ether layer was dried over anhydrous sodium sulfate and distilled. The yield of methyl cyclopentyl ketone (b.p. 160–163°) was 2.3 g. (30% of the theoretical).

Methyl Cyclopentyl Ketone from Dicyclopentylcadmium and Acetyl Chloride.—A Grignard solution was prepared from 7.5 g. (0.05 mole) of cyclopentyl bromide and 1.2 g. (0.05 mole) of magnesium turnings in 25 ml. of anhydrous ether. The Grignard reagent was formed with great ease. When the reaction was complete and had been refluxed for 20 minutes, the solution was chilled in a Dry Ice–acetone-bath and 4.6 g. (0.025 mole) of anhydrous cadmium chloride were slowly added. The reaction mixture was vigorously agitated throughout the addition and care was taken to keep the temperature low. When the addition was complete, the suspension was allowed to stand 20 minutes at the Dry Ice-bath temperature. A solution of 3.5 ml. of acetyl chloride in 10 ml. of anhydrous ether was then slowly added while cooling was maintained. After 5 minutes the cooling bath was removed and the reaction mixture was allowed to warm up to room temperature. The mixture was finally refluxed for 20 minutes. After standing overnight it was decomposed with ice and dilute sulfuric acid. The ether layer was washed with dilute alkali, which removed part of the yellow color, and with distilled water. The light amber-colored ether solution was dried over sodium sulfate and distilled. The colorless distillate, boiling at 160–163°, amounted to 1.8 g. (30% of the theoretical).

***spiro*-(Cyclopentane-1,3′-*pseudo*-2-methylindole)**.—To a solution of 11.2 g. (0.09 moles) of methyl cyclopentyl ketone in 68 ml. of glacial acetic acid was added 9.6 ml. (0.09 moles) of phenylhydrazine. The solution was refluxed for an hour, then cooled and made basic with potassium hydroxide. The basic solution was thoroughly extracted with ether, the ether solution was dried over sodium sulfate followed by potassium hydroxide pellets. Evaporation of the ether solution left 1.6 g. of a dark red oil, which was distilled *in vacuo* in a small sausage flask. The first fraction was a yellow oil, distilling at 100° (bath) and 35 mm. The second fraction (120–145°) at 2 mm. was an orange oil which partly crystallized in colorless plates, m.p. 125–128°. This crystalline material was identified as N-acetylphenylhydrazine. (*Anal.* Calcd. for $C_8H_{10}ON_2$: C, 63.98; H, 6.71; N, 18.66. Found: C, 64.00; H, 6.46; N, 18.87.) The extraction of the ether mother liquor with 0.1 *N* hydrochloric acid and addition of picric acid yielded a crystalline picrate. Recrystallization from acetone furnished yellow needles, m.p. 188–192°, orange yellow melt.

Anal. Calcd. for $C_{13}H_{15}N \cdot C_6H_3O_7N_3$: C, 55.07; H, 4.38. Found: C, 54.88; H, 4.18.

Hydrochloride.—A small amount of the picrate was converted into the hydrochloride in the usual fashion. The hydrochloride, after recrystallization from ethyl alcohol ether, melted at 180–184°.

Anal. Calcd. for $C_{13}H_{15}N \cdot HCl$: C, 70.41; H, 7.27. Found: C, 70.50; H, 7.38.

***spiro*-(Cyclopentane-1,3′-*pseudo*-2-ethylindole) (XXIV)**.—To an ether solution of excess ethylmagnesium iodide was added 630 mg. of *spiro*-(cyclopentane-1,2′-*pseudo*-indoxyl) (II) in 6 ml. of tetrahydrofuran. An orange precipitate formed immediately. The solution was refluxed for 45 minutes and, since the precipitate had not dissolved, 40 ml. of tetrahydrofuran was added and refluxing was continued for another hour. The reaction mixture was then cooled and decomposed with water and dilute alkali. The ether layer was separated, dried over sodium sulfate and evaporated. The syrupy residue was triturated with 0.1 *N* hydrochloric acid and the resulting solution treated with aqueous picric acid. The picrate was recrystallized from methanol (yield 270 mg.). Two more recrystallizations from methanol yielded yellow needles with a greenish tinge, m.p. 142–144°.

Anal. Calcd. for $C_{14}H_{17}N \cdot C_6H_3O_7N_3$: C, 56.07; H, 4.71. Found: C, 55.79; H, 4.93.

A mixed melting point with the picrate of 11-ethyltetrahydrocarbazolenine (m.p. 148–150°) showed a large depression (123–130°).

Hydrochloride.—The picrate in ether suspension was treated with alkali to liberate the free base. After drying of the ether phase over sodium sulfate dry hydrogen chloride produced the hydrochloride. This hydrochloride crystallized from water in colorless prisms, m.p. 181–183°, sublimation in rods starting at 130°, darkening from 170°. A mixed melting point with 11-ethyltetrahydrocarbazolenine hydrochloride (m.p. 176–181°) showed a depression (169–181°).

11-Ethyltetrahydrocarbazolenine Hydrochloride,—The 2-ethylcyclohexanone used in the Fischer indolenine synthesis[9,10] was prepared by condensing 3 moles of cyclohexanone with 1 mole of acetaldehyde,[28,29] dehydration of the resulting ketole with iodine,[30] and hydrogenation of the 2-ethylidenecyclohexanone.[31] The hydrochloride of the indolenine was prepared from ethereal solution using dry hydrogen chloride. The salt formed hexagonal prisms from ethanol-ether (1:2), m.p. 176–181°, transformation to smaller aggregates 120–150°, sintering 168°, clear melt.

Anal. Calcd. for $C_{14}H_{17}N \cdot HCl$: C, 71.27; H, 7.66. Found: C, 71.06; H, 7.93.

Picrate.—The picrate, prepared in the usual manner, formed golden yellow prisms on recrystallization from methanol, m.p. 148–150°.

Acknowledgment.—We are indebted to Research Corporation, New York, for a grant-in-aid in support of this investigation.

[28] Vavon and Mitchovitch, *Bull. soc. chim.*, [4] **45**, 964 (1929).

[29] Grignard and Dubien, *Ann. chim.*, [10] **1**, 288 (1924).

[30] Hibbert, THIS JOURNAL, **37**, 1748 (1915).

[31] Garland and Reid, *ibid.*, **47**, 2333 (1925).

CAMBRIDGE 38, MASSACHUSETTS RECEIVED JUNE 22, 1950

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NEW MEXICO HIGHLANDS UNIVERSITY]

The Ultraviolet Absorption Spectra of Acrylic Acids and Esters

BY HERBERT E. UNGNADE AND ISHMAEL ORTEGA

The literature reports a number of absorption spectra for various acrylic acids but the differences among authors in the location and extinction values of the maxima even for the same type of acid exceed the experimental error of the method. As an example, Dimroth[1] summarizing the data for crotonic acid and other acids of the type RCH═CH—COOH (I) gives λ_{max}(EtOH) 204–205 mμ, log ε 4.06–4.14. Later precise measurements by Van der Hulst[2] and by Lauer, Gensler and Miller[3] locate the maximum for the acids (I) at 210 mμ (log ε 4.5). Rusoff, *et al.*,[4] report an even higher wave length for the maximum (213 mμ) but a lower extinction value (log ε 4.2). There is little doubt that all investigators were dealing with the stable *trans*-isomers and with reasonably pure compounds.

According to Caliezi and Schinz[5] the absorption curves of α,β-unsaturated acids show a maximum at about 230 mμ. Other investigators fail to find a maximum in the observed region and report only general absorption, *e.g.*, Jones, Shen and Whiting[6] who measured the acids $R_2C(OH)C(COOH)$═

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[1] Dimroth, *Angew. Chem.*, **52**, 551 (1939).

[2] Van der Hulst, *Rec. trav. chim.*, **54**, 639 (1935).

[3] Lauer, Gensler and Miller, THIS JOURNAL, **63**, 1153 (1941).

[4] Rusoff, Platt, Klevens and Burr, *ibid.*, **67**, 678 (1945).

[5] Caliezi and Schinz, *Helv. Chim. Acta*, **32**, 2557 (1949).

[6] Jones, Shen and Whiting, *J. Chem. Soc.*, 230 (1950).

CH_2 found no maximal absorption above 214 mμ.[6a]

Acrylic acids in which the beta carbon is part of a ring have been reported to have maxima of 225 mμ (6-membered ring, log ε 3.3[7] and 4.2[8]) and 222 mμ (5-membered ring, log ε 4.1–4.4[9]).

The present investigation has established that all acrylic acids in alcoholic solution show a distinct maximum in the region between 210–225 mμ excepting only acrylic acid itself and its esters[10] which undoubtedly have a maximum just below the range of the Beckman instrument. The extinction values at the maxima and to some extent even the wave lengths of the maxima have been found to vary with concentration. This deviation from Beer's law is most pronounced in the region of the maxima, less so at 300 mμ and each series of curves obtained by varying the concentration contains an isosbestic point or region. The observed variations in extinction and wave length due to concentration are sufficiently large to explain some of the disagreements in the literature.

A comparison of simple aliphatic acrylic acids or esters shows a red shift for the introduction of each successive alkyl group (Table I). It appears immaterial whether the group is substituted alpha or beta or whether it contains one or more carbons. Branching at the α-carbon of the substituent group may possibly increase the shift.[11]

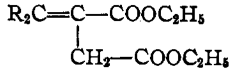
TABLE I

ABSORPTION SPECTRA OF ACYLIC ACRYLIC ACIDS AND ESTERS

Compound	Mole/liter × 10^3	λ_{max}, mμ	log ϵ_{max}	I. P.,[a] mμ	log $\epsilon_{I. P.}$	log ϵ_{300}
$CH_2=CHCOOMe$	0.248	..[b]	..	220	2.64	1.45
	.498	..[b]	..	220	2.65	1.20
	.880	..[b]	..	220	2.71	1.13
$CH_2=CHCOOBu$	.366	..[b]	..	220	2.70	1.21
	.466	..[b]	..	220	2.71	0.93
	1.090	..[b]	..	220	2.73	1.11
$CH_2=CMeCOOMe$	0.296	(212)[c]	(3.78)	230	2.59	1.37
	.592	214.5	3.36	230	2.58	1.07
	1.280	212	3.35	230	2.60	0.59
$CH_2=CMeCOOEt$	0.114	214	3.77	230	2.66	1.58
	.154	(211)[c]	(3.87)	230	2.68	1.59
	.324	212	3.85	230	2.69	1.44
	.393	214	3.73	230	2.60	1.10
$CH_2=CMeCOOBu$	.264	213	3.83	230	2.70	1.28
	.375	213	3.81	230	2.69	1.20
	.820	216	3.54	230	2.64	0.56
	1.460	..[d]	..	230	2.66	.68
$Me_2C=CHCOOEt$	0.153	217	4.14	240	3.33	1.89
	.460	..[d]	..	240	3.32	1.41
$Me_2C=CHCOOH$[e]	.210	216	4.00	240	3.23	1.62
	.536	217	3.71	240	3.17	1.00

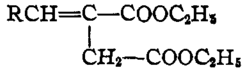
[a] Isosbestic point. [b] Below the range of the instrument. [c] No maximum below 211 mμ. [d] Too concentrated to determine. [e] An example of $CH_3CH=CRCOOH$ has been reported by Kropman and Warren (*J. Chem. Soc.*, 700 (1950)) with maxima of 215 mμ (*cis*, log ε 3.61) and 218 mμ (*trans*, log ε 3.97) in alcohol.

At the maximum, the shift per alkyl group amounts to approximately 4 mμ when acids of equivalent concentrations are compared,[12] the isosbestic point, however, is shifted 10 mμ to longer wave lengths (Fig. 1). Since this point falls well within the range of most instruments, simple acrylates and acrylic acid can be measured as well as substituted acids.



$R_2C=C(CH_2-COOC_2H_5)-COOC_2H_5$

A, λ_{max} 218–220



$RCH=C(CH_2-COOC_2H_5)-COOC_2H_5$

B, λ_{max} 213–213.5

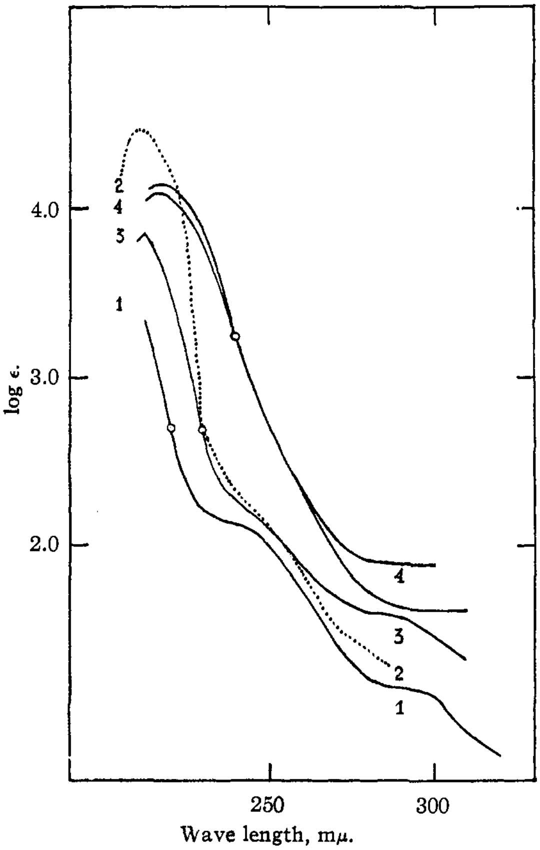
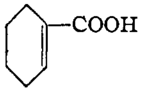
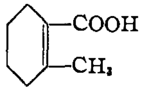


Fig. 1.—Ultraviolet absorption spectra of acyclic acrylic acids and esters: 1, $CH_2=CHCOOR$ (0.88 mole/liter × 10^{-3}); 2, $RCH=CHCOOH$[8]; 3, $CH_2=CMeCOOR$ (0.324 mole/liter × 10^{-3}); 4, $Me_2C=CHCOOEt$ (0.153 mole/liter × 10^{-3}) and $Me_2C=CHCOOH$ (0.210 mole/liter × 10^{-3}). The isosbestic points are marked by circles.

The concentration dependence of the absorption spectra is retained when the double bond of acrylic acid becomes part of a six-membered ring. The concentration effects are much larger than in the open-chain acids while the red shift due to alkyl substituents is decreased. The maxima are useless for structural work (Table II) but a shift of 5 mμ per alkyl is observed at the isosbestic point (Fig. 2). It is therefore possible to distinguish between tetra-



II



III

(6a) NOTE ADDED IN PROOF.—Additional absorption values have been reported recently for $RC(CH_3)=CHCOOH$, λ_{max} 219 mμ (log ε 3.92) and λ_{max} 217 mμ (log ε 4.03) by Cason and Sumrell, THIS JOURNAL, **72**, 4838 (1950), and for $RC(CH_3)=CHCOOEt$, λ_{max} 215 mμ (log ε 4.1) by Caliezi and Schinz, *Helv. Chim. Acta*, **33**, 1134 (1950).

(7) Vodoz and Schinz, *Helv. Chim. Acta*, **33**, 1040 (1950).

(8) Ruegg, Dreiding, Jeger and Ruzicka, *ibid.*, **33**, 889 (1950).

(9) Heusser, Eichenberger and Plattner, *ibid.*, **33**, 1089 (1950).

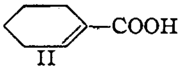
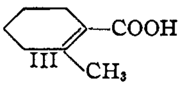
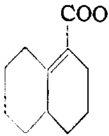
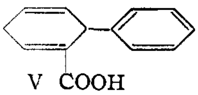
(10) Acrylic acids and their esters yield identical curves in ethanol so that a direct comparison is possible.

(11) Overberger and Roberts, THIS JOURNAL, **71**, 3618 (1949).

(12) Overberger and Roberts[11] have observed a similar shift for the esters A and B (presumably at equivalent concentrations in alcohol).

TABLE II

ABSORPTION SPECTRA OF CYCLIC ACRYLIC ACIDS

Compound	Mole/liter × 10^3	λmax. mμ	log ϵ_{max}	I. P., mμ	log $\epsilon_{I. P.}$	log ϵ_{300}
 II	0.050	218	3.90	240	3.01	2.00
	.144	217	3.93	240	3.01	1.95
	.289	217.5	3.94	240	3.01	1.62
 III	.167	216.5	3.97	245	3.06	2.34
	.334	218.5	3.94	245	3.06	2.27
	.694	[a]	..	245	3.06	2.25
 IV	.095	218	3.97	245	2.98	2.13
	.199	218	3.99	245	2.98	1.82
	.898	220	3.98	245	2.98	1.20
 V	.090	...[b]	..	260	2.92	2.25
	.188	212	3.98	260	2.89	2.07
	.600	225[c]	3.67[c]	260	2.89	1.95
	1.04	220[c]	3.39[c]	260	2.90	1.59

[a] Too concentrated to determine. [b] No maximum above 210 mμ. [c] Instrumental deviation from Beer's law.

hydrobenzoic acid (II) and the tetrahydro-*o*-toluic acid (III).[13]

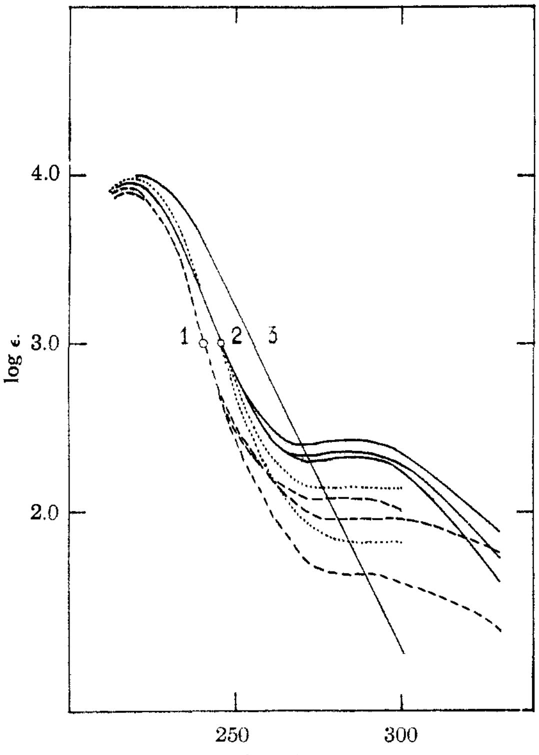
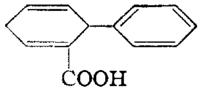
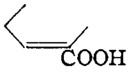


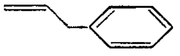
Fig. 2.—Ultraviolet absorption spectra of cyclic acrylic acids: 1, — — — — acid (II); 2, ——— acid (III), and .... acid (IV); 3, ——— 3-acetoxy-Δ^{5}-(6)-*nor*-cholestene-7-carboxylic acid (VIII).

It is also possible to assign a structure to the octahydro-1-naphthoic acid (IV), m.p. 158–159°, which has been obtained by dehydrobromination of 1-bromo-1-decahydronaphthoic acid.[14] Its absorption curve coincides with that of (III); the double bond is therefore located 1,9 rather than 1,2.[15]

Inasmuch as the absorption curves for cyclic acrylic acids are known, it is possible to predict spectra for compounds such as (V)[13] which contains the chromophores (VI) and (VII). Addition


V


VI


VII

of the extinction values for (II) and (VII) has given a composite curve similar to the one observed (Fig. 3).[16] The spectrum of the acid (V) is of considerable interest in view of the large changes with concentration. Curves 4 and 5 (Fig. 3) show instrumental failure below 235 mμ, curve 1 has no maximum above 210 mμ so that only one concentration furnishes a useful maximum (curve 2).

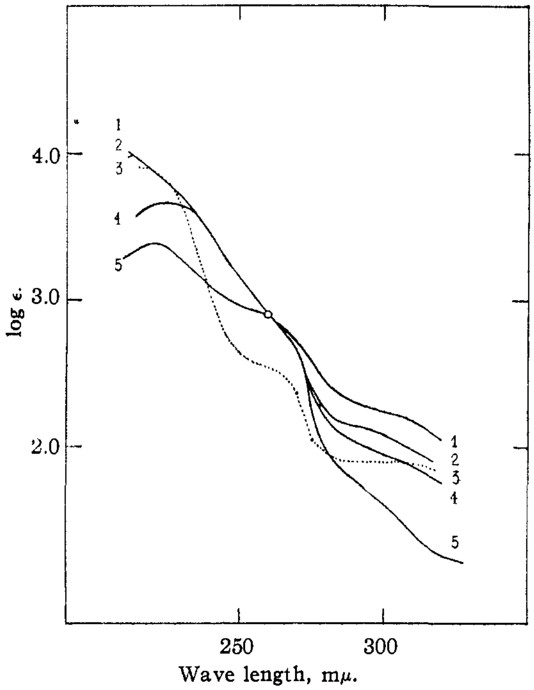


Fig. 3.—Ultraviolet absorption spectra of acid (V): 1, 0.090 mole/liter × 10^{-3}; 2, 0.188 mole/liter × 10^{-3}; 3, calculated curve; 4, 0.600 mole/liter × 10^{-3}; 5, 1.04 mole/liter × 10^{-3}.

If the double bond of acrylic acid is incorporated in a five-membered ring, the absorption curve is displaced 10 mμ further to the red than the curve

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[13] The authors are indebted to Dr. John Meek, University of Colorado, for a sample of this compound.

[14] Ungnade and Morriss, THIS JOURNAL, **72**, 2114 (1950).

[15] Careful repetition of the earlier work has given only one single crystalline bromo acid, m.p. 146–148°, from all-*cis*-decahydro-1-naphthoic acid which in turn yields only one single unsaturated acid. In view of the established *trans*-elimination mechanism (Cristol, *ibid.*, **69**, 338 (1947)), the bromo acid will have bromine and bridge hydrogens *trans* to one-another.

[16] The values for allylbenzene were taken from the literature.[17] Recent work by Braude[18] and deviations among published curves for allylbenzene (*cf.*, Campbell, Linden, Godshalk and Young, *ibid.*, **69**, 882 (1947)) make it likely that the spectrum of allylbenzene varies with concentration, so that better agreement between the curves may be expected between 230 and 272 mμ if the compounds were run in the same concentration.

[17] Jones, *Chem. Revs.*, **32**, 36 (1943).

[18] Braude, Fawcett and Timmons, *J. Chem. Soc.*, 1019 (1950).

for the corresponding acid in the six-ring series (Fig. 2). The curve for the five-ring acid, 3-acetoxy-Δ^5-(6)-*nor*-cholestene-7-carboxylic acid (VIII)[19] parallels those of the other cyclic acids near the isosbestic points and very likely has a maximum in the vicinity of 218 mμ.

It has been observed that the acrylic acids and esters show weak fluorescence in ultraviolet light. While dimerization of the acids cannot be eliminated as a factor in the deviation from Beer's law, the deviation may be ascribed in part to "superposition of transmitted light and scattered fluorescence emission."[18]

Experimental

Materials.—The simple acrylates and methacrylates were commercial products.[20] β,β-Dimethylacrylic acid, m.p. 68–69°, was prepared according to "Organic Syntheses"[21] and was purified by crystallization from petroleum ether. Its ester, b.p. 112–114° (2 mm.), was obtained in 69.5% yield from the silver salt and ethyl iodide.

3,4,5,6-Tetrahydrobenzoic Acid (II).—Cyclohexanecarboxylic acid (5 g.) heated with bromine (6.25 g.) and phosphorus trichloride (4 drops) at 60–70° for 3 hours gave 61.8% of crude bromo acid. Dehydrobromination by refluxing with 3.65 g. of collidine yielded 22.3% of pure tetrahydrobenzoic acid boiling at 131–132° (13 mm.).

2,3,4,5,6,7,8,10-Octahydro-1-naphthoic Acid (IV).[22]—Decahydro-1-naphthoic acid was converted to the 1-bromo-acid described previously.[14] Digestion and crystallization from Skellysolve F yielded one pure bromo acid, m.p. 146–148°, which on dehydrobromination with collidine gave an excellent yield of the octahydronaphthoic acid, m.p. 158–159°.

Ultraviolet Absorption Spectra.—Accurately weighed (±0.01 mg.) acrylic acids and esters were dissolved in 95% alcohol and diluted to an exact volume with the same solvent. Further dilutions were made from the same stock solution. All determinations were made in matched quartz cells of 1 cm. length with a Beckman spectrophotometer with freshly prepared solutions.

Summary

It has been shown that acrylic acids and esters exhibit maximal absorption roughly between 210 and 225 mμ. Large deviations from Beer's law are found in all these acids and an accurate comparison of similarly constituted acids can be made only at the isosbestic points.

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[19] Woodward and Clifford, THIS JOURNAL, **63**, 2727 (1941).

[20] The authors are indebted to Rohm and Haas Co., Philadelphia, for generous samples of these compounds.

[21] *Organic Syntheses*, **23**, 27 (1943).

[22] Experimental by Vernon Kerr, New Mexico Highlands University.

LAS VEGAS, NEW MEXICO RECEIVED JULY 14, 1950

[CONTRIBUTION OF THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, BUREAU OF MINES]

Characterization of the Phenolic Fraction of Coal-hydrogenation Asphalt

BY RALPH HUSACK AND CALVIN GOLUMBIC

A study of the phenolic constituents of coal hydrogenation asphalt was made by the countercurrent distribution method The results of this study showed the presence of two groups of phenols. One group, which was extracted by aqueous alkali comprised alkylphenols and phenylphenols. The other group was soluble only in Claisen alkali and was probably a mixture of phenols with polynuclear structures. Close agreement between experimental and theoretical distribution curves indicated a considerable degree of homogeneity for each group with respect to partition coefficient. The oxygen content of the asphalt fraction extracted by Claisen alkali comprised about one-third of the total oxygen in the asphalt. Most of this oxygen was accounted for as hydroxyl. Only about 30% of the oxygen in the non-extracted fraction could be definitely ascribed to hydroxyl oxygen.

It has been postulated that asphalt is the primary product formed in the high-pressure hydrogenolysis of coal.[1] That portion of the coal-hydrogenation product which is soluble in benzene, but insoluble in *n*-hexane, will be referred to as asphalt for the purposes of this paper. The nature of the oxygenated constituents of asphalt has now been studied with the ultimate aim of obtaining better understanding of the type of oxygen linkages in coal. Little or no information exists on this subject, yet this knowledge is highly desirable because (a) one of the critical steps in the hydrogenolysis of coal occurs at the site of carbon–oxygen bonds,[2] and (b) the oxygen content of coal is intimately associated with its coking properties.[3]

Asphalt was separated into acidic (phenolic) and non-acidic portions by a procedure based on that described by Woolfolk, *et al.*,[4] for the recovery of phenols (tar acids) from coal-hydrogenation oils. In this procedure, alcoholic (Claisen) alkali is employed as the phenol extractant in preference to aqueous alkali because it was found to increase the phenol recovery. DeWalt and Glenn[5] have recently reported a similar observation. With asphalt, the recovery of phenolic material is increased 50% by the use of Claisen alkali. In view of these results, it may not be valid to assume, as Green and Mukherji[6] have done, that aqueous alkali alone can be used to distinguish between alcoholic and phenolic groups in coal tar resins.

To obtain some definitive indication of the molecular structures present in the phenolic fraction of coal-hydrogenation asphalt, this fraction was studied by the countercurrent distribution method,[7] which is particularly suitable for the qualitative and quantitative analysis of phenolic mixtures.[8,9] Application of this technique, together with spec

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[1] M. G. Pelipetz, E. M. Kuhn, S. Friedman and H. H. Storch, *Ind. Eng. Chem.*, **40**, 1259 (1948); S. Weller, E. L. Clark and M. G. Pelipetz, *ibid.*, **42**, 334 (1950).

[2] H. H. Storch, C. H. Fisher, C. O. Hawk and A. Eisner, Bureau of Mines Tech. Paper 654, 1943, 50 pp.

[3] Blayden, Riley and Shaw, *Fuel*, **25**, 13 (1946).

[4] Woolfolk, Golumbic, Friedel, Orchin and Storch, Bur. Mines Bull. 487, in press.

[5] DeWalt and Glenn, paper presented before the Division of Gas and Fuel Chemistry, 116th meeting, A. C. S., Atlantic City, September, 1949.

[6] Green and Mukherji, *J. Soc. Chem. Ind.*, **67**, 438 (1948).

[7] Craig, *J. Biol. Chem.*, **155**, 519 (1944).

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