With alkaline potassium permanganate, an acid resulted, m. 233–5° (uncorr.), apparently isopropyl *m*-phthalic acid (m. 236°) and, by further oxidation, an acid, m. 195–8°, which gave an impure ethyl ester, m. 102–5°. The latter is, therefore, probably the dimethylphthalide *m*-carboxylic acid, which m. 205–6°, and its ethyl ester at 105–6°.

Unfortunately, the reactions were not carried out with enough material to adequately purify these oxidation products and more definitely establish their identity, but it is hoped to complete this part of the work at a later date.

Reduction of Cymene 3-Carboxylic Acid.—A solution of the acid in glacial acetic acid was mixed with a solution of colloidal platinum, and the resulting homogeneous solution shaken mechanically for 20 hours while it was subjected to treatment with hydrogen at 13 lbs. pressure. No reduction occurred, the original acid being recovered unchanged. Experiments on the reduction of an amyl alcohol solution of the acid by metallic sodium are under way and will be reported later.

Summary of Results.

1. The syntheses of *p*-cymene 2-carboxylic acid and of *p*-cymene 3-carboxylic acid, have been accomplished from the corresponding bromo cymenes, and numerous derivatives of these acids prepared and studied.
2. The statements in the literature concerning cymene 2-carboxylic acid and its salts have been tested and corrected. The following hitherto unknown derivatives have been prepared: methyl ester, ethyl ester, acid chloride, acid anilide, diacyl hydrazine, the furodiazole condensation product from the latter, the cymyl hippuric acid and its ethyl ester.
3. Cymene 3-carboxylic acid is entirely new. In addition to the free acid, the following derivatives have been synthesized and examined: Na, K, Ca, Ba, Cu and Ag salts, methyl ester, ethyl ester, phenyl ester, acid chloride, acid amide, acid anilide, diacyl hydrazine, the furo- and *N*-phenyl pyrrodiazole condensation products from the latter, and the cymyl hippuric acid.
4. The bromination product of cymene has been shown to be a mixture of 2- and 3-bromo derivatives, and not a pure 2-bromo derivative as hitherto assumed.

New York, N. Y.

[Contribution from the Mellon Institute of the University of Pittsburgh.]

THE HYDROLYSIS OF CHLOROPENTANES AS AFFECTED BY HIGH PRESSURE: SYNTHETIC FUSEL OIL.

By Harry Essex, Harold Hibbert and Benjamin T. Brooks.

Received May 6, 1916.

The recent work of Meyer and Bergius[1] on the conversion of chlorobenzene and chloronaphthalene into phenol and α-naphthol, respectively,

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[1] *Ber.*, 47, 3155 (1914).

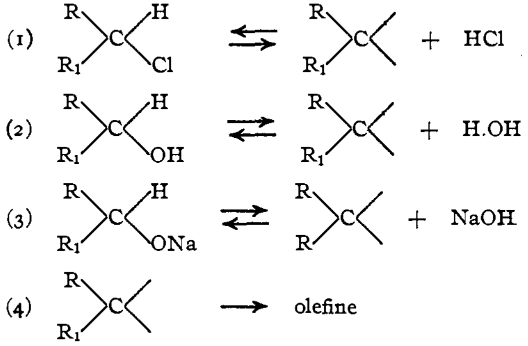
by heating the chlorides with aqueous alkalies at about 300° and 1500 pounds' pressure, showed that the yields were increased by pressure and to a very striking degree. We have employed similar conditions and also much higher pressures with chloropentanes with the object of studying their conversion into the amyl alcohols. Obviously the two cases show several marked points of difference. Benzene dissociates on heating to about 550°, giving hydrogen and diphenyl,[1]

$$2C_6H_5 — H — (2C_6H_5 — + 2H) — C_6H_5.C_6H_5 + H_2.$$

The temperature at which the dissociation of chlorobenzene first becomes appreciable must be somewhat lower than this, although Meyer and Bergius heated chlorobenzene with water vapor at atmospheric pressure at 500° without any noticeable reaction.

In the presence of considerable excess of 15% NaOH solution at 300°, Meyer and Bergius obtained first diphenyl ether and finally, after longer heating, nearly theoretical yields of phenol. Dilute alkalies, lime, sodium carbonate and borax solutions had very little effect on chlorobenzene under the same conditions of pressure and temperature. Our findings on the behavior of chloropentane differ very markedly from their results. With the alkyl chloride, we obtained practically the same yields of alcohol with sodium carbonate as with caustic soda and even larger yields with sodium acetate than with sodium carbonate under conditions otherwise substantially the same. The amount of diamyl ether formed was usually very small, never exceeding 8%. When glacial acetic acid is employed as a solvent, the relatively more stable amylacetate is obtained in much larger yields and at much lower pressures.

These results appear to be explained in a very satisfactory manner by Nef's[2] theory of the manner in which the alkyl halides dissociate and then react with other substances by addition.



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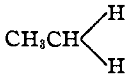
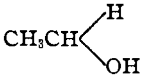
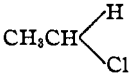
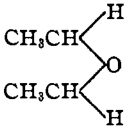
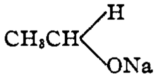
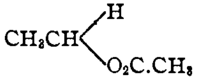
[1] Cf. Engler, *Das Erdöl,* Vol. I, 576.

[2] THIS JOURNAL, 26, 1570 (1904); *Ann.*, 309, 126; 318, 1.

The relative ease with which some of the compounds of the ethane series, the hydrocarbon, alkyl chloride, alcohol, ether and sodium alcoholate appreciably decompose is shown in the following:[1]

Substance.	Temperature.
Ethane  $CH_3CH{<}^{H}_{H}$	800°
Ethyl alcohol  $CH_3CH{<}^{H}_{OH}$	650°
Ethyl chloride  $CH_3CH{<}^{H}_{Cl}$	510–530°
Ethyl ether  $\begin{matrix}CH_3CH{<}^{H} & \\ & {>}O \\ CH_3CH{<}_{H} & \end{matrix}$	550°
Sodium ethylate  $CH_3CH{<}^{H}_{ONa}$	250°
Ethyl acetate  $CH_3CH{<}^{H}_{O_2C.CH_3}$	"low red heat"[2]

Comparative data for the corresponding compounds of the *n*-pentane series are lacking. The relative stability of the primary derivatives of *n*-pentane is undoubtedly of the same order, with respect to one another, as in the ethane series. The same probably holds in the series of secondary derivatives. The chloropentanes employed in this work were prepared from petroleum pentane, as herein described, and consisted of the 1, 2 and 3 monochloro derivatives.

The effect of caustic alkali in producing increased yields of amylene, as compared with sodium carbonate, borax and sodium acetate, finds a ready explanation in the low dissociation temperature of the sodium alcoholate. This would have the effect of increasing the concentration of the dissociated methene, which has the result of increasing the amount of olefine formed,[3] as is expressed by Equations 3 and 4. To produce

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[1] Nef, *Loc. cit.*

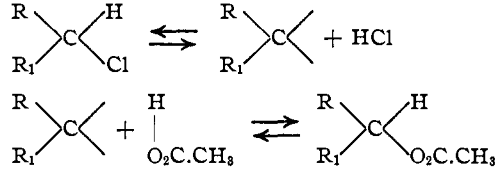
[2] Oppenheim and Precht, *Ber.*, 9, 325 (1876).

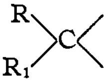
[3] Nef, *Ann.*, 318, 1 (1901) has shown that when isoamyl chloride, bromide and iodide are heated with alcoholic sodium ethylate, the chloride gives the greatest yield of isoamyl ethyl ether and the iodide the largest yield of amylene, which he explains by assuming that the rate of the addition of alcohol to the dissociated methene is not sufficient to combine with the latter as fast as formed, resulting in its partial rearrangement to amylene.

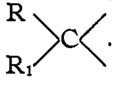
large yields of amyl alcohol in the presence of caustic alkali, the temperature should not exceed that at which the dissociation of sodium amylate takes place to a sensible degree. But this temperature is so much lower than the temperature at which the dissociation of the chloride becomes appreciable that the formation of alcohol or alcoholate is extremely slow. Higher yields of alcohol are therefore obtained when employing temperatures sufficient to dissociate the chloride at a fairly rapid rate, 215°, and solutions of a weak base or the alkali salt of a very weak acid, so that the HCl split off is taken up. It should be pointed out that, excepting the olefine, the alcohol is the most stable substance in the system.

In the presence of glacial acetic acid much higher yields of alkyl acetate than of alcohol are obtained when water is employed as the solvent, the conditions of temperature and pressure being the same in the two cases.[1]

(5)



This may be due to the fact that glacial acetic acid is more highly dissociated than water. It would then be expected that dissociated methene of a given concentration would react more rapidly with acetic acid than with water, or, in other words, a lower temperature (lower concentration) of  should suffice to produce a given yield of product, *i. e.*, acetate. Higher yields are obtained when anhydrous sodium acetate is added to the mixture than when glacial acetic acid alone is employed, the function of the sodium acetate apparently being to take up the hydrogen chloride with the formation of sodium chloride and the liberation of acetic acid.

It now remains to consider the effect of pressure on the two systems chloropentane and water; and chloropentane, water and alkali. It is obvious that in the case of chloropentane alone the effect of increased pressure will be to prevent the dissociation as indicated in Equation 1. Increased pressure should effect the dissociation of the alcohol, Equation 2, in the same direction. As has been noted above, the addition of caustic alkali causes increased formation of olefine at the expense of alcohol, which we interpret as being brought about by the effect of caustic alkali in increasing the concentration of . Increase of pressure should, therefore, tend to confine the reactions which take place to

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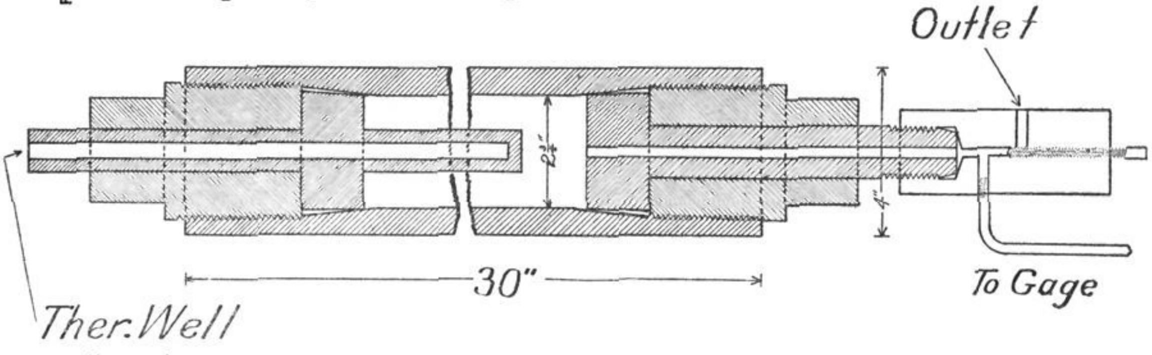
[1] The data on these experiments are reserved for later publication.

those expressed by (1) and (2). If the volume change of Equation 2 is greater than that of Equation 1, then increase in pressure should cause the alcohol to become relatively more stable with respect to the chloride; in other words, the difference of temperature between the "decomposition temperature" of amyl alcohol and amyl chloride becomes greater at high pressures. Probably a similar difference in stability would be found in the case of ethyl chloride and ethyl alcohol at high pressure.

We have found that heating monochloropentane with water vapor at atmospheric pressure until decomposition becomes appreciable leads to the formation of amylene almost exclusively. In the same way, Meyer and Bergius[1] found that by heating chlorobenzene and water vapor at atmospheric pressure to temperatures at which decomposition could be noted, namely, nearly 600°, only 10% of phenol was formed after "several hours" heating in an apparatus arranged for circulating and repeatedly heating the vapors.

Experimental.

The pressure bomb employed was very simple in construction, a piece of seamless steel tubing 30 inches long, internal diameter 2.5 inches and 0.75 inch thickness of wall. The open ends were carefully machined and threaded so as to be closed by conical plugs forced in to place by heavy forged steel screw plugs. The conical plugs, sealing the interior chamber, were kept centered during the closing operation by the centering pins passing through the screw plugs, and were tapered a few degrees less than the seat machined in the tube, as shown in the sketch. A valve was provided for escape of gas, such as CO_2, produced in some of the reactions. The temperature in the bomb was read by a thermocouple placed in the thermometer-well shown and the pressure indicated on an hydraulic gage, reading to ten thousand pounds per square inch. The heating was accomplished electrically by means of a simply constructed nichrome wire resistance furnace and it was found possible to control the temperature in the bomb to about ±2° of the desired point. In order to attain pressures higher than were given by water and the reaction products, ether was added in some cases, and in many cases the bomb was filled completely with the liquid mixture.



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[1] *Loc. cit.*

Meyer and Bergius mention the use of cuprous chloride as a catalyst accelerating the reaction in the case of chlorobenzene. In our work with amyl chlorides, we were unable to detect any effect in the rate or character of the reaction which could be attributed to this substance. Basic lead carbonate was also tried, but without result.

In working up the resulting reaction mixtures, the liquid layer was separated, washed with water, dried with anhydrous sodium sulfate and fractioned. The fusel oil distils over in the fraction boiling above 115°, but, since appreciable quantities distil with the fraction-boiling point 100–115°, this fraction was acetylated and refractioned. The acetylated product obtained, boiling above 115°, was then calculated back to amyl alcohol. The unchanged chlorides, contained in the fusel oil fraction, were found by analyzing for chlorine by the method of Drogin and Rosanoff[1] and making the necessary correction. That the polymerization of the amylene, formed as a by-product, to diamylene occurs to slight extent under the conditions prevailing in these experiments is indicated by the following distillation results:

FRACTIONAL DISTILLATION OF ALCOHOL PORTION.

Distillation temperatures.	Quantity per cent.
115–125°	22.8
125–140°	53.1
140–150°	2.7
150–170°	11.7[2]
170–190°	5.5
Residue and loss	4.2
	100.0

That the large yields, generally obtained in the experiments in which ether was added to the reaction mixture, are due primarily to the resulting higher pressure and not to any catalytic or solvent action is indicated by the equally large yields in those experiments in which the conditions were substantially the same, but containing no ether in the reaction mixture, and also by the fact that, comparing a series in which ether was introduced, those carried out at the higher pressures gave much higher yields of alcohol, other factors remaining the same.

WITH SODIUM HYDROXIDE OR POTASSIUM HYDROXIDE.

Mixture in bomb.	Time of heating.	Temperature.	Maximum pressure.	Yield of fused oil.
100 g. chloride; 5 g. Cu_2Cl_2 212 cc. 25% sol. KOH	8 hrs.	190°	240 lbs.	0.0%
213 g. chloride; 20 g. Cu_2Cl_2 740 cc. 25% sol. NaOH	8 1/2 hrs.	250°	1200 lbs.	20.5%

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[1] THIS JOURNAL, 38, 711 (1916).

[2] This fraction also contained diamyl ether.

Mixture in bomb.	Time of heating.	Temperature.	Maximum pressure.	Yield of fused oil.	Unchanged chlorides
WITH SODIUM HYDROXIDE OR POTASSIUM HYDROXIDE.					
213 g. chloride; 20 g. Cu_2Cl_2 480 cc. 16.5% sol. NaOH 300 cc. ether	9 hrs.	300°	3200 lbs.	20.0%	
213 g. chloride; 20 g. Cu_2Cl_2 480 cc. 16.5% sol. NaOH 500 cc. ether	9 hrs.	250°	4200 lbs.	33.0%	
213 g. chloride; 20 g. Cu_2Cl_2 80 g. NaOH (580 cc. sol.) 500 cc. ether	8 hrs.	210°	3300 lbs.	38.0%	
WITH SODIUM CARBONATE.					
213 g. chloride 424 cc. 25% Na_2CO_3 25 g. basic Pb carbonate	30 hrs.	150°	Below 200 lbs.	0.0%	
213 g. chloride; 8 g. Cu_2Cl_2 424 cc. 25% sol. Na_2CO_3	8 hrs.	250°	1100 lbs.	13.6%	
213 g. chloride 424 cc. 25% sol. Na_2CO_3 25 g. freshly pptd. basic Pb carbonate	4 hrs. at 250° and 4 hrs. at 300°	250–300°	1100–2100 lbs.	15.0%	
213 g. chloride; 200 cc. ether 424 cc. 25% sol. Na_2CO_3 25 g. basic Pb carbonate	8 hrs.	250°	1050 lbs.	9.0%	
213 g. chloride; 300 cc. ether 425 cc. 25% Na_2CO_3 25 g. basic Pb carbonate	10 hrs.	250°	1400 lbs.	25%	
300 g. chloride; 20 g. Cu_2Cl_2 149 g. Na_2CO_3 (596 cc. sol.) 470 cc. ether	11 hrs.	225°	4700 lbs.	36%	7%
260 g. chloride; 400 cc. ether 193 g. Na_2CO_3 (517 cc. sol.) 34 g. $Pb(OH)_2$	8 hrs.	250°	4700 lbs.	35%	
290 g. chloride 215 g. Na_2CO_3 (577 cc. sol.)	17 hrs.	210°	3300 lbs.	37.5%	
300 g. chloride; 460 cc. ether 223 g. Na_2CO_3 (596 cc. sol.) 20 g. Cu_2Cl_2	8 hrs.	235°	6000 lbs.	51.2%	
WITH SODIUM ACETATE.					
236 g. chloride; 20 g. Cu_2Cl_2 300 g. $NaCH_3CO_2$ (700 cc. sol.)	9 hrs.	250°	1400 lbs.	31%	
WITH WATER ALONE.					
300 g. chloride; 20 g. Cu_2Cl_2 600 cc. H_2O	6 hrs.	250°	1700 lbs.	23%	

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