

obtained (Fig. 9), namely, 15,800 cal. per mole, or about the same as that calculated for the addition reaction.

Summary

The reaction between phenols and paraformaldehyde in the presence of a weak alkaline catalyst has been studied with ordinary phenol, eight alkylated phenols and saligenin.

The addition of formaldehyde apparently follows a first order rate law. The rate constants decrease in the following order: 3,5-xyleneol > *m*-cresol > 2,3,5-trimethylphenol > phenol > 3,4-xyleneol > 2,5-xyleneol > *p*-cresol > saligenin > *o*-cresol > 2,6-xyleneol.

2,6-Xyleneol reacts with exactly one-half mole of formaldehyde under these conditions, and the chief reaction product is the diphenylmethane derivative.

The observed velocity constants are composites of the rates of addition of the first, second and third moles of formaldehyde. The behavior of saligenin indicates that the second mole of formaldehyde is added at about one-third the rate of the first.

The effects of variation in phenol-formaldehyde ratio, catalyst concentration and temperature are discussed and illustrated graphically.

A bromination procedure has been used to gain an insight into the condensation processes, which involve the conversion of methylol to methylene

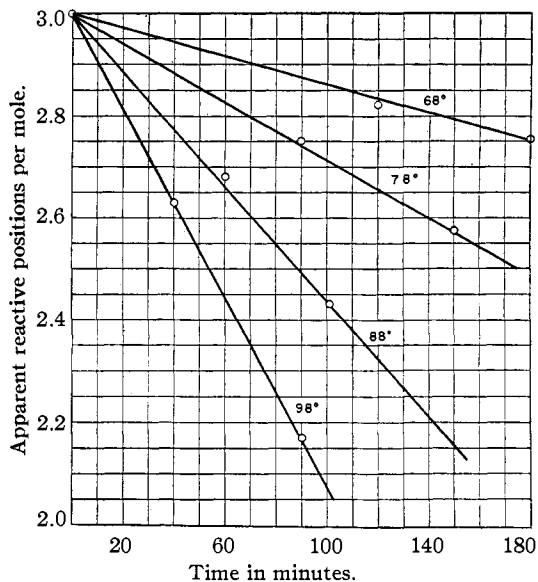


Fig. 11.—The condensation reaction: variation with temperature for *m*-cresol + paraformaldehyde.

groups. These reactions are very slow compared to the addition reactions.

The condensation rates for the phenolic systems studied are in the same relative order as the addition rates, except that a saligenin-formaldehyde mixture condenses at a rate about equal to that of a phenol-formaldehyde mixture.

A method is given for estimating the average chain length from the formaldehyde addition and bromination data.

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[CONTRIBUTION NO. 89 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Nature of Oils Obtained from the Hydrogenation of a Few Typical Bituminous Coals¹

BY CLAIRE D. LECLAIRE

From a study of the oils resulting from the high pressure hydrogenation of the extract and residue from the benzene extraction of Pittsburgh coal, Biggs and Biggs and Weiler² concluded that the benzene soluble and insoluble parts of this coal are similar in their essential chemical structure and that the oils formed by their hydrogenation are chiefly polycyclic hydroaromatic hydrocarbons. This conclusion is supported by further data described in the present paper, which

(1) Original manuscript received March 16, 1940.

(2) (a) B. S. Biggs, *THIS JOURNAL*, **58**, 1020 (1936); (b) B. S. Biggs and J. F. Weiler, *ibid.*, **59**, 369 (1937).

summarizes hydrogenation studies not only of Pittsburgh coal, but also of Pocahontas no. 3, High Splint, and Illinois no. 6 coals.³ These latter three coals were selected to determine the dependence of the nature of the hydrogenation products on the rank and type of certain bituminous coals. The hydrogenations were carried out in the presence of Adkins catalyst at 350°, a temperature that gave good yields of petroleum ether soluble products and avoided extensive degradation of the hydrocarbon structures.

(3) Wm. B. Warren, *Ind. Eng. Chem.*, **30**, 136 (1938).

TABLE I
YIELDS AND ANALYSES OF HYDROGENATION PRODUCTS
From (1) Pocahontas no. 3, (2) Pittsburgh, (3) High Splint, and (4) Illinois no. 6 Coals

	Pet. ether soluble	Fraction, g.	% of original carbon	Mol. wt. in biphenyl	Mol. % petroleum ether soluble	Average molecular formulas					
						C	H	OH	N	S	
1st fraction -165 (5 mm.)	}	1	16.9	8.5	178	34.5	12.8	22.1	0.10	0.014	0.025
		2	22.1	12.4	171	33.2	12.4	20.2	.15	.044	.011
		3	17.8	9.7	188	27.3	13.3	22.9	.20	.046	.014
		4	24.2	15.5	174	43.8	12.6	22.5	.13	.025	.008
2nd fraction 165-205 (5 mm.)	}	1	8.2	4.2	241	12.3	17.7	26.8	.21	.024	.025
		2	16.0	9.0	235	17.4	17.0	25.2	.25	.079	.018
		3	13.9	7.7	238	16.9	17.0	27.9	.34	.046	.000
		4	11.8	7.6	251	14.9	18.2	29.0	.16	.047	.008
3rd fraction 205-265 (5 mm.)	}	1	14.5	7.5	287	18.4	21.0	30.6	.16	.045	.003
		2	16.2	9.2	285	14.5	20.8	29.0	.24	.118	.000
		3	20.1	11.3	290	19.9	21.0	30.7	.25	.114	.006
		4	18.1	11.6	299	19.1	21.6	32.6	.22	.013	.007
4th fraction 265-310 (5 mm.)	}	1	21.0	11.0	398	19.2	29.5	39.7	.23	.065	.007
		2	15.1	8.7	391	9.9	28.6	38.6	.31	.106	.005
		3 ^a	38.6	21.9	421	26.2	30.9	43.6	.30	.147	.009
		4 ^a	24.3	15.9	417	18.4	30.6	45.4	.26	.057	.000
Residue from distillation	}	1	22.6	11.9	527	15.6	39.2	50.2	.24	.113	.015
		2	51.8	29.3	532	25.0	38.9	49.4	.35	.213	.023
		3	21.9	12.5	646	9.7	47.7	65.2	.29	.286	.000
		4	7.8	5.1	641	3.8	47.3	61.3	.28	.188	.004
Benzene sol. P. E. insoluble	}	1	22.0	11.9	492		37.5	32.5	.31	.186	.025
		2	13.0	7.6	555		41.7	39.9	.54	.321	.033
		3	5.5	3.3	555		42.5	37.5	.38	.190	.014
		4	5.0	3.4	498		37.4	36.3	.12	.053	.039
Hydrogenation residue	}	1		19.3							
		2		6.5							
		3		11.1							
		4		5.8							
Carbon loss	}	1		25.7							
		2		17.3							
		3		22.5							
		4		35.1							

^a Upper distillation temperature (3) and (4), 330°.

Experimental

The coals were hydrogenated by the stepwise procedure described by Biggs.¹ Adkins⁴ calcium-copper-chromium oxide was used as a catalyst, and the petroleum ether soluble oils were removed after each hydrogenation until there was almost complete conversion to soluble products. The coal (200 g. of -200 mesh) was mixed with 20 g. of catalyst in a 1-liter stainless steel bomb, and hydrogenated at 1800-2000 lb./sq. in. initial hydrogen pressure and 350° for twelve hours. Three hours were required to bring the bomb to the reaction temperature. After each hydrogenation the contents of the bomb were transferred to a Soxhlet thimble and extracted with benzene. The material insoluble in benzene was set aside for further hydrogenation. The greater part of the benzene was evaporated from the extract, which was then poured into more than ten times its volume of petroleum ether. The material insoluble in petroleum ether was filtered from the solution, was com-

bined with the benzene insoluble portion and 20 g. of additional Adkins catalyst, and was rehydrogenated.

The petroleum ether soluble portion was freed of solvent and set aside. After performing the cycle of hydrogenation and extraction processes ten times, the combined petroleum ether soluble portion was hydrogenated at 270° in benzene using Adkins catalyst, and then at 270° in cyclohexane using Raney nickel catalyst. The final hydrogenation product from each coal was freed of cyclohexane and distilled at 5 mm. pressure in an asbestos insulated unpacked 11 inch column. The vapor temperatures of distillation were: (1) -165°; (2) 165-205°; (3) 205-265°; (4) 265°. The upper limit of temperature of the fourth fraction varied between 310 and 330°. Some decomposition occurred during the later stages of the distillation. The fractions were colorless or nearly colorless oils with the exception of the fourth, which was fluorescent and too viscous to flow at room temperature. The residue was a resinous solid. Each fraction was characterized by initial boiling point, molecular weight, density, refractive index, dispersion, aniline point, and determination of carbon,

(4) R. Connor, K. Folkers and H. Adkins, *THIS JOURNAL*, **54**, 1139 (1932).

TABLE II
 PROPERTIES OF THE PARTLY SATURATED PETROLEUM ETHER SOLUBLE PRODUCTS
 From (1) Pocahontas no. 3, (2) Pittsburgh, (3) High Splint, and (4) Illinois no. 6 Coals

		Initial b. p. at 746 mm.	Density	Molecular volume	Aniline point, °C.	n_D^{20}	Specific refraction	$\frac{n_F - n_C}{d}$
1st fraction -165 (5 mm.)	1	228	0.900	198	46	1.4883	0.3202	0.01132
	2	205	.898	191	28	1.4875	.3206	.01026
	3	225	.892	211	36	1.4823	.3202	.00979
	4	220	.888	196	45	1.4809	.3203	.00995
2nd fraction 165-205 (5 mm.)	1	310	.964	250	41	1.5222	.3165	.01131
	2	305	.964	244	16	1.5245	.3177	.01208
	3	305	.950	251	35	1.5123	.3161	.01082
	4	305	.950	264	48	1.5117	.3157	.01045
3rd fraction 205-265 (5 mm.)	1	380	1.003	286	40	1.5430	.3141	.01239
	2	385	1.007	284	20	1.5502	.3164	.01326
	3	377	0.985	294	37	1.5351	.3160	.01197
	4	375	.985	304	50	1.5319	.3144	.01153
4th fraction 265-310 (5 mm.)	1		1.047	380	47	1.5710	.3138	.01213
	2		1.038	377	21	1.5670	.3147	.01672
	3 ^a		1.034	407	51	1.5655	.3152	.01744
	4 ^a		1.030	405	58	1.5580	.3130	.01323
Residue from distillation	1				59			
	2				41			
	3				57			
	4				76			

^a Upper distillation temperature (3) and (4), 330°.

hydrogen, hydroxyl, nitrogen and sulfur contents. These data are recorded in Tables I and II. The average molecular formulas represent the results obtained from the analytical data. The value reported for hydrogen is that obtained by combustion less the hydroxyl hydrogen determined with acetic acid in pyridine.⁵

The molecular weight of each fraction of the petroleum ether soluble oil was determined cryoscopically in biphenyl. Measurements at different concentrations showed the molecular weight to be independent of the concentration. The mean of two values that checked closely was used in calculating the average value for the fraction. The benzene soluble-petroleum ether insoluble material showed increasing values in apparent molecular weight with concentration, indicating a strong associating tendency; the molecular weights for this material given in Table I were obtained by extrapolation to zero concentration. The index of refraction and the dispersion were determined with an Abbe refractometer.

These oils, which had received only one hydrogenation over Raney nickel, were not completely saturated as is shown by their aniline points, specific dispersion, and refractive index. To saturate them completely each fraction was hydrogenated with about two times its weight of Raney nickel in 300 ml. of cyclohexane at 270°. After distilling off the cyclohexane under reduced pressure, the properties of the oils were again determined. A modified Menzies-Wright ebullioscopic apparatus with benzene as the solvent was used in determining the molecular weights of the saturated oils.⁶ The properties of the saturated oils are given in Tables III and IV.

(5) M. Freed and A. M. Wynne, *Ind. Eng. Chem., Anal. Ed.*, **8**, 278 (1936).

(6) W. E. Hanson and J. R. Bowman, *ibid.*, **11**, 440 (1939).

Discussion

Bone and co-workers,⁷ Juettner⁸ and Kent⁹ have shown the presence of aromatic rings in coal by the separation and identification of benzene carboxylic acids obtained from the oxidation of coal. The physical properties of the hydrogenation products from coal obtained by Biggs and Weiler² suggested the presence of cyclic structures, and pure aromatic hydrocarbons have been isolated from similar material by Biggs.¹⁰ Aromatic structures are also indicated from the work of Weiler¹¹ on the chlorination of coal.

McAllister and Davis¹² have shown that molecular volume plotted as a function of molecular weight for the saturated homologous series of paraffins, paraffin substituted cyclohexanes, and paraffin substituted decalins, etc., gave a series of parallel lines as shown in Fig. 1. The number of rings in a perhydroaromatic compound thus determines its position in this family of lines. The molecular volumes and molecular weights of the saturated oil fractions from the hydrogenation of coal are plotted and their position in relation to

(7) W. A. Bone, L. Horton and S. G. Ward, *Proc. Roy. Soc. (London)*, **A127**, 480 (1930).

(8) B. Juettner, *THIS JOURNAL*, **59**, 1472 (1937).

(9) C. R. Kent, *Australian Chem. Inst. J. & Proc.*, **6**, 127 (1939).

(10) B. S. Biggs, *THIS JOURNAL*, **58**, 484 (1936).

(11) J. F. Weiler, *ibid.*, **58**, 1112 (1936).

(12) E. N. McAllister and G. N. B. Davis, *Ind. Eng. Chem.*, **22**, 1326 (1930).

TABLE III

PROPERTIES OF THE PETROLEUM ETHER SOLUBLE OILS AFTER THE SECOND HYDROGENATION WITH RANEY NICKEL
From (1) Pocahontas no. 3, (2) Pittsburgh, (3) High Splint, and (4) Illinois no. 6 Coals

Pet. ether soluble	Mol. wt.	Density	Molecular vol.	Index of refraction	$\frac{n_D - n_C}{d}$	Specific refraction	Aniline point	Hydroxyl per mol.	
1st fraction	1	208	0.880	236	1.4772	0.00979	0.3211	60.3	0.08
	2	209	.875	239	1.4742	.00978	.3213	61.0	.02
	3	198	.877	226	1.4742	.00952	.3207	59.6	.10
	4	189	.875	216	1.4744	.00979	.3215	60.6	.07
2nd fraction	1								
	2								
	3	254	.917	277	1.4941	.00983	.3176	70.4	.21
	4	253	.921	275	1.4963	.00959	.3172	71.5	.13
3rd fraction	1	306	.967	316	1.5171	.00958	.3129	79.0	.28
	2	320	.962	331	1.5146	.00970	.3134	77.8	.38
	3	316	.956	331	1.5118	.00967	.3139	79.5	.12
	4	323	.958	337	1.5132	.01032	.3139	80.0	.05
4th fraction	1	422	1.003	421	1.5372	.01017	.3114	85.0	.27
	2	382	1.000	382	1.5388	.01066	.3132	62.8	
	3	420	0.998	421	1.5370	.01013	.3131	82.5	.10
	4	424	1.000	424	1.5358	.01045	.3119	88.0	.13

TABLE IV

COMPOSITION OF THE SATURATED OILS IN PERCENTAGE BY WEIGHT OF LINEARLY OR ANGULARLY CONDENSED RINGS AND PARAFFIN SIDE CHAINS AND IN PERCENTAGE OF CARBON AND HYDROGEN DERIVED FROM FIG. 2 TOGETHER WITH THE CARBON AND HYDROGEN PERCENTAGES BY ANALYSIS

From (1) Pocahontas no. 3, (2) Pittsburgh, (3) High Splint, and (4) Illinois no. 6 Coals

	Av. no. of rings, %	Composition in % by wt. assuming hydrocarbon		Composition					
		Naphthene	Paraffin side chains	By analysis			Other elements by difference	From Fig. 2	
				C	H			C	H
1st fraction	1	87-2; 13-3	69.7	30.3	84.9	13.1	2.0	86.3	13.7
	2	85-2; 15-3	68.8	31.2	85.1	13.0	1.9	86.3	13.7
	3	85-2; 15-3	73.7	26.3	86.3	12.6	1.1	86.3	13.7
	4	100-2	73.0	27.0	86.2	13.0	0.8	86.2	13.8
2nd fraction	1								
	2								
	3	3-2; 97-3	75.0	25.0	86.9	12.6	0.5	86.7	13.3
	4	98-3; 2-4	76.3	23.7	86.5	12.7	0.8	86.7	13.3
3rd fraction	1	69-4; 31-5	86.2	13.8	87.0	12.0	1.0	87.0	13.0
	2	64-4; 36-5	83.4	16.6	86.8	12.3	0.9	87.0	13.0
	3	78-4; 22-5	81.6	18.4	86.3	11.8	1.9	87.1	12.9
	4	71-4; 29-5	82.8	17.2	86.8	12.0	1.2	87.2	12.8
4th fraction	1	5-5; 95-6	83.2	16.8	87.9	11.4	0.7	87.5	12.5
	2	97-5; 3-6	79.0	21.0					
	3	53-5; 47-6	77.5	22.5	87.4	11.7	0.9	87.3	12.7
	4	18-5; 82-6	81.2	18.8	87.2	11.8	1.0	87.5	12.5

the parallel lines indicate their approximate number of rings per average molecule to be: first fraction, two rings; second fraction, three rings; third fraction, four to five rings; fourth fraction, six to seven rings, with the exception of the oil from Pittsburgh coal which has a lower molecular weight and fewer rings per molecule. A similar plot of the partly saturated oils shows about the same number of rings per molecule. Unfortunately, after determining the properties of the

second fraction of the oils from Pocahontas no. 3 and Pittsburgh coal there was not sufficient oil for further hydrogenation studies. The properties of these two fractions are probably very similar to the second fractions from Illinois no. 6 coal and High Splint coal as shown by the similarity of the four fractions of the partly saturated oils from these coals.

A method of determining the nature of the saturated hydrocarbons in petroleum oils has been

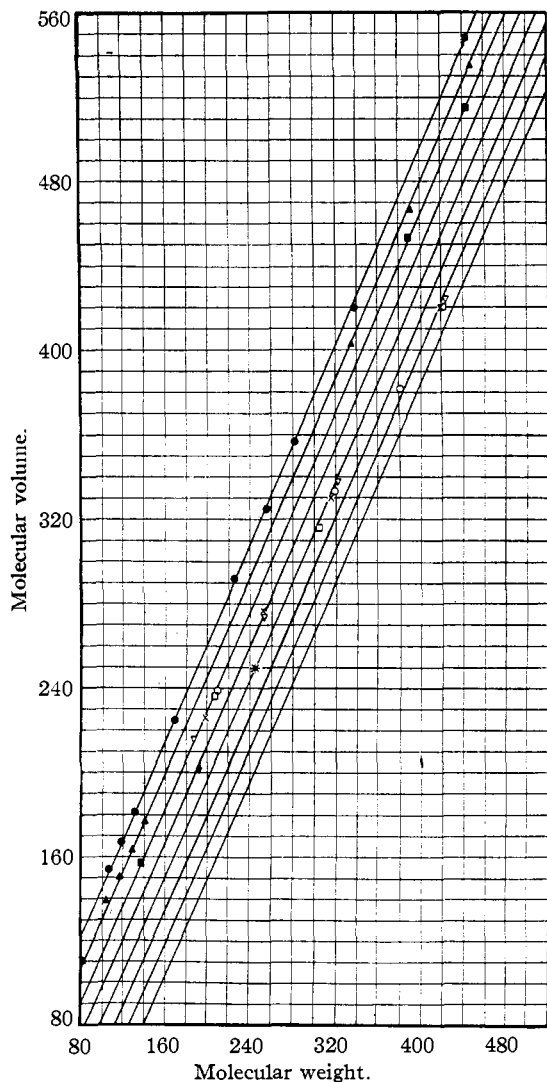


Fig. 1.—Molecular volume versus molecular weight of paraffinic and perhydroaromatic hydrocarbons and derivatives including the hydrogenation products from four coals: paraffins, ●; cyclohexane derivatives, ▲; decalin derivatives, ■; perhydrophenanthrene, ◆; perhydrochrysene, *; Pocahontas no. 3, □; High Splint, ×; Pittsburgh, ○; Illinois no. 6, ▽.

developed by Waterman and co-workers,¹³ based on the relation between specific refraction and molecular weight of different types of hydrocarbon, using the atomic refractions for carbon and hydrogen of Eisenlohr¹⁴ which were shown to be in agreement with their experimental values. In Fig. 2 this method has been applied to the saturated products obtained from the hydrogenation of the four coals. Specific refractions, cal-

culated from atomic refractions, are plotted against molecular weight for the side chain homologs of saturated, linearly or angularly condensed six-membered ring hydrocarbons. The specific refractions of the saturated fractions from the hydrogenation of the four coals plotted in the figure show that the oils are composed, for the most part, of cyclic structures. The number of rings calculated from the position in the diagram are given in Table IV. It seems logical, because of studies previously mentioned, to assume that the rings are six-membered and that they are probably of a condensed ring structure; moreover, the dimethyl naphthalenes isolated in previous studies¹⁰ indicate that the non-ring atoms are probably present as paraffin side chains rather than a mixture of completely naphthenic and paraffinic molecules. The estimation of the number of rings (Table IV) in the average molecule of each fraction thus is based on the assumption that the rings are linearly or angularly condensed perhydroaromatic six-membered carbon structures, and the percentage of paraffin side chains by weight are calculated from the remaining non-ring atoms. Although there are small differences in fractions boiling in the same range, the similarity of these fractions for the different coals is the most noticeable feature brought out in Tables III and IV.

The effect of unsaturation on the properties of

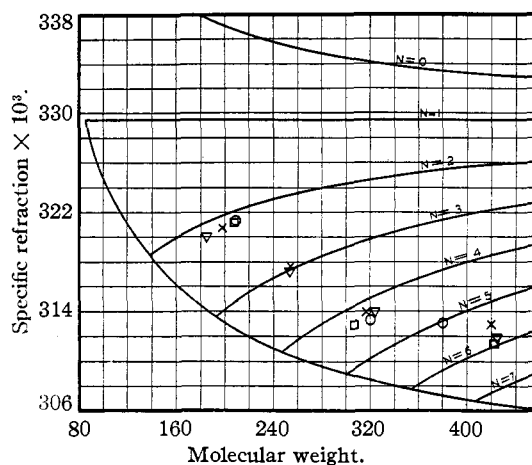


Fig. 2.—Molecular weight versus specific refraction of paraffins and paraffin side chain homologs of linearly or angularly condensed perhydroaromatic hydrocarbons. The points for such hydrocarbons lie on the line $n = 0$, $n = 1$, $n = 2$, etc., where n is the number of rings in the molecule. The saturated hydrogenation products of the four coals are represented as follows: Pocahontas no. 3, □; High Splint, ×; Pittsburgh, ○; Illinois no. 6, ▽.

(13) J. C. Vlughter, H. I. Waterman and H. A. van Westen, *J. Inst. Petroleum Tech.*, (a) **21**, 661, (b) 707 (1935).

(14) F. Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1910-1911).

the oil from the hydrogenation of coal is shown by a comparison of Table II with Table III. The index of refraction of the saturated products has decreased as a result of saturation. The specific refraction $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$ should also decrease with increasing saturation and it is therefore surprising to find an increase in specific refraction of the first and second fractions of the oils after a second hydrogenation with Raney nickel. This increase in specific refraction can be accounted for by a cleavage of ring members to paraffin side chains which causes a sufficient decrease in density to increase the specific refraction. The cleavage of rings with the formation of side chains probably occurs throughout all the fractions, but results in an increase in specific refraction only in the first and second fractions where the ratio of the bonds cleaved to bonds saturated is greater than with the incompletely saturated oils from the third and fourth fractions that have more unsaturation and more rings per molecule. The first fractions, therefore, show the greatest percentage of paraffin side chains. The number of rings in the average molecule increases with molecular weight as shown in Table IV. The original units from which the molecules under consideration are derived are probably composed of somewhat more rings than are indicated by the hydrocarbon units represented in Table IV. The agreement between the composition calculated from Fig. 2 and that obtained by analysis (Table IV) is satisfactory in view of the fact that the composition given from Fig. 2 supposes the molecule to be a hydrocarbon whereas in none of the fractions does the percentage of carbon and hydrogen add up to 100%.

Waterman¹³ has pointed out that specific dispersion is a property which varies with unsaturation. Von Fuchs and Anderson¹⁵ find $(n_t - n_c)/d$ preferable to Waterman's $(n_g - n_c)/d$ because the former can be determined with an Abbe refractometer. Paraffins, naphthenes and naphthenes having paraffin side chains are reported by von Fuchs and Anderson to have dispersion values which vary from 0.0095 to 0.0102, the values for aromatic hydrocarbons being more than twice as great. The values of specific dispersion for the oils which are not completely saturated range from 0.0097 in the first fraction to 0.0174 in the higher fractions. That the second hydrogenation

with Raney nickel has almost completely saturated the oils is shown by the low values of their specific dispersion. The fourth fraction of oil from Pittsburgh and the third and fourth fraction from Illinois no. 6 coal have somewhat higher specific dispersions than values given for saturated naphthenes and paraffins, but the unsaturation indicated by their higher specific dispersion is very small if the high values of dispersion for aromatic compounds be used as a criterion. If saturated, these fractions would show a lower specific refraction and a slightly greater number of rings per molecule.

The aniline points (Table III) of the saturated oils show a large increase over those of the partly saturated oils, and if the aniline points and molecular weights are plotted in Waterman's curve¹² of isoaniline points, the oils appear to be (with the possible exception of the fourth fraction from Pittsburgh coal), for all practical purposes, completely saturated.

The percentage of other atoms, obtained by subtracting the sum of the carbon and hydrogen percentages from 100, are small and should not affect the foregoing conclusions.

Although the increase observed in the unsaturated oils after saturation may be due, in part, to the different methods of determining molecular weights, it seems more likely that this increase is due chiefly to the loss of part of the lower molecular weight hydrogenation products with the cyclohexane during the removal of the solvent under reduced pressure. The increase in molecular weight does not affect the conclusions drawn in the preceding discussion. The following discussion is based on the molecular weights of the unsaturated products.

Comparison of the Coals.—Table V and Fig. 3 show the distribution in mole per cent. of petroleum ether soluble material on the basis of

TABLE V
CUMULATIVE MOLE PER CENT. OF PETROLEUM ETHER SOLUBLE PRODUCTS

Mol. wt. less than	Pocahontas no. 3	Pittsburgh	High Splint	Illinois no. 6
189	34.5	33.1	27.3	44.0
251	46.8	40.5	44.2	58.8
299	65.2	55.1	64.1	78.0
421	84.4	81.3	74.1	94.3
646	100.0	100.0	100.0	100.0

the average molecular weight of each fraction. The three coals—Pocahontas no. 3, Pittsburgh, and High Splint—yield products that show dis-

(15) G. H. von Fuchs and A. P. Anderson, *Ind. Eng. Chem.*, **29**, 319 (1937).

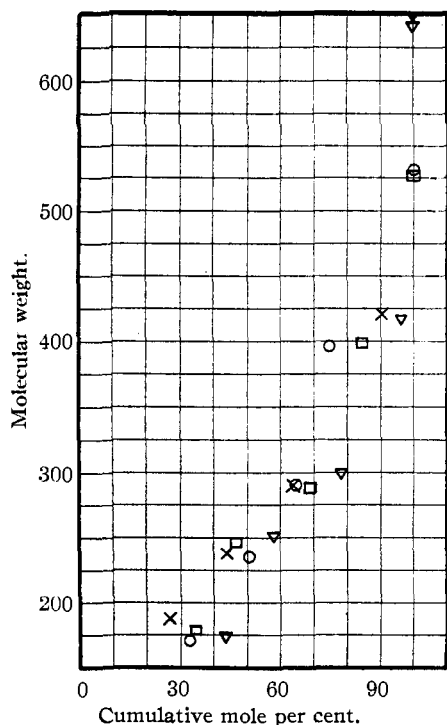


Fig. 3.—Cumulative mole per cent. of petroleum ether soluble hydrogenation products *versus* the average molecular weight: Pocahontas no. 3, □; High Splint, ×; Pittsburgh, O; Illinois no. 6, ∇.

tributions which are not greatly different. Illinois no. 6 coal, which yields 78% of the petroleum ether soluble material consisting of molecules having a molecular weight of less than 299, differs appreciably from the other three coals which show only 65 mole per cent. of a similar material. Corresponding values for the hydrogenation products from the residue and extract from the benzene pressure extraction of Pittsburgh coal, as determined by Biggs and Weiler,² are in agreement with the results of this investigation. A comparison of the results of Biggs' and Weiler's work with those of the present investigation is given in Fig. 4. The first fraction of the oil from the residue was separated into the five fractions represented by the first five points; the average molecular weight calculated from these points falls just above that obtained from the first fraction derived from the whole coal. While not identical, because the fractions were taken at different temperatures, the curves from the extract, residue, and whole coal lie sufficiently close together to indicate that the hydrogenation products from these sources are of similar chemical nature, and therefore that the extract, residue,

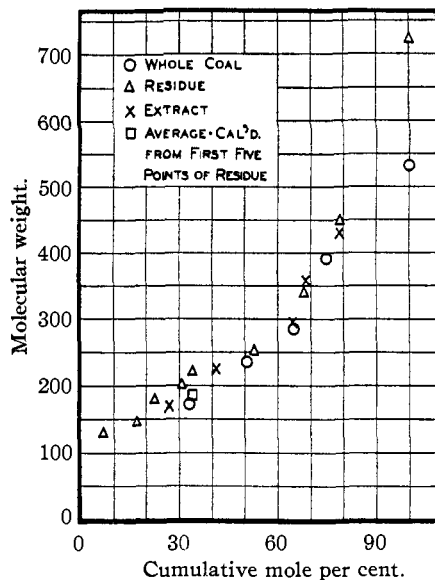


Fig. 4.—Molecular weight *versus* cumulative mole per cent. of petroleum ether soluble hydrogenation products from Pittsburgh coal and from the extract and residue obtained by extraction of Pittsburgh coal with benzene at 260°.

and whole coal are composed of similar building units.

The cumulative weight per cent. of carbon found in the different products (Table I) obtained from each of the four coals is plotted against the molecular weight in Fig. 5. The points nearest the abscissa represent the carbon lost in the process of hydrogenation. Inasmuch as manipula-

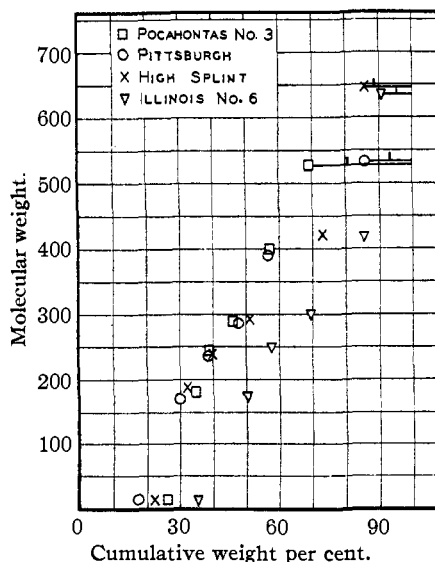


Fig. 5.—Molecular weight *versus* cumulative weight per cent. of carbon in products from the hydrogenation of four coals.

tive losses were carefully minimized, the greater part of this carbon is probably discharged as gaseous hydrocarbons with the hydrogen at the end of the hydrogenation. For the purpose of plotting, these hydrocarbons are assumed to be methane, although gaseous hydrocarbons of higher molecular weight are known to be present. The points near the top of the figure show the molecular weight of the residue from the distillation of the petroleum ether soluble material and represent the sum of the carbon loss and the carbon in the petroleum ether soluble products. The lines connecting these points to the 100% line represent the carbon in the benzene soluble-petroleum ether insoluble material (left of division), the molecular weight of which is not used in this figure, and the carbon remaining in the hydrogenation residue, the molecular weight of which is unknown. The small size of the carbocyclic building units in Illinois no. 6 coal, as compared to the other three coals, is clearly demonstrated in the figure.

In order to show the correlation between the yield of petroleum ether soluble material and the rank of the coal, the coals are arranged in Table VI in order of decreasing rank, which is also the order of decreasing carbon content, increasing oxygen content, and increasing volatile matter.

TABLE VI
RELATION OF COAL RANK TO YIELD OF OXIDATION AND HYDROGENATION PRODUCTS

	Poca- hontas no. 3	Pitts- burgh	High Splint	Illinois no. 6
% Carbon ^a	90.9	85.0	83.8	80.6
% Oxygen ^a	2.0	6.9	8.1	10.5
% Volatile matter ^a	16.3	37.1	38.9	40.3
% Loss of carbon on hydrogenation ^b	25.7	17.3	22.5	35.1
% of total carbon hy- drogenated to P. E. soluble products	43.1	68.6	63.1	55.7
Weight % of carbon in hydrogenation residue	19.3	6.5	11.1	5.8
Yield of mellitic acid on oxidation ⁵	10.9	5.5	5.0	4.3
Total acids after KMnO ₄ oxidation ⁵	25.8	28.1	14.4	19.3

^a Ash and moisture-free basis. ^b Largely gas loss.

Since coalification is characterized by increasing condensation to cyclic structures, the coals are also arranged in order of decreasing condensation, as shown by the decreasing yields of mellitic acid. High Splint coal, appearing just below Pittsburgh coal in rank, differs from the other three coals in

type. The large residue from the hydrogenation of the splint coal has been attributed to a characteristic constituent, opaque attritus.¹⁶

The physical properties of the oils from the hydrogenation of High Splint coal are not decidedly different from the same fractions of the other three coals. The uniformity of the products obtained by hydrogenation of these different coals, regardless of rank or type, indicates a marked similarity in chemical structure.

Table VI shows that the highest yields of petroleum ether soluble material are obtained from a coal of intermediate rank. Increased formation of gaseous hydrocarbons lowers the yield of liquid products obtained in hydrogenating a coal of lower rank; whereas with a coal of higher rank both increased formation of gaseous hydrocarbons and increased amounts of carbon remaining in the residue lower the yield of liquid products. An explanation of this result may lie in the fact that oxygen-to-carbon linkages are quite susceptible to rupture under hydrogenation treatment¹⁷ and when dispersed throughout the coal they serve as a point for attack and breakdown of the coal structure. In Illinois coal the oxygen is so generously distributed throughout the coal structure that the coal on hydrogenation is broken into units, a considerable part of which are low molecular weight gaseous products, and the remainder of the units are, on the average, smaller than those obtained from the other three coals. High rank Pocahontas coal does not, however, give good yields of petroleum ether soluble products because there is not sufficient oxygen dispersed throughout the coal structure to permit the breakdown of the coal to units of a size that are soluble in petroleum ether; a large fraction of the carbon remains in high molecular weight structures in the residue. The maximum yields of petroleum ether soluble oils are obtained in a medium rank bituminous coal such as Pittsburgh or High Splint coal where sufficient oxygen, dispersed throughout the coal, serves as a point for attack and facilitates breakdown of the coal structure to units of intermediate molecular weight which are soluble in petroleum ether.

Summary

An investigation of the hydrocarbon oils from the hydrogenation of four coals has shown that

(16) C. H. Fisher, *et al.*, *Ind. Eng. Chem.*, **31**, 1155 (1939).

(17) E. M. Van Duzee and Homer Adkins, *THIS JOURNAL*, **57**, 147 (1935).

regardless of the rank or the type of these coals, the products are similar, and that the general properties correspond to condensed carbocyclic structures with paraffin side chains. Although it seems probable that this type of structure predominates, the presence of purely cyclic and paraffinic structures cannot be excluded.

The lower rank coal of high oxygen content gives on hydrogenation units which have, on an average, lower molecular weights than the units

from higher rank coals of low oxygen content.

On hydrogenation, the extract and residue from the benzene extraction of coal give hydrocarbons which are similar in nature to those obtained from the hydrogenation of the unextracted coal.

The maximum yields of petroleum ether soluble products are obtained by hydrogenation of medium rank coals.

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Another Type of Free Radical in the Group of Thiazines and Some Other Related Heterocyclic Rings

BY L. MICHAELIS, S. GRANICK AND M. P. SCHUBERT

Among the thiazine dyestuffs it was those with two auxochromic groups, such as thionine and methylene blue, for which formation of very stable semiquinone radicals in strongly acid solution was first discovered.¹ Later, certain thiazine-, oxazine-, and selenazine dyestuffs containing only one auxochromic group, either an amino group, or a hydroxyl group, were shown to be capable of forming semiquinone radicals even to a still higher extent.² Herefrom the problem arises how thiazine, oxazine, and selenazine³ themselves, containing no auxochromic groups, behave. Our concern is essentially the problem whether there is a reversible univalent oxidation product, a free radical.

It has been shown by R. Pummerer and S. Gassner⁴ and by Kehrman and Diserens⁵ that an oxidation product of thiazine on the oxidation level of a "meriquinone" easily can be obtained.

(1) L. Michaelis, M. P. Schubert and S. Granick, *THIS JOURNAL*, **62**, 204 (1940).

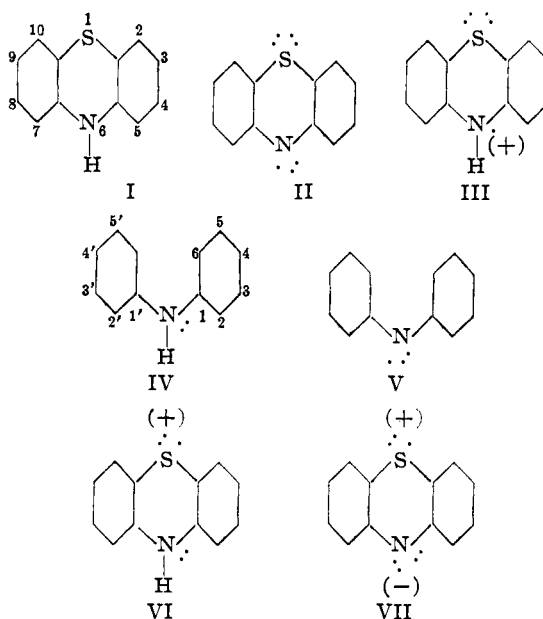
(2) S. Granick, L. Michaelis and M. P. Schubert, *ibid.*, **62**, 1802 (1940).

(3) The parent substance or nucleus of a thiazine dye, stripped of all side chains is a substance which can exist in various oxidation levels. The fully reduced form is best known. It is thiodiphenylamine. An analogous name for the parent substance of the oxazines, namely, oxydiphenylamine, would be ambiguous. Bernthsen³ [*Ber.*, **20**, 942 (1887)] for this reason named it phenazoxin. To avoid all difficulties in nomenclature we shall use the name *phenothiazine*, or even abbreviated, if no ambiguity arises, *thiazine*, for the parent substance, or skeleton, of the thiazine dyes and when we wish to distinguish the various reversible oxidation levels in which it may exist, we use the prefix *r*-, *s*-, or *t*-, for the reduced, semi-oxidized, and totally oxidized (quinonoid) forms, in the same way as for the dyestuffs themselves.¹ Then *r*-thiazine is the same as thiodiphenylamine. In the same sense we speak of *r*-, *s*-, and *t*-oxazine and selenazine.

(4) R. Pummerer and S. Gassner, *Ber.*, **46**, 2310 (1913).

(5) Kehrman and Diserens, *ibid.*, **48**, 318 (1915).

A substance on a holoquinoid oxidation level can be prepared also. This holoquinoid product although easy to prepare in the form of its perbromide, is much less stable, and under our working conditions, by oxidizing the *r*-form in 80% acetic acid, has no noticeable stability at all. We are here mainly interested in the "meriquinoid" product and shall show that this is a free radical. If the two positions 3 and 9 (in formula I) are



methylated, the radical is even more stable due to the blocking of the very reactive H atoms in para position to the N. Whereas the radicals of the thiazine dyes proper are formed only in rather