Although the reported values of the chain length are qualitative, they are to our knowledge the first measured values of the chain length for isomerization, especially at conditions where little side reaction occurs. In our opinion, these data support the chain carbonium ion mechanism as proposed by Pines rather than the various molecular mechanisms that have been advanced.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER COMPANY, WILMINGTON, DELAWARE]

Hydroxyl Spectra of *o*-*t*-Butylphenols

BY ROBERT F. GODDU

RECEIVED JANUARY 19, 1960

The free hydroxyl stretching vibration in most free phenols is observed close to 3608 cm.$^{-1}$. Most previously reported intramolecular interactions shift the band to lower frequency. However in 2,6-di-*t*-butyl-substituted phenols it is at 3643 cm.$^{-1}$. This is due to the interaction between two electropositive groups rather than between the hydroxyl proton and an electronegative group. In mono-*o*-*t*-butylphenols there are two free hydroxyl stretching bands which are attributed to two conformations of the hydroxyl group relative to the *t*-butyl group. One band is at the same frequency as found for hydroxyl groups in free phenols, the other is at the frequency of 2,6-di-*t*-butyl-substituted phenols. From the intensities of the two bands it is calculated that about 8% of the molecules are in the higher frequency configuration when the 6-position is free and about 17% are in the same form when a methyl group is in the 6-position. Data are included from both the 3600 cm.$^{-1}$ fundamental hydroxyl region and the 7100 cm.$^{-1}$ first overtone region.

The interaction between phenolic hydroxyl groups and *ortho* substituents was initially observed by Wulf, Liddel and Hendricks[1] in the 7100 cm.$^{-1}$ (1.4 μ) overtone hydroxyl stretching region. This interaction, observed as doublet hydroxyl bands in *ortho*-halo-phenols, was explained by Pauling[2] as being due to the existence of *cis*- and *trans*-orientations of the hydroxyl group which lies in the plane of the benzene ring. Recent work by Baker[3] in the fundamental hydroxyl stretching region has reaffirmed the earlier work and in addition explained more fully the observed frequency shifts.

In addition to *ortho*-halo substitution, shifts of the hydroxyl stretching band to lower frequencies are caused by a wide variety of intramolecular interactions. Many of these interactions are described by Flett[4] in his review of work on hydroxyl spectra. More recently Baker[5] and Baker and Shulgin[6] have discussed other types of intramolecular bonds in phenols. All of these interactions require coplanarity of the hydroxyl group and the benzene ring. Also all of these interactions were with an electronegative group and the shift of the hydroxyl band was to lower frequency.

A recent paper by the author[7] on the determination of phenolic hydroxyl gave considerable data on the free hydroxyl stretching band in the neighborhood of 3610 cm.$^{-1}$ (2.77 μ). It was noted that most free phenolic hydroxyl groups absorbed at 3608 ± 2 cm.$^{-1}$ (2.772 ± 0.001 μ). Notable exceptions included phenols in which di-*ortho* substitution was present. In particular, di-*o*-*t*-butyl substitution shifted the free hydroxyl band to higher frequency (3643 cm.$^{-1}$ or 2.745 μ). This shift is larger than that usually attributed to the electron donating effect of alkyl groups alone when in the *m*- or *p*-positions.[5] In the table of data included in this earlier paper were three mono-*o*-*t*-butyl-substituted compounds. These latter compounds had weak absorption bands at 3643 cm.$^{-1}$ (2.745 μ) and strong bands at 3608 cm.$^{-1}$ (2.772 μ). With the limited data on these mono-*ortho*-substituted isomers, it was not clear if the higher frequency band were real or possibly due to an impurity.

Discussion of Results

A considerable number of *t*-butyl-substituted phenols have now been investigated. A typical spectrum is in Fig. 1 and the data obtained in the fundamental hydroxyl region are in Table I.

The constancy of the fraction of the total absorptivity which is observed at 3642 ± 2 cm.$^{-1}$ (2.746 ±

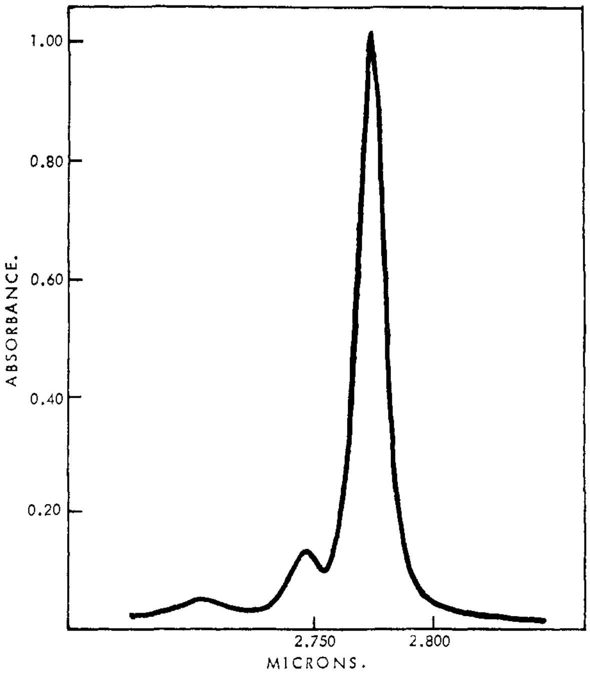

Fig. 1.—Hydroxyl spectrum of 2-*t*-butyl-5-methylphenol in the 2.75-μ region, 6.6 millimolar solution in carbon tetrachloride and run in 1-cm. cell.

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[1] O. R. Wulf, U. Liddel and S. B. Hendricks, THIS JOURNAL, **58**, 2287 (1936).

[2] L. Pauling, *ibid.*, **58**, 94 (1936).

[3] A. W. Baker, *ibid.*, **80**, 3598 (1958).

[4] M. St. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957).

[5] A. W. Baker, *J. Phys. Chem.*, **62**, 744 (1958).

[6] A. W. Baker and A. T. Shulgin, THIS JOURNAL, **80**, 5358 (1958).

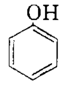
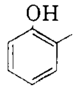
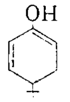
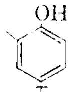
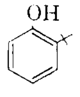
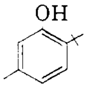
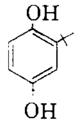
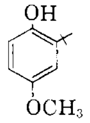
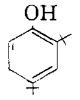
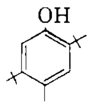
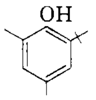
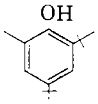
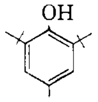
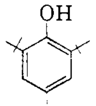
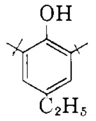
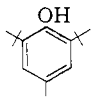
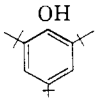
[7] R. F. Goddu, *Anal. Chem.*, **30**, 2009 (1958).

0.001 μ) would indicate that the peak is real and not due to an impurity. This indicates that there are two orientations or configurations of the hydroxyl group relative to the tertiary butyl group. These two orientations have an energy barrier between them. It is tempting to speculate that the lower frequency peak is probably due to an orientation of the hydroxyl group *trans* to the tertiary butyl group, but this is not proven in this work. Since the free electron pairs on the oxygen take up space as well as the hydrogen atom and since the exact charge distribution in *o*-*t*-butylphenols is not known, we cannot be sure which orientation is responsible for each peak. We shall, therefore, refer to the two peaks as low and high frequency forms. The difference in force constant of the two bands is observed as a shift of about 33 cm.$^{-1}$. In contrast to the usual intramolecular bonding, this type of shift might well be called intramolecular repulsion.

Since the molar absorptivities of free, unhindered phenolic hydroxyl groups are about equivalent to those of completely hindered hydroxyl groups, it appears reasonable to use the peak absorptivity to calculate directly the per cent. of the phenolic hydroxyl groups in the high and low frequency orientations. When only one *ortho*-position is occupied, about 8% of the molecules have the higher

TABLE I

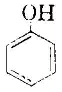
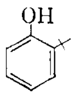
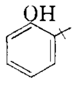
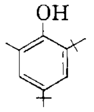
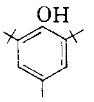
DATA ON PHENOLS AT 2.7 μ

Phenol[a]	ν max., cm.$^{-1}$	λ max., μ	Molar absorp. ε, l./mole cm.[b]	Higher freq. form, %
	3609	2.771	193	
	3609	2.771	172	
	3608	2.772	202	
	3611	2.769	168	
	3643 3605	2.745 2.774	15 167	8.2
	3640 3605	2.747 2.774	16 150	9.6
	3643 3611	2.745 2.769	13 174	7.4
	3644 3611	2.744 2.769	14 168	7.5
	3643 3606	2.745 2.773	15 183	7.6
	3642 3604	2.746 2.775	16 169	8.7
	3646 3615	2.742 2.766	26 123	17.5
	3643 3613	2.745 2.768	25 127	16.5
	3643	2.745	212	
	3643	2.745	205	
	3643	2.745	191	
	3640	2.747	197	
	3642	2.746	187	

[a] +, denotes a *t*-butyl groups; –, denotes a methyl group. [b] Solutions were about 2 to 6 millimolar in carbon tetrachloride and run in 1 cm. cells.

TABLE II

DATA ON PHENOLS AT 1.4 μ

Phenol[a]	ν max., cm.$^{-1}$	λ max., μ	Molar absorp. ε, l./mole cm.[b]	Higher freq. form, %
	7059	1.417	3.30	
	7124 7049	1.404 1.419	0.24 3.23	7.4
	7124 7054	1.404 1.418	0.24 3.66	6.6
	7128 7068	1.403 1.415	0.37 3.00	11
	7128	1.403	2.12	

[a] +, denotes a *t*-butyl groups; –, denotes a methyl group. [b] Solutions were 30 millimolar in carbon tetrachloride and run in 10-cm. cells.

frequency orientation. Substitution of a methyl group in the free *ortho*-position changes this value, as would be expected so that 17% of the molecules then have the high frequency orientation. It would be expected that substitution of bulkier groups in the 6-position would increase the absorptivity of the high frequency peak until the di-*o*-*t*-butylphenol situation was achieved.

Subsequent to this work with the fundamental hydroxyl band, a few compounds were run at the first overtone of the free hydroxyl stretching band at 1.4 μ in order to get comparative data. These data in Table II confirm the conclusions drawn from Table I. The values for the per cent. high frequency form are slightly lower but are of the same order of magnitude.

This work, in addition to the data presented, points out the value of high resolution spectra in dilute solutions for detecting minor intramolecular interactions of hydroxyl groups. Similar interactions may be detectable between *t*-butyl groups and other functional groups. Such correlations are valuable in establishing molecular configurations and explaining the reactivity of the various functional groups.

Experimental

The work at 2.7 μ was carried out on a Beckman Model DK-2 Spectrophotometer using a 2x expanded scale, scanning time of 20, time constant 0.2 and sensitivity such that a slit width of 0.12 mm. was obtained at 3619 cm.$^{-1}$ (2.763 μ) (half-intensity band-width 8 cm.$^{-1}$ or 6 mμ). The work at 1.4 μ was done on a Cary Model 14 Spectrophotometer using a slit width of 0.15 mm. at 7143 cm.$^{-1}$ (1.400 μ) (half-intensity band-width 2.6 cm.$^{-1}$ or 0.53 mμ) and a recording speed of 5Å./sec. Slit widths were set with a cell filled with dry carbon tetrachloride in the reference beam. Further details on methods of calculation, cells and solvents are in the earlier paper.[7]

All compounds are believed to be 95% pure or better. While a few were commercial samples, most were prepared here.[8]

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(8) Prepared by the Naval Stores Research Division of this Research Center. The author is particularly indebted to Drs. C. E. Smith, L. J. Filar and R. A. Bankert.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY, CAMPUS STATION, SOCORRO, NEW MEXICO]

The Volume Change of Activation in the Decomposition of Aromatic Diazonium Salts

BY K. R. BROWER

RECEIVED JANUARY 28, 1960

The volume changes of activation for the decomposition of various benzenediazonium fluoroborates in aqueous solution are nearly equal and surprisingly large. It is suggested that the leaving group does not move independently of its water of solvation and has in effect a large cross-sectional area. The product ratio for the decomposition of *p*-nitrobenzenediazonium ion in solutions containing bromide ion is insensitive to pressure and the involvement of a bimolecular process is therefore doubtful.

Introduction

The effects of hydrostatic pressure on the rates of many bimolecular reactions have been measured and the volume changes of activation calculated therefrom, but very few unimolecular reactions have been so treated. It has been shown that solvolyses of certain alkyl halides for which the S_N1 mechanism may be reliably postulated are accelerated by pressure and therefore have negative volume changes of activation.[1] This effect is ascribed to electrostriction of solvent by the polarized transition state and is analogous to the effect of pressure on the ionization constants of water and other weak acids. Measurements have also been made on the acid-catalyzed hydrolysis of formals, acetals and ethyl orthoformate which is believed to be a two step process involving equilibrium-controlled transfer of a proton followed by slow unimolecular decomposition.[2]

As an example of a simple one-stage unimolecular process uncomplicated by large changes in polarization the decomposition of aromatic diazonium salts in aqueous solution shows promise. The kinetics have been extensively investigated and except for one case which will be discussed in the next section, have been shown to be first-order with rates nearly independent of the kind and concentration of anions.[3] The effects of substituents on the rates of reaction are consistent with a carbonium-ion mechanism; for example, a *p*-nitro group greatly decreases the rate, whereas it would be expected to favor nucleophilic attack by water if such were involved.[4]

Measurement of the sign and magnitude of the volume change of activation for diazonium ion decomposition could be expected to answer at least the first and perhaps both of these two questions: whether nucleophilic attack by water occurs and whether a simple bond-breaking process results in a measurable increase in molecular volume. A negative volume change would conclusively establish the bimolecular mechanism since the reaction of a neutral molecule with an ion could only cause a slight release of electrostricted solvent,[5] and a net decrease of volume could only result from contraction along the reaction coördinate. A considerable positive volume change would tend to confirm the carbonium-ion mechanism, and its magnitude might be expected to correlate with the reactivity.

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(1) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953); H. G. David and S. D. Hamann, *ibid.*, **50**, 1188 (1954).

(2) J. Koskikallio and E. Whalley, *ibid.*, **55**, 809 (1959).

(3) H. Euler, *Ann.*, **325**, 292 (1902); J. C. Cain, *Ber.*, **38**, 2511 (1905); H. Pray, *J. Phys. Chem.*, **30**, 1417, 1477 (1926); J. E. Taylor and T. J. Feltis, THIS JOURNAL, **74**, 1331 (1952); E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 948 (1940).

(4) M. L. Crossley, R. H. Kienle and C. H. Benbrook, THIS JOURNAL, **62**, 1400 (1940).

(5) C. T. Burris and K. J. Laidler, *Trans. Faraday Soc.*, **51**, 1497 (1955).