

12. *Studies of Dipole Moments, and Sorption Characteristics at the Solution-Solid Interface, of a Series of Substituted Phenols.*

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Sorption of a series of substituted phenols from cyclohexane on activated alumina has been studied, and evidence provided that sorption is unimolecular. From the isotherm data, standard thermodynamic free-energy changes have been calculated. The apparent dipole moments of the phenols in cyclohexane and dioxan have been determined from measurements on dilute solutions. Increases in O-H bond moment, brought about by hydrogen bonding between the hydrogen atom of the hydroxyl group and the oxygen atom of the dioxan molecule, have been calculated. The results indicate that hydrogen-bond formation is responsible for the sorption process, the magnitude of the standard free-energy decrease on sorption being a reflection of the intensity of the O-H bond moment. Dipole moments of the *para*-substituted phenols in cyclohexane agree with the calculated values, indicating no interaction between the groups in the *para*-positions. The moment of 2,4,6-tribromophenol is almost identical with that of phenol, whereas the moment of 2,4,6-tri-*t*-butylphenol is between those of phenol and *t*-butyl alcohol. It is concluded that the large *t*-butyl groups in the *ortho*-positions cause steric inhibition of mesomerism in 2,4,6-tri-*t*-butylphenol.

SORPTION of a solute in solution by a solid surface is a spontaneous process, associated with a decrease in free-energy whose magnitude might be expected to manifest the intensity of the electrical forces between the sorbent surface and the sorbate molecule.

Many attempts have been made to correlate the dipole moment of the sorbate with sorbability, but Heymann and Boye,¹ Sata and Kurano,² Arnold,³ and Bhatnagar, Kapur, and Bhatnagar⁴ all conclude that it has no significance in explaining the mechanism of sorption from solution.

Molecules are sorbed with the functional group or groups in contact with the sorbent surface, and this investigation is an attempt to determine the importance of essential bond polarity in relation to thermodynamic free-energy decrease on sorption. Sorption of a series of substituted phenols from cyclohexane on activated alumina has been studied, and standard free-energy decreases associated with the sorption process evaluated. Dipole moments of the sorbates in cyclohexane and dioxan have also been determined.

EXPERIMENTAL

(1) *Sorption Studies.*—(a) *Materials.* Activated alumina suitable for chromatographic analysis, and passing a 120 mesh B.S. sieve, was stored in bulk.

Cyclohexane, dried first with anhydrous calcium chloride, then with sodium wire, was distilled, and the fraction boiling at 80.8°/760 mm., was collected.

Phenol, m. p. 41.5°, *p*-cresol, m. p. 35.0°, *p*-chlorophenol, m. p. 43.0°, and *p*-bromophenol, m. p. 64.0° were distilled, and recrystallised from light petroleum (b. p. 40–60°) *p*-*t*-Butylphenol, prepared by the Friedel-Crafts reaction from phenol and *t*-butyl chloride in the

¹ Heymann and Boye, *Kolloid Z.*, 1932, **59**, 153.

² Sata and Kurano, *ibid.*, 1932, **60**, 137.

³ Arnold, *J. Amer. Chem. Soc.*, 1939, **61**, 1911.

⁴ S. S. Bhatnagar, Kapur, and M. S. Bhatnagar, *J. Indian Chem. Soc.*, 1940, **17**, 361.

presence of anhydrous aluminium chloride and recrystallised from light petroleum, had m. p. 99.0°. Mesitol, prepared by fusion of mesitylenesulphonic acid with potassium hydroxide at 270–330° and recrystallised from methanol–water, had m. p. 70.0°. 2,4,6-Tri-*t*-butylphenol was prepared by passing isobutene into a solution of phenol in benzene, with sulphuric acid as catalyst; it was recrystallised from alcohol and had m. p. 131.0°. 2,4,6-Trichlorophenol, recrystallised from alcohol–water, had m. p. 69.0°. 2,4,6-Tribromophenol, prepared by direct bromination of phenol and recrystallised from alcohol–water, had m. p. 93.5°.

(b) *Method of sorption.* Solutions of graded concentration of each sorbate were prepared. 2.0 g. portions of alumina dried at 110° for 48 hr. were transferred directly from the drying oven to 50 ml. portions of solution contained in glass stoppered flasks. The flasks were shaken, sealed with a viscous solution of cellulose acetate in acetone, immersed in a thermostat at 35°, and allowed to attain equilibrium. After seven days the flasks were removed, and the equilibrium concentrations determined absorptiometrically on a Unicam SP.500 instrument. From initial and equilibrium concentrations amounts of solute sorbed were calculated.

TABLE I. *Sorption and free-energy data*

10^3x_0	10^3c	c/x_0	$-\Delta G^\circ$ (cal. mole ⁻¹)	10^3x_0	10^3c	c/x_0	$-\Delta G^\circ$ (cal. mole ⁻¹)
Phenol				<i>p</i> -Cresol			
0.450	0.10	—	6860	0.350	0.10	—	6720
0.520	0.25	0.48	—	0.540	0.20	—	6560
0.620	0.40	—	6220	0.680	0.48	0.70	6270
0.720	1.08	1.50	5640	0.720	0.60	—	6060
0.770	2.46	3.20	5200	0.740	0.80	—	5900
0.840	6.71	7.99	4750	0.760	1.06	1.40	5780
0.880	12.28	13.95	—	0.780	1.56	2.00	5600
0.900	18.23	20.25	3770	0.830	6.78	8.17	—
				0.820	12.37	15.09	—
<i>p</i> - <i>t</i> -Butylphenol				<i>p</i> -Chlorophenol			
0.280	0.05	—	7000	0.360	0.10	—	6740
0.440	0.20	0.45	6430	0.490	0.49	1.00	6250
0.550	1.16	2.10	5650	0.560	0.85	1.52	5810
0.590	2.17	3.68	5200	0.630	1.67	2.65	5400
0.630	6.36	10.10	4530	0.720	4.46	6.20	4830
0.645	8.82	13.67	—	0.763	7.03	9.22	—
0.655	12.24	18.69	—	0.770	10.49	13.62	4350
<i>p</i> -Bromophenol				Mesitol			
0.370	0.10	—	6750	0.128	0.01	—	7400
0.470	0.28	0.60	6470	0.186	0.04	—	6950
0.510	0.30	—	6270	0.251	0.13	—	6340
0.590	1.00	1.70	5630	0.304	0.35	—	5860
0.650	2.59	3.98	5080	0.346	0.80	2.32	5420
0.687	4.54	6.61	—	0.391	1.83	4.68	—
0.710	7.81	11.00	4480	0.441	4.05	9.19	4590
0.714	10.78	15.10	—	0.471	6.67	14.17	—
				0.490	9.52	19.42	—
2,4,6-Tri- <i>t</i> -butylphenol				2,4,6-Trichlorophenol			
0.054	2.10	39.60	—	0.260	0.05	—	6970
0.070	3.09	44.20	3710	0.400	0.20	—	6370
0.078	3.83	49.10	3640	0.470	0.63	1.35	5910
0.084	4.49	53.40	3580	0.540	1.55	2.87	5320
0.095	7.09	74.60	3320	0.566	2.31	4.09	—
0.102	9.17	89.90	3190	0.619	3.99	6.44	—
0.110	12.08	109.80	3070	0.620	6.68	10.77	4640
2,4,6-Tribromophenol							
0.360	0.11	0.30	6690				
0.380	0.15	0.39	6520				
0.420	0.29	0.70	6150				
0.450	0.54	1.21	5830				
0.464	0.90	1.93	—				
0.470	1.30	—	5320				

(c) *Sorption results.* From the straight-line nature of the plots of c/x_0 against c , evidence was obtained of the applicability of the Langmuir equation to the sorption systems studied:

$$c/x_0 = 1/x_1 b + c/x_1 \dots \dots \dots (1)$$

where c = equilibrium concentration in moles. l^{-1} , x_0 = moles of solute sorbed per 2 g. of alumina at equilibrium, x_1 = moles sorbed per 2 g. of alumina at saturation, and b = constant. Slopes were measured and x_1 calculated for each sorbate.

If t = thickness of sorbed film in cm., and s = surface area of 2 g. of alumina in $cm.^2$, then the standard free-energy change per mole (ΔG°) on sorption is

$$\Delta G^\circ = -RT \ln (10^8 x_0/stc) \dots \dots \dots (2)$$

TABLE 2

100w	ϵ	n_D	100w	ϵ	n_D	100w	ϵ	n_D	100w	ϵ	n_D
Phenol in cyclohexane			Phenol in dioxan			<i>p</i> -Chlorophenol in cyclohexane			<i>p</i> -Chlorophenol in dioxan		
0·000	2·0214	1·4240	0·000	2·2135	1·4200	0·000	2·0218	1·4238	0·000	2·2113	1·4202
0·258	2·0265	1·4242	0·196	2·2235	—	0·225	2·0302	1·4240	0·290	2·2344	—
0·571	2·0340	1·4243	0·290	2·2278	—	0·398	2·0361	1·4242	0·482	2·2505	—
0·779	2·0381	1·4245	0·411	2·2346	—	0·615	2·0443	1·4243	0·673	2·2657	—
1·091	2·0441	1·4249	0·482	2·2380	—	0·822	2·0513	1·4245	0·864	2·2809	1·4213
1·250	2·0478	—	0·575	2·2427	—	1·002	2·0578	1·4246	2·240	—	1·4230
2·065	—	1·4256	0·860	—	1·4212	2·333	—	1·4248	3·820	—	1·4250
3·416	—	1·4268	1·975	—	1·4227	4·191	—	1·4273			
3·798	—	1·4271	2·750	—	1·4238						
<i>p</i> -Cresol in cyclohexane			<i>p</i> -Cresol in dioxan			<i>p</i> -Bromophenol in cyclohexane			<i>p</i> -Bromophenol in dioxan		
0·000	2·0185	1·4238	0·000	2·2135	1·4198	0·000	2·0205	1·4238	0·000	2·2077	1·4199
0·293	2·0237	1·4240	0·207	2·2223	—	0·236	2·0265	1·4241	0·105	2·2138	—
0·543	2·0282	1·4242	0·382	2·2293	—	0·427	2·0318	1·4242	0·207	2·2191	—
0·817	2·0327	1·4244	0·418	2·2313	—	0·542	2·0341	1·4243	0·340	2·2272	—
1·060	2·0374	1·4246	0·579	2·2381	—	0·826	2·0414	1·4245	0·434	2·2327	—
1·292	2·0415	1·4247	0·758	2·2455	—	1·042	2·0464	1·4247	0·582	2·2410	1·4206
1·909	—	1·4250	0·863	—	1·4209				2·932	—	1·4234
			1·906	—	1·4222				5·465	—	1·4265
			2·901	—	1·4235						
<i>p</i> - <i>t</i> -Butylphenol in cyclohexane			<i>p</i> - <i>t</i> -Butylphenol in dioxan			2,4,6-Trichlorophenol in cyclohexane			2,4,6-Trichlorophenol in dioxan		
0·000	2·0212	1·4238	0·000	2·2147	1·4199	0·000	2·0194	1·4238	0·000	2·2122	1·4199
0·301	2·0249	1·4240	0·094	2·2178	—	0·249	2·0225	1·4242	0·200	2·2173	—
0·524	2·0292	1·4242	0·190	2·2217	—	0·549	2·0251	—	0·482	2·2246	—
0·833	2·0335	1·4244	0·313	2·2255	—	0·944	2·0294	—	0·674	2·2296	—
1·026	2·0362	1·4246	0·408	2·2293	—	1·281	2·0332	1·4250	0·864	2·2347	1·4209
1·323	2·0407	1·4247	0·502	2·2320	1·4205	1·653	2·0368	—	1·500	—	1·4217
1·420	—	1·4249	2·912	—	1·4230	2·871	—	1·4260	2·240	—	1·4226
1·704	—	1·4252	5·769	—	1·4261	3·746	—	1·4267	3·140	—	1·4238
Mesitol in cyclohexane			Mesitol in dioxan			2,4,6-Tribromophenol in cyclohexane			2,4,6-Tribromophenol in dioxan		
0·000	2·0208	1·4238	0·000	2·2110	1·4202	0·000	2·0203	1·4240	0·000	2·2134	1·4200
0·261	2·0241	—	0·196	2·2165	1·4205	0·235	2·0223	—	0·106	2·2156	—
0·497	2·0274	1·4241	0·382	2·2220	—	0·371	2·0230	—	0·491	2·2225	—
0·546	2·0278	—	0·580	2·2275	—	0·760	2·0265	1·4245	0·569	2·2242	—
0·719	2·0301	1·4243	0·770	2·2336	—	1·059	2·0291	1·4248	0·712	2·2267	—
0·943	2·0328	1·4245	0·960	2·2390	—	1·560	2·0325	—	0·902	2·2303	1·4212
1·961	—	1·4255	1·000	—	1·4215	2·622	—	1·4260	1·250	—	1·4216
4·215	—	1·4267	1·620	—	1·4223	3·991	—	1·4271	2·070	—	1·4226
			1·940	—	1·4227				2·970	—	1·4238
			2·390	—	1·4233						
2,4,6-Tri- <i>t</i> -butylphenol in cyclohexane			2,4,6-Tri- <i>t</i> -butylphenol in cyclohexane			2,4,6-Tri- <i>t</i> -butylphenol in dioxan			2,4,6-Tri- <i>t</i> -butylphenol in dioxan		
0·000	2·0203	1·4240	1·342	2·0338	—	0·000	2·2112	1·4202	0·860	2·2237	1·4211
0·510	2·0251	—	1·604	—	1·4253	0·310	2·2158	—	2·000	—	1·4222
0·865	2·0284	—	1·809	2·0374	—	0·490	2·2183	—	2·953	—	1·4230
1·040	—	1·4246	3·860	—	1·4265	0·670	2·2209	—	5·736	—	1·4258
1·270	—	1·4250									

Assuming that sorption is unimolecular, we took the thickness of the sorbed layer to be 4×10^{-8} cm. The surface area of 2 g. of alumina was determined⁵ by Brunauer, Emmett, and Teller's method from the sorption of carbon dioxide at -78.5° as 1.504×10^6 cm.². Introducing the sorption data into eqn. (2), we calculated standard thermodynamic affinities for each sorbate and plotted them against x_0 . Sorption and free-energy data are in Table 1.

(2) *Dipole Moments.*—(a) *Materials.* Dioxan and benzene were repeatedly refluxed with sodium, and then fractionally distilled under anhydrous conditions.

(b) *Apparatus and methods.* Dielectric constants and refractive indices of solutions of graded concentrations of each sorbate in cyclohexane and dioxan were determined. All measurements were made at 25.0° .

Dielectric constants, accurate to ± 0.0002 , were measured with a heterodyne-beat apparatus by using the substitution technique. The linear condenser was calibrated in "steps" with a small fixed condenser. The dielectric cell was of the type first used by Sayce and Briscoe,⁶ and the interior walls were silvered by Sugden's method.⁷ The dielectric constants of the solutions were calculated relative to the value of 2.2725 at 25° for pure benzene.

Refractive indices were measured with an Abbé refractometer of high accuracy.

The results are summarised in Table 2, where the symbols have their usual significance.

The molar orientation polarisation at infinite dilution, $P_{2\infty}$, of each phenol was calculated from the equation:

$$P_{2\infty} = 3M_2 v_1 \{ \alpha / (\epsilon_1 + 2)^2 - \nu / (n_1^2 + 2)^2 \} \dots \dots \dots (3)$$

in which M_2 = molecular weight of solute, v_1 , ϵ_1 , n_1 , are specific volume, dielectric constant, and refractive index respectively of the solvent at 25.0° , $\alpha = (d\epsilon/dw)_{w=0}$, $\nu = (dn^2/dw)_{w=0}$. α and ν were determined from the limiting slopes of the plots of ϵ against w , and n_D^2 against w .

Dipole moments (μ) were calculated from the equation:

$$\mu = 0.012812 (P_{2\infty} \times T)^{\frac{1}{2}} \dots \dots \dots (4)$$

DISCUSSION

Polarisation and sorption data are summarised in Table 3.

As is to be expected from the Van der Waals group diameters [CH_3 4.0 Å, Cl 3.6 Å, Br 3.9 Å, $\text{C}(\text{CH}_3)_3$ 5.6 Å⁸], the x_1 values of 2,4,6-tribromophenol and mesitol lie between those for 2,4,6-trichlorophenol and 2,4,6-tri-*t*-butylphenol.

The x_1 value for phenol indicates that the area occupied per molecule is 27 sq. Å. This is near to the value (24 sq. Å) quoted by Adam⁹ for phenols and other simple *para*-substituted benzene derivatives at zero compression, and therefore supports the view that the sorption is unimolecular.

Table 3 indicates that dipole moment of the sorbate determined in either cyclohexane or dioxan is unrelated to comparable free-energy decrease on sorption. The results with mesitol and 2,4,6-tri-*t*-butylphenol suggest that the difference between the moments in dioxan and cyclohexane moves in a direction parallel to ΔG° , but a plot shows that this difference is not a satisfactory magnitude for comparison. If, however, the mechanism of sorption involves hydrogen-bond formation between the hydrogen atom of the hydroxyl group and the sorbent surface, then it is reasonable to suppose that the magnitude of the O-H bond moment may be significant in interpreting variations in sorption affinity. Few and Smith^{10,11} and Smith¹² have determined the dipole moments of aniline and nuclear-substituted anilines in dioxan and benzene, and note that in most cases dipole moments in dioxan are higher than the corresponding ones in benzene. These workers attribute the

⁵ Jackson, M.Sc. Thesis, Leeds, 1958.

⁶ Sayce and Briscoe, *J.*, 1925, 315.

⁷ Sugden, *J.*, 1933, 768.

⁸ Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, 1940.

⁹ Adam, "The Physics and Chemistry of Surfaces," Oxford Univ. Press, 1941.

¹⁰ Few and Smith, *J.*, 1949, 753.

¹¹ *Idem*, *J.*, 1949, 2781.

¹² Smith, *J.* 1953, 109.

TABLE 3. Polarisation and sorption data.

Compound	Solv.*	10 ³ α	10 ² ν	$P_{2\infty}$ (c.c.)	μ (D)	$-\Delta G^\circ$ (cal. mole ⁻¹) at † $\theta = 0.7$	10 ⁵ κ_1 (eqn. 1)	Previous * values μ (D)
Phenol	C	2090	24	41.7	1.43	6100	91.7	B 1.53(4) ^a
Phenol	D	5023	39	71.0	1.86			
<i>p</i> -Cresol	C	1800	17	42.4	1.44	6500	82.0	B 25° 1.64, ^b B 1.57 ^c
<i>p</i> -Cresol	D	4251	37	68.5	1.83			
<i>p</i> - <i>t</i> -Butylphenol	C	1470	23	44.6	1.48	6300	66.5	
<i>p</i> - <i>t</i> -Butylphenol	D	3582	31	80.5	1.98			
<i>p</i> -Chlorophenol	C	3590	23	103.5	2.25	6000	77.0	B 25° 2.68, ^d B 2.22 ^e
<i>p</i> -Chlorophenol	D	8055	36	162.2	2.82			
<i>p</i> -Bromophenol	C	2510	23	94.4	2.15	6200	72.2	D 2.78, ^e B 2.12, ^e B 25° 2.25 ^e B30° 1.36 ^f
<i>p</i> -Bromophenol	D	5773	34	154.3	2.75			
Mesitol	C	1260	20	34.6	1.30	5400	50.6	
Mesitol	D	2921	37	56.4	1.66			
2,4,6-Trichlorophenol	C	1050	22	39.0	1.38	6000	66.6	B 1.62 ^g
2,4,6-Trichlorophenol	D	2600	35	72.1	1.88			
2,4,6-Tribromophenol	C	760	22	42.4	1.44	6800	48.6	B 1.56 ^g
2,4,6-Tribromophenol	D	1865	36	80.1	1.98			
2,4,6-Tri- <i>t</i> -butylphenol	C	970	19	49.2	1.55	3280	14.2	
2,4,6-Tri- <i>t</i> -butylphenol	D	1465	28	50.1	1.57			

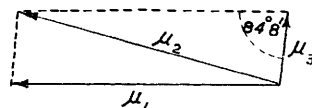
* C = Cyclohexane; D = dioxan; B = benzene.

† $\theta = \frac{\text{Moles sorbed per 2 g. of alumina at equilibrium}}{\text{Moles sorbed per 2 g. alumina at saturation}}$. Although the plots of $-\Delta G^\circ$ against κ_0 offered little choice of attributing good typical values of $-\Delta G^\circ$, it was considered that at a surface coverage of $\theta = 0.7$ reasonably comparable values are obtained.

^a Hulett, Pegg, and Sutton, *J.*, 1955, 3901. ^b Williams, *J. Amer. Chem. Soc.*, 1928, **29**, 683. ^c Donle and Gehrckens, *Z. phys. Chem.*, 1932, **13**, B, 316. ^d Williams and Fogelberg, *J. Amer. Chem. Soc.*, 1930, **52**, 1356. ^e Anzilotti and Curran, *ibid.*, 1943, **65**, 607. ^f Brown, de Bruyne, and Gross, *ibid.*, 1934, **56**, 1291. ^g Hassel and Naeshagen, *Z. physikal. Chem.*, 1931, **12**, B, 79.

higher moments in dioxan to hydrogen bonding between the hydrogen atoms of the amino-group and the oxygen atoms of the dioxan molecule. The dipole moments of the phenols can be explained in the same way, since the values in dioxan are all greater than the corresponding ones in cyclohexane. When the electronegative oxygen atom of dioxan

FIG. 1. Calculation of the angle which the C-OH group moment in phenol makes with the C-O bond.



approaches the hydrogen atom of the hydroxyl group, and a hydrogen bond forms, the valency electrons of the O-H bond will presumably be displaced to a limited extent towards the oxygen atom of the hydroxyl group, thereby increasing the bond moment.

In calculating increases in O-H bond moment, arising from hydrogen bonding, a C-O-H valency angle of 115° is assumed.¹³ The angle which the C-OH group moment in phenol makes with the C-O bond is calculated by Marsden and Sutton's method¹⁴ from the dipole moments of phenol μ_1 (1.43 D), *p*-cresol μ_2 (1.44 D), and toluene μ_3 (0.37 D) to be $84^\circ 8'$ (Fig. 1).

The moments $\mu_{\text{O-H}}$ and $\mu_{\text{O-C}}$ associated with the O-H and O-C bonds in phenol are calculated to be 1.57 D and 0.52 D respectively, the oxygen atom being at the negative end of each dipole (Fig. 2). Assuming that the increase in O-H bond moment due to hydrogen bonding in dioxan is equal to the decrease in C-O bond moment due to an increased mesomeric effect, we can calculate this bond-moment increment $\Delta\mu$ from equation (5):

$$\mu_{\text{D}}^2 = (1.57 + \Delta\mu)^2 + (\mu_{\text{PhX}} + 0.52 - \Delta\mu)^2 + 2(1.57 + \Delta\mu)(\mu_{\text{PhX}} + 0.52 - \Delta\mu) \cos 115^\circ \quad (5)$$

¹³ Anzilotti and Curran, *J. Amer. Chem. Soc.*, 1943, **65**, 607.

¹⁴ Marsden and Sutton, *J.*, 1936, 599.

where μ_D is the observed dipole moment in dioxan and μ_{PhX} the moment of the mono-substituted benzene compound in dioxan. The following values have been taken for the moments of the parent monosubstituted benzenes: toluene 0.37, *t*-butylbenzene 0.53, chlorobenzene -1.58, and bromobenzene -1.56, it being assumed that these moments determined in benzene, remain unaltered in dioxan.

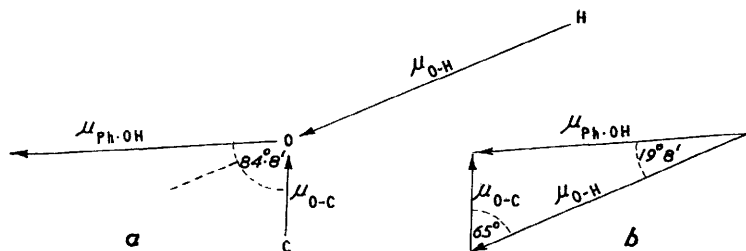


FIG. 2. Calculation of μ_{O-H} and μ_{O-C} in phenol.

Smith and Walshaw,¹⁵ in their studies of the dipole moments of *para*-substituted anilines, calculated by vector combination the additional moments along the N-C bond ($\Delta\mu_{vect}$) required to explain the observed increased dipole moments in dioxan. It is

TABLE 4.

Compound	$\Delta\mu_{vect}$ (D)	μ_B (D)	Compound	$\Delta\mu$ (D)	μ_C (D)
Aniline	0.33	1.53 ¹⁰	Phenol	0.35	1.43
<i>p</i> -Toluidine	0.31	1.32 ¹⁵	<i>p</i> -Cresol	0.41	1.44
<i>p</i> -Chloroaniline	0.40	3.01 ¹¹	<i>p</i> -Chlorophenol	0.35	2.25
<i>p</i> -Bromoaniline	0.38	3.01 ¹⁵	<i>p</i> -Bromophenol	0.32	2.15
<i>p</i> - <i>t</i> -Butylaniline	—	—	<i>p</i> - <i>t</i> -Butylphenol	0.57	1.48
2,4,6-Trichloroaniline	—	—	2,4,6-Trichlorophenol	0.37	1.38
2,4,6-Tribromoaniline	0.33	1.73 ^a	2,4,6-Tribromophenol	0.44	1.44
2,4,6-Tri- <i>t</i> -butylaniline	—	—	2,4,6-Tri- <i>t</i> -butylphenol	0.13	1.55
Mesidine	0.19	1.40 ²¹ 1.45 ¹²	Mesitol	0.20	1.30

μ_B = dipole moment in benzene; μ_C = dipole moment in cyclohexane.

^a Few and Smith, *J.*, 1949, 2663. Other refs. as in text.

expected that hydrogen bonding in dioxan would affect to approximately the same extent the electron-density distribution along the O-C bond in the case of *para*-substituted phenols ($\Delta\mu$). Table 4 shows that $\Delta\mu_{vect}$ values are comparable in magnitude with $\Delta\mu$ values, thus providing grounds for the application of eqn. (5).

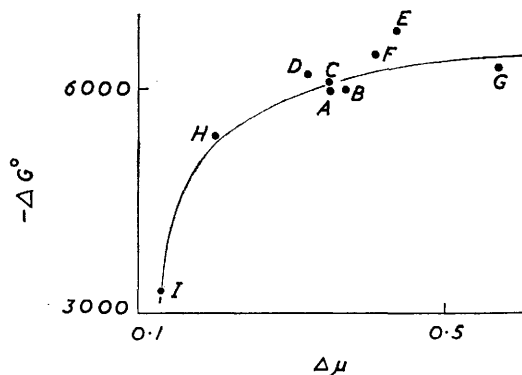


FIG. 3. Relationship between free energy decrease on sorption, and O-H bond moment increment.

A, *p*-Chlorophenol; B, 2,4,6-Trichlorophenol; C, Phenol; D, *p*-Bromophenol; E, 2,4,6-Tribromophenol; F, *p*-Cresol; G, *p*-*t*-Butylphenol; H, Mesitol; I, 2,4,6-Tri-*t*-butylphenol.

Evidence that hydrogen bonding contributes to the mechanism of sorption of the phenols on alumina is provided by a comparison of free-energy decreases with $\Delta\mu$ values (Fig. 3). The relatively small values of $\Delta\mu$ and $-\Delta G^\circ$ for 2,4,6-tri-*t*-butylphenol indicate

¹⁵ Smith and Walshaw, *J.*, 1957, 3217.

that the steric effect of the large *t*-butyl groups in the *ortho*-positions permit only weak hydrogen bonding with either the dioxan molecule or the sorbent surface. Some steric opposition to hydrogen bonding exists in the case of mesitol, but the effect is much less pronounced, as is evident from the greater values of $\Delta\mu$ and $-\Delta G^\circ$.

Presence of the groups CH_3 , Cl, or Br *para* to the hydroxyl group produces little change in either the O-H bond-moment increment of phenol or the sorptive affinity of the compound for alumina, indicating negligible interaction between the two groups in the *para*-positions. Confirmation is provided by agreement between calculated and observed dipole moments of the *para*-substituted phenols. Assuming no interaction between the groups in the *para*-positions, we calculated the following moments in cyclohexane from equation (6): phenol 1.43, *p*-cresol 1.44, *p*-*t*-butylphenol 1.47, *p*-chlorophenol 2.24, *p*-bromophenol 2.22. The absence of interaction between *para*-groups seems surprising in

$$\mu_{\text{calc.}}^2 = 1.43^2 + \mu_{\text{PhX}}^2 + 2(1.43)(\mu_{\text{PhX}}) \cos 84^\circ 8' \quad \dots \quad (6)$$

view of Hulett, Pegg, and Sutton's¹⁶ observations that changes of dipole moment which occur when trimethylamine forms complexes with *p*-cresol, phenol, and *p*-chlorophenol in cyclohexane increase with the acid dissociation constants in water, presumably because of an increase of the O-H bond moment. They also observe fairly good proportionality between the square of the dipole-moment change and the association constant for the complex in cyclohexane.

Moments of the symmetrically trisubstituted phenols summarised in Table 4 are noteworthy in the light of Smith's¹⁷ review of dipole-moment evidence for steric inhibition of mesomerism. In support of the evidence obtained by Smith and Walshaw¹⁸ against any appreciable steric inhibition of mesomerism in 2,4,6-tribromoaniline, the moment of 2,4,6-tribromophenol is found to be almost identical with that of phenol. The moment of 2,4,6-tri-*t*-butylphenol is intermediate between that of phenol and *t*-butyl alcohol (1.66 D),¹⁹ and it is concluded that mesomerism is hindered sterically in the trisubstituted phenol by the large *t*-butyl groups in the *ortho*-positions. The moment of 2,4,6-trichlorophenol is slightly smaller than that of phenol, and this could be explained by the electron attraction of the *ortho*-chlorine atoms slightly increasing the mesomeric effect of the hydroxyl group. The moment of mesitol in benzene has been reported to be much lower than that of phenol,²⁰ and the present measurements in cyclohexane confirm this order. This result is hard to understand since some inhibition of mesomerism is present in durenol, the moment of which is reported to be much higher than that of phenol.²¹

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¹⁶ Hulett, Pegg, and Sutton, *J.*, 1955, 3901.

¹⁷ Smith, "Electric Dipole Moments," Butterworths Scientific Publications, London, 1955, p. 211.

¹⁸ Smith and Walshaw, *J.*, 1957, 4527.

¹⁹ Maryott, *J. Amer. Chem. Soc.*, 1941, **63**, 3079.

²⁰ Brown, De Bruyne, and Gross, *ibid.*, 1934, **56**, 129.

²¹ Ingham and Hampson, *J.*, 1939, 981.