was effected by the dropwise addition with stirring of 25 cc. of saturated ammonium chloride solution. The ether layer was washed with water and dried over anhydrous magnesium sulfate. The addition of ethereal hydrogen chloride precipitated 3.50 g. of crude colorless hydrochloride. This was dissolved in methanol and dry ether was added just to faint turbidity. On cooling, 0.18 g. of solid separated which could not be identified. The further addition of several portions of ether, each followed by periods of cooling brought about the crystallization of 2.02 g. (51%) of the dehydrated product in the form of yellow round clumps, m.p. 172–174°.

*Anal.* Calcd. for $C_{25}H_{29}NO{\cdot}HCl$: C, 75.83; H, 7.64. Found: C, 75.41; H, 7.57.

NORTH CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY][1]

# The Oxidation of Di-*t*-butylpyrogallol by Oxygen in Alkaline Solution. II. Absorption Spectra of the Products

BY FRED STITT, GLEN F. BAILEY, GALVIN B. COPPINGER AND TOD W. CAMPBELL

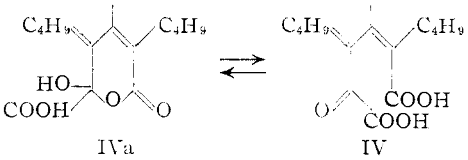
RECEIVED SEPTEMBER 8, 1953

Ultraviolet and infrared absorption spectra are presented for four crystalline products of oxidation of di-*t*-butylpyrogallol by oxygen in alkaline solution and for six related products. The spectra are discussed in relation to the structures assigned to these compounds on the basis of chemical and spectroscopic data. The principal types of structures involved are substituted α-pyrones, cyclopentenedione and cyclopentanediones.

In an earlier paper[2] spectroscopic evidence was referred to in arriving at the probable structures of four crystalline compounds isolated as products of oxidation of di-*t*-butylpyrogallol in alkaline solution. Both the ultraviolet and infrared absorption spectra of these products and some of their derivatives are presented here for purposes of characterization and for discussion in relation to the structures assigned to them. The compounds are referred to here by the same Roman numerals as were used before.[2] Since proof of the proposed structures cannot now be made by reliable interpretation of the available absorption spectra, the discussion is limited to examination of the compatibility of the spectra with the assigned structures.

The ultraviolet absorption spectra were obtained on a Cary Model 11 Recording Spectrophotometer and the infrared spectra were recorded on a Beckman Model IR-3 Spectrophotometer with sodium chloride optics.

**Compound IV.**—Although the ultraviolet spectrum of compound IV (Fig. 1), a dibasic acid, resembles in general appearance that of simple carboxylic acids,[3] the molar absorption coefficient is of a higher order of magnitude. At 220 mμ, ε is about 10,000, suggesting[4] either diene conjugation or unsaturation α,β to either a keto or carboxyl group, the wave length of maximum absorption being depressed by substituent groups. The infrared spectrum of compound IV as a solid suspended in mineral oil (Fig. 6a) shows the bands in the 3.8μ region most characteristic of carboxylic acids[5] and shows a rather sharp band at 3320 cm.$^{-1}$ which is strong evidence for presence of an OH group not part of a carboxyl group.[5] Of the carbonyl band peaks at 1707 and 1734 cm.$^{-1}$, the former is due to the carboxyl group[5] and the latter is approximately that expected for a δ-lactone carbonyl group. Although apparently no examples of carbonyl frequencies of δ-lactones with α,β-unsaturation are available for comparison, a frequency of about 1720 cm.$^{-1}$ is predicted, on the assumption that the effect of conjugation is about the same as observed for aliphatic esters and γ-lactones.[6–8] The position of the remaining peak in the double bond region at 1629 cm.$^{-1}$ is typical of a carbon–carbon double bond conjugated to a carbonyl group.[6] Thus all of these most reliably interpreted features of the infrared spectrum of compound IV are in agreement with the assignment of the lactol structure IVa to the solid state with equilibrium in solution between the lactol structure and the keto–dibasic acid structure IV



IVa IV

In view of the similar environment of methyl groups in all *t*-butyl groups, one expects to find certain frequencies characteristic of *t*-butyl groups. An examination of the infrared spectra of a number of hydrocarbons containing *t*-butyl groups[9,10] showed that bands near 1470, 1395, 1365, 1260, 1200 and 920 cm.$^{-1}$ appear in the spectra of *t*-butyl compounds, those near 1365 and 1470 cm.$^{-1}$ being

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[1] United States Department of Agriculture, Agricultural Research Administration, Bureau of Agricultural and Industrial Chemistry, Albany, California.

[2] T. W. Campbell, THIS JOURNAL, **73**, 4190 (1951); compare H. Schulze and W. Flaig, *Ann.*, **575**, 231 (1952).

[3] I. I. Rusoff, J. R. Platt, H. B. Klevens and G. O. Burr, THIS JOURNAL, **67**, 673 (1945).

[4] See *e.g.*, E. A. Braude, *Ann. Rept. Chem. Soc.*, 105 (1945).

[5] M. St. C. Flett, *J. Chem. Soc.*, 962 (1951).

[6] R. S. Rasmussen, *Fortschr. Chem. org. Naturstoffe*, **5**, 331 (1948).

[7] R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

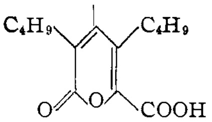
[8] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 877 (1951).

[9] American Petroleum Institute Research Project 44, Carnegie Inst. of Technology, Catalog of Infrared Spectral Data: Serial No. 442, 2,2-Dimethylpropane, Shell Development Co., Emeryville, Calif.; serial no. 471, *t*-butylbenzene, U. S. Naval Research Lab., Washington, D. C.; serial no. 559, *t*-butylcyclohexane, Nat. Bur. Std., Radiometry Section, Washington, D. C.; serial no. 579, 2,2,5-trimethylhexane, U. S. Naval Research Lab., Washington, D. C.; serial no. 586, 3,3-dimethyl-1-butene, U. S. Naval Research Lab., Washington, D. C.; serial no. 808, 2,2-dimethylbutane, The Texas Co., Beacon, New York; serial no. 959 3-*t*-butylthiophene, Socony Vacuum Laboratories, Paulsboro, New Jersey.

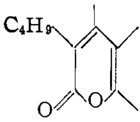
[10] N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

strongest and those near 1470, 1395 and 920 cm.$^{-1}$ occurring frequently as double bands. Many of these bands are identifiable in the infrared spectra of the compounds discussed in this paper, each of which (with one exception) contains two *t*-butyl groups. A doublet occurs at about 1464 and 1484 cm.$^{-1}$ with the two components of nearly equal intensity in all except the mull samples, where mineral oil interferes. In all samples another doublet occurs near 1368 and 1403 cm.$^{-1}$, with the former component the more intense. In three compounds (VI, VII, XXI) a third component occurs near 1385 cm.$^{-1}$, all three components being of about the same intensity. These three compounds each contain an OH group attached to a cyclopentene ring and the 1385 cm.$^{-1}$ component is ascribed to this OH group.[10] All of these frequencies have their origins in motions involving the bending of CH (or OH) bonds. A moderately strong band originating primarily in C–C stretching motion[11] of the *t*-butyl groups is found near 1260 cm.$^{-1}$, but is not always distinct from absorption due to other skeletal frequencies. Other expected bands at lower frequencies due to *t*-butyl groups are relatively weak and are not always definitely recognizable.

**Compound V.**—Compound V and its decarboxylation product, compound XVI, were assigned the following α-pyrone structures

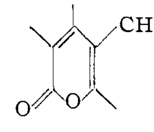


V



XVI

The ultraviolet spectra of compounds V and XVI are very similar (Fig. 1), the wave length of maximum absorption and the maximum molar absorption coefficient being somewhat greater for V than for XVI as might be expected for the increased conjugation due to the COOH group of structure V. In alkaline solution the ultraviolet spectrum of XVI is unchanged, but that of V undergoes a slight bathochromic hyperchromic shift: $\lambda_{\max}$ 305 mμ, $\epsilon_{\max}$ 8450. These ultraviolet spectra differ markedly from that of coumalic acid[12] (Fig. 5) the spectrum of which is in essential agreement with the partial spectrum shown by Fried and Elderfield[13] for methyl coumalate in ether. On the other hand the spectrum shown by these authors[13] for an alcohol solution of 5-methyl-α-pyrone

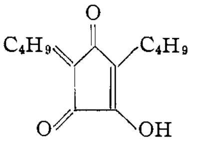


is very similar to those of V and XVI. Spectra of additional related compounds are needed to clarify this situation.

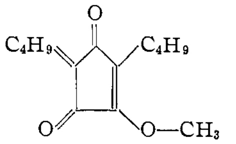
The infrared spectra of compound V (Fig. 6b) and of coumalic acid (Fig. 6c) both show the structure in the 3.8 μ region characteristic of carboxylic acids.[5] In the double bond stretching region, compound V shows four distinct peaks at 1749, 1667, 1634 and 1567 cm.$^{-1}$. The first of these is assigned to the δ-lactone[6–8] carbonyl group, the second to the carboxyl[5] carbonyl, the third to conjugated double bonds,[6] and the last to a frequency originating in the highly conjugated α-pyrone ring. The absorption of coumalic acid in the 6 μ region is complex, showing maxima or shoulders at 1742, 1721, 1703, 1684, 1658, 1629 and 1545 cm.$^{-1}$. Although correlation of the highest of these frequencies with the lactone carbonyl group seems justified, this leaves the origin of the deepest maximum at 1721 cm.$^{-1}$ unexplained. One possible explanation for the large number of bands in this region is that the crystalline structure of coumalic acid may be such that lactone and carboxyl carbonyl groups each occur in more than one type of environment. Detailed assignment of the various peaks is not at present feasible, nor is it clear to what extent interactions in the solid state complicate the spectrum in this region.

Compound XVI shows several real differences between the infrared spectra of the solid (Fig. 6d) and of solutions in carbon tetrachloride (2–7.7 μ) and in carbon disulfide (7.7–15 μ) (Fig. 6e), but on the whole the results are very similar. In the 6μ region the solid shows maxima at 1706, 1639, 1580 and 1538 cm.$^{-1}$, whereas in solution maxima occur at 1721, 1683, 1642 and 1562 cm.$^{-1}$. It is noteworthy that the highest of these frequencies is lower than the frequencies assigned to δ-lactone carbonyl groups in compounds IV and V, although it does coincide with the frequency of maximum absorption in coumalic acid. It is not clear from the evidence now available whether the structure assigned compound XVI is compatible with its absorption spectrum. Unfortunately coumalin (α-pyrone) was not available for comparison of its spectrum with those included here.

**Compound VI.**—Compound VI and its methylation product have been assigned the cyclopentenedione structures



VI



XIXa

These compounds have very similar ultraviolet spectra (Fig. 2), VI differing from XIXa by showing a reversible bathochromic shift of 20 mμ in 0.08 *N* alkaline methanol solution (Fig. 4). This shift is attributed to the equivalence of the three oxygen atoms in the anion form of VI rather than to enolization such as accounts for a similar shift in cyclic β-diketones.[14]

The presence of the OH group in compound VI is clearly indicated by the peak at 3435 cm.$^{-1}$ in the infrared spectrum (Fig. 6f). The strongest band in the spectrum occurs at 1695 cm.$^{-1}$, a frequency much lower than would be expected if compound VI had an α-pyrone type structure. This

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(11) N. Sheppard, *Trans. Faraday Soc.*, **46**, 527 (1950).

(12) We are indebted to Dr. J. F. Carson of this Laboratory for the coumalic acid, which was prepared in accordance with R. H. Wiley and N. R. Smith, *Org. Syntheses*, **31**, 23 (1951).

(13) J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 566 (1941).

(14) E. R. Blout, V. W. Eaeger and D. C. Silverman, THIS JOURNAL, **68**, 566 (1946).

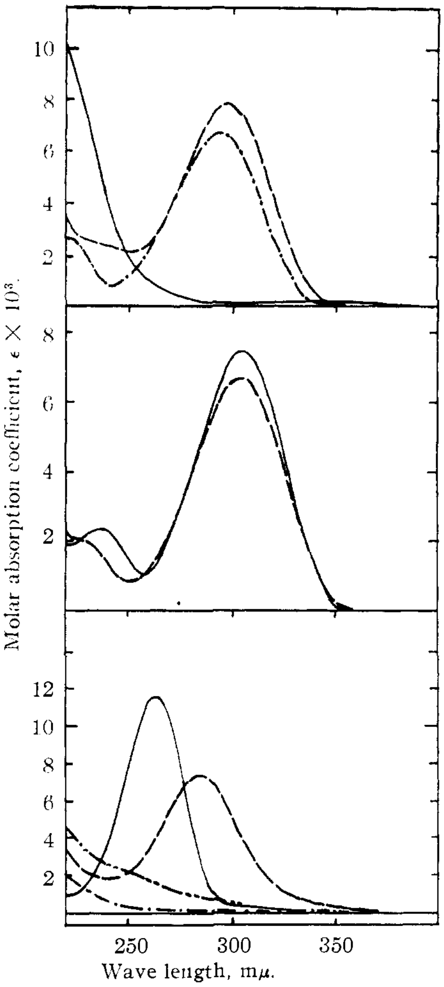


Fig. 1.—Ultraviolet absorption spectra in neutral methanol solution: (top) ——, compound IV; ------, compound V, $\epsilon_{max}$ 7570; —·—·—, compound XVI, $\epsilon_{max}$ 6550.

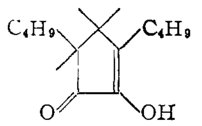
Fig. 2.—Ultraviolet absorption spectra in neutral methanol solution (middle): ——, compound VI, $\epsilon_{max}$ 7410; ------, compound XIX, $\epsilon_{max}$ 6600.

Fig. 3.—Ultraviolet absorption spectra in neutral methanol solution (bottom): ——, compound VII, $\epsilon_{max}$ 11,540; – – –, compound XXI, $\epsilon_{max}$ 7450; —·—·—·—, compound XXIII; —··—··—··—··, compound XXIIIa.

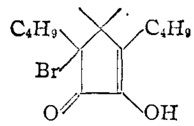
frequency is somewhat lower than has been found for carbonyl groups conjugated to a cyclopentene ring[8] (1715 cm.$^{-1}$).

The infrared spectrum of compound XIX (Fig. 6g) differs markedly from that of compound VI. Strong maxima are observed at 1718 and 1634 cm.$^{-1}$. The former of these agrees well with the value 1715 cm.$^{-1}$ observed for carbonyl groups conjugated to a cyclopentene ring[8] and the latter is typical of conjugated double bonds.[6] A possible explanation for the marked differences in spectra in the 6 μ region for compounds VI and XIXa is the difference in vibrational interaction of the bonds concerned. In VI the masses attached to carbon atoms 1, 3 and 5 are approximately the same, whereas this is not true in XIXa.

**Compound VII.**—Compound VII and its partial bromination product, XXI, have been assigned the structures



VII



XXI

The ultraviolet spectrum of VII (Fig. 3) shows maximum absorption at 261 mμ, about where one would predict for a trisubstituted 2-cyclopentenone in which one of the substituents is an OH group.[15,16] Like compound VI, compound VII is very weakly acidic, with a reversible bathochromic shift of nearly 40 mμ, substantially all the change taking place as the alkali concentration is changed from 0.002 $N$ to 0.08 $N$ (Fig. 4). The bathochromic shift of 21 mμ caused by bromine substitution in going from VII to XXI is of the same order of magnitude observed for bromine substitution in an α,β-unsaturated ketone system.[16] The hydroxyl

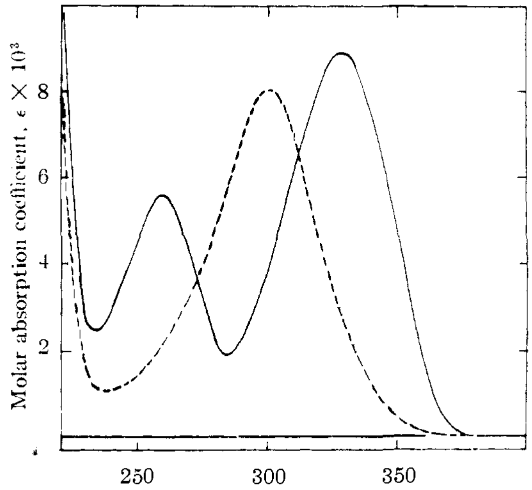


Fig. 4.—Ultraviolet absorption spectra in alkaline methanol solution (0.08 $N$ NaOH): ——, compound VI, $\epsilon_{max}$ 8890; - - - -, compound VII $\epsilon_{max}$ 8040.

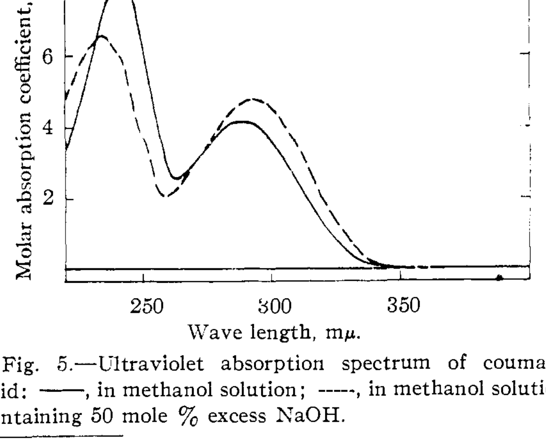


Fig. 5.—Ultraviolet absorption spectrum of coumalic acid: ——, in methanol solution; -----, in methanol solution containing 50 mole % excess NaOH.

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(15) H. S. French, This Journal, **74**, 514 (1952); H. S. French and M. E. T. Holden, *ibid.*, **67**, 1239 (1945).

(16) K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

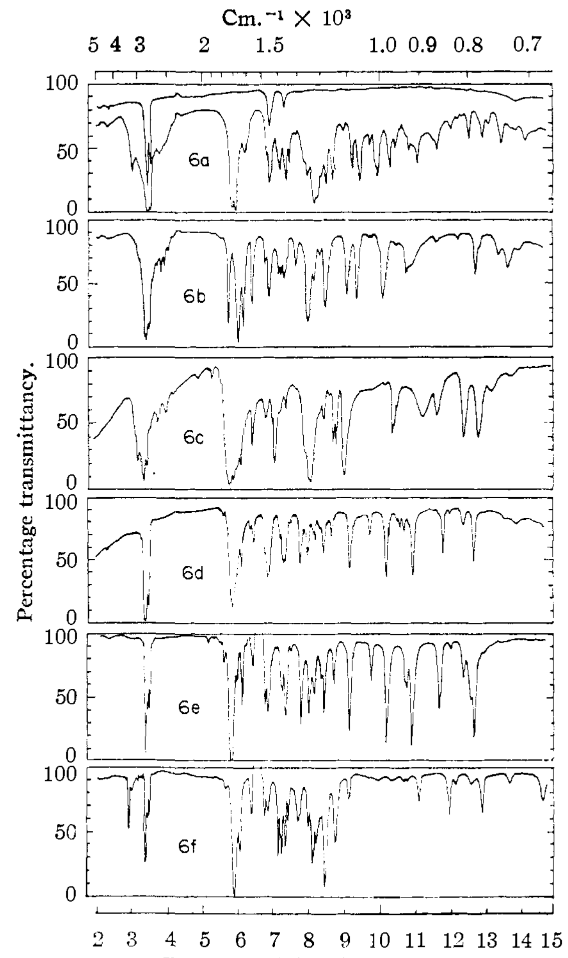
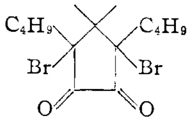
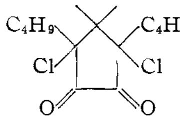


Fig. 6a–6d.—Infrared absorption spectra of mineral oil mull samples: 6a, upper curve, mineral oil; lower curve, compound IV. 6b, compound V; 6c, coumalic acid; 6d, compound XVI.

groups of VII and XXI are clearly indicated by the band at 3470 cm.$^{-1}$ in their infrared spectra (Fig. 6h, 6i). In the 6$\mu$ region sharp absorption maxima are found at 1703 and 1658 cm.$^{-1}$ for VII and 1712 and 1658 cm.$^{-1}$ for XXI. The higher value for each compound agrees satisfactorily with the value (1715 cm.$^{-1}$) observed for a carbonyl conjugated to a cyclopentene ring,[8] although the lower value is somewhat higher than usually found for a conjugated C=C bond.[6]

When compound VII was more completely brominated, two bromine atoms were introduced giving rise to compound XXIII, or compound XXIIIa in the case of chlorination, to which 1,2-cyclopentanedione structures were assigned.


XXIII


XXIIIa

The ultraviolet spectra of these compounds (Fig. 3) show no strong absorption maxima above 220 m$\mu$, as is to be expected since here there is no possibility of enolization to form $\alpha,\beta$-unsaturated ketone structures.[17] The infrared spectra of these compounds (Figs. 6j, 6k) are very similar over the region measured, all of the vibrations involving significant motions of the halogen atoms occurring above 15 $\mu$. Only a single maximum occurs in the 6 $\mu$ region, in accordance with observations on simple acyclic $\alpha$-diketones.[18] The observed frequencies, 1758 cm.$^{-1}$ for XXIII and 1767 cm.$^{-1}$ for XXIIIa, are somewhat higher than the value 1745 cm.$^{-1}$ expected for cyclopentanones[6,8] probably due to the electron-attracting effect of the halogen substituents.

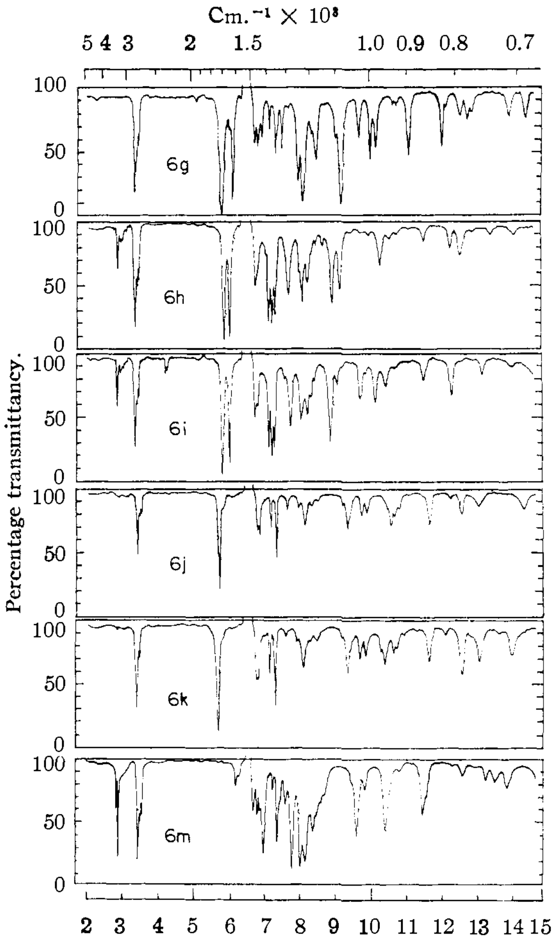


Fig. 6e–6m.—Infrared absorption spectra of compounds in carbon tetrachloride solutions (2–7.7 $\mu$) and in carbon disulfide solutions (7.7–15 $\mu$). Solvent absorbs strongly between 6.4 and 6.7 $\mu$. Path length 0.463 mm. 6e, compound XVI, 0.083 *M;* 6f, compound VI, 0.043 *M;* 6g, compound XIXa, 0.052 *M;* 6h, compound VII, 0.051 *M;* 6i, compound XXI, 0.048 *M;* 6j, compound XXIII, 0.031 *M;* 6k, compound XXIIIa, 0.048 *M;* 6m, 2,6-di-*t*-butylpyrogallol, 0.049 *M*.

**Di-*t*-butylpyrogallol.**—The ultraviolet spectrum of this starting material has been reported.[19] Its infrared spectrum is shown in Fig. 6m for characterization purposes. The presence of distinct

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[17] A. E. Gillam, J. I. Lynas-Grey, A. R. Penfold and J. L. Simonsen, *J. Chem. Soc.*, 60 (1941).

[18] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, This Journal, **71**, 1068 (1949).

[19] T. W. Campbell and G. M. Coppinger, *ibid.* **73**, 2708 (1951).

maxima at 3625 and 3545 cm.$^{-1}$ will be noticed indicating OH stretching frequencies of both "free" and internally H-bonded OH groups.[20]

Although a number of approximate coincidences of wave lengths of infrared absorption bands will be noticed in comparing the spectra of compounds assigned closely related structures in the above discussion, it is thought that more data on compounds of known similar structures should be available before further generalizations are made relating particular bands to particular structural features.

ALBANY 6, CALIFORNIA

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[20] L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

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[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

# Nuclear Structure of the Water-soluble Polycarboxylic Acids from the Oxidation of Bituminous Coal: The Hydrogenolysis Reaction[1]

BY JACOB ENTEL

RECEIVED FEBRUARY 4, 1954

To ascertain the nature of the nuclei of the yellow, water-soluble, polycarboxylic aromatic acids produced by the controlled oxidation of aqueous alkaline suspensions of bituminous coals these acids have been subjected to a series of reactions which have converted the carboxyl groups to methyl groups, and which have led to the isolation and identification of individual compounds. Herein is described the application of this series of reactions. Phthalan, 5-methylphthalan, 2-methylcyclohexanemethanol, 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetramethylbenzene have been isolated and identified from the fraction boiling at 195–207° (760 mm.) which was obtained from the hydrogenolysis of the butyl esters of these acids. Since further work on this problem is not planned for the near future, the results of preliminary investigations of those hydrogenolysis fractions boiling above 207° (760 mm.) are also presented. From these fractions pentamethylbenzene has been isolated and identified. Two compounds—4,5- and 4,7-dimethylphthalan—have been isolated, but it has not been possible to determine which of these compounds is the 4,5- or 4,7-dimethylphthalan. The data also indicated the presence of such compounds as polymethylbiphenyls, polymethylphthalans, polymethylhexahydrophthalyl alcohols, lactones of polymethyl-2-hydroxybicyclohexyl-2′-carboxylic acid and polymethylcyclohexanemethanols. The significance of these compounds in establishing the nuclear structure of the acids obtained from the alkaline oxidation of coal is discussed.

In the controlled oxidation of aqueous alkaline suspensions of bituminous coals, yellow, water-soluble, polycarboxylic aromatic acids are produced in yields of 50–60% by weight of coal charged.[2] These acids have been the subject of extensive investigations because of their potential commercial value and their significance in structural studies on coal.

In order to ascertain the nature of the nuclei to which the carboxyl groups are attached, these acids have been subjected to the following series of reactions: (1) esterification, (2) hydrogenolysis of the resulting esters, (3) precision fractional distillation of the hydrogenolysis products, (4) adsorption of selected distillation fractions on selective adsorbents, (5) precision fractional distillation of the products obtained by the adsorption procedure and (6) identification of individual compounds by chemical, spectroscopic and other physical means. The procedures, results and discussion of steps 1–3 inclusive have been described in detail elsewhere.[2]

The data obtained from the fractional distillation of 1920 g. of the hydrogenolysis products of the butyl esters of these acids[2] indicated that this material consisted essentially of a mixture of three classes of compounds: (a) oxygenated materials, (b) aromatic hydrocarbons and (c) alicyclic hydrocarbons. Initial separation of this mixture of classes from each other facilitates the isolation and identification of the individual compounds which comprise these hydrogenolysis products. The feasibility of effecting this type of separation by adsorption on bentonite and silica-gel has been shown.[3]

In this work primary interest was in those materials with boiling ranges higher than the previously identified trimethylbenzenes.[2] Accordingly, the fractions which were obtained from the fractional distillation of 1920 g. of hydrogenolysis materials[2] and which boiled above 195° at 760 mm. pressure were composited as shown in Table I, preparatory to separation by adsorption on bentonite and silica-gel.

TABLE I

PROPERTIES OF THE COMPOSITE DISTILLATION FRACTIONS OF THE HYDROGENOLYSIS PRODUCTS

| Fraction | B.p., °C./760 mm. | Mol. wt. range | Wt., g. |
|---|---|---|---|
| I | 195–207 | 126–140 | 87 |
| II | 212–263 | 144–174 | 180 |
| III | 280–317 | 186–218 | 173 |
| IV | >320 | 220–250 | 213 |
| V | ..... | 250–300 | 145 |
| Residue | ..... | Avg. 545 | 598 |

This paper describes the work up of fraction I, *in toto*, to show the feasibility of the previously outlined series of reactions in isolating and identifying individual components of the hydrogenolysis products of the esters of the acids obtained by the oxidation of bituminous coals. As work on this problem has been postponed indefinitely, the results of a preliminary investigation of fractions II–V inclusive are also presented.

## Experimental

**Selective Adsorption.**—22.6 g. of durene (1,2,4,5-tetramethylbenzene) was removed from fraction I by fractional freezing. The remaining 64 g. was dissolved in 640 ml. of pentane and subjected to a bentonite–silica gel adsorption sequence[3] with results shown in Fig. 1.

The bentonite column was developed with anhydrous ether after 1800 ml. of pentane had failed to elute the oxy-

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[1] Presented in part before the Division of Gas and Fuel Chemistry, American Chemical Society, April 21, 1953, Pittsburgh, Penna.

[2] C. H. Ruof, T. R. Savich and H. C. Howard, THIS JOURNAL, **73**, 3873 (1951).

[3] J. Entel, C. H. Ruof and H. C. Howard, *Anal. Chem.*, **25**, 616 (1953).