height of 3500 calories per mole may be used, in the temperature range of interest, in estimating their thermodynamic contributions from the tables of Pitzer and Gwinn[6] without introducing an error larger than the other uncertainties. With estimated values for the three remaining frequencies, the thermodynamic properties can be calculated with an accuracy adequate for engineering purposes in the initial or appraisal stages.

Acknowledgment.—One of us (W. F. E.) wishes to thank the Research Corporation for a grant which made the purchase of the fast Raman spectrograph possible.

Summary

1. The Raman spectrum of C_3F_8 has been obtained in the liquid state at $-65°$.

2. The infrared spectrum has been obtained at 25° and at pressures ranging from 1.5 to 500 mm.

3. Although it is not now possible to make an accurate assignment of the observed frequencies, it is believed that twenty-two of the twenty-seven fundamentals have been located.

Iowa City, Iowa
St. Paul, Minn.
Received January 9, 1950

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[6] K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

[Contribution from the Ovaltine Research Laboratories]

The Ultraviolet Absorption Spectra of Some Hydroxynaphthalenes

By C. Daglish

In a preliminary note[1] it was shown that the "apparent vitamin C"[2] of the walnut was probably a hydrojuglone derivative. The evidence for this was based on the findings that it could be hydrolyzed to juglone, and that its ultraviolet absorption curve showed similarities with those of α-hydrojuglone and the reduced form of acetoxyjuglone. It is now known that this substance is glycosidal in nature with the sugar moiety attached at the 5-position of α-hydrojuglone. Although a full description of its isolation and the determination of its structure will be published in the near future, several points arose during the spectroscopic examination of similar compounds that suggested further examination of the hydroxynaphthalenes in order to correlate, if possible, structure with absorption curves.

Discussion of Results

Naphthalene in 95% ethanol (Fig. 1), showed three well-defined regions of absorption with the values

$\lambda_{max.}$ Å., *ca.*	2200	2500–2900	2950–3200
log ε	5	3.2–3.7	2.3–2.5

Similar curves have been reported for hexane solutions[3,4] and the three absorbing regions ascribed[4] to separate states of electronic excitation of the molecule. The presence of these three regions in the curves of most of the simple derivatives examined suggested that absorption was due to the naphthalene molecule as a whole. However the curve was affected both by the nature and the position in the molecule, of the substituent, as previously shown by de Laszlo.[5]

Monohydroxynaphthalenes.—Compared with that of naphthalene, the curve of 1-naphthol in ethanol (Fig. 1) showed a general shift to the red end of the spectrum, with an overlapping of the second and third bands, and a loss of the well-defined subsidiary peaks. The 2200-Å. band was also broadened. However, there was not the increase in intensity found for hexane solutions of the alkyl naphthalenes.[3] 2-Naphthol (Fig. 1) showed no such general bathochromic effect save in the third region, which showed also a tenfold increase in intensity. This had the effect of splitting the lower intensity portion of the curve into two. This division was seen in almost all of the further substituted 2-naphthols, and was quite characteristic.

Lewis and Calvin[6] suggested that light was absorbed by polarized forms which contribute to the general resonance structure of the molecule. By suppressing the electron-donating hydroxyl groups by acetylation, diminution of the particular polarized structures responsible for the curves of 1- and 2-naphthols would be expected. The curves in Fig. 3 of the acetoxynaphthalenes show that there was a reversion to the original naphthalene curve, though with less well-defined subsidiary peaks, the 1-derivative being distinguished by less resolution of the low intensity region. In these acetates, the acetyl group also acted as an electron-acceptor, since the curves obtained were almost identical with those of the corresponding sulfonic acids (Fig. 2).

The distinctions between the 1- and 2-derivatives in neutral and acid solutions were again observed in alkaline solution (Figs. 9 and 14). In both derivatives, although there was a further bathochromic shift and a general smoothing of the curve, the characteristic three peaks were present in 2-naphthol but two only in the 1-derivative.

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[1] Daglish and Wokes, *Nature*, **162**, 179 (1948).

[2] Wokes, *et al.*, *ibid.*, **152**, 15 (1943).

[3] Morton and de Gouveia, *J. Chem. Soc.*, 916 (1934).

[4] Hirshberg and Jones, *Can. J. Research*, **27**, Sect. B, 437 (1949).

[5] de Laszlo, *Proc. Roy. Soc.* (*London*), **A111**, 355 (1926).

[6] Lewis and Calvin, *Chem. Revs.*, **25**, 273 (1939).

The introduction of further groups into the naphthol molecule, especially electron-accepting sulfonic acid groups, would stabilize the dipole. This would then contribute more to the resonance of the molecule and lower its energy level. The general shape of the curve would not be altered by this further substitution, but there should be a slight shift toward the red end of the spectrum. This was found to be approximately true, as shown by the curves in Figs. 4, 5 and 6 and the data of Tables I and II.

TABLE I

ULTRAVIOLET ABSORPTION IN ACID ETHANOL OF 1-NAPHTHOLSULFONIC ACIDS

1-OH		1-OH 2-SO₃H		1-OH 4-SO₃H		1-OH 5-SO₃H		1-OH 6-SO₃H	
λmax.	log ε	λmax.	log ε	λmax.	log ε	λmax.	log ε	λmax.	log ε
2330	4.52	2370	4.58	2340	4.50	2410	4.46	2450	4.57
		$\underline{2400}$	4.57						
$\underline{2850}$	3.65	2865	3.64						
2955	3.71	2940	3.64	3000	3.85			$\underline{2960}$	3.51
$\underline{3080}$	3.60	3140	3.51	$\underline{3200}$	3.64	3115	3.66	3040	3.52
3230	3.42	3280	3.57			$\underline{3230}$	3.62	3190	3.48
								3340	3.50

Figures underlined denote inflections.

TABLE II

ULTRAVIOLET ABSORPTION IN ACID ETHANOL OF 2-NAPHTHOLSULFONIC ACIDS

2-OH		2-OH 1-SO₃H		2-OH 6-SO₃H		2-OH 3,6(SO₃H)₂		2-OH 6,8(SO₃H)₂	
λmax.	log ε	λmax.	log ε	λmax.	log ε	λmax.	log ε	λmax.	log ε
2260	4.86	2290	4.78	2330	4.85	2370	4.89	2370	4.75
		$\underline{2450}$	3.99						
		$\underline{2570}$	3.38						
2650	3.59	2690	3.59			$\underline{2600}$	3.51		
2740	3.67	2780	3.67	$\underline{2720}$	3.66	2730	3.62	$\underline{2780}$	3.65
2850	3.52	2900	3.58	2800	3.71	2825	3.61	2870	3.75
				$\underline{2880}$	3.62	$\underline{2950}$	3.37	$\underline{2950}$	3.69
3200	3.24	3215	3.39	3190	3.11	$\underline{3320}$	3.20	$\underline{3300}$	3.44
3300	3.31	3330	3.43	3320	3.13	3420	3.23	3380	3.48

The above results with simple substituent groups agree with those found by Hirshberg and Jones,[4] who, using the postulates of Scheibe[7,8] and of Lewis and Calvin,[6] interpreted them as the effect of excitation of polarized structures by vectorized electric moments of light. They[4] associated the second naphthalene band with a vector along an axis parallel to the linkage common to the two rings. From their results and the present findings, it would appear that the low intensity third region of absorption was associated with an electric vector normal to the first.

Naphthalenediols.—de Laszlo,[9] using hexane solutions of the fourteen isomeric dichloronaphthalenes, was able to distinguish these spectroscopically as *aa*, *ab*, and *bb* compounds. All the naphthalenediols have not been examined in the present study, but sufficient differences have been found to suggest that the above classification is, for these, an over-simplification of the problem.

The introduction of the second hydroxyl into the corresponding position in the unattacked ring as the first, as in 1,5-naphthalenediol, had very little effect upon the wave length of absorption, as shown in Fig. 7. Morton and Stubbs[10] found with benzene that, when the introduction of a transparent group into the molecule had an appreciable effect upon the wave length, the introduction of a second such group had very much less effect. In the case of the 1,5 diol, although there was no further change in position, the intensity of absorption was almost double that of the monohydroxy compound. This is shown in Tables III and IV, which contain data on the corresponding mono- and disulfonic acids (Figs. 2 and 8) to show that with these also, the approximate doubling of intensity holds.

TABLE III

ULTRAVIOLET ABSORPTION IN ETHANOL OF 1- AND 1,5-DERIVATIVES

1-OH		1,5-(OH)₂			1-SO₃H		1,5-(SO₃H)₂		
λmax.	log ε	λmax.	log ε	log dε	λmax.	log ε	λmax.	log ε	log dε
2330	4.52	2260	4.85	0.33	2240	4.84	2270	4.82	
$\underline{2850}$	3.65	$\underline{2880}$	3.78	.13			$\underline{2670}$	3.59	
2955	3.71	2990	3.89	.18	2745	3.77	2770	3.88	0.11
$\underline{3080}$	3.60	3160	3.80	.20	2830	3.83	2830	3.98	.15
3230	3.43	3300	3.74	.31	$\underline{2930}$	3.65	2980	3.84	.19
					3150	2.63	3180	2.93	.30

Figures underlined denote inflections.

TABLE IV

ULTRAVIOLET ABSORPTION IN KCl–BORATE BUFFER *p*H 10 OF 1- AND 1,5-HYDROXYNAPHTHALENES

1-OH		1,5-(OH)₂		
λmax.	log ε	λmax.	log ε	log dε
2450	4.31	2250	4.55	0.24
$\underline{3245}$	3.78			
3315	3.79	3300	3.96	0.17
		$\underline{3400}$	3.94	

Introduction of the second group into the similar position in the same ring, as in 1,4-naphthalenediol, gave an entirely different absorption curve as shown in Figs. 7 and 9. There was a marked bathochromic shift from that of the mono-derivative with approximately the same intensity of absorption. These differences were maintained in alkaline as well as neutral and acid solutions.

The apparent difference in the polarizations of the molecule responsible for the curves of the 1,4- and 1,5-diols, depends largely upon the suppression of the ionization of the two opposed hydroxyls in the same ring of the 1,4-diol. A similar effect is seen in the decrease of acidic dissociation of benzoic acid on para substitution of hydroxyl. It is also suggested by the curves obtained on 5-acetoxy- and 5-glucosido-1,4-naphthohydroquinones (Fig. 10). As shown above, acetylation of 1-naphthol gave a curve similar to that of the parent compound, whilst the observed curves of the substituted 1,4-diols

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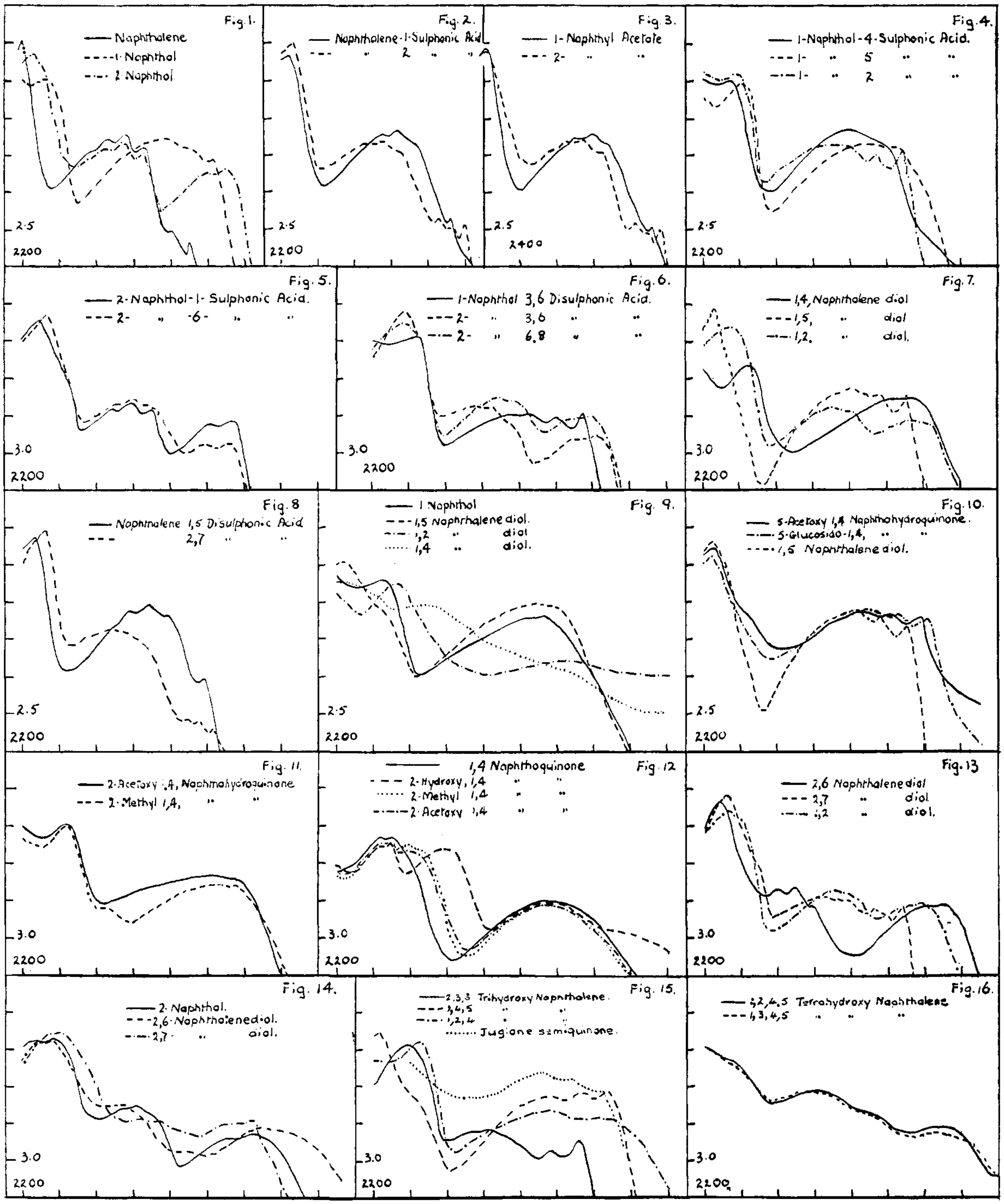
(7) Scheibe, *Kolloid Z.*, **82**, 1 (1938).

(8) Scheibe, *Angew. Chem.*, **42**, 631 (1939).

(9) de Laszlo, THIS JOURNAL, **50**, 892 (1928).

(10) Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).



Figs. 1–16.—The ultraviolet absorption spectra of some hydroxynaphthalenes.

Figs. 1–16.—The wave lengths along the abscissa axes are marked at intervals of 200 Å. The ordinate marks indicate the logarithm of the molecular extinction coefficient at intervals of 0.5 unit. The curves in Figs. 1, 2, 3 and 12 were obtained on solutions in 95% ethanol; those in Figs. 9 and 14, in buffer *p*H 10, and the remainder in 95% ethanol containing 5% (by vol.) reagent hydrochloric acid.

agreed more with that of the 1,5- rather than with that of the 1,4-diol. The introduced electron-attracting acetyl (or glucose) group allows greater ionization of the opposed hydroxyls to give the polarization present in the 1,5-diol.

The effect of further substitution in the same ring as the hydroxyls is shown in Fig. 11 which gives the curves for 2-acetoxy- and 2-methyl-1,4-

naphthohydroquinones. The methyl group, being of similar electronic character to the hydroxyls already present, tends to augment the existing condition, and the curve obtained is almost identical with that of the 1,4-diol. The opposite electronic nature of the acetyl group, though considerably weakened by its position, is shown in the broadening of the curve. The almost identical curves obtained for 2-acetoxy- and 2-methyl-1,4-naphthoquinone, which lie in an intermediate position between the unsubstituted quinone and its 2-hydroxy derivative (Fig. 12), also emphasize the effect of the 2-position upon the acetyl group.

Examination of the curves for the 2,6- and 2,7-diols, as well as that for the 2,7-disulfonic acid (Figs. 13, 14 and 8), showed that these were comparable to those of the mono 2-derivatives, though the increase in intensity observed with the 1,5-diol was absent.

Since it appears that the different portions of the naphthalene curve are varied according to whether the polarization of the molecule takes place vertically or horizontally, and that these polarizations are stabilized by substitution in the 1- or 2-positions, it would follow that the 1,2-diol curve would be different from those described above. Figures 7 and 9 show that there is the general bathochromic shift common to the 1-substituted compounds, with the three regions of the 2-derivatives, and a total disappearance of fine structure.

Hence when two like groups are substituted in the naphthalene molecule, there are spectroscopically more forms than the *aa*, *ab* and *bb* suggested by de Laszlo,[9] depending upon whether or not the groups are in the same or different rings.

Trihydroxynaphthalenes.—The difficulties encountered in attempting to interpret the curves of the naphthalenediols became more acute with the higher substituted derivatives and, at this stage, only three trihydroxy compounds were studied. These were the 1,4,5-(all α-compound), the 2,3,6-(all β-) and the 1,2,4-(in which all the groups are in one ring) derivatives. The curves for these are given in Fig. 15.

The curve of 2,3,6-trihydroxynaphthalene showed strong connections with that of the 2-derivatives previously described, though there was a shift of the high intensity region toward the red end of the spectrum, and some simplification of the lower intensity one. This simplification was further seen in the curves of the two tetrahydroxy compounds in Fig. 16.

1,4,5- showed only the two portions of the curve common to all 1-derivatives with yet a further bathochromic shift. The three subsidiary peaks present were possibly those shown by 1-naphthol and 1,5-diol. Evidence for this was gained during one preparation of the hydroxy compound by sodium hydrosulfite reduction of juglone, when a compound was isolated which gave the curve shown in Fig. 14. This, though evidently of a semiquinone nature, was unstable to ultraviolet light, and the curve quickly changed to that of the 1,4,5-trihydroxy derivative. However, the similarity of its curve to that of the 1,5-diol suggested that the curve for the trihydroxy compound was that of the diol, modified by the presence of the hydroxyl at position 4.

1,2,4-Trihydroxynaphthalene gave a curve, which like that of the 1,2-diol, was neither truly representative of the 1- nor the 2-substituted types, so far encountered. Besides a large bathochromic shift, the two lower portions of the curve shown by most 2-derivatives, had become almost fused, with the third region represented only by a large inflection.

Experimental

Ultraviolet absorption data were obtained with a Beckman spectrophotometer using 1-cm. cells. The spectra were measured on solutions in 95% ethanol, in 95% ethanol containing 5% reagent hydrochloric acid and in a chloride-borate buffer at *p*H 10. It was found that many of the higher hydroxy derivatives, particularly the naphthohydroquinones, were unstable in neutral solution especially when exposed to ultraviolet light, but were sufficiently stable in the acid ethanol to allow measurements to be made. This solvent also minimized the dissociation of acidic compounds, particularly the hydroxyquinones, hence gave a more truly representative curve. Attention to this necessity was drawn recently by Spruit.[11]

As many of the alkaline solutions were unstable, fresh dilutions were made for each maximum and minimum of the curves. The molar extinction values in Table V were calculated with respect to the free sulfonic acids though measurements were made on solutions of the alkali salts.

Compounds Examined

Naphthalenesulfonic Acids.—Commercial samples of the alkali metal salts were recrystallized before use.

TABLE V

WAVE LENGTHS AND INTENSITIES OF THE ABSORPTION MAXIMA IN ETHANOL, ACID ETHANOL AND BUFFER *p*H 10

Figures underlined denote inflections

	Ethanol		Acid ethanol		Buffer *p*H 10	
Compound	$\lambda_{max.}$	log ϵ	$\lambda_{max.}$	log ϵ	$\lambda_{max.}$	log ϵ
Naphthalene	2200	5.01				
	$\underline{2580}$	3.57				
	2660	3.71				
	2755	3.76				
	$\underline{2840}$	3.59				
	2860	3.59				
	$\underline{2970}$	2.51				
	3010	2.48				
	$\underline{3040}$	2.36				
	3120	2.24				
1-Naphthyl acetate	2210	4.92				
	$\underline{2620}$	3.58				
	2700	3.74				
	2800	3.80				
	$\underline{2880}$	3.65				
	3120	2.52				
	$\underline{3160}$	2.27				

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(11) Spruit, *Rec. trav. chim.*, **68**, 316 (1949).

TABLE V (*Continued*)

Compound	Ethanol $\lambda_{max.}$	Ethanol log ϵ	Acid ethanol $\lambda_{max.}$	Acid ethanol log ϵ	Buffer pH 10[e] $\lambda_{max.}$	Buffer pH 10[e] log
Naphthalene-2-sulfonic acid	2270	5.00	2270	4.98		
	2580	3.55	2570	3.52		
	2665	3.66	2660	3.66		
	2745	3.69	2750	3.69		
	2840	3.55	2840	3.55		
	3060	2.65	3060	2.67		
	3130	2.53	3130	2.57		
	3200	2.58	3200	2.62		
2-Naphthyl acetate	2210	4.88				
	2600	3.59				
	2740	3.71				
	2835	3.54				
	3030	2.59				
	3085	2.46				
	3170	2.50				
1,2-Naphthalenediol			2340	4.69	2350	4.24
			2900	3.61		
			3340	3.44	3450	3.20
1,4-Naphthalenediol			2440	4.18	2300	4.22
			2750	3.08	2670	3.95
			3265	3.72	3400	3.12
			3340	3.72		
2,6-Naphthalenediol	2280	4.86	2290	4.83	2300	4.61
	2600	3.66	2600	3.66	2350	4.61
	2690	3.60	2695	3.67	2700	3.73
	2790	3.43	2790	3.43	3050	3.12
	3400	3.42	3400	3.42	3500	3.43
	3490	3.44	3490	3.43	3700	3.33
2,7-Naphthalenediol	2320	4.88	2320	4.92	2390	4.72
	2855	3.53	2855	3.54	2820	3.55
	2950	3.49	2950	3.50	2900	3.54
	3130	3.37	3130	3.37		
	3180	3.30	3180	3.30	3260	3.46
	3280	3.43	3280	3.43	3400	3.50
Naphthalene-2,7-disulfonic acid	2330	4.94	2325	4.97	2310	4.96
	2550	3.50	2550	3.53	2550	3.47
	2660	3.59	2665	3.63	2665	3.58
	2740	3.58	2740	3.62	2730	3.58
	3080	2.41	3080	2.42	3080	2.52
	3150	2.38	3150	2.40	3150	2.52
	3230	2.25	3230	2.29	3230	2.51
1,2,4-Trihydroxynaphthalene			2450	4.61	2650	4.38
			2850	3.43	3000	3.90
			3150	3.67	3300	3.38
			3450	3.56	4600	3.49
1,4,5-Trihydroxynaphthalene			2220	4.70	2600	3.96
			3155	3.81	3100	3.08
			3330	3.90		
			3475	3.92	3500	3.15
2,3,6-Trihydroxynaphthalene	2390	4.54	2390	4.56	2430	4.54
	2750	3.40	2750	3.40	2500	4.49
	2820	3.41	2825	3.42	2840	3.51
	3000	3.19				
	3160	3.15	3160	3.15	3170	3.31
	3310	3.27	3310	3.26	3310	3.41
2-Acetoxy-1,4-naphthalenediol			2440	4.53		
			3100	3.81		
			3235	3.84		
2-Methyl-1,4-naphthalenediol			2450	4.49		
			2655	3.40		
			3245	3.71		
			3325	3.70		
5-Acetoxy-1,4-naphthalenediol			2260	4.73		
			2950	3.79		
			3050	3.88		
			3220	3.85		
			3380	3.81		
5-Glucosido-1,4-naphthalenediol			2250	4.62		
			3080	3.89		
			3260	3.84		
			3410	3.77		
1,4-Naphthoquinone	2460	4.34			2300	4.22
	2510	4.34			2670	3.95
	2600	4.05				
	3380	3.50			3400	3.12
2-Hydroxy-1,4-naphthoquinone			2440	4.23		
			2490	4.28		
			2780	4.18		
			3330	3.47		
2-Acetoxy-1,4-naphthoquinone			2450	4.26		
			2500	4.28		
			2600	4.15		
			3300	3.44		
			3360	3.46		
2-Methyl-1,4-naphthoquinone			2455	4.27		
			2510	4.30		
			2585	4.22		
			2650	4.19		
			3355	3.43		
1,2,4,5-Tetrahydroxynaphthalene			2350	4.36		
			2820	3.95		
			3505	3.44		
			4030	2.75		
1,3,4,5-Tetrahydroxynaphthalene			2800	3.94		
			3450	3.37		
			4000	2.76		

1-, 2-, 1,5-, 1,6-, 2,6- and 2,7-naphthols were obtained by caustic fusion of the corresponding sulfonic acids. In this connection it was found that both 1-hydroxy-2-sulfonic acid and 2-hydroxy-1-sulfonic acid gave only 2-naphthol in the melt. **1,2- and 1,4-Naphthalenediols** and their acetoxy, methyl and hydroxy derivatives were obtained by sodium hydrosulfite reduction of ethereal solutions of the corresponding quinones.[12] **Juglone** was synthesized by the method of Bernthsen and Semper.[13] **1,2-Naphthoquinone** was prepared from 2-naphthol.[14] **2-Hydroxy-1,4-naphthoquinone** was obtained by hydrolysis[15] of the 2-acetoxy compound, prepared from 1,2-naphthoquinone by the method of Thiele and Winter.[16] The melting points of the above compounds were checked against published data.

5-Glucosido-1,4-naphthalenediol was isolated as a pale buff colored powder, m. p. 165°, from the winter buds of the walnut. An account of its isolation and identification is now in the press.[17]

Summary

1. A comparative study has been made of the

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[12] Fieser, THIS JOURNAL, **70**, 3169 (1948).

[13] Bernthsen and Semper, *Ber.*, **20**, 934 (1887).

[14] Fieser, "Org. Syntheses," Coll. Vol. II, 1943, pp. 34, 430.

[15] Hooker, THIS JOURNAL, **58**, 1214 (1936).

[16] Thiele and Winter, *Ann.*, **311**, 345 (1900).

[17] Daglish, *Biochem. J.* (1950).

ultraviolet absorption spectra of some thirty hydroxynaphthalenes.

2. The correlation of spectra with molecular structure has been attempted.

3. It appears that the changes produced in the naphthalene curve on substitution are due chiefly to the stabilization of polarized structures along two axes in the molecule, normal to one another.

KING'S LANGLEY, HERTS., ENG.

RECEIVED FEBRUARY 17, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Copolymerization of Butyl Vinylsulfonate. Comments on Sulfur Shell Expansion[1]

BY C. G. OVERBERGER, DAVID E. BALDWIN AND HARRY P. GREGOR

Since the development of the copolymer composition[2] equation, a large amount of copolymerization data has been obtained in the form of reactivity ratios. Such studies permit one to obtain, by a simple experimental procedure, useful information relating to the reactivity of double bonds toward radicals[3a,3b,3c] and polar factors[3d,3e,3f] in radical reactions. In particular, we were interested in information regarding the expansion of the sulfur shell in radical transition states.

This paper describes the copolymerization of butyl vinylsulfonate with vinyl acetate, vinyl chloride, styrene, methyl acrylate and vinylidene chloride.

Heuer[4] has described the copolymerization of small quantities of vinylsulfonic acid or one of its soluble salts with aqueous suspensions of vinyl acetate, vinyl chloride and other monomers, but no polymer analyses are reported. Since the polymers gave stable emulsions, it was concluded that vinylsulfonic acid entered the copolymer chain. Alderman and Hanford[5] reported a very slow bulk polymerization of vinylsulfonic acid and ethyl vinylsulfonate catalyzed by ultraviolet irradiation or benzoyl peroxide. They also reported copolymers prepared in bulk of ethyl vinylsulfonate and vinylsulfonic acid with vinyl acetate, methyl methacrylate and methyl-α-chloroacrylate and other monomers, but no polymer analyses were reported. The emulsion copolymerization of vinylsulfonic acid with chloroprene was likewise reported and it was shown by analyses that some vinylsulfonic acid had entered the chain.

Experimental

Materials.—The styrene, vinyl acetate, vinylidene chloride, methyl acrylate and vinyl chloride were commercial products, and except for the vinyl chloride, were fractionally distilled through a 12-inch "Vigreux" column immediately before use. The vinyl chloride was passed through two bubblers containing 10% sodium hydroxide solution, one containing solid flake sodium hydroxide, and one containing "Drierite" before being condensed in a receiver cooled in a Dry Ice-acetone-bath and protected from moisture with a drying tube. The *n*-butyl vinylsulfonate was prepared by the method of Whitmore and Landau.[6] From 187.5 g. (1.5 moles) of sodium sulfite and 427.5 ml. (937.5 g., 4.95 moles) of ethylene dibromide was obtained 413 g. of crude dry salts which, with 225 g. (1.1 moles) of phosphorus pentachloride, yielded 195.5 g. (65%) of 2-bromoethanesulfonyl chloride, n^{25}D 1.5230, b. p. 85° at 3 mm. (82° at 5 mm., n^{25}D 1.5227).[6] From 327.5 g. (1.58 moles) of 2-bromoethanesulfonyl chloride and 107.3 g. (1.45 moles) of *n*-butyl alcohol there was obtained 90 g. (36%) of *n*-butyl vinylsulfonate, b. p. 89° at 5 mm., n^{25}D 1.4410 (116° at 15 mm., n^{25}D 1.4416)[6]. The *n*-butyl vinylsulfonate was redistilled immediately before use.

Procedure.—With the exception of the vinyl chloride samples the monomers (40 millimoles of total monomers) were weighed into small test-tubes on an analytical balance, cooled, mixed well, and transferred to ampoules containing 0.0484 g. (2×10^{-4} mole, 0.5 mole %) of benzoyl peroxide which were then chilled thoroughly and sealed. The vinyl chloride samples were made up by adding the approximate desired amount of vinyl chloride to weighed ampoules containing known amounts of butyl vinylsulfonate and 0.05 g. (approximately 0.5 mole %) of benzoyl peroxide, after which the ampoules were sealed and reweighed on an analytical balance and the amount of vinyl chloride used obtained by difference. The above quantities were doubled in cases where a low yield of copolymer was anticipated. When the degree of conversion was judged to be near 10%, as evidenced by the change in viscosity, the ampoules were removed, chilled, and opened. In each case where the sample contained 90 mole % or more of butyl vinylsulfonate far less than 10% polymerization was achieved in several days of heating. The copolymers from the samples containing 95, 90 and 70 mole % of vinylidene chloride precipitated from the monomer mixtures during the reaction. Each polymerization mixture was diluted with 1-5 ml. of the solvent for the copolymer, poured dropwise with stirring into 150 ml. of the precipitant, and the tube rinsed with 1 ml. of solvent. The styrene copolymers were precipitated in methanol, redissolved in 5 ml. of methyl ethyl ketone and reprecipitated twice more. Several drops of 1:1 hydrochloric acid were added at the end of each precipitation to coagulate the copolymer. The vinylidene chloride copolymers from the monomer mixtures containing 50 mole % or more of vinylidene chloride were purified by the same technique except that 10-15 ml. of hot dioxane was used as a solvent in each case. Those from the mixtures containing 30 mole % of vinylidene chloride were too soft to handle if the methanol was at room temperature and reprecipitation and drying were carried out at 5-10°. The copolymer from the mixture containing 5 mole % of vinyl-

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(2) (a) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); (b) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944); (c) Wall, *ibid.*, **66**, 2050 (1944).

(3) (a) Lewis, Mayo and Hulse, *ibid.*, **67**, 1701 (1945); (b) Alfrey, Merz and Mark, *J. Polymer Sci.*, **1**, 37 (1946); (c) Lewis, Walling, Cummings, Briggs and Mayo, THIS JOURNAL, **70**, 1519 (1948); and succeeding papers, among which are Mayo, Lewis and Walling, *ibid.*, **70**, 1529 (1948); (d) Walling, Briggs, Wolfstirn and Mayo, *ibid.*, **70**, 1537 (1948); (e) Alfrey and Price, *J. Polymer Sci.*, **2**, 101 (1947); (f) Price, *ibid.*, **3**, 772 (1948).

(4) Heuer, German Patent 724,889 (1942); *C. A.*, **37**, 5808 (1943); Heuer, U. S. Patent 2,300,920 (1942).

(5) Alderman and Hanford, U. S. Patent 2,348,705 (1944).

(6) W. F. Whitmore and Landau, THIS JOURNAL, **68**, 1797 (1946).