just alkaline with sodium hydroxide, a slight precipitate filtered off and the filtrate hydrogenated in a Parr apparatus with Raney catalyst. After 4 hours the calculated amount of hydrogen was absorbed, the catalyst was filtered and the filtrate acidified with acetic acid. The crude yield of 2,6-di-(*p*-hydroxy-β-phenethyl)-pyridine was 10 g., m.p. 171–174°; recrystallized twice from dilute ethanol for analysis, m.p. 180–181°. *Anal.* Calcd. for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63. Found: C, 78.78; H, 6.56.

To a solution of 3.19 g. (0.01 mole) of the hydroxy compound dissolved in 320 cc. of 1% sodium hydroxide solution, there was added dropwise with stirring a solution of 10.2 g. of iodine and 10.2 g. of potassium iodide in 100 cc. of water. The solution was stirred for an additional hour, filtered and then acidified with sulfur dioxide. The precipitated tetraiodo compound was filtered and air-dried; yield 7.2 g., m.p. 150–157°. Attempts to recrystallize the product from dilute ethanol, dilute acetic acid or alcohol–ether resulted in liberation of iodine with the formation of tarry products.

(18) **2-(*p*-Hydroxy-β-phenethyl)-piperidine and 2-[β-(4-hydroxycyclohexyl)-ethyl]-piperidine.**—A solution of 7.5 g. (0.04 mole) of 4′-hydroxy-α-dihydrostilbazole in 150 cc. of dry *n*-butanol was refluxed in an oil-bath at approximately 180° and treated rather rapidly with 14 g. (0.6 mole) of sodium. After 1.5 hours, an additional 50 cc. of butanol was added. After 3 hours at 175–180°, the sodium had been consumed. The solvent was removed by steam distillation and a small amount of solid filtered from the steam distillation residue. The 2-(*p*-hydroxy-β-phenethyl)-piperidine was precipitated by careful acidification with acetic acid; yield 6.6 g. (85%), m.p. 197–198°. Recrystallization from toluene raised the m.p. to 198.5–199.5°. *Anal.* Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33. Found: C, 76.13; H, 9.26.

Twenty grams (0.1 mole) of 4′-hydroxy-α-stilbazole was hydrogenated in 250 cc. of ethanol for 9 hours at 80° at an initial pressure of 1,200 p.s.i. The catalyst was then filtered and the solvent evaporated. Leaching the residue with hot dilute sodium hydroxide solution left, as an insoluble residue, 4.0 g. (18%) of substantially pure perhydro compound, 2-[β-(4-hydroxycyclohexyl)-ethyl]-piperidine, m.p. 174–175.5. Recrystallization from dilute ethanol raised the m.p. to 176–177.5° using Raney nickel catalyst. *Anal.* Calcd. for $C_{13}H_{25}NO$: C, 73.88; H, 11.92; N, 6.63. Found: C, 74.21; H, 11.87; N, 6.51.

The alkali soluble fraction was precipitated by careful acidification with acetic acid, yielding 8.0 g. (38%), of 2-(*p*-hydroxy-β-phenethyl)-piperidine, m.p. 195.5–196.5°. Recrystallization from toluene raised the m.p. to 198.5–199.5°, not depressed by admixture with a sample prepared by sodium-butanol reduction.

Summary

A series of diiodohydroxydihydrostilbazoles and α-(3,5-diiodo-4-hydroxy-styryl)-α′-methyl pyridine and α-quinoline compounds have been prepared for pharmacological examination as X-ray diagnostic agents. None of the compounds showed cholecystographic properties in dogs.

BLOOMFIELD, N. J.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photochemical Decomposition of Gaseous Di-*t*-butyl Peroxide[1]

BY LEON M. DORFMAN[2] AND Z. W. SALSBURG[3]

The extensive investigations of Vaughan and his co-workers[4,5,6,7] on the thermal decomposition of the alkyl peroxides have led to considerable interest in di-*t*-butyl peroxide. As a result of this work the mechanism of the pyrolysis of this compound is reasonably well understood.

Very little is recorded in the chemical literature, on the photolysis of alkyl peroxides. The above authors[6] have reported one run on the photolysis of liquid di-*t*-butyl peroxide but no investigations of the photochemical decomposition of this compound in the gaseous phase have yet been reported.

Di-*t*-butyl peroxide, because of its relatively high stability at temperatures below 80°, lends itself to a study of the reactions of the methyl radical, which are currently of much interest, as well as those of the butoxy radical. Its use as a radical source in reaction initiation is well established[8] at temperatures above 100°. It may also be used for this purpose at room temperature since the photolysis will provide radicals.

The present investigation has been carried out over a temperature range from 25 to 75° using both filtered light and the full light of the mercury arc where necessary in order to obtain sufficient quantities of liquid products for accurate analysis.

Experimental Details

Di-*t*-butyl peroxide, obtained from the Shell Development Company, was purified by distillation at reduced pressure using a column packed with glass beads. The liquid was distilled at a temperature of 40–45° over the pressure range 55–70 mm. The middle third of the distillate was retained, then dried over anhydrous copper sulfate and subsequently bulb-to-bulb distilled in the vacuum system before being stored over a mercury cut-off in a storage bulb painted black. Prior to each run the peroxide was degassed for at least one hour at Dry Ice temperature. The refractive index of the purified liquid was found to be $n^{20}\text{D}$ 1.3889. This compares with previously listed values[4,9] of 1.3890 and 1.3872. After the liquid had been stored for over two months the refractive index was found to be unchanged.

A Hanovia Alpine burner type S-100 was used as the light source in all runs. For the low intensity runs in which only gaseous products were analyzed, this mercury arc was used in conjunction with a chlorine gas filter (460 mm. pressure, 50-mm. path length) and a Corning No. 9863 filter of standard thickness. These filters provided light consisting chiefly of 2537 and 2650 Å. The intensity was further reduced, when desired, by interposing a neutral density filter in the beam. For these runs with the filtered light the reaction vessel consisted of a cylindrical quartz cell, 200 mm. in length and 22 mm. inside diameter. The light beam had an incident diameter of 14.1 mm. and an emergent diameter of 14.3 mm. The absorbed light intensity was determined with the use of a photocell, and the necessary corrections[10,11] for multiple reflections were made.

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Gaseous acetone provided a satisfactory actinometer since it has been shown[12,13] that the quantum yield of carbon monoxide formation is unity at temperatures in excess of 100°.

In the low intensity runs, the gaseous products, pumped off at −135° using a Toepler pump, were determined quantitatively by combustion on a hot platinum wire. These methods have been described by various authors.[11,13,14] Acetone was first identified as a product by infrared absorption, but no quantitative analysis could be carried out at the low intensities because of the extremely small amounts. Consequently this phase of the work was left for the high intensity runs.

For the high intensity runs with the full arc a quartz cell of 45 mm. diameter and 80 mm. length was used. The beam was of such dimensions as to practically fill the cell. The determination of absorbed intensity was carried out here for only one run by using a uranyl oxalate actinometer behind the cell, first with the cell empty, then immediately afterward during the run.

With the full arc ethane was the only gaseous product within experimental error. This was verified by mass spectrometric analysis at the National Bureau of Standards. The ethane was distilled off at −150°, frozen in liquid nitrogen and subsequently measured with an ordinary mercury manometer at room temperature. Analyses of acetone and *t*-butyl alcohol were carried out as follows.

The acetone was determined using hydroxylamine hydrochloride according to the procedure given by Maltby and Primavesi[15] with the following modifications. The Beckman *p*H meter, rather than an indicator, was used to follow the titration and to determine the end-point. A 20 to 30% excess of hydroxylamine hydrochloride was used, rather than the larger excess recommended above, since this procedure was found to give a sharper end-point. The di-*t*-butyl peroxide was necessarily present during the determination of acetone and was found to give a blank. By titrating several amounts of pure peroxide and interpolating for the amount of peroxide present in each run a blank was determined which, in each case, amounted to less than 10% of the acetone present.

The *t*-butyl alcohol was determined using Denige reagent in a method adopted from Robey and Robertson.[16] The following procedure was carried out simultaneously on a sample of pure peroxide, a series of standard *t*-butyl alcohol solutions, and the unknown sample. To each sample 1 ml. of soluble starch solution and 2 ml. of Denige reagent were added. The solution was then heated in a water-bath at 45° for 10 minutes and then diluted to 50 ml. The finely divided precipitate formed was then determined nephelometrically. It was found necessary to prepare a fresh starch solution before each determination. After correcting for the blank given by the peroxide the concentration of the *t*-butyl alcohol was determined from a working curve obtained from the analyses of the standard solutions.

Three samples of the gaseous products which, on the basis of the results obtained with the filtered light were assumed to consist only of ethane, were sent to the National Bureau of Standards for mass spectrographic analysis. Except for a small amount of acetone in one sample and a slight presence of peroxide which had been pumped over, these analyses showed the gas to be over 97% ethane. Less than a few hundredths of a per cent. of methane was present. This analysis was also used to correct the data obtained for the three runs.

In order to avoid photochemical decomposition of the acetone formed in the reaction, the runs with the full mercury arc were interrupted after each 5-minute exposure period and ethane and acetone removed from the peroxide at −40°. This was done by distilling these products, along with some peroxide which was always present in excess, into a cold finger maintained at −195°. At the end of the run the substrate was combined with this distillate before carrying out the analyses. As shown by the absence of any significant amount of carbon monoxide in the products this procedure was successful in preventing photolysis of the acetone.

Several dark runs at temperatures of 75° and higher were made for periods as long as 13 hours. The dark reaction was found to be negligible at temperatures below 80°.

Results and Discussion

Ethane and methane were found to be the only gaseous products of the photochemical decomposition. Acetone and *t*-butyl alcohol are the only liquid products for which we have carried out analyses. These compounds have been identified by previous workers[4,5,6,9,17] as products of the thermal decomposition of the peroxide.

A series of runs was carried out using the full arc and the rates of formation of acetone and of ethane were determined. These results are shown in Table I.

TABLE I

RATIO OF ACETONE TO ETHANE FORMED IN THE PHOTOLYSIS OF DI-*t*-BUTYL PEROXIDE

Temp., °C.	Press., mm.	Rates of formation, moles/hour × 10^5 Ethane	Rates of formation, moles/hour × 10^5 Acetone	$R_{\text{acetone}}/R_{\text{ethane}}$
30.0	33.2	3.38	6.82	2.02
29.0	29.5	1.97	4.10	2.08
27.2	28.5	2.06	4.00	1.94
26.2	27.6	2.55	4.98	1.95
29.4	33.8	2.08	5.16	2.48

The work[4] on the thermal decomposition has indicated that the initial step in the reaction is a scission of the O–O bond to form two butoxy radicals. These workers have suggested[6] that this is also the primary step in the photochemical decomposition

$$(CH_3)_3COOC(CH_3)_3 + h\nu = 2(CH_3)_3CO \qquad (1)$$

and that acetone is formed by the loss of a methyl group from the butoxy radical

$$(CH_3)_3CO = CH_3COCH_3 + CH_3 \qquad (2)$$

The methyl radicals may then combine to form ethane.

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

Since ethane is the only gaseous product at high intensities, this scheme would require that

$$R_{\text{acetone}} = 2R_{\text{ethane}}$$

where R represents the rate of formation of product. As may be seen in the last column of Table I, this relationship is quite closely obeyed, thus supporting the validity of these modes of formation of the two products.

The runs in which analyses were carried out for both *t*-butyl alcohol and ethane are shown in Table II.

TABLE II

FORMATION OF *t*-BUTYL ALCOHOL AND ETHANE IN THE PHOTOLYSIS OF DI-*t*-BUTYL PEROXIDE

Run	Temp., °C.	Press., mm.	Rates of formation, moles/hour × 10^5 Ethane	Rates of formation, moles/hour × 10^5 *t*-Butyl alc.	$R_{\text{alcohol}}/R_{\text{acetone}}$
6	27.5	31.0	3.83	1.70	0.22
7	28.8	32.0	4.49	2.33	.26
8[a]	30.0	36.0	7.85	4.80	.31

[a] The absorbed intensity in Run No. 8, determined by uranyl oxalate actinometry is $I_a = 10.6 \times 10^{-5}$ einstein/hour. The quantum yields of products, therefore, are $\Phi_{\text{ethane}} = 0.74$ and $\Phi_{\text{alcohol}} = 0.45$. Since the yield of acetone has been shown (Table I) to be twice that of ethane, the quantum yield of acetone is $\Phi_{\text{acetone}} = 1.48$.

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The quantum yields obtained in Run 8 are only approximate because of the polychromatic nature of the light. Nevertheless, the value of $\Phi_{\text{ethane}} = 0.7$ obtained in this run is in reasonably good agreement with the value of 0.64 at room temperature obtained by more precise measurements with the filtered light at the higher intensity.

It has been suggested[5] that the *t*-butyl alcohol is formed through hydrogen abstraction by the butoxy radicals. Since the acetone has been removed at frequent intervals during these runs, and no added compounds are present, this abstraction can take place only from the peroxide itself.

$$(CH_3)_3CO + (CH_3)_3COOC(CH_3)_3 = (CH_3)_3COH + CH_2(CH_3)_2COOC(CH_3)_3 \quad (4)$$

If there is no chain process involved in the photochemical decomposition the following relationship should hold.

$$\Phi_{\text{acetone}} + \Phi_{\text{alcohol}} \leqq 2$$

The quantum yields obtained in Run 8 yield a value of 1.93 ± 0.25 for this sum of quantum yields. Provided the primary quantum yield is nearly unity, this would seem to indicate that no important chain process is involved at room temperature. A primary quantum yield of unity is quite probable in this photolysis. The O–O bond strength[4,18] is less than 40 kcal./mole. Consequently an energy excess of some 60 kcal./mole greater than the amount necessary for bond rupture is present following the initial absorption.

Methane is formed in appreciable quantities only at very low intensities in the gas phase photolysis. A series of runs using filtered light have been carried out over a temperature range from 25 to 75° with a 40-fold variation in absorbed intensity. Quantum yields have been determined for some of the runs and the results are listed in Table III.

TABLE III

FORMATION OF GASEOUS PRODUCTS IN THE PHOTOLYSIS OF DI-*t*-BUTYL PEROXIDE

Temp., °C.	Press., mm.	Absorbed intensity, quanta/sec. × 10^{-12}	Fraction of gaseous products Ethane	Fraction of gaseous products Methane	R_{ethane}, molecules/sec. × 10^{-12}	Φ_{ethane}
25.9	26.8	...	0.98	0.02	37.3	..
25.6	26.4	...	.95	.04	18.7	..
27.0	28.0	16.3	.94	.05	10.4	0.64
27.6	29.5	1.45	.75	.25	0.50	.35
59.8	31.2	...	.99	..	9.1	..
60.1	48.2	13.8	.80	.20	11.2	.81
75.2	31.9	10.4	.97	..	10.2	.98
75.7	28.4	...	.98	..	8.6	..
74.8	30.6	...	.66	.34	0.97	..
75.0	30.5	...	.75	.25	.97	..

As may be seen from Table III the fraction of methane in the gaseous products increases with decreasing absorbed intensity. This is to be expected since the abstraction of hydrogen by the methyl radicals

$$CH_3 + (CH_3)_3COOC(CH_3)_3 = CH_4 + CH_2(CH_3)_2COOC(CH_3)_3 \quad (5)$$

will be favored in competition with the association reaction (3) as the intensity is decreased to lower values.

The quantum yield of gaseous product increases with increasing temperature. This observation is consistent with the results obtained in the work on the thermal decomposition where it has been reported[5] that an increase in temperature favors the loss of a methyl group from, rather than abstraction by, the butoxy radical.

The higher quantum yield of ethane formation at 75° indicates the possibility of short chains at this higher temperature. Szwarc and Roberts[18] have reported the presence of short chains in the pyrolysis at temperatures above 120°. The chains result from the decomposition of the peroxide radical formed in the abstraction reactions (4) and (5) to give isobutylene oxide[6] and a butoxy radical.

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Summary

1. The photo-chemical decomposition of gaseous di-*t*-butyl peroxide has been investigated over a temperature range from 25 to 75°.

2. The rates of formation of ethane, methane, acetone and *t*-butyl alcohol have been determined. Methane is a major product only at very low intensities, its quantum yield increasing as the intensity is decreased.

3. The quantum yield of gaseous product increases as the temperature is raised.

4. There is no evidence of a chain reaction at room temperature, but the possible existence of short chains at elevated temperatures is indicated.

SCHENECTADY, N. Y. RECEIVED JULY 5, 1950

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