[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

# THE DECOMPOSITION OF ORGANIC COMPOUNDS AT HIGH TEMPERATURES AND PRESSURES[1,2]

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## Introduction

The purpose of this investigation was the determination of the effect of high temperatures upon organic compounds at constant volume.

Numerous experiments have been carried out on decomposition of organic compounds at high temperatures by various methods, such as passing the vapors through hot tubes in the presence of catalysts or by electrical discharge, but, for the most part, these have been carried out under atmospheric pressure. Sealed tubes and autoclaves have been used but these are not designed to withstand extremes of temperature and pressure. Very few experiments have been made at temperatures above 250° and at pressures greater than a few hundred atmospheres. It seemed desirable to study the decomposition of pure organic compounds when heated at constant volume and the consequent pressure at temperatures from 250–525°.[4]

## Apparatus and Procedure

The apparatus used in these experiments was designed to withstand a pressure of 20,000 atmospheres at 400°, at which temperature the tensile strength of the chrom-vanadium[5] steel used is at a maximum. The design was such that at the weakest place in the structure the wall was three-fourths of an inch in thickness. The bomb which was used was of the same design as that used by Morey[6] except that the chamber was made longer so as to contain 100 cc. A thermocouple well was bored down the center of the plunger to within one-half inch of the reaction chamber. The bomb was heated in an electric furnace which was controlled by means of an automatic regulator[7] to which the thermocouple was connected, and in series with three lamp-banks, two of which were connected to the regulator through relays. By this means it was possible to maintain any given temperature between 250 and 525°, within ±2° for any desired length of time.

The threads were dusted with graphite, which was used as a lubricant. The bomb was then sealed with a copper gasket and made tight by means of a long handled, double ratchet wrench. The heating was usually for two hours for the initial run, the

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[1] In memory of Ira Remsen.

[2] Presented at the Richmond meeting of the American Chemical Society, April, 1927.

[3] From the Ph.D. dissertation of Lee R. Herndon, June, 1928.

[4] This was made possible by the use of a type of bomb developed in the Geophysics Laboratory and brought to our attention by Dr. F. R. Bichowsky.

[5] Procured from the Midvale Steel Co., Philadelphia, Pa.

[6] Morey, THIS JOURNAL, 36, 215 (1914).

[7] Leeds and Northrup Co., Philadelphia, Pa.

time being lengthened if necessary to effect decomposition. At the desired time the bomb was removed from the furnace and allowed to cool spontaneously to room temperature. It was then set in the holding device, and the wrench applied very slowly until the gaseous products could be heard to escape, then the wrench was quickly removed and the bomb transferred to the water-bath and gas collecting apparatus. This was an inverted 14-liter bottle filled with water. Through the stopper passed a funnel and a tube to discharge the water displaced by the gas. After the gas had escaped the bomb was taken from the bath, dried, opened and the liquid products were removed by means of a pipet. If there were two layers, these were weighed separately. The gaseous products were measured and analyzed and the liquid products subjected to distillation and the products identified as far as possible.

The bombs withstood all pressures to which they were subjected except in one case. In one run with ethylene glycol at 400° the bomb burst. A slit about three inches long opened in the side. The furnace was wrecked but little other damage was done as there were no flying pieces of metal. The bursting was probably due to the thermal expansion of the liquid glycol due to the bomb being too nearly filled with the charge.

## Results

**Alcohols.**—The aliphatic alcohols, methyl-, ethyl-, propyl-, *iso*propyl-, *n*-butyl-, *iso*butyl-, *sec.*-butyl-, *tert.*-butyl- and *n*-amyl-; the aromatic, benzyl- and phenylethyl; and the terpene, fenchyl alcohol have been decomposed by heating at temperatures above 400° for two hours. Temperatures were chosen such that decomposition was not quite complete in this time. All of the above mentioned alcohols yielded a great variety of products. There seem to be two simultaneous reactions: (1) dehydration and subsequent polymerization of the hydrocarbon residues, and (2) dehydrogenation followed by the splitting off of carbon monoxide and then polymerization. Three distinct types of compounds were derived from these decompositions: (1) gaseous, (2) water-insoluble portion, (3) water and water-soluble portion.

The gaseous products were analyzed in a number of cases, the results of which are given in the following table.

Table I

Percentage Composition of the Gaseous Products from Alcohols

| Alcohol | $CO_2$ | $CH_4$ | $CH_2{=}CH_2$ | CO | $C_2H_6$ | $H_2$ |
|---|---|---|---|---|---|---|
| Methyl | 8.1 | 41.8 | 0.8 | 3.1 | .. | 39.4 |
| Ethyl | 10.2 | 31.8 | 8.0 | 7.6 | 36.6 | .. |
| *n*-Propyl | 9.8 | 36.8 | 2.0 | 21.6 | .. | 20.0 |
| *Iso*propyl | 8.6 | .. | 18.4 | 2.8 | 51.2 | 12.6 |
| Benzyl | 14.2 | 4.2 | 0.6 | 64.6 | .. | 11.0 |
| Phenylethyl | 10.4 | 5.8 | .. | 44.6 | .. | 33.0 |
| Fenchyl | 10.0 | 32.2 | 2.4 | 51.0 | .. | .. |

Methyl alcohol gave exceptional results in that no liquid hydrocarbon or insoluble portion was obtained, the products of decomposition being gaseous with the exception of water. Peytral[8] and Ipatiev[9] state that

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[8] Peytral, *Compt. rend.*, **165**, 703 (1917).

[9] Ipatiev, *Ber.*, **34**, 3579 (1901); **35**, 1047 (1902).

the products are all gaseous, the decompositions taking place according to the following reactions

$$CH_3OH = H_2 + CH_2O \quad (1)$$
$$CH_2O = CO + H_2 \quad (2)$$

In the bomb the above reactions appear to be accompanied by hydrogenation. That reaction (2) takes place is proved by the presence of carbon monoxide in the gaseous product; however, the dioxide is present to a greater extent than the monoxide. This may be accounted for by the reaction:

$$2CO = CO_2 + C \quad (3)$$

which Briner and Wroczynski[10] found to take place at 320–330° and 400 atmospheres.

Ethyl alcohol showed dehydrogenation, dehydration and polymerization of the hydrocarbon residue to compounds of wide boiling range, as shown in Table II, which also shows the density and bromine absorption for each cut.

TABLE II

FRACTIONAL DISTILLATION OF 591 G. OF UPPER LAYER FROM 30 RUNS OF 59 G. EACH OF ETHYL ALCOHOL AT 425° FOR TWO HOURS

| Fraction | *T*, °C. | G. | Density | Br abs., g. per cc. |
|---|---|---|---|---|
| 1 | 18– 30 | 22 | 0.6252 | 0.1122 |
| 2 | 30– 40 | 24 | .6380 | .1047 |
| 3 | 40– 50 | 32 | .6830 | .1327 |
| 4 | 50– 63 | 107 | .7034 | .1421 |
| 5 | 63– 80 | 22 | .7120 | .2468 |
| 6 | 80– 98 | 32 | .7252 | .1701 |
| 7 | 98–106 | 28 | .7430 | .2262 |
| 8 | 106–119 | 28 | .7552 | .2337 |
| 9 | 119–138 | 51 | .7647 | .2075 |
| 10 | 138–160 | 31 | 0.7751 | 0.2019 |
| 11 | 160–166 | 38 | .7936 | .2188 |
| 12 | 166–195 | 43 | .8134 | .1927 |
| 13[a] | 90–110 | 47 | .8430 | .1627 |
| 14[a] | 110–130 | 28 | .8509 | .1208 |
| 15[a] | 130–150 | 15 | .8526 | .1458 |
| 16[a] | 150–170 | 15 | .8591 | .1645 |
| 17[a] | 170–200 | 13 | .9243 | .1533 |
| 18[a] | 200–270 | 15 | .9710 | .0195 |

[a] At 15 mm.

Unsaturation was also evident in the gaseous product. This unsaturation cannot be entirely credited to the lack of hydrogen in the decomposition products because the gaseous portion from *iso*propyl alcohol was even more unsaturated than that from ethyl alcohol and still contained about 12% hydrogen.

*Sec.*-butyl alcohol was exceptional in so far as no gaseous product was obtained.

*Tert.*-butyl alcohol was almost completely decomposed when heated at 400° for two hours, yielding nearly the theoretical quantity of water, showing that the primary reaction is dehydration. This was the lowest temperature at which any of the alcohols underwent complete decomposition.

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[10] Briner and Wroczynski, *Compt. rend.*, **150**, 1324 (1910).

Benzyl alcohol yielded carbon monoxide as the chief gaseous product. The toluene formed must have resulted from hydrogenation, since both water and hydrogen were present in the final products of the decomposition.

**Hydrocarbons.**—Normal heptane, the only aliphatic hydrocarbon subjected to 400° for two hours, underwent slight decomposition into simpler products as well as some of more complex character. The simpler products were gaseous, while the most complex were of the character of lubricating oil. The mechanism given by Thorpe and Young[11] for butane is

$$CH_3CH_2CH_2CH_3 = CH_3CH_3 + CH_2{=}CH_2$$

but Pease[12] has shown it to be

$$CH_3CH_2CH_2CH_3 = CH_4 + CH_3CH{=}CH_2 \qquad (1)$$
$$CH_3CH_2CH_2CH_3 = H_2 + CH_3CH_2CH{=}CH_2 \qquad (2)$$

In the bomb the normal saturated hydrocarbon yields simpler saturated hydrocarbons together with unsaturated hydrocarbons, which under the influence of heat and pressure polymerize to give higher hydrocarbons. Each fraction contained some unsaturates, since each took up an appreciable quantity of bromine.

Benzene is quite stable at 400° and was only slightly decomposed when heated at 500° for two hours. More complete decomposition was effected by heating at 525° for forty-eight hours, but even then the decomposition was incomplete, 27% of the benzene being recovered. With the exception of the hydrogen the decomposition products were solids. Diphenyl, *m*-diphenyl- and *p*-diphenylbenzenes were formed in quantities sufficient for identification, while other products of higher boiling point did not yield readily to the action of solvents or the formation of derivatives.

Toluene decomposed almost completely when heated at 525° for ten hours, with the deposition of some carbon. Distillation of the resulting product indicates the formation of xylenes and a number of isomers with the empirical formula $C_{14}H_{14}$, which boil over the range of 278–300°.

Other aromatic hydrocarbons with side chains, such as ethylbenzene, *iso*propylbenzene, *tert.*-butylbenzene and unsymmetrical diphenylethane behave much as does toluene.

**Acids.**—Acetic acid at temperatures above 400° decomposes into gaseous products rather than yielding liquid products of varied boiling points, as is shown by the distillation range of the product.

Adipic acid at 450° for three hours breaks down completely into liquid and gaseous products with the deposition of carbon. The liquid portion was in two layers, the upper being a dark brown oil, while the lower layer was colorless and mostly water.

Benzoic acid heated at 400° for two hours yielded a thick, black sub-

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[11] Thorpe and Young, *Proc. Roy. Soc.*, **21**, 184 (1873).

[12] Pease, This Journal, **50**, 1779 (1928).

stance which was chiefly undecomposed benzoic acid with a little carbon and some gas as decomposition products.

Citric acid decomposes at 400° into two liquid layers, a large quantity of gas and a little carbon. The upper layer was composed of hydrocarbons, while the lower layer contained acetone, acetic acid and water.

Stearic acid when heated at 400° for two hours gave a pale yellow, soft solid which appeared to be the unchanged acid.

**Aldehydes.**—Acetaldehyde at 335° for two hours gave two liquid layers of almost equal volume and two liters of gas. The upper layer gave a wide variety of products, as indicated by the boiling range of 55–360°. The lower layer distilled over a narrow range, 79–100°, the major portion within the last 5°. The gaseous product contained carbon dioxide, carbon monoxide, unsaturated hydrocarbons and methane.

Benzaldehyde at 400° for two hours gives benzene as the principal product as well as other higher boiling products.

**Chloroform.**—Chloroform decomposed at 425° yielding chlorine, and possibly hydrogen chloride, with two liquid layers and a pale yellow solid which had the correct melting point for hexachloro-ethane. Work was discontinued on this product because of the corrosive effect of the products of decomposition on the bomb.

**Ester.**—Ethyl acetate above 400° for two hours decomposes into two liquid layers, a little gas and a small amount of carbon. The upper layer, consisting mostly of hydrocarbons, had a very wide boiling range, indicating a large number of compounds. The lower layer was chiefly water with some acetic acid formed by hydrolysis and a soluble ferrous salt, possibly the acetate.

**Ether.**—Diethyl ether decomposes when heated at 400° for two hours yielding acetaldehyde, considerable gas and a liquid distilling over the range of 22–48°.

**Glycols.**—Ethylene glycol decomposes into two liquid layers and some gas when heated at temperatures considerably below 400°.

Diethylene glycol undergoes almost complete decomposition at 400° for two hours. The products of decomposition consist of some gas and two immiscible liquids. The liquids show a very marked change in character from the original. In addition to having distillation ranges lower than the boiling point of pure diethylene glycol, the lower layer is chiefly water, as is the case with the lower layers of the alcohols, while the upper layer is composed of hydrocarbons of a wide boiling range.

**Acetone.**—Acetone at 400° for two hours decomposes into two layers, the lower of which is chiefly water and the upper layer of an oily consistency.

**Benzophenone.**—Benzophenone appears to be quite stable at 400° for two hours.

**Phenol.**—Phenol is stable at 400° and decomposes only slightly when heated at 525° for two and one-half hours.

**Quinol.**—Quinol undergoes some decomposition at 400° in two hours. The product from one experiment was not of sufficient quantity to justify attempts at identification.

**Sucrose.**—Cane sugar gave a black, porous mass when heated at 425° for two hours.

TABLE III

SUMMARY OF RESULTS

| Cpd. | Temp., °C. | Time, hours | Charge, g. | Product Upper | Product Lower | Gas, liters | Dist. range, °C. | Cpds. identified and remarks |
|---|---|---|---|---|---|---|---|---|
| Methyl alcohol | 400 | 2 | 60 | 39 | .. | 10 | 64–100 | $H_2O$, $CH_3OH$, $CO_2$, CO, $CH_2$, $H_2$ |
| | 435 | 2 | 50 | 20 | .. | Much | ..... | |
| | 450 | 2 | 60 | 20 | .. | 15 | ..... | |
| | 475 | 2 | 60 | 48 | .. | Much | 64– 99 | |
| Ethyl alcohol | 425 | 2 | 59 | 17f[a] | 15 | 14.5 | Upper, 18–270; lower, 30–102 | $CH_3COOH$, $CH_3CHO$ $H_2O$, CO, $CO_2$, $CH_4$, $C_2H_4$, $C_2H_6$ |
| | 460 | 2 | 59 | 9f | 15 | 19 | | |
| | 425[b] | 2 | 59 | 19.7f | 16.7 | 14.5 | | |
| Propyl alcohol | 400 | 2 | 40 | 40 | .. | ... | ..... | One layer |
| | 415 | 2 | 40 | 29 | .. | Little | 27–115 | ............... |
| | 425 | 2 | 40 | 19f | 7 | Much | 27–105 | $C_2H_5CHO$, $H_2O$, $CO_2$, CO, $H_2$, $C_2H_4$, $CH_4$ |
| | 425 | 2 | 48 | 30f | 7 | Much | 35–165 | |
| | 425 | 2 | 60 | 12f | 7 | 11.5 | ..... | |
| *Iso*propyl alcohol | 400 | 2 | 42 | 42 | .. | ... | 79– 82 | ............... |
| | 425 | 2 | 42 | 23 | .. | Little | 57– 85 | ............... |
| | 425 | 2 | 42 | 3f | 29 | ... | ..... | $CH_3COCH_3$, $H_2O$, $CO_2$, $C_2H_4$, CO, $C_2H_6$, $H_2$ |
| | 425 | 8 | 42 | 11f | 15r | ... | ..... | |
| | 435 | 8 | 42 | 7f | 117 | ... | ..... | |
| | 465 | . | 52 | 16f | 16 | Much | 56–100 | |
| | 435 | 2 | 60 | 26f | 26 | 3 | 35–112 | |
| Butyl alcohol | 400 | 2 | 40.5 | 40 | .. | ... | 65–119 | Colorless liquid, $H_2O$ |
| | 435 | 2 | 40.5 | 21f | 4 | Much | 52–200 | |
| *Iso*butyl alcohol | 400 | 2 | 60 | 42 | .. | Little | 40–112 | ............... |
| | 400 | 4 | 60 | 11f | 1 | Much | ..... | ............... |
| | 400 | 16 | 60 | 8f | 3 | Much | ..... | ............... |
| | 425 | 2 | 60 | 7f | 2 | Much | ..... | ............... |
| | 450 | 2 | 60 | 8f | 2 | Much | ..... | ............... |
| | 475 | 2 | 60 | 3f | 2 | 18 | ..... | ............... |
| *Sec.*-butyl alcohol | 400 | 2 | 41 | 41 | .. | None | 23–102 | $C_2H_5OH$ |
| | 425 | 2 | 41 | 38f | 3 | ... | ..... | ............... |
| *Tert.*-butyl alcohol | 400 | 2 | 39 | 20f | 11 | ... | 26–200 | ............... |
| | 300 | 2 | 39 | 26 | .. | ... | 80– 98 | f liquid |
| *n*-Amyl alcohol | 425 | 2 | 60 | 35f | 10 | 5 | 30–215 | $H_2O$ |
| | 450 | 2 | 60 | 38f | 5 | Little | 35–215 | ............... |
| | 450 | 16 | 15 | 7 | 3 | 18 | ..... | ............... |
| Benzyl alcohol | 425 | 2 | 50 | 38 | 5 | 3 | 78–305 | $C_6H_6$, $C_6H_5CH_3$, BzOH, $CO_2$, CO, $C_2H_4$, $CH_4$, $H_2$ |
| | 425 | 2 | 50 | 43 | 5 | Little | 83–100 | |

TABLE III (*Continued*)

| Cpd. | Temp., °C. | Time, hours | Charge, g. | Product Upper | Product Lower | Gas, liters | Dist. range, °C. | Cpds. identified and remarks |
|---|---|---|---|---|---|---|---|---|
| Phenylethyl alcohol | 425 | 2 | 50 | 42 | 6 | 1.5 | 60–330 | $CH_3OH$, $C_6H_5CH_3$, $CO_2$, $CH_4$, $H_2$, CO, $H_2O$ |
|  | 425 | 2 | 50 | 43 | 6 | Little | ..... |  |
| Fenchyl alcohol | 435 | 2 | 75 | 57.3 | 1 | 2.5 | 30–335 | $H_2O$, $CO_2$, $C_2H_4$, CO, $CH_4$ |
| Acetic acid | 350 | 2 | 79 | 49 | .. | ... | 114–118 | .............. |
|  | 412 | 2 | 79 | 41 | .. | 3.7 | 110–118 | ............... |
| Adipic acid | 450 | 3 | 60 | 3 | 15 | Much | ..... | ............... |
| Benzoic acid | 400 | 2 | 15 | 12 | .. | Little | ..... | ............... |
| Citric acid | 400 | 2 | 50 | 10 | 8 | Much | ..... | $H_2O$, $CH_3COCH_3$, $CH_3COOH$ |
|  | 250 | 2 | 50 | 14 | 10 | Much | ..... |  |
| Stearic acid | 400 | 2 | 15 | 15 | .. | Little | ..... | Yellow solid |
| Acetaldehyde | 425 | 2 | 60 | 8 | 12 | Much | ..... | ............... |
|  | 325 | 2 | 60 | 20 | 17 | 2 | 55–360 | $CO_2$, $C_2H_4$, CO, $CH_4$ |
| Benzaldehyde | 400 | 2 | 52 | 33 | .. | Much | 81–297 | $C_6H_6$ $C_6H_5COOH$ |
|  | 400 | 2 | 52 | 36 | .. | Much | 81–297 |  |
| *n*-Heptane | 400 | 2 | 52 | 29 | .. | 5 | 27–295 | ............... |
| Benzene | 400 | 2 | 66 | 55 | .. | 0.5 | 68– 80 | f liquid |
|  | 400 | 24 | 66 | 66 | .. | ... | 75– 80 | f liquid |
|  | 450 | 24 | 66 | 50 | .. | ... | 70– 80 | f liquid |
|  | 500 | 2 | 66 | 63 | .. | Little | 69– 82 | f liquid |
|  | 600 | . | 66 | 17 | .. | ... | 250–280 | Solid |
|  | 500 | 18 | 66 | 60 | .. | 5.5 | 70–310 | Solid |
|  | 500 | 24 | 66 | 66 | .. | ... | 80–254 | f liquid, diphenyl |
|  | 525 | 4 | 66 | 65 | .. | ... | 80–500 | f liquid |
|  | 525 | 24 | 66 | 59 | .. | Little | 80–260 | Liq., solid diphenyl |
|  | 525 | 48 | 66 | 50 | .. | Much | 80–500 | $H_2$, $C_6H_5C_6H_5$, *m*-$C_6H_4(C_6H_5)_2$, *p*-$C_6H_4(C_6H_5)_2$ |
|  | 525 | 48 | 66 | 55 | .. | Much | 80–500 |  |
|  | 525 | 48 | 66 | 58 | .. | Much | 80–500 |  |
| Toluene | 400 | 2 | 43 | 43 | .. | ... | 108–110 | ............... |
|  | 500 | 2 | 43 | 43 | .. | ... | 97–110 | ............... |
|  | 525 | 10 | 57 | 54 | .. | ... | 100–300 | $C_6H_6$ |
|  | 525 | 48 | 57 | 35 | .. | ... | ..... | ............... |
| Ethylbenzene | 400 | 2 | 44 | 43 | .. | ... | 130–138 | ............... |
|  | 400 | 8 | 58 | 54 | .. | ... | 130–140 | ............... |
|  | 450 | 2 | 58 | 51 | .. | ... | 125–145 | ............... |
|  | 450 | 2 | 66 | 66 | .. | ... | 124–140 | ............... |
|  | 450 | 10 | 66 | 66 | .. | Little | 108–140 | ............... |
|  | 450 | 24 | 58 | 27 | .. | Much | ..... | Solid, 14 g. |
|  | 500 | 2 | 66 | 41 | .. | ... | 97–140 | $C_6H_6$, |
|  | 500 | 2 | 66 | 66 | .. | Little | 105–305 | $C_6H_5CH_3$ |
|  | 500 | 2 | 66 | 62 | .. | Little | 105–305 |  |
| *Iso*propyl benzene | 450 | 3 | 57 | 50 | .. | Little | 140–200 | ............... |
| *Tert.*-butylbenzene | 450 | 2 | 59 | 51 | .. | Little | 105–175 | $C_6H_5CH_3$ |
| Diphenylethane | 425 | 16 | 55 | 34 | .. | 2 | 80–360 | ............... |

TABLE III (*Concluded*)

| Cpd. | Temp., °C. | Time, hours | Charge, g. | Product Upper | Product Lower | Gas. liters | Dist. range, °C. | Cpds. identified and remarks |
|---|---|---|---|---|---|---|---|---|
| Chloroform | 425 | 2 | 112 | 35 | 23 | ... | 100–109 | $Cl_2$, HCl, $C_2Cl_6$ |
| Ethyl acetate | 400 | 2 | 42 | 19 | 11 | Little | 39–178 | $CH_3COCH_3$, $CH_3COOH$, $H_2O$, $CH_3CHO$ |
|  | 425 | 2 | 42 | 18 | 9 | Little | 33–200 |  |
| Ether | 400 | 2 | 36 | 18 | .. | Much | 22–48 | $CH_3CHO$ |
| Glycol | 400 | 2 | 64 | 15 | 19 | 13.6 | 68–101 | ............... |
|  | 350 | 4 | 84 | 2 | 82 | 1.5 | 67–205 | ............... |
| Diglycol | 400 | 2 | 56 | 10 | 14 | Much | 50– 90 | ............... |
|  | 400 | 2 | 56 | 10 | 24 | 5 | 65–101 | $C_2H_5OH$, $H_2O$ |
|  | 400 | 22 | 56 | 8 | 18 | Much | ..... | ............... |
| Acetone | 400 | 2 | 26 | 26 | .. | ... | 56– 60 | ............... |
|  | 400 | 2 | 39 | 30 | 5 | Little | 53–170 | $H_2O$ |
| Benzophenone | 400 | 2 | 37 | 36 | .. | ... | 293–310 | ............... |
| Phenol | 400 | 2 | 50 | 50 | .. | ... | ..... | ............... |
|  | 500 | 2.5 | 50 | 50 | .. | ... | 80–187 | ................. |
| Quinol | 400 | 2 | 44 | 38 | .. | Little | 98–280 | ............... |
| Sucrose | 425 | 2 | 15 | 15 | .. | ... | ..... | ............... |

[a] The figures for the third run with ethyl alcohol are the average of those obtained in 30 runs under the same conditions.

[b] f = fluorescent.

## Summary

A study has been made of the decomposition of organic compounds at constant volume, constant temperature (between the limits of 300–525°), at consequent pressure and for periods of time ranging from two to forty-eight hours, the temperature and duration of heating depending upon the stability of the compound under investigation.

The following substances have been heated: methyl-, ethyl-, *n*-propyl-, *iso*propyl-, *n*-butyl-, *iso*butyl-, *sec.*-butyl-, *tert.*-butyl-, *n*-amyl, benzyl-, phenylethyl and fenchyl alcohols; acetic, adipic, benzoic, citric and stearic acids; acetaldehyde and benzaldehyde; *n*-heptane; benzene, toluene, ethylbenzene, *iso*propylbenzene, *tert.*-butylbenzene; unsymmetrical diphenylethane; chloroform; ethyl acetate; diethyl ether; ethylene and diethylene glycols; acetone and benzophenone; phenol; quinol; and sucrose.

The products of decomposition have been separated and identified as far as possible.

BALTIMORE, MARYLAND