at a distance of 6" from a 200-watt incandescent tungsten filament lamp, while both lamp and flask were submerged in an ice-bath. During the first minute the temperature of the reactants rose to 26° and then slowly dropped to 0°. The reactants were irradiated for 35 minutes. Gas phase infrared spectra of the recovered olefins showed no detectable *cis–trans*-isomerization. In experiments where short irradiation periods were used, excess benzenesulfonyl iodide was removed by washing with an aqueous solution of potassium iodide and sodium bisulfite. Removal of solvent *in vacuo* left 48.7 g. (101% of theoretical yield based on benzenesulfonyl iodide) of liquid crude 2-benzenesulfonyl-3-iodobutanes, $n^{25}D$ 1.582. Experiments in which *trans*-2-butene was used gave essentially identical results, no isomerization of unreacted olefin and a similar product, $n^{25}D$ 1.586. The infrared spectra of the crude products from both olefins were superimposable when taken neat or in cyclohexane solvent.

In paired experiments 10.0 g. of each of these crude products was recrystallized from a solution of 80 ml. of *n*-heptane and 10 ml. of benzene to separate at 0° 3.46 and 3.45 g. of a solid product, respectively. The crude solids (m.p. 65.5–68.5°, mixed m.p. not depressed) had identical infrared spectra when taken in CS_2 solution (~ 1 g./100 ml. solution). Two recrystallizations from 95% ethanol raised the melting point to 70.0–70.5°, but did not change the infrared spectra noticeably. Attempts to separate the other isomer in pure condition were not successful.

The halogen content of the β-iodosulfones was determined argentometrically after liberating I^- by treating the sample with excess sodium methoxide solution (halogen-free). Calcd. for $C_{10}H_{13}SO_2I$: I, 39.1. Found for (a) crystalline isomer: I, 39.1; (b) crude product from *cis*-2-butene (VII): I, 38.5; (c) crude product from *trans*-2-butene (VIII): I, 36.8.

Infrared spectra of the pure solid isomer in CS_2 solution (1.50 g./100 ml. soln.) indicated absorption bands at 3.27, 3.36, 3.44, 7.25, 7.39, 7.58, 7.66, 7.80, 8.00, 8.08, 8.45, 8.67, 8.72, 9.20, 9.43, 9.75, 9.91, 10.01, 10.42, 11.90, 13.15, 13.50, 13.80, 14.48. The infrared spectra of the mixture of liquid isomers VII and VIII were identical and in CS_2 solution (2.21 g./100 ml. solution) showed all of the bands of the solid isomer and several additional bands. We list here only the new bands (indicated by *) and those bands which showed a larger extinction coefficient in the mixture. This procedure does not detect all of the bands of the liquid isomer. Some of the absorption bands of the liquid isomer appear at 7.25, 8.04*, 9.06*, 9.35*, 9.62*, 10.55*, 11.05*, 12.20*, 13.80, 14.45.

Dehydrohalogenation of the Diastereomeric 2-Benzenesulfonyl-3-iodobutanes.—The liquid mixtures of diastereoisomers were dehydrohalogenated by boiling under reflux with 10 g. of pyridine in 100 ml. of benzene. The pyridine was removed by washing with 10% hydrochloric acid and water, and the benzene solution was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was distilled at 1 mm. pressure through a 6" Vigreux column.

The unsaturated sulfone prepared from 10 g. of VII was separated into two fractions: (1) b.p. 115°, $n^{25}D$ 1.5542, 1.08 g.; (2) b.p. 115–117°, $n^{25}D$ 1.5570, 0.79 g. Schlieren were evident in both fractions. There was an accidental loss of an indeterminate amount of crude product.

The product from 5.0 g. of VIII was similarly distilled: (1) b.p. 118°, $n^{25}D$ 1.5540, 1.40 g.; (2) b.p. 118°, $n^{25}D$ 1.5560, 1.40 g. Schlieren were evident in both fractions.

The product from 3.0 g. of crystalline 2-benzenesulfonyl-3-iodobutane was treated similarly, yielding a crystalline unsaturated sulfone, b.p. 128–132°, 0.70 g., m.p. 50–51°. Recrystallization from ethanol raised the m.p. to 51°. Calcd. for $C_{10}H_{12}SO_2$: S, 16.3. Found: S, 17.1.

Infrared spectra of the combined fractions 1 and 2 of the unsaturated sulfones from VII and VIII were identical. The absorption bands of the mixture showed all the bands observed in the spectrum of the solid isomer and several which were absent in the latter. The absorption bands found for the unrecrystallized solid isomer in CS_2 solution (1.42 g./100 ml. solution) appeared at 3.26, 3.36, 3.43, 3.52, 6.05, 7.25, 7.48, 7.60, 7.74, 8.49, 8.54, 8.80, 9.20, 9.35, 9.75, 10.00, 10.95, 11.75, 13.20, 13.75, 14.50. The new bands (*) which are attributable to the liquid unsaturated sulfone and the bands which had a larger extinction coefficient than the corresponding band in the solid isomer were detected from the spectrum of the liquid products in CS_2 (1.87 g./100 ml. solution): 3.36, 3.43, 8.00*, 8.69*, 9.20, 9.63*, 10.55*, 12.03*, 15.42*.

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[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF GULF RESEARCH & DEVELOPMENT CO., MELLON INSTITUTE, AND THE UNIVERSITY OF PITTSBURGH]

Steric and Resonance Effects in the *t*-Butyl and Isobutylphenols[1]

BY ROBERT S. BOWMAN, DONALD R. STEVENS AND W. E. BALDWIN[2]

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The six mono *t*-butyl and isobutylphenols, the *t*-butyl and isobutyl phenyl ethers, *t*-butylbenzene and isobutylbenzene have been subjected to vapor phase thermal decomposition. Pronounced "*ortho*" or steric effects are observed in the *o*-*t*-butyl- and *o*-isobutylphenols. These effects are manifested in increased rates of dissociation and greater production of propylene when compared to the *meta* and *para* isomers. An effect attributable to phenolic resonance polarization is indicated in the *para* isomers, and is reflected by increased rates of dissociation and greater production of isobutane (from *p*-*t*-butylphenol) and propane (from *p*-isobutylphenol) when compared to their *meta* isomers. In general, the *m*-butylphenols resemble more closely their parent hydrocarbons, the butylbenzenes. Reaction routes are postulated in an attempt to elucidate the differences in decomposition rates and products. All of the thermal decompositions produced complex gaseous mixtures except in the case of *t*-butyl phenyl ether. In this instance, phenol and isobutylene were formed almost exclusively. Further confirmation of considerable steric interaction in the *o*-*t*-butyl- and isobutylphenols was afforded by (a) an investigation of the partial steric hindrance to hydrogen bonding in solution, using infrared absorption spectroscopy; and (b) a kinetic study of the rate of thermal dissociation of *o*-*t*-butylphenol. The rate of pressure rise in this reaction obeys first-order kinetics. The activation energy was found to be 58.4 kcal./mole.

The presence of steric strain in phenols in which one or both of the *ortho* positions are occupied by bulky alkyl substituents such as *t*-butyl groups is indicated by the ease with which the group is expelled as the olefin under the influence of various acidic reagents at 125–250°.[3] At lower temperatures in the presence of sulfuric acid the *t*-butyl group in the case of *o*-*t*-butylphenol has been observed to migrate to the non-hindered, stable *para* position.[4]

This present investigation was undertaken in order to study the manifestation of these "*ortho*

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[1] Abstracted from a dissertation submitted by Robert S. Bowman to the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree, 1950.

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[3] D. R. Stevens, *Ind. Eng. Chem.*, **35**, 655 (1943).

[4] H. Hart, THIS JOURNAL, **71**, 1966 (1949).

effects" under the conditions of vapor phase thermal dissociation, using the *t*-butyl- and isobutylphenols as the test compounds. A second objective of this work was to note and define any effects attributable to the resonance polarization of the *ortho* and *para* carbons in the phenol nucleus. The inclusion of infrared absorption studies for the estimation of intermolecular hydrogen bonding was made in order to obtain a comparison between a *t*-butyl and an isobutyl group relative to their respective hindrance capacities. The pronounced effect of steric "interaction" in *o-t*-butylphenol invited a more quantitative investigation of the pyrolysis reaction. Accordingly, rate studies were made at various temperatures which then allowed the calculation of the composite energy of activation. Finally, the pyrolyses of the two isomeric butyl phenyl ethers, *t*-butyl and isobutyl phenyl ether, and the two parent hydrocarbons, *t*-butyl- and isobutylbenzene, were included in the research program in order to provide any additional information which might be useful in the interpretation of the butylphenol decompositions.

Experimental

The syntheses of the ten *t*-butyl and isobutyl compounds were achieved, for the most part, by conventional procedures and techniques. Thus, it will suffice to present a general description of the preparations and a table containing some physical properties of the compounds. Attention should be drawn, however, to a convenient preparation of *o-t*-butylphenol in good yield by direct alkylation with isobutylene, a process which affords *o-t*-butylphenol and *p-t*-butylphenol in the ratio of two to one. These results can be interpreted to indicate that the *o*- and *p*-carbons of phenol are about equally activated.

It is also pertinent to include a more detailed account of the synthesis of *m*-isobutylphenol, a new butylphenol isomer.

Materials.—In the *t*-butyl series, four of the five compounds were obtained by direct alkylation with gaseous isobutylene. Thus, *t*-butylbenzene was prepared by the butylation of benzene in the presence of the hydrate of BF_3 ($BF_3 \cdot H_2O$), while the butylation of phenol in the presence of varying amounts of sulfuric acid afforded the *o*- and *p-t*-butylphenols and *t*-butyl phenyl ether. The concentration of sulfuric acid was found to exert a pronounced influence on the course of phenol butylation. For the exclusive preparation of *p-t*-butylphenol, a 5% by weight charge of concentrated sulfuric acid is employed at 70°, while the preparation of *o-t*-butylphenol as the major product is achieved by reducing the sulfuric acid concentration to 0.1% and using lower reaction temperatures (40–45°). Under these "mild" conditions, the protonic attacks are insufficient to displace the sterically strained *o-t*-butyl group. Finally, by lowering the reaction temperature to 10°, and employing the dilute sulfuric acid catalyst and diethyl ether as the solvent, the extent of carbon alkylation is greatly reduced so that under these conditions the major product is *t*-butyl phenyl ether. The technique of preparing *t*-alkyl phenyl ethers by alkylation at low temperature and low catalyst concentration is described elsewhere.[5]

The syntheses of *m-t*-butylphenol was accomplished by a route similar to that of Read and Mullin[6] who prepared *m-n*-butylphenol. The procedure, starting with *t*-butylbenzene, was modified slightly in that the intermediate *p*-nitro-*t*-butylbenzene was reduced catalytically in 90% yield to *p-t*-butylaniline at room temperature and pressure, using hydrogen and a palladium–charcoal catalyst. This catalyst is prepared *in situ* and is described in more detail under the synthesis of *m*-isobutylphenol.

In the isobutyl series, both *o*- and *p*-isobutylphenols were prepared *via* the Fries rearrangement of phenyl isobutyrate. The resulting *o*- and *p*-hydroxyisobutyrophenones were reduced to the phenols by the Clemmensen reduction.

Isobutylbenzene was obtained in good yield by the Wolff–Kishner reduction of isobutyrophenone, using the Huang-Minlon modification. The Williamson reaction of isobutyl bromide with sodium phenoxide afforded isobutyl phenyl ether.

The preparation of *m*-isobutylphenol was accomplished by a four-step process, starting with isobutyrophenone. The nitration of isobutyrophenone, using fuming nitric acid in acetic anhydride at 0°, according to the method of Morgan and Hickenbottom,[7] formed a low melting solid product (m.p. 37°) in 60–70% yield, found to be *m*-nitroisobutyrophenone. Oxidation of this product formed *m*-nitrobenzoic acid (m.p. 141°). The reduction of the nitro compound to *m*-aminoisobutyrophenone was performed catalytically in glacial acetic acid, at room temperature and pressure, using hydrogen and a palladium–charcoal catalyst. The catalyst is prepared conveniently *in situ* by adding 8 g. of a 10% palladium chloride to the hydrogenation mixture containing 20 g. of Norite A boneblack. The amine was recovered by benzene extraction of the reaction mixture which had been made alkaline with sodium hydroxide. Diazotization and hydrolysis to the *m*-hydroxyisobutyrophenone in hydrochloric acid then followed without isolating the amine. The hydroxy compound was obtained from the nitro compound in 19% yield. The m.p. of the semicarbazone is 188° (darkening). The final reduction to *m*-isobutylphenol was achieved in 82% yield, using the Huang-Minlon modification of the Wolff–Kishner procedure. The *m*-isobutylphenol is liquid at room temperature and boils at 129.5° at 20 mm. pressure. The acetic acid derivative obtained upon reaction with chloroacetic acid melts at 90.5°. The observed neutral equivalent is 209.1, an average of two determinations. The calculated value is 208.0.

The six butylphenols were characterized as the aryloxyacetic acids, as listed in Table I.

TABLE I

PROPERTIES OF THE BUTYL COMPOUNDS

Compound	B.p., °C., at 20 mm.	M.p., °C.	Refractive index at 20°	Acetic acid derivative M.p., °C.	Neutral equivalent Obsd.	Calcd.
o-t-Butylphenol	113.0	...	....	148.0	209.0	208.0
m-t-Butylphenol	129.5	43.0	....	116.5	209.7	208.0
p-t-Butylphenol	130.0	100.0	....	96.5	209.0	208.0
o-Isobutylphenol	116.5	...	....	96.5	208.3	208.0
m-Isobutylphenol	129.5	...	....	90.5	209.1	208.0
p-Isobutylphenol	131.0	48.0	....	109.5	209.5	208.0
t-Butylbenzene	168.8[a]	...	1.4880			
Isobutylbenzene	67.5	...	1.4854			
t-Butyl phenyl ether	80.0	...	1.4869			
Isobutyl phenyl ether	93.0	...	1.4929			

[a] At 741 mm. All of the recorded temperatures are corrected values.

Pyrolyses.—Thermal decompositions of each of the ten butyl compounds were performed statically at 420.0 ± 0.1° and at initial pressures of 150 to 400 mm. The system, as detailed in Fig. 1, is so designed that the pyrolyses occur in a completely sealed, Pyrex glass system. A glass crescent gage, A, affords the means by which the pressure changes within the reaction system can be followed without exposing the organic vapors to any extraneous materials, other than the glass surfaces.

The greatest portion of the total reaction volume is confined in a 120-ml. glass reaction bulb, which contains a thermocouple well, and which is joined to the sample bulb and crescent gage by means of 2-mm. capillary tubing. The capillary system and the crescent gage are maintained at a temperature slightly below (app. 2°) the reaction bulb temperature by means of an insulated electrical winding of nichrome wire (not shown). The collective volume of the capillary system and the crescent gauge bellows is about 3 ml., which constitutes 2.5% of the total volume of the reaction system. The furnace is electrically heated, and it contains a second winding of Hitempco resistance wire which, when used in conjunction with a thyratron controller unit,

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[5] D. R. Stevens, *J. Org. Chem.*, **20**, 1232 (1955).

[6] R. R. Read and D. B. Mullin, THIS JOURNAL, **50**, 1763 (1928).

[7] G. T. Morgan and W. J. Hickenbottom, *J. Chem. Soc.*, **119**, 1884 (1921).

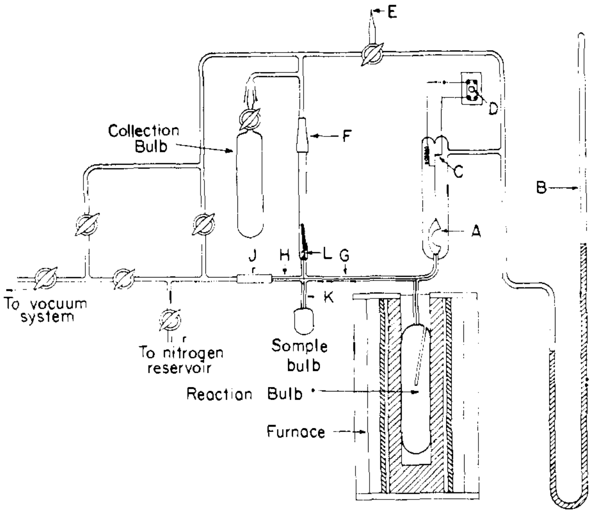

Fig. 1.—Apparatus used for the vapor phase thermal decompositions.

provides a temperature control of ±0.1 at 420°. The temperature gradient from the center of the reaction bulb to either end of the bulb is 2° at 420°.

The pyrolyses are performed as follows: A sample bulb unit is connected to the exterior system at F by means of a short piece of rubber pressure tubing and is then sealed by a torch to the capillary system at G. Approximately 0.2 cc. of liquid sample is then introduced into the sample bulb through H which is then connected to the vacuum system at J by a short piece of rubber pressure tubing. The unit is then wound with insulated heating wire, after which it is brought to temperature and flushed with dry nitrogen gas. The entire system is then degassed under high vacuum after which a portion of the liquid sample is allowed to vaporize into the vacuum system in order to ensure complete degassing of the sample. The sample bulb is then cooled and the capillary is sealed off with a torch at H. The sample is then warmed and allowed to vaporize into the evacuated reaction system, which is at the predetermined temperature, until the desired vapor pressure, 150 to 400 mm., is reached. At this point the liquid sample is quickly isolated from the reaction system by sealing off the capillary at K. The initial pressure is recorded and the change in pressure is noted at specific time intervals until the desired total change in pressure within the isolated system has been reached. A metal plunger encased in a glass capsule is then raised by means of a magnet and is allowed to drop and break the thin glass tip at L which permits the gaseous products to flow into a previously degassed and evacuated 100-cc. collection bulb at room temperature. The gaseous products so obtained were analyzed in a type 21-102 mass spectrometer (Consolidated Engineering Co.).

The kinetic data for *o*-*t*-butylphenol were obtained from pyrolyses performed at four different temperatures. These include 383.0, 392.6, 403.2 and 413.3°.

Infrared Studies.—The infrared analyses for the detection of intermolecular hydrogen bonding were made on 0.01, 0.1 and 1.0 *M* solutions of the phenols in carbon tetrachloride, using a model 12C Perkin–Elmer infrared spectrometer.

Results

The ten butylated compounds were found to undergo considerable thermal dissociation at 420.0°. In all instances, except with *t*-butyl phenyl ether, the pyrolyses proceeded at measurable rates, yielding gaseous, complex mixtures containing olefinic and paraffinic fragments composed chiefly of hydrocarbons ranging from methane to C_4-compounds. *t*-Butyl phenyl ether was observed to decompose practically spontaneously to produce phenol and isobutylene almost exclusively. Phenol was identified by the ultraviolet absorption spectrum obtained on an "isoöctane" rinse of the product collection bulb. Isobutyl phenyl ether, yielding propane, carbon monoxide and isobutylene as the major products, constitutes the only instance in which a gaseous oxygen-containing product was detected in the cleavage fragments.

Rates of Decomposition.—On the basis of thermal decomposition as noted in the percentage pressure rise *vs.* time plots, contained in Fig. 2, the compounds can be arranged in the following order of decreasing thermal stability: *m*-*t*-butylphenol > *t*-butylbenzene > *p*-*t*-butylphenol > isobutylbenzene > *m*-isobutylphenol > *p*-isobutylphenol > *o*-*t*-butylphenol > *o*-isobutylphenol > isobutyl phenyl ether > *t*-butyl phenyl ether. Thus, the ethers are observed to be least stable, while the hydrocarbons and the *m*-butylphenols are the most stable.

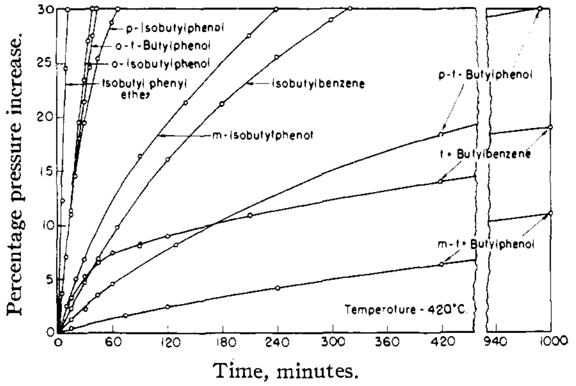

Fig. 2.—Pressure rise data.

It is recognized that the rate of pressure increase within a thermostated, static system does not afford an infallible means of diagnosing a pyrolysis reaction. Nevertheless, this convenient and widely applied technique reveals a pattern of stability which is common to both series of *t*-butyl and isobutylphenols. The order of decreasing stability is *meta* > *para* > *ortho*. A major distinction between the two series of phenols is the smaller observed difference in stability between the *ortho* and *para* isomers in the isobutylphenol series.

The rather pronounced decrease in rate of pressure rise after the rapid initial rise in the case of *t*-butylbenzene is believed to be attributable to the presence of a small amount of the thermally unstable "triisobutylenes." These materials are formed as by-products during the preparation of *t*-butylbenzene, and they are not completely separable from *t*-butylbenzene by fractional distillation.

The more detailed study of the pyrolysis of *o*-*t*-butylphenol revealed that the decomposition, as measured by rates of pressure rise in the closed system, can be expressed kinetically as a first-order reaction during the first 20 to 30% pressure rise. After this point the rates fell off appreciably. Consequently, the rate constant *k* at a given temperature was obtained by averaging the values for the reasonably linear first-order portion of the reaction, using the expression

$$k = \frac{1}{t}\, 2.3 \log \frac{1}{x}$$

where x, the mole fraction of *o*-*t*-butylphenol at time t, $= (P_t - 2\,\Delta P)/p_t$. The observed pressure in mm. at time t is designated by P_t, while ΔP is the pressure change. This treatment is based on the observation that the total pressure rise ceases after about 95% increase. Therefore the reaction is assumed to be a pressure-doubling type.

The rate constants (as $k \times 10^4$) for each of four different temperatures are contained in Table II. These values were obtained by averaging the rate constants from three runs at each temperature.

The plot of log $(1/k)$ *vs.* $1/T$, °K., as shown in Fig. 3, indicates a straight line relationship. The activation energy, calculated from the slope of the curve in accordance with the Arrhenius equation, is 58.4 kcal./mole.

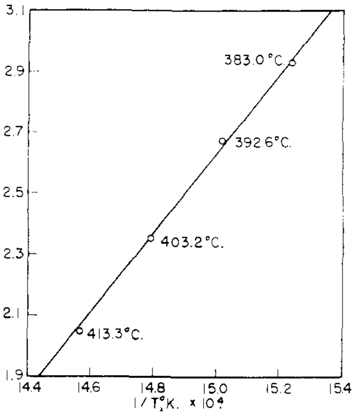

Fig. 3.—Plot of log $1/k$ *vs.* $1/T$, °*K* for the thermal decomposition of *o*-*t*-butylphenol.

Results based on total pressure change of a complex reaction in a closed system are always open to question, and consequently no pretense of precise interpretation of the data is intended. However, if one assumes that the initiating and rate-controlling step in the pyrolysis of *o*-*t*-butylphenol is the cleavage of a "strained" C–CH_3 bond in the *t*-butyl group, one can further assume that a measured increment of pressure rise during the early stages of the reaction can provide a measure of the decrease in the concentration of *o*-*t*-butylphenol. Further, it can be said that the results are reasonable, that the composite activation energy is lower than the values of 60 to 80 kcal./mole reported for most organic thermal decompositions.

Products of Decomposition.—From an inspection of the gross analyses of the gaseous products of decomposition, in Table III, it is again evident that a similarity exists between the two series of *t*-butyl and isobutyl compounds. Thus, both *ortho* isomers yield a preponderance of olefins, while the *meta* and *para* isomers, as well as the hydrocarbons, produce larger amounts of paraffins. In these analyses, the C_3- and C_4-hydrocarbons include the composite values for propane, propylene, isobutane and isobutylene. Only minor amounts of *n*-butane and insignificant quantities of C_5 or higher hydrocarbons were found.

The above values, in mole per cent., were obtained by averaging the data from three runs performed on each compound. Only in the case of *t*-butylbenzene was there any appreciable variation in composition of the cleavage products with contact time, an observation which again may arise from the presence of small amounts of thermally unstable "triisobutylenes" in the sample of *t*-butylbenzene.

The individual analyses are recorded in Table IV. They again show some general similarities between the two series of butylphenols, and they reveal the variation in cleavage products as a function of the location of the butyl group. A preponderance of propylene characterizes the pyrolyses of the *ortho* compounds, while pronounced methane production attends the pyrolyses of the *meta* compounds. *p*-*t*-Butylphenol and *p*-isobutylphenol yield somewhat less methane than their *meta* isomers and they afford relatively large amounts of isobutane and propane, respectively. The gaseous hydrocarbon products from isobutylbenzene are strikingly similar to those from *m*-isobutylphenol.

Infrared Absorption.—The infrared absorption curves for the *ortho* and *meta* isomers are presented in Figs. 4 and 5 wherein the transmitted energy is plotted *vs.* wave number. Thus the absorption maxima are represented by minima. The absorption band at 3615 cm.$^{-1}$ (2.7μ) is the characteristic band of an unperturbed hydroxyl group while that at 2940 cm.$^{-1}$ (3.4μ) is the carbon–hydrogen absorption band. The broader bands around 3330 cm.$^{-1}$ (3.0μ) in sufficiently concentrated solutions are characteristic of hydroxyl groups in the hydrogen-bonded complexes. The curves for each isomer are displaced with respect to one another along the vertical axis in order to facilitate comparison.

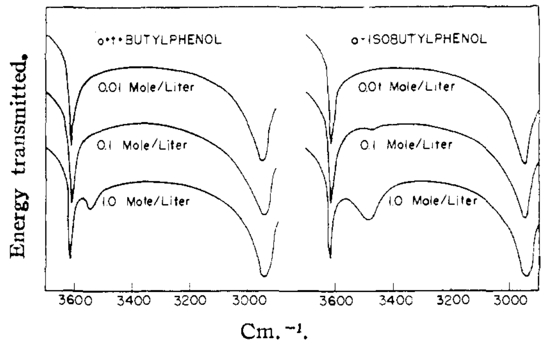

Fig. 4.—Infrared absorption spectra in the hydroxyl region for the *o*-butylphenols.

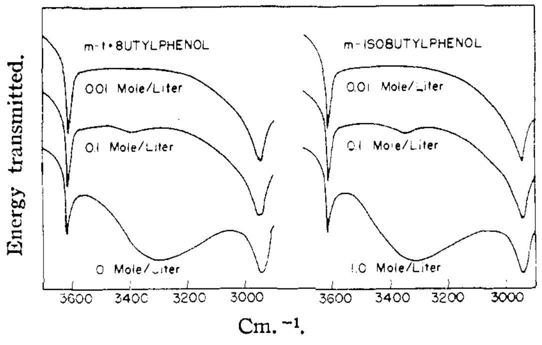

Fig. 5.—Infrared absorption spectra in the hydroxyl region for the *m*-butylphenols.

TABLE II

KINETIC DATA FOR THE THERMAL DECOMPOSITION OF *o-t*-BUTYLPHENOL

Temperature, °C.	$k \times 10^4$
383.0	11.72 ± 0.44
392.6	21.12 ± .60
403.2	44.39 ± .59
413.3	89.75 ± .85

TABLE III

COMPOSITION OF THE GASEOUS HYDROCARBONS IN THE DECOMPOSITION PRODUCTS

Compound decomposed	Mole per cent. paraffins	Mole per cent. olefins	Mole per cent. C_3- and C_4-hydrocarbons
o-t-Butylphenol	25	74	75
o-Isobutylphenol	29	69	71
m-t-Butylphenol	83	10	24
m-Isobutylphenol	78	17	22
p-t-Butylphenol	86	12	38
p-Isobutylphenol	87	11	38
t-Butylbenzene	65	27	33
Isobutylbenzene	68	25	30

TABLE IV

INDIVIDUAL GASEOUS HYDROCARBONS IN THE DECOMPOSITION PRODUCTS

	Mole per cent. of various gaseous cleavage products					
Compound pyrolyzed	Methane	Propane	Propylene	Isobutane	Isobutylene	Hydrogen
o-t-Butylphenol	20	3	56	..	16	1
o-Isobutylphenol	24	3	66	..	2	2
m-t-Butylphenol	66	12	6	2	4	7
m-Isobutylphenol	69	6	14	..	2	5
p-t-Butylphenol	58	9	4	17	8	2
p-Isobutylphenol	57	28	8	..	2	2
t-Butylbenzene[a]	41	10	6	8	19	8
Isobutylbenzene	60	6	19	..	5	7
t-Butyl phenyl ether	1	1	..	4	93	..
Isobutyl phenyl ether[b]	9	26	7	3	22	..

[a] Some ethane, 3 mole per cent., also was found. [b] Products included 24% carbon monoxide and 7% ethane.

The curves of the two *para* isomers are not included, for they were found to be identical with those from the *meta* isomers.

Discussion

The pyrolyses data become more revealing when they are considered as differences in rates and products as functions of the structure and location of the butyl groups. If one assumes that the resonance polarization in phenol affords equal electron enrichment of the *ortho* and *para* carbons, the steric effects will be observed by comparing the behaviors between the *ortho* and *para* isomers. To detect the effects accorded to the resonance-electron enrichment it is necessary to compare the behaviors of the *meta* isomers with those of the *para* isomers.

Steric Effects.—The greater rates of dissociation of *o-t*-butyl- and *o*-isobutylphenol, when compared to their *para* isomers, reflect the presence of steric strain in the *ortho* isomers. On the basis of these differences it appears that the "steric interaction" is greater in *o-t*-butylphenol than in *o*-isobutylphenol. The observation that the rate difference between the *o*- and *p-t*-butylphenols is greater than that between the *o*- and *p*-isobutylphenols affords this conclusion. It is in accord with the results of the infrared studies on hydrogen bonding, and with an examination of the Taylor–Hirschfelder atom models. The rate data also suggest that the *t*-butyl group is inherently more stable toward thermal dissociation than the isobutyl group.

On the basis of the major hydrocarbon products, propylene and methane, which are formed from the two *ortho* isomers, one can postulate that the sterically crowded butyl groups undergo C–C cleavage to yield methyl radicals and the corresponding *o*-hydroxyphenylisopropyl radicals. These large radicals then dissociate into *o*-hydroxyphenyl radicals and a lower olefin, propylene. Some of the methyl radicals strip hydrogen atoms from donor molecules and appear as methane.

The production of isobutylene from *o-t*-butylphenol can be interpreted as a result of C–H bond scission on the *t*-butyl group, additionally motivated by steric strain, to form the *o*-hydroxyphenylisobutyl radical which decomposes into isobutylene and the *o*-hydroxyphenyl radical. In *o*-isobutylphenol, the loss of an H atom from the isobutyl group produces an *o*-hydroxyphenylbutyl radical which can dissociate into propylene and a resonance-stabilized benzyl radical. This reaction, leading to propylene, seems particularly plausible if the tertiary H atom favored by a lower C–H bond energy, or a primary H atom, favored statistically, is cleaved out initially. Thus, both reactions depicted above, involving the initial loss of a methyl group or a hydrogen atom, can lead to the formation of propylene from *o*-isobutylphenol. The data, correspondingly, show that this isomer affords the greatest amount of propylene.

The pyrolyses of the *para* isomers may occur in a more unimolecular manner in which the major reaction is the expulsion of methane. The relatively small amounts of propylene and isobutylene found in the reaction products can be interpreted to reflect a much reduced methyl radical contribution to the over-all process, when compared to the *ortho* isomers.

Resonance Effects.—The fact that the *meta* isomers and the two butylbenzenes dissociate at markedly slower rates than the *para* isomers is indicative of a phenolic resonance contribution to the pyrolysis reaction, an effect which reduces the bond energies in the *p*-butyl groups. Although the decompositions of the *meta* and *para* isomers are characterized by preponderant methane production, the increase in isobutane formation (from *p-t*-butylphenol) and propane production (from *p*-isobutylphenol) are significant differences. In *p-t*-butylphenol a weakening of the C–C bond between the phenyl ring and the *t*-butyl group may exist because of the repulsive forces between two adjacent centers of high electron density. The *para* carbon of the phenol nucleus is electron enriched by the +T resonance polarization while an enhanced degree of electron density is conferred upon the central carbon atom of the *t*-butyl group because of the electron-repelling character of the methyl groups (hyperconjugation). As a result, an electrostatic repulsion reduces the C–C bond energy and increases the probability of cleavage into *p*-hydroxyphenyl and *t*-butyl radicals. The latter, to which resonance stability can be assigned because of the nine equivalent hyperconjugate forms, acquire H atoms upon collision with donor molecules to form isobutane.

In *p*-isobutylphenol, one can postulate a weakening of the bond between the α- and β-carbons of the isobutyl group. Here, the β-carbon atom requires a higher electron density because of the two electron-repelling methyl groups. The α-carbon is electron enriched by induction from the *para* carbon of the phenol nucleus. The repulsive forces then increase the probability of cleavage between the α- and β-carbons to form *p*-hydroxybenzyl and isopropyl radicals, both of which are resonance stabilized. Collision of the isopropyl radicals with H-donor molecules produces propane.

Theoretically, the butylbenzenes should resemble more closely their *m*-hydroxy derivatives for in both series the butyl groups are attached to phenyl carbons which have lower electron densities than the *ortho* and *para* carbons of the phenol nucleus. The data, accordingly, confirm this point, particularly in the isobutyl series, and thereby substantiate the proposal that butyl groups attached to high electron density phenyl carbon atoms have less thermal stability.

Decomposition of the Phenyl Ethers.—From the nature of the pyrolysis products, in Table IV, it is evident that the interposition of an oxygen atom between the butyl and phenyl groups imparts a profound change in the course of thermal dissociation, when compared to the butylphenols. If the appearance of isobutane can be taken as indicative of the transitory formation of *t*-butyl and isobutyl radicals, one must conclude that the formation of these radicals is not a major contribution to the over-all pyrolyses in both ethers.

The almost exclusive formation of isobutylene from *t*-butyl phenyl ether suggests a direct cleavage into isobutylene and phenol. The reaction may be conceived to proceed through a concerted mechanism involving a cyclic intermediate whereby incipient bonding occurs between the oxygen atom and a methyl hydrogen atom. The shift of electrons into the new bond reduces the bond energies of the O–C, and in the particular C–H bond in which the H atom is undergoing reattachment. Total O–H bonding and cleavages of the two weakened bonds results in the expulsion of isobutylene and the formation of phenol. This reaction is favored by a large statistical factor because of the nine equivalent hydrogen atoms.

The isobutyl phenyl ether, reported by Bamberger[8] to decompose into phenol and a sulfuric acid-soluble butene (presumably isobutylene), undergoes decomposition along two major routes to yield isobutylene, propane and carbon monoxide as the principal products. The production of isobutylene, by the process proposed for *t*-butyl phenyl ether, is of lower probability because of the single requisite β-hydrogen atom in the isobutyl group. The formation of almost equimolar quantities of propane and carbon monoxide suggests a molecular cleavage into benzene and an oxygen-containing fragment, such as isobutyraldehyde, which then decomposes into carbon monoxide and propane.

Hindrance to Hydrogen Bonding.—A more quantitative picture of the *ortho* steric effect is afforded by the infrared absorption data. From an inspection of the absorption curves, it is seen that for the dilute solutions, only the sharp bands at 3,615 and 2,940 cm.$^{-1}$ exist, indicating the absence of hydrogen bonding. A partial steric hindrance to hydrogen bonding is distinctly revealed, however, upon comparing the spectra from the 1.0 *M* solutions. Whereas the *meta* and *para* isomers show strong hydrogen bonding, as evidenced by the broad absorption band around 3,330 cm.$^{-1}$, a shift of about 300 cm.$^{-1}$, the two *ortho* isomers show much smaller bands at 3,545 and 3,475 cm.$^{-1}$ shifts of only 70 and 140 cm.$^{-1}$, respectively, for *o*-*t*-butylphenol and *o*-isobutylphenol. In the *meta* and *para* isomers, therefore, a close approach by interaction with several molecules is permitted, thereby forming a "hydrogen bonded polymer" which causes a large shift in the frequency of the hydroxyl band and a broad contour of the band. In the *ortho* isomers, however, the spatial proximity of the bulky alkyl groups allows the close approach of probably only one or two molecules, which accounts for the sharpness and smaller frequency shift of the hydroxyl band.

It is evident that the *t*-butyl group effects a smaller spectral shift (70 cm.$^{-1}$) than the isobutyl group which shows a shift of 140 cm.$^{-1}$ and a broader absorption band. It is apparent, therefore, that a *t*-butyl group is more effective than an isobutyl group in sterically screening a neighboring hydroxyl group from intermolecular hydrogen bonding. In other words, the *t*-butyl group has a greater hindrance capacity, an observation that is in accord with the results of thermal dissociation studies on the two series of *t*-butyl- and isobutylphenols.

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(8) E. Bamberger, *Ber.*, **19**, 1870 (1886).