[CONTRIBUTION FROM THE EMERYVILLE LABORATORIES OF THE SHELL DEVELOPMENT COMPANY]

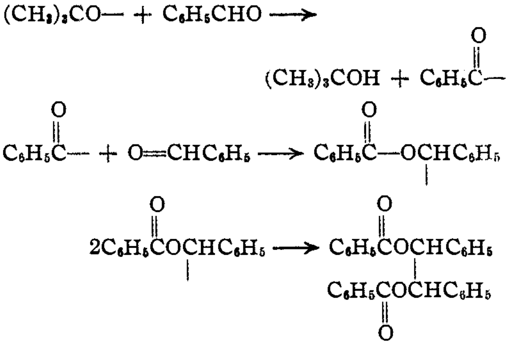
The Reaction of Di-*t*-butyl Peroxide and Benzaldehyde

BY FREDERICK F. RUST, FRANK H. SEUBOLD AND WILLIAM E. VAUGHAN

The interaction of benzaldehyde and di-*t*-butyl peroxide in the absence of base leads to the formation of *sym*-diphenylethylene glycol dibenzoate in a clean-cut synthesis. This reaction bears a striking resemblance to the classical Cannizzaro disproportionation. Although the careful study of Alexander[1] has disproved the contention of Kharasch and Foy[2] that peroxides are necessary for the Cannizzaro reaction, the present results suggest the possibility of an analogous reaction proceeding by a free radical rather than an ionic mechanism. The formation of *t*-butyl alcohol in the presence of the aldehyde implies that the di-*t*-butyl peroxide initially dissociates into two *t*-butoxy radicals which may abstract hydrogen atoms from copresent molecules.

The suggested steps are as follows

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO— \quad (1)$$



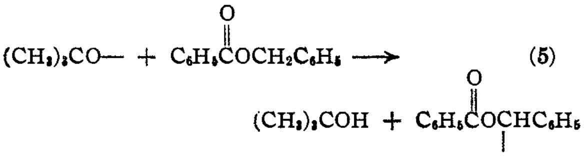
$$(CH_3)_3CO— + C_6H_5CHO \longrightarrow (CH_3)_3COH + C_6H_5\overset{O}{\overset{\|}{C}}— \quad (2)$$

$$C_6H_5\overset{O}{\overset{\|}{C}}— + O{=}CHC_6H_5 \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}—O\underset{|}{C}HC_6H_5 \quad (3)$$

$$2C_6H_5\overset{O}{\overset{\|}{C}}O\underset{|}{C}HC_6H_5 \longrightarrow \begin{array}{c} C_6H_5\overset{O}{\overset{\|}{C}}O\underset{|}{C}HC_6H_5 \\ C_6H_5\underset{\underset{O}{\|}}{C}OCHC_6H_5 \end{array} \quad (4)$$

No benzyl benzoate was isolated or indicated. Its apparent absence suggests that the ester radical formed in step 3 is incapable of abstracting a hydrogen atom from benzaldehyde. Instead two such radicals eventually recombine with remarkable specificity to form the glycol diester.

The validity of this latter assumption is enhanced by the preparation of the same compound by interaction of benzyl benzoate and di-*t*-butyl peroxide (Reaction 1 followed by 5 and 4)



$$(CH_3)_3CO— + C_6H_5\overset{O}{\overset{\|}{C}}OCH_2C_6H_5 \longrightarrow (CH_3)_3COH + C_6H_5\overset{O}{\overset{\|}{C}}O\underset{|}{C}HC_6H_5 \quad (5)$$

Further evidence for this mechanism is gained from the synthesis of the glycol diester from benzaldehyde by means of benzoyl peroxide. In this case benzoate radicals, rather than *t*-butoxy, are formed in the primary step 1 and these then react with the aldehyde (step 2).

Experimental

Benzaldehyde and Di-*t*-butyl Peroxide.—Benzaldehyde[3] (200 ml., 2.0 moles) and di-*t*-butyl peroxide[4] (50 ml., 0.274 mole) were refluxed at 109° and at 130°. The conditions and results are summarized in the table

Temperature, °C.	109	130
Time of run, hr.	63	30
Gas evolved,[a] mole	0.014	0.019
t-Butyl alcohol recovered, mole	0.31	0.40
Peroxide reacted, mole	0.18	0.20

[a] Carbon number 0.9, therefore methane.

A large quantity of crystalline material which precipitated from the reaction mixture (at 130°) was separated by filtration and washed with hot ethanol. It was identified as the *meso* form of *sym*-diphenylethylene glycol dibenzoate by the following determinations:

	Found	Calcd. $C_{28}H_{22}O_4$
Carbon, %	79.5	79.6
Hydrogen, %	5.3	5.2
Saponification equiv.	212.5	211
Melting point, °C.	244	244[5]

The filtrate from the crystalline dibenzoate was distilled at 1.5–2.0 mm. and 100° to remove all volatile material; this distillation provided the means for determining the amounts of *t*-butyl alcohol and unreacted peroxide. The rosin-like residue was apparently a mixture of diphenylethylene glycol dibenzoate stereoisomers. Its analysis was

	Found	Calcd. for $C_{28}H_{22}O_4$
Carbon, %	79.2–79.3	79.6
Hydrogen, %	5.3–5.3	5.2
Molecular wt. (ebull.)	408	422
Saponification equiv.	211	211

The total yield of the glycol diester was 85% based on the peroxide consumed:

Di-*t*-butyl peroxide	input	40 g.	0.274 mole
	recovered	10	.068
	consumed	30	.206
$C_{28}H_{22}O_4$ ester	produced	74	.175

In an effort to isolate benzyl alcohol as evidence for the formation of benzyl benzoate, a saponification reaction mixture of the product was diluted with ether and the precipitated sodium benzoate filtered off. The ether and ethanol were evaporated and the gummy residue heated under vacuum so as to distill any benzyl alcohol which might be present. No distillate was obtained, however, and it must be assumed that benzyl benzoate was absent or present in minor amount only.

Benzyl Benzoate and Di-*t*-butyl Peroxide.—Benzyl benzoate (223 g., 1.05 moles) and di-*t*-butyl peroxide (50 g., 0.34 mole) were heated at 130° for forty-eight hours. During this time 0.123 mole of gas was evolved and collected over brine. Analysis showed it to be 95%

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[1] Alexander, THIS JOURNAL, **69**, 289 (1947).

[2] Kharasch and Foy, *ibid.*, **57**, 1510 (1935).

[3] Redistilled from Eastman Kodak Co. white label product.

[4] Prepared in accordance with directions given by Vaughan and Rust, U. S. Patent 2,403,771 (July 9, 1946); for a similar procedure see Milas and Surgenor, THIS JOURNAL, **68**, 205 (1946).

[5] Paal, *Ber.*, **17**, 909 (1884).

methane, which arises from the reaction of methyl radicals. In conformity with the decomposition of *t*-butoxy radicals by the mechanism

$$(CH_3)_3CO— \longrightarrow CH_3 + CH_3COCH_3 \qquad (6)$$

an almost equivalent amount of acetone (0.10 mole) was recovered by fractionation of the reaction product. *t*-Butyl alcohol (0.24 mole) and unreacted peroxide (0.08 mole) were also recovered by fractionation.

The product was filtered to separate the precipitated *meso*-diphenylethylene glycol dibenzoate which melted at 244–246° and had a saponification equivalent of 211 after washing with hot ethanol.

Benzaldehyde and Benzoyl Peroxide.—Benzaldehyde (106 g., 1.00 mole) and benzoyl peroxide (21 g., 0.09 mole) were heated at 80° for *ca.* eighteen hours, during which time all of the peroxide reacted. The evolved gas consisted of 0.009 mole of carbon dioxide and 0.007 mole of carbon monoxide. After removal of the excess aldehyde the liquid product yielded 6.0 g. (0.014 mole) of crystalline *meso*-diphenylethylene glycol dibenzoate (m. p. 244–245°). The residue was not further investigated.

Summary

1. A remarkably clean-cut disproportionation reaction of benzaldehyde leading to *sym*-diphenylethylene glycol dibenzoate is effected by either di-*t*-butyl peroxide or benzoyl peroxide.

2. The mechanism advanced for the formation of the diester is supported by the synthesis of the same compound from benzyl benzoate and di-*t*-butyl peroxide.

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The Heat of Combustion of 2,2'-bis-(4-Hydroxyphenyl)-propane

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Introduction

The heat of combustion of 2,2'-bis-(4-hydroxyphenyl)-propane was measured and the data combined with values for the heats of formation of water and carbon dioxide to obtain a value for the heat of formation of this compound. For brevity in the text, the above substance will be called by its trade name, "Bis-phenol-A."

Experimental

The Calorimeter and its Calibration.—The calorimeter was substantially of the type described by Dickinson.[1] The construction of the constant-temperature jacket differs from the Bureau of Standards model, but there was no change in operating principles or in the design of the calorimeter itself.

A schematic diagram of the apparatus is shown in Fig. 1. The calorimeter can E was enclosed in the constant-temperature jacket, which was a covered cylindrical tank. The inner boundary of the jacket was a copper vessel D, called the well. This was of such shape and dimensions that a 1-cm. air gap was provided between the well and the calorimeter, the form of which is shown by the isometric projection G. The well was isolated in the jacket, being anchored to three plastic supports. Two tubes attached to the water-tight cover extended through the top of the jacket to provide ports for insertion of the thermometer and for coupling the calorimeter stirrer to its drive pulley at A. All surfaces were nickel-plated and polished.

In operation the jacket was filled with water to the level indicated by the overflow C. Two propellers (as shown at B) provided vigorous circulation. Constant temperature was maintained by intermittently energized heaters, which were soldered to the flow tubes surrounding the propellers and controlled by a sensitive thermostat (not shown). The well was exposed for introducing and removing the calorimeter by draining water through cocks F. To avoid delay in starting an experiment, the jacket was drained only to the level of the upper of these cocks in between runs. This arrangement (which approaches the Richards submarine calorimeter[2] eliminates the troublesome water cap of the Dickinson model, and simplifies the construction.

Temperature measurements were made using a platinum resistance thermometer of the calorimetric type in conjunction with a Type G-2 Mueller resistance bridge and a sensitive galvanometer. By controlling the amount of material burned in each experiment, the temperature rise was held substantially constant. Each combustion was initiated at 24.000° and the temperature of the calorimeter rose to an average of 26.000 ± 0.003°. The improved ignition technique of Huffman and co-workers was used.[3]

The double-valved bomb was machined from S. A. E. 1040 steel, following the design of Atwater and Snell[4] and was lined with platinum. The arrangement of platinum firing electrodes was similar to that of Prosen and Rossini.[5] This consists in having one electrode in the form of a tube connected to one of the valves, and extending close to the bottom of the bomb, permitting continuous flushing with oxygen and convenient removal of the gaseous products of combustion for analysis whenever desired. The sealing gasket was made of du Pont Teflon (polytetrafluoroethylene). Repeated combustions of Bis-phenol-A, benzoic acid and certain chlorinated hydrocarbons (which form extremely corrosive combustion products) resulted in no visible attack on this material and no anomalous combustion data were obtained when such a gasket was used. The volume of the bomb was 0.328 liter, and all combustions were carried out under an initial oxygen pressure of 30 atmospheres and with 0.1 ml. of water added to the bomb.

The energy equivalent of the calorimeter was determined by combustion of benzoic acid (National Bureau of Standards Standard Sample 39f), having for its isothermal heat of combustion at 25°, and under standard specified conditions,[6] the value $-\Delta U_B/M$ = 26,429.4 N. B. S. international joules per gram. Since the conditions in these experiments were not quite those of the standard

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[1] Dickinson, *Bull. Bur. Standards*, **11**, 189 (1915).

[2] Richards and Jesse, THIS JOURNAL, **32**, 268 (1910).

[3] (a) Huffman and Ellis, *ibid.*, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935); (c) Huffman, *ibid.*, **60**, 1171 (1938).

[4] Atwater and Snell, *ibid.*, **25**, 659 (1903).

[5] Prosen and Rossini, *J. Research Natl. Bur. Standards*, **27**, 289 (1941).

[6] Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942), revised for a new value for the density of benzoic acid. See Jessup, *ibid.*, **36**, 421 (1946), and Supplementary Note of February 12, 1946, to N. B. S. Certificate for Standard Sample 39f.