 56° (acetone), (2) 79° (methyl ethyl ketone), (3) higher boiling carbonylic compounds.

TABLE I

KETONE PRODUCTS FORM DI-*t*-BUTYL PEROXIDE

Ketone	Cc./min. N. T. P.	n^{20}_D Found	n^{20}_D Lit.	Deriv.	M. p., °C. Deriv.	M. p., °C. Mixed
Acetone	274	1.3589	1.3589	....	..	...
Methyl ethyl	21	1.3790	1.3788	*p*-Nitrophenylhydrazone	128[a]	128

[a] Literature value (Huntress and Mulliken, "Identification of Pure Organic Compounds") was 128–129°.

Di-*t*-butyl Peroxide and Nitric Oxide.—A mixture of the peroxide (67 cc./min.), nitric oxide (175 cc./min.), and nitrogen (50 cc./min.) was passed through the tube at 225° for one hundred and forty minutes, the liquid product being collected in ether cooled with Dry Ice. Distillation (after addition of Cellosolve to furnish a high boiling residue) gave a fraction of b. p. 83–85° which was collected in ether. Treatment of one third of the distillate with hydrogen chloride gas according to the method of Dunston and Bossi[8] yielded one gram of the hydrochloride [m. p. 136–137°, lit.[8] 136°; % Cl (Volhard) 20.8, calcd. for $(CH_2NOH)_3 \cdot HCl$, 20.66]. A second portion of the distillate was converted to the benzoate derivative [m. p. 168–168.5° (decomp.), lit.[8] 168.5° (decomp.); % N (Dumas) 9.29, 9.30; % C 64.40, 64.67; % H 4.80, 5.02; theory 9.39, 64.42, 4.73, respectively]. Characteristic behaviors of formaldoxime—condensation to a white, insoluble solid upon standing, and violet coloration with cupric sulfate–potassium hydroxide solution—were also observed with the crude product.

Decomposition of Di-*t*-amyl Peroxide.—Di-*t*-amyl peroxide and nitrogen (*ca.* 100 cc./min. of each) were passed through the tube at 235°. The liquid product contained 87–88% acetone, 4–5% methyl ethyl ketone (aqueous azeotrope, b. p. 73°), and higher boiling ketones. The gaseous products, separated by low temperature distillation, were as in Table II.

TABLE II

GASEOUS DECOMPOSITION PRODUCTS OF DI-*t*-AMYL PEROXIDE

Gas	Cc./min.
n-C_4H_{10}	66.6
C_2H_6	19.5
C_3H_8	5.9
C_2H_4	5.2
CH_4	4.3
C_4H_8	1.4

4. **Di-*t*-butyl Peroxide and Isopropylbenzene (liquid phase).**—A solution of di-*t*-butyl peroxide (0.27 mole) and

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(8) W. R. Dunston and A. L. Bossi, *J. Chem. Soc.*, **73**, 353 (1898).

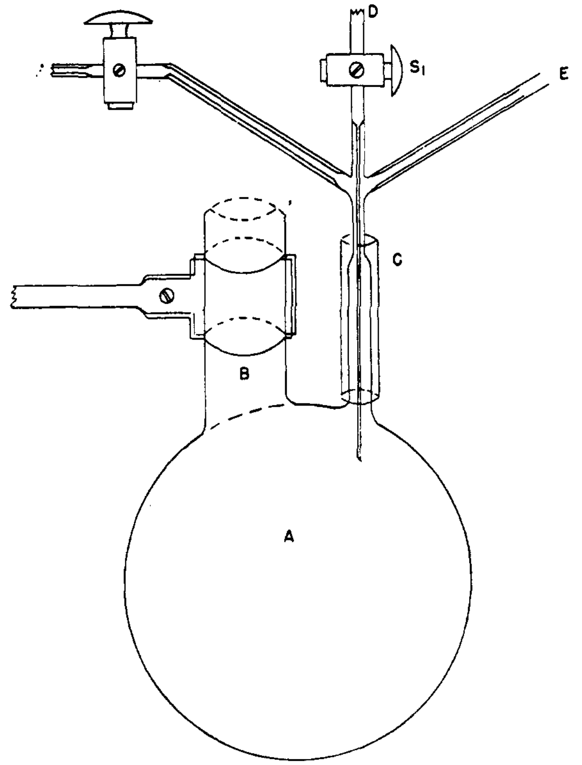

Fig. 2.—Reaction vessel for peroxide decompositions. Legend (see text): A, 500 cc. bulb; B, butt-sealed, heavy wall tube for clamping; C, copper sheath, partially immersed in oil-bath, for heating inlet line; D, inlet for liquid peroxide; E, lead to gage; F, lead to Toepler pump.

isopropylbenzene (1.44 moles) was heated in an oil-bath at 130° for thirty hours. The following products were obtained: *t*-butyl alcohol (0.24 mole), methane (0.06 mole), 2,3-dimethyl-2,3-diphenylbutane (0.07 mole) (C, 90.65; H, 9.3; mol. wt., 242; theory C, 90.75; H, 9.25; mol. wt., 238).

Decomposition of Di-*t*-butyl Peroxide

Kinetic Order.—If the pyrolysis follows the over-all stoichiometries

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_2CO + C_2H_6 \quad (6)$$

or

$$\longrightarrow CH_3COCH_3 + CH_3COC_2H_5 + CH_4$$

the peroxide pressure, $(A - x)$, is related to P, the total pressure, by

$$(A - x) = A - (P - P_0)/2 \quad (7)^9$$

where P_0 is the initial total pressure, obtained by a short extrapolation. The initial peroxide pressure, A, is obtained from

$$A = P_0 - P_{N_2} \quad (8)$$

where P_{N_2} is the nitrogen pressure, obtained by analysis of the product gases. log $(A - x)$ as a function of time is illustrated in Fig. 3 from which it is clear that, at least in the first 30–40%, the decomposition follows a first order expression. Data for typical runs are given in Table III. As the reaction approaches completion, a slight curvature is noticeable (Fig. 4) and upon complete decomposition, the total pressure of the products is found to be slightly less than three times the initial peroxide pressure. If the experimental ratio (2.88) is used to calculate values for $(A - x)$, adherence to the first order expression is indicated for virtually the entire reaction.[10] We have preferred, however, to use equation (7) since during the early stages of the reaction, where all rate measurements were made, the discrepancy between assumed and observed stoichiometries is within experimental error (Table IV). The initial rate constant calculated in this manner is essentially independent of pressure over the range 50–380 mm. (Table V).

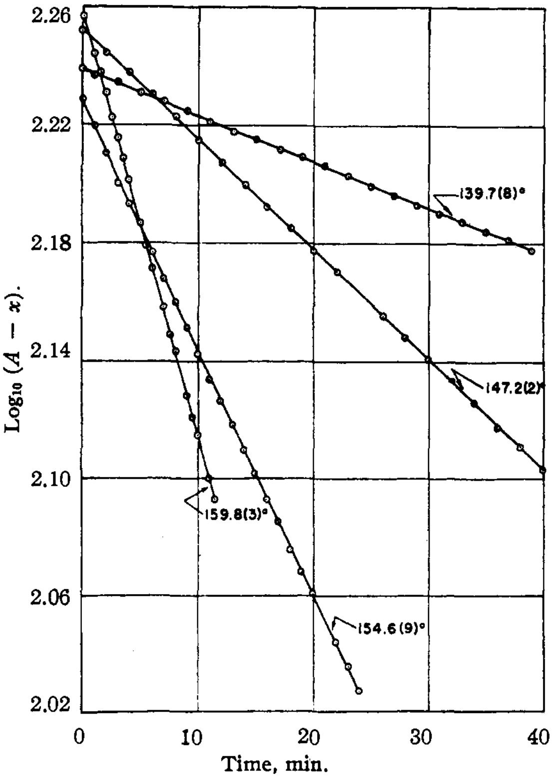

Fig. 3.—Decomposition of di-*t*-butyl peroxide, 140–160°.

Homogeneity.—Although the fate of methyl radicals produced during the reaction is modified by the surface of the confining vessel, the decomposition itself is apparently homogeneous. As shown in Table VI, the rate constant is not affected by the presence of Pyrex rod packing (2 mm. diameter) sufficient to produce an elevenfold change in surface–volume ratio of the vessel.

Tests for a Chain Reaction.—A number of well recognized chain inhibiting reagents have

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[9] Since the higher ketones are also probably formed by substitutive methylation, their production should not alter the pressure change during decomposition.

[10] It should be mentioned that the apparent decrease in rate is not traceable to interaction with reaction products since addition of a spent mixture does not influence the decomposition of a fresh peroxide charge.

TABLE III

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE—TYPICAL RUNS

Temperature, 154.6(9)°				Temperature, 147.2(2)°			
Time, min.	Total press., mm.	$(A - x)$, mm.	$k \times 10^4$ [a] (sec.$^{-1}$)	Time, min.	Total press., mm.	$(A - x)$, mm.	$k \times 10^4$ [b] sec.$^{-1}$
0	173.5	169.3		0	182.6	179.5	
2	187.3	162.4		2	190.5	175.5	
3	193.4	159.3	3.38	6	201.7	169.9	
5	205.3	153.4	3.17	10	213.6	164.0	
6	211.3	150.4	3.20	14	224.3	158.6	
8	222.9	144.0	3.28	18	235.0	153.3	
9	228.6	141.7	3.31	20	240.4	150.6	1.46
11	239.8	136.1	3.37	22	245.4	148.1	1.41
12	244.4	133.8	3.19	26	255.6	143.0	1.44
14	254.5	128.8	3.06	30	265.2	138.2	1.43
15	259.2	126.4	3.16	34	274.4	133.6	1.43
17	268.7	121.7	3.15	38	283.3	129.1	1.43
18	273.9	119.1	3.31	40	288.0	126.8	1.43
20	282.0	115.0	3.15	42	292.0	124.8	1.43
21	286.8	112.6	3.12	46	300.2	120.7	1.41
			Av. 3.22 ± 0.08				Av. 1.43 ± 0.01

[a] Calculated for successive three-minute intervals. [b] Calculated for successive twenty minutes intervals.

TABLE IV

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE. RATE CONSTANTS AND YIELDS

			Product yields,[a] %			
Temp., °C.	Peroxide press., (mm.)	$k \times 10^4$, sec.$^{-1}$	Ketone	Ethane	Methane	Total paraffin
139.7(8)	163	0.589 ± 0.007	99			
	163	.620 ± .008	97	88	11	99
	173	.596 ± .007				
		Mean 0.60				
147.2(2)	180	1.43 ± 0.01				
154.6(9)	168	3.22 ± .18	97			
	169	3.22 ± .08	97			
		Mean 3.22				
159.8(3)	181	5.53 ± 0.16	105	103	6	109

[a] The yields are based on the amount of peroxide decomposed, as calculated from the total pressure increase by equation (7).

TABLE V

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE. EFFECT OF INITIAL PRESSURE ON INITIAL RATE CONSTANT

Temperature, 147.2(2)°

Initial peroxide press., mm.	$k \times 10^4$, sec.$^{-1}$
51.6	1.38 ± 0.0
66.3	1.33 ± .02
167	1.40 ± .02
179 + 190 mm. N_2	1.49 ± .02
180	1.43 ± .01
386	1.48 ± .01
	Mean 1.41

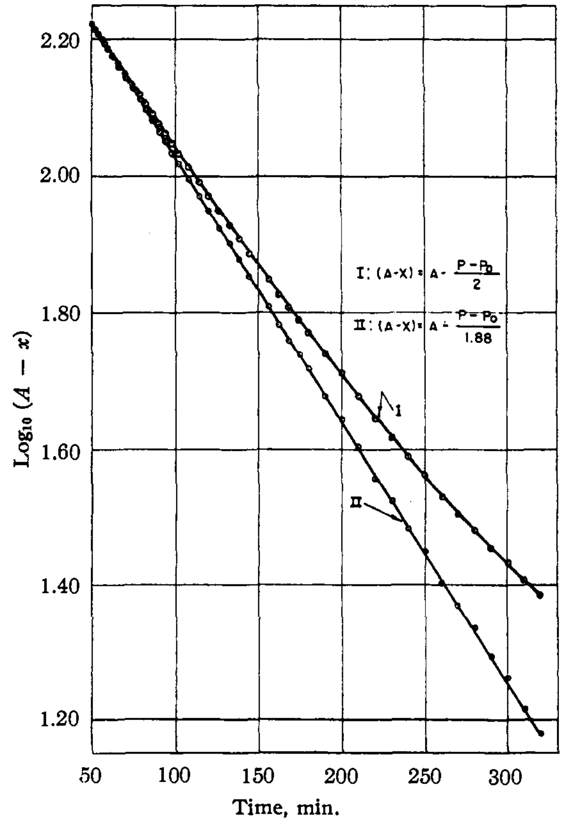

Fig. 4.—Decomposition of di-*t*-butyl peroxide, *ca.* 90% completion, temperature 147.2(2)°.

been added in attempts to detect chain processes in the di-*t*-butyl peroxide decomposition. In the first of these tests the peroxide and additive were passed through a heated tube[4] and the unreacted peroxide collected and measured. From the results, summarized in Table VII, it is clear that neither nitric oxide nor propylene appreciably affects the decomposition velocity. That methyl radicals react readily under the experimental conditions with both additives is shown by the isolation of products derivable only from these sources. The formation of formaldoxime has been postulated previously[11] but apparently this is the first report of its isolation from a methyl radical–

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[11] For example, see Taylor and Bender, *J. Chem. Phys.*, **9**, 761 (1941); Forsyth, *Trans. Faraday Soc.*, **37**, 312 (1941).

TABLE VI

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE. EFFECT OF REACTOR SURFACE: VOLUME RATIO

Temperature, 147.2(2)°; peroxide pressure, 170–215 mm.

Vessel	*S/V*, cm.$^{-1}$	$k \times 10^4$, sec.$^{-1}$	Product yields, % Ketone	Ethane	Methane	Total paraffin
Unpacked	0.61	1.41 ± 0.01[a]	99[b]	..	..	99+[b]
Packed	2.07	1.42 ± .01	103	94	6	100
Packed	6.96	1.49 ± .02	102	90	13	103

[a] Average of four runs. [b] Estimated from the data of Table IV.

nitric oxide combination. Formaldoxime is probably further attacked by methyl radicals since when an excess of peroxide is used, a complex product is obtained. The reaction products with propylene are discussed in detail in the succeeding paper.[4]

TABLE VII

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE. EFFECT OF CHAIN INHIBITORS

Temperature, 209–210°; flow rates, 100 cc./min. (N.T.P.), peroxide, 200 cc./min. (N.T.P.), additive; residence time, 2.5–2.6 minutes.

Additive	Peroxide dec., %	Product
Nitrogen	95	....
Nitric oxide	94	Formaldoxime
Propylene	95	C_4H_8, C_4H_{10}, C_5H_{12}, etc.

In a closed system oxygen causes a slight acceleration in the rate of pressure increase, but apparently the velocity of decomposition is not affected since the production of ketone is virtually unchanged (Table VIII).

TABLE VIII

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE. EFFECT OF OXYGEN

Temperature, 147.2(2)°; reaction time, 47 min.

Peroxide, mm.	Oxygen, mm.	Oxygen consumed, mm.	Ketone produced, mm. Found	Calcd.[a]
170.1	41.4	37.2	113	112

[a] Assuming the rate constant (1.41×10^{-4} sec.$^{-1}$) at this temperature for an oxygen-free system.

It should be noted that the major gaseous oxidation product of methyl radicals at this temperature is carbon monoxide, in contrast to the formaldehyde and methanol reported for the reaction at 0°.[12] A test for aldehyde with Schiff reagent on the liquid product was negative.

Mechanism and Activation Energy.—A summary of all data presented above leads to the conclusion that the decomposition of di-*t*-butyl peroxide is a homogeneous, first order, nonchain process. The suggested mechanism (equations (1), (2) and (3)) yields the rate equation

$$-\frac{d[(CH_3)_3COOC(CH_3)_3]}{dt} = \frac{d[C_2H_6]}{dt} = \frac{{}^1/_2 d[(CH_3)_2CO]}{dt} = k_1[(CH_3)_3COOC(CH_3)_3]$$

from which it is seen that k_1 and the experimentally determined rate constant should be identical. In support of this, the calculated energy of activation, E_1, for (1) is in close agreement with the experimental value. Since (1) is postulated as a unimolecular dissociation reaction, E_1 may be taken equal to the energy of dissociation.[13] The latter value has been calculated from the heat of combustion of the peroxide and other thermochemical data.[14]

The combustion heats for the peroxide and *t*-butyl alcohol lead to the equation

$$\underset{1282.6}{C_4H_9O_2C_4H_9(g)} + \underset{68.4}{H_2(g)} \longrightarrow \underset{2(640.7)}{2C_4H_9OH(g)}; \quad \Delta H_{298} = -69.6; \ \Delta E = \Delta H.$$

$$D_{O-O} \text{ (in peroxide)} = 2D_{O-H} - D_{H-H} - 69.6$$

The value of D_{O-H} in *t*-butyl alcohol is computed from

$$\underset{686.3}{C_4H_{10}(g)} + {}^1/_2O_2(g) \longrightarrow \underset{640.7}{C_4H_9OH(g)}; \quad \Delta H_{298} = -45{,}6; \ \Delta E = -45.3.$$

$$D_{O-H} = D_{C-H} + {}^1/_2D_{O-O} \text{ (in oxygen)} - D_{C-O} + 45.3 = 105.2 \text{ kcal./mole}$$

Hence $E_1 = D_{O-O}$ (in peroxide) = 39 kcal./mole.[15]

The data of Table IV, plotted in the conventional manner in Fig. 5, yield an experimental activation energy of 39.1 ± 0.5 kcal./mole.

Calculation of the pre-exponential factor gives, for the rate constant $k = 3.2 \times 10^{16}(e^{-39,100/RT})$.

The entropy of activation is the abnormally high[16] value + 14.5 E.U. at 160°.

Decomposition of Di-*t*-amyl Peroxide

Milas and Surgenor[1] have shown that the decomposition of di-*t*-amyl peroxide over glass wool yields, mainly, *n*-butane and acetone with small amounts of ethane, propane and methyl ethyl ke-

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(12) Bates and Spence, THIS JOURNAL, 53, 1689 (1931); also *Trans. Faraday Soc.*, 27, 468 (1931).

(13) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

(14) (a) Data from this Laboratory: Di-*t*-butyl peroxide: heat of combustion = 1273 kcal./mole for (1) 25°; heat of vaporization = 9.6 kcal./mole. *t*-Butyl alcohol: heat of combustion = 629.4 kcal./mole for (*s*) 25°; heat of fusion = 1.6 kcal./mole; heat of vaporization = 9.7 kcal./mole; (b) Rossini, *J. Research Natl. Bur. Standards*, 15, 357 (1935): Isobutane; heat of combustion = 686.3 kcal./mole for (g) 25°; (c) Baughan and Polanyi, *Trans. Faraday Soc.*, 39, 19 (1943): D_{C-O} in *t*-butyl alcohol = 85.0 kcal./mole. D_{C-H} in isobutane (for the *t*-hydrogen) = 86.0 kcal./mole; (d) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 134–135: D_{H-H} in hydrogen = 4.454 e. v./mole. D_{O-O} in oxygen (normal atoms) = 5.11 e. v./mole.

(15) Pauling ("The Nature of the Chemical Bond," Cornell University Press (1939)) estimated D_{O-O} in hydrogen peroxide as 34.9 kcal./mole while Skinner (*Trans. Faraday Soc.*, 41, 645–662 (1945)) gives the much higher value 52 kcal./mole. However, recently Glockler and Matlack, (*J. Chem. Phys.*, 14, 504 (1946)) using methods similar to those of Skinner, reported that the latter's value is much too high and that 34.9 is the better figure.

(16) For example, the activation entropies for the decomposition of nitrogen pentoxide and dimethyl ether are, respectively, −2.5 and +2.5 E. U.

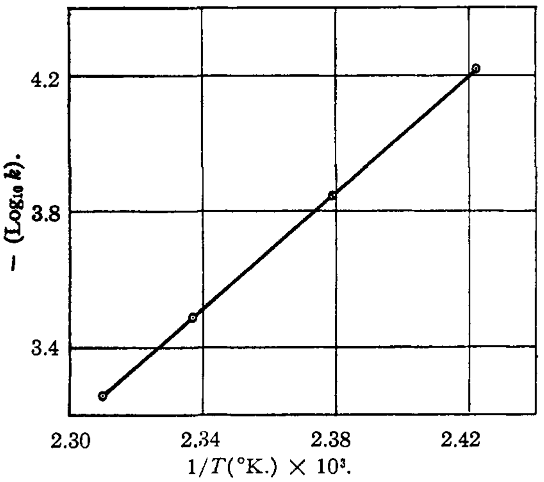

Fig. 5.—Decomposition of di-*t*-butyl peroxide, effect of temperature.

tone. With a larger bore, unpacked tube we find, in addition, small amounts of ethylene, methane and unidentified higher ketones. These additional products are attributed to free radical processes in the gas phase, the ethylene (and perhaps some methane) being ascribed to disproportionation reactions and the rest to alkyl radical attack on the primary ketone products.

Kinetic Order.—Since all products except ethylene are derivable from processes which should give rise to a three-fold pressure increase, the instantaneous values of the di-*t*-amyl peroxide pressure were also calculated from equation (7). A typical experiment is illustrated in Table IX and the summarized data for the decomposition at 132–150° are given in Table X and Fig. 6. (As before, the rate constants and ketone yields were computed from measurements taken during the first third of the reaction. No hydrocarbon yields are given because of difficulty in recovering the butane quantitatively.)

TABLE IX

DECOMPOSITION OF DI-*t*-AMYL PEROXIDE—TYPICAL RUN

Temperature, 142.2(4)°

Time, min.	Total press., mm.	$A - x$, mm.	$k \times 10^4$,[a] sec.$^{-1}$
0	165.6	157.4	
2	173.5	153.4	
4	182.8	148.8	
6	190.8	144.8	
8	198.3	141.0	
10	205.7	137.3	2.28
12	212.4	134.0	2.25
14	218.8	130.8	2.15
16	225.9	127.2	2.16
18	232.8	123.8	2.17
20	238.1	121.1	2.09
22	244.6	117.9	2.14
24	250.6	114.9	2.16
26	256.2	112.1	2.11
28	261.6	109.4	2.06
30	267.4	106.5	2.14
			Av. 2.15 ± 0.04

[a] Calculated for ten-minute intervals.

TABLE X

DECOMPOSITION OF DI-*t*-AMYL PEROXIDE. RATE CONSTANTS AND YIELDS

($A - x$) calculated from equation (7); peroxide pressure, 150–70 mm.

Temp., °C.	Rate constant $k \times 10^4$, sec.$^{-1}$	Ketone yield,[a] %
132.2(2)	0.721 ± 0.15	97
	.759 ± .14	95
	.683 ± .13	98
	Mean 0.72	97
136.7(4)	1.15 ± 0.02	95
142.2(4)	2.11 ± 0.04	
	2.15 ± .04	
	2.38 ± .17 (?)	96
	2.20 ± .04	
	2.18 ± .07	99
	Mean of four 2.16	97
149.7(3)	4.69 ± 0.09	106
	4.96 ± .09	92
	Mean 4.8	99

[a] See footnote [a], Table IV.

However, with this peroxide the rate constant is not pressure independent, regardless of whether it is calculated by use of equation (7) or the empirical equation

$$A - x = A - \frac{P - P_0}{n - 1} \quad (8)$$

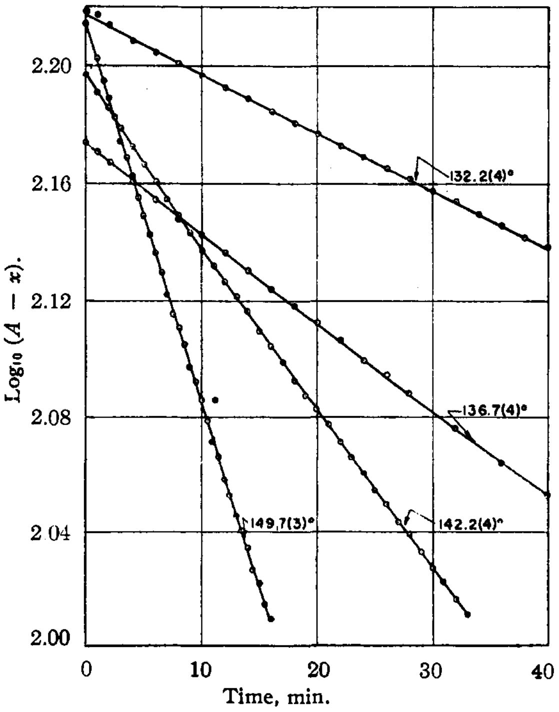

Fig. 6.—Decomposition of di-*t*-amyl peroxide. 130–150°.

where n is the observed ratio of final to initial pressure. The values of n, obtained by completely decomposing the peroxide at *ca.* 150°, are given in Table XI, together with the rate "constants" calculated therefrom.

TABLE XI

DECOMPOSITION OF DI-*t*-AMYL PEROXIDE. EFFECT OF INITIAL PRESSURE

Temp., °C.	Peroxide press., mm.	$k \times 10^4$, sec.$^{-1}$	
136.7(4)	46.6	1.06	
	149.2	1.15	
	339	1.34	
	352	1.34	
142.4(4)	155	2.16	
	360	2.41	
149.7(3)	41.1	5.02	4.43 for n = 3.19
	55.0	4.93	4.56 for n = 3.12
	155	5.04	4.84 for n = 3.06
	184 + 257 CO_2	5.12	
	339	5.61	

Furthermore, in the higher pressure runs, a definite falling off of the rate is noticeable before the decomposition is 30% complete. These results probably indicate that the principal mode of decomposition is first order but that a higher order process is also occurring.

Homogeneity.—No appreciable difference in rate was observed when the pyrolysis was carried out in the packed vessel (Table XII). It is concluded, therefore, that the decomposition takes place only in the gas phase.

Activation Energy.—Since the decomposition of di-*t*-amyl peroxide is not strictly first order, the over-all activation energy, 37 kg.-cal./mole (Fig. 7), does not represent the energy requirements of any single process. Presumably, however, a closer approximation to the activation energy for scission of the oxygen-oxygen bond could be obtained from low pressure data where effects of higher order processes would be minimized. Extrapolation to zero pressure of the values (for n = 3) in Table XI yields E = 41 kcal./mole. Hence, it is probable that the true value of E_1 is between 37 and 41 kcal./mole.

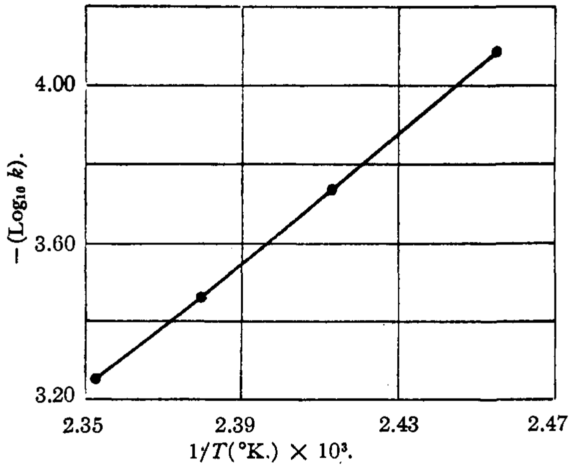

Fig. 7.—Decomposition of di-*t*-amyl peroxide, effect of temperature.

TABLE XII

DECOMPOSITION OF DI-*t*-AMYL PEROXIDE. EFFECT OF REACTOR SURFACE:VOLUME RATIO

Temperature, 142.2(4)°; pressure, 150–170 mm.

Vessel	S/V, cm.$^{-1}$	Initial rate constant $k \times 10^4$, sec.$^{-1}$	Ketone yield, %
Unpacked	0.61	2.16 ± 0.03	97
Packed	7.0	2.14 ± .02	101

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Summary

1. The vapor phase decomposition of di-*t*-butyl peroxide at 140–160° is a homogeneous, first order, non-chain reaction, the rate constant for which is given by $k = 3.2 \times 10^{16}(e^{-39,100/RT})$. The rate-determining step is the scission of the oxygen-oxygen bond and the experimental activation energy closely approximates the calculated strength of this bond.

2. The decomposition proceeds through the formation of *t*-butoxy and methyl radicals. The primary reaction product of the latter and nitric oxide has been identified as formaldoxime.

3. The principal decomposition products are ethane and acetone. However, some methyl radicals react with acetone to yield methane and methyl ethyl and higher ketones. A small fraction of the peroxide may decompose in another manner.

4. The pyrolysis of di-*t*-amyl peroxide at 130–150° is a homogeneous, approximately first order reaction. The over-all activation energy is 37 kcal./mole and that for the initial step is estimated as 37–41 kcal./mole. The predominant products are n-butane and acetone, but methane, ethane, ethylene, propane and methyl ethyl and higher ketones are also found in small amounts. All products can be accounted for by the intermediate formation of *t*-amyloxy, ethyl and methyl radicals.

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