TABLE I

| Compound | M. p., °C. | Solvent | Formula | Analyses, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Calcd. | | | | Found | | | |
| | | | | C | H | N | S | C | H | N | S |
| *p*-Acetylaminobenzenesulfon- | | | | | | | | | | | |
| -4-sulfonic acid anilide[a] | ..... | Water | $C_{14}H_{13}O_6N_2S_2Na$ | 42.86 | 3.31 | 7.14 | 16.35 | 43.04 | 3.59 | 7.06 | 16.03 |
| -4-sulfamido-anilide[b] | 279–280 | 50% EtOH | $C_{14}H_{15}O_5N_3S_2$ | 45.53 | 4.1 | 11.4 | 17.37 | 45.29 | 4.28 | 11.55 | 17.54 |
| -4-carboxy-anilide | 253–254 | 50% EtOH | $C_{15}H_{14}O_5N_2S$ | 53.89 | 4.19 | 8.38 | 9.60 | 54.04 | 3.97 | 8.50 | 9.41 |
| -3-carboxy-anilide | 274–275 | Ethylene glycol | $C_{15}H_{14}O_5N_2S$ | 53.89 | 4.19 | 8.38 | 9.60 | 53.71 | 4.04 | 8.43 | 9.83 |
| -2-carboxy-anilide | 240 | 30% EtOH | $C_{15}H_{14}O_5N_2S$ | 53.89 | 4.19 | 8.38 | 9.60 | 54.20 | 4.04 | 8.46 | 9.73 |
| -di-(β-hydroxyethyl)-amide | 161–162 | Water | $C_{12}H_{18}O_5N_2S$ | 47.68 | 5.96 | 9.27 | 10.61 | 47.56 | 6.00 | 8.96 | 10.39 |
| -glycine[c] | 237.5–238.5 | 60% EtOH | $C_{10}H_{12}O_5N_2S$ | 44.12 | 4.41 | 10.29 | 11.78 | 44.26 | 4.62 | 10.46 | 11.56 |
| *p*-Aminobenzenesulfon | | | | | | | | | | | |
| -4-sulfonic acid anilide[a,f] | ..... | [e] | $C_{12}H_{11}O_5N_2S_2Na$ | 41.14 | 3.14 | 8.00 | 18.31 | 40.82 | 3.23 | 7.76 | 18.47 |
| -4-sulfamido anilide·HCl[b] | 224–225 | 10% EtOH[d] | $C_{12}H_{13}O_4N_3S_2 \cdot HCl$ | 39.62 | 3.85 | 11.56 | 17.63 | 39.50 | 3.68 | 11.54 | 17.64 |
| -4-carboxy-anilide[g] | 202 | 25% EtOH | $C_{13}H_{12}O_4N_2S$ | 53.42 | 4.11 | 9.59 | 10.97 | 53.17 | 4.38 | 9.71 | 10.77 |
| -3-carboxy-anilide | 196–197 | 25% EtOH | $C_{13}H_{12}O_4N_2S$ | 53.42 | 4.11 | 9.59 | 10.97 | 53.57 | 4.27 | 9.29 | 10.81 |
| -2-carboxy-anilide[a] | 315 (dec.) | Water | $C_{13}H_{11}O_4N_2SNa$ | 49.68 | 3.50 | 8.92 | 10.20 | 49.76 | 3.67 | 8.65 | 10.28 |
| -di-(β-hydroxyethyl)-amide | 110–111 | 10% EtOH | $C_{10}H_{16}O_4N_2S$ | 46.16 | 6.15 | 10.77 | 12.32 | 46.22 | 6.15 | 10.58 | 12.40 |
| -glycine[c] | 150–151 | Water | $C_8H_{10}O_4N_2S$ | 41.74 | 4.35 | 12.17 | 13.93 | 41.82 | 4.23 | 11.89 | 13.98 |
| *p*-Uraminobenzene-sulfonamide | 208–209 | Water | $C_7H_9O_3N_3S$ | 39.07 | 4.19 | 19.54 | 14.90 | 39.22 | 3.94 | 19.65 | 15.08 |

[a] Analyzed as sodium salt. [b] Previously described by Buttle, Gray, and Stephenson[4] and Rosenthal, Bauer, and Branham.[5] [c] Mentioned but not described by Kamlet at American Chemical Society Meeting, Rochester, N. Y., September, 1937. [d] From 10% alcohol a product melting at 132° was obtained. This is a mixture of the salt and free base as was shown by analysis. In order to obtain the pure salt it is necessary to add a trace of hydrochloric acid to the dilute alcohol used for crystallizing. [e] Sodium salt purified by precipitation with acetone. [f] Reported but not described by Dochez and Slanetz [*Science*, **87**, 142 (1938)]. [g] Reported but not described by Bauer and Rosenthal [*Public Health Reports*, **53**, 40 (1938)].

***p*-Uraminobenzenesulfonamide.**—The procedure used in this preparation is that of Buck and Ferry.[8]

A mixture of 34.4 g. of *p*-aminobenzenesulfonamide and 24 g. of nitrourea in 50 cc. of alcohol was warmed gently until evolution of gas ceased. The alcohol was then boiled off and the resulting solid recrystallized from water.

The author wishes to thank Mr. Harold Emerson for the micro-analyses reported.

The pharmacology of these compounds will be reported later.

## Summary

New water-soluble derivatives of *p*-aminobenzenesulfonamide (sulfanilamide) have been prepared and described.

KALAMAZOO, MICH. RECEIVED JANUARY 24, 1938

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(8) Buck and Ferry, THIS JOURNAL, **58**, 854 (1936).

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[CONTRIBUTION FROM THE LABORATORY OF THE R. & H. CHEMICALS DEPT., E. I. DU PONT DE NEMOURS & CO., INC.]

# Sodium Naphthalene. II. Preparation and Properties of Dihydronaphthalene Dicarboxylic Acids

BY J. F. WALKER AND N. D. SCOTT

The ease with which sodium naphthalene is prepared from sodium and naphthalene in such solvents as dimethyl ether and the glycol diethers[1] makes it an excellent starting material for the preparation of dihydronaphthalene dicarboxylic acids and related compounds. Schlenk and Bergmann[2] previously have reported the isolation of a dihydronaphthalene dicarboxylic acid from the products obtained by the carbonation of lithium naphthalene in ethyl ether, but the extreme slowness with which lithium naphthalene is formed in this solvent makes this method unsatisfactory as a preparative procedure. The formation of sodium naphthalene in dimethyl ether or dimethyl glycol ether, however, is extremely rapid and good yields of crystalline isomeric dihydronaphthalene dicarboxylic acids can be obtained by following the proper carbonation technique.

When carbon dioxide is passed into a solution of sodium naphthalene at room temperature, the main reaction product is a mixture of resin-like acids and considerable carbon dioxide is liberated when the crude sodium salts are acidified. However, when the carbonation is carried out at low temperatures such as −70 to −80°, more than 80% of the theoretical yield of isomeric crystalline dihydronaphthalene dicarboxylic acids is produced and very little carbon dioxide is set free on work-

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(1) Scott, Walker and Hansley, THIS JOURNAL, **58**, 2442 (1936).

(2) Schlenk and Bergmann, *Ann.*, **463**, 91 (1928).

ing up the product. In this behavior sodium naphthalene seems to resemble organic lithium compounds which give the expected carboxylic acids only when added to solid carbon dioxide or sprayed into carbon dioxide gas, giving ketones and lithium carbonate under ordinary conditions.[3] Although we were unable to isolate any pure chemical compounds from the resin-like acid fraction obtained from sodium naphthalene, it is quite possible that keto acids or other ketonic compounds are present in this product.

Good yields of the dihydronaphthalene dicarboxylic acids can be obtained at temperatures considerably higher than −70° if the sodium naphthalene is carbonated at low concentration. This can be done conveniently by carbonating the sodium compound as it is formed.[4] This method is of particular value since thus it is possible to use all the naphthalene in the charge. As stated in our previous paper the amount of sodium which will dissolve in a solution of naphthalene is only one atom per molecule of hydrocarbon. Accordingly, although carbonation of preformed sodium naphthalene solution gives a good yield of acids as based on sodium, half of the naphthalene remains unchanged.

In working up the crude sodium salts obtained by carbonating sodium naphthalene, two fractions of crystalline acids differing considerably in melting point, solubility and other characteristics are readily isolated. Both of these products are dihydronaphthalene dicarboxylic acids showing the theoretical neutralization equivalent required by the empirical formula $C_{10}H_8(COOH)_2$. The chemical reactions of the two fractions show that one fraction consists mainly of a dihydronaphthalene-1,4-di-carboxylic acid, whereas the other fraction contains an acid having a carboxyl group in the beta- or 2-position and is apparently a dihydronaphthalene-1,2-dicarboxylic acid.

When sodium naphthalene is carbonated under optimum conditions, the yield of crystalline acids is better than 80% of the theoretical as based on sodium reacted. The crude 1,4-acid is obtained in a yield of 45 to 50%, whereas the yield of crude 1,2-acid is only 28 to 32%. Approximately equivalent results are obtained whether dimethyl ether or dimethyl glycol ether is used as a solvent. Higher yields of 1,2-acid can be obtained by carbonating sodium naphthalene which has been precipitated by chilling a solution of this compound in diethyl glycol ether. Under these conditions a 62% yield of the 1,2-acid is obtained. This difference in yield is probably due to the state of the sodium naphthalene rather than any specific difference in the solvent used. Sodium naphthalene cannot be precipitated quantitatively from dimethyl ether or dimethyl glycol ether by chilling to temperatures attainable with solid carbon dioxide.

The product fraction containing the 1,4-acid (melting range 210–225°) is practically insoluble in hot or cold water and is purified by recrystallization from *n*-propyl alcohol. The recrystallized acid melts at 229–230°. Its structure is proved by the fact that it gives naphthalene-1,4-dicarboxylic acid on oxidation with bromine in glacial acetic acid.

Further proof for the structure of this acid is found in the fact that it gives alpha-naphthoic acid on oxidation with alkaline ferricyanide. The reaction probably takes place as shown

$$C_{10}H_8(COONa)_2 + NaOH + {}^1/_2\,O_2 = C_{10}H_7COONa + Na_2CO_3$$

This procedure is apparently an excellent method for converting dihydroaromatic dicarboxylic acids to monocarboxylic aromatic acids and appears to apply generally to the acids of this class obtained by carbonation of sodium addition compounds of polynuclear aromatic hydrocarbons such as naphthalene, phenanthrene, diphenyl, anthracene, and acenaphthene.[5] It is not only of value as a preparative procedure but is also useful in determining structure since it makes it possible to determine the position of one of the carboxyl groups in the parent acid.

The dihydronaphthalene-1,4-dicarboxylic acid obtained from sodium naphthalene is probably identical with the acid isolated by Schlenk from the carboxylation products of lithium naphthalene[2] and which he reported as melting at 226–227°. Schlenk believed his acid to be a 1,4-derivative because 1,4-dihydronaphthalene was obtained in the reaction of lithium naphthalene with water.

The other acid fraction (melting range 140–180°) obtained from sodium naphthalene is extremely soluble in hot water and organic solvents such as propyl alcohol. It can be crystallized from water or a mixture of isopropyl ether and hexane. It appears to be somewhat unstable and is hard to purify. The purest samples obtained in our work melted in the range 185–190°. On

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[3] Gilman and Van Ess, This Journal, 55, 1258 (1933).

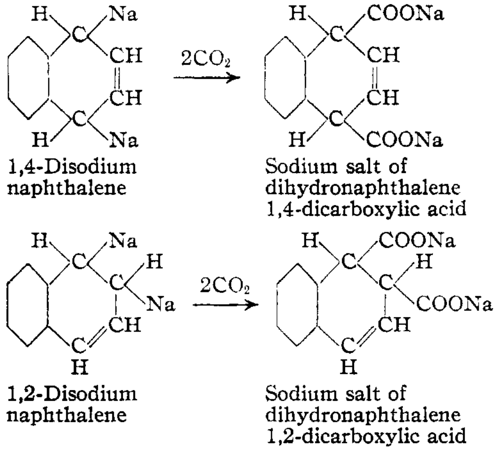
[4] Walker, U. S. Patent 2,033,056 (1936).

[5] Scott and Walker, U. S. Patent 2,054,100 (1936).

oxidation with alkaline ferricyanide it gives a good yield of beta-naphthoic acid. Apparently no alpha-naphthoic acid is obtained by this reaction. When heated at 200° it loses approximately one molecule of water, probably forming an anhydride. The 1,4-acid does not lose water at this temperature. These facts show that this acid probably contains two adjacent carboxyl groups, one of which is in position 2. It is our belief that this acid is a dihydronaphthalene-1,2-dicarboxylic acid. Unfortunately, the reaction with bromine in glacial acetic acid does not give the expected naphthalene-1,2-dicarboxylic acid. A bromo acid was obtained as the product of this reaction.

It seems probable that sodium naphthalene may consist of a mixture of 1,4- and 1,2-disodium naphthalenes analogous in structure to the two known dihydronaphthalenes: 1,4-dihydronaphthalene and 1,2-dihydronaphthalene. Carboxylation of these products would give 1,4- and 1,2-acids as shown in the diagram. This hypothesis is in good agreement with our findings.

CARBONATION OF SODIUM NAPHTHALENE



1,4-Disodium naphthalene

Sodium salt of dihydronaphthalene 1,4-dicarboxylic acid

1,2-Disodium naphthalene

Sodium salt of dihydronaphthalene 1,2-dicarboxylic acid

## Experiments

### Preparation of Dihydronaphthalene Dicarboxylic Acids

**Preparation of Sodium Salts. A. Carbonation of Preformed Sodium Naphthalene.**—Normal solutions of sodium naphthalene were prepared as described in our previous paper. (1) In the case of diethyl glycol ether one-half to three-quarters normal solutions were prepared. The solutions were cooled by means of a bath of solid carbon dioxide and methanol and carbonated with constant agitation, maintaining the desired temperature throughout the reaction.

When glycol ethers had been used as solvents, the sodium salts were filtered from the reaction mixture, unreacted naphthalene was removed by washing with fresh solvent, and the product was dried under reduced pressure. When dimethyl ether had been used as a solvent, it was allowed to distil from the reaction mixture, leaving the crude sodium salts and unreacted naphthalene.

**B. Carbonation of Sodium Naphthalene as Formed.**—In this procedure carbonation was commenced as soon as the sodium naphthalene formation had begun. Carbon dioxide was passed over the surface of the reaction mixture at a rate sufficient to keep the solution colorless but not fast enough to bleach the green surface of the sodium particles. Sodium was added in increments until 30% more than the theoretical amount had been added. The unreacted sodium was removed and weighed when the preparation was complete. The crude salts were isolated as described in A.

**Isolation of Dihydronaphthalene Dicarboxylic Acids from Crude Sodium Salts.**—The crude salts were dissolved in water and the solution filtered or extracted with an organic solvent to remove naphthalene. The salts were dissolved with caution as they sometimes contained sodium particles. The 1,4-acid fraction was then precipitated by acidifying with hydrochloric acid in the presence of peroxide-free isopropyl ether. The crystalline precipitate was filtered off, washed with additional ether and dried. The 1,2-acid fraction was obtained by crystallization on concentrating the isopropyl ether extract. When no further crystals could be obtained by addition of petroleum ether to the mother liquor, the residual solvent was evaporated leaving the resin-like acid.

The crude 1,4-acid melted in the range 210 to 225°. Pure dihydronaphthalene-1,4-dicarboxylic acid obtained by crystallization from *n*-propyl alcohol melted at 229–230°. This acid dissolved in cold water (25°) to the extent of about 0.1% and in hot water (95–100°) to the extent of about 2%.

*Anal.* Calcd. for $C_{12}H_{10}O_4$: C, 66.02; H, 4.62. Found: C, 66.35; H, 4.74.

The low melting 1,2-acid fraction melted in the range 140 to 180°. Recrystallization from isopropyl ether gave a product melting at 185 to 190°. It dissolved in approximately its own weight of hot water, but only 2.5% dissolved in water at 25°.

*Anal.* Calcd. for $C_{12}H_{10}O_4$: C, 66.02; H, 4.62. Found: C, 66.06; H, 4.87.

Both crystalline acids had neutralization equivalents of 109, the theoretical value for dihydronaphthalene dicarboxylic acid.

TABLE I

YIELDS OF DIHYDRONAPHTHALENE DICARBOXYLIC ACIDS OBTAINED BY CARBONATION OF PREFORMED SODIUM NAPHTHALENE

| Solvent | Carbonation temp., °C. | Yields crude acid fractions, % calculated on sodium basis 1,4-acids | 1,2-acids | Resin-like acids | Total acids |
|---|---|---|---|---|---|
| Dimethyl glycol ether | 29–36 | 7 | — | 44 | 51 |
| Dimethyl ether | Approx. −30 | 25 | — | 49 | 74 |
| Dimethyl ether | −68 to −73 | 44 | 32 | 18 | 94 |
| Dimethyl glycol ether | −60 to −70 | 44 | 30 | 9 | 83 |
| | −76 to −82 | 51 | 29 | 4 | 84 |
| Diethyl glycol ether (sodium naphthalene suspension) | −60 to −70 | 28 | 63 | — | 91 |
| | −65 to −70 | 28 | 64 | — | 92 |

The resin-like acid fraction was a brown tarry material from which we were unable to isolate any pure chemical compounds. It had a neutralization equivalent of 150–160.

**Yields of Acids Obtained.**—Table I shows the yields of crude acids obtained by the carbonation of preformed sodium naphthalene at various temperatures in dimethyl ether, dimethyl glycol ether, and diethyl glycol ether. As will be seen the best yields of crystalline acids are at temperatures below −60°.

Table II shows the results obtained when sodium naphthalene is carbonated as formed. Higher yields of crystalline acids are obtained at a given temperature by this procedure.

TABLE II

YIELDS OF DIHYDRONAPHTHALENE DICARBOXYLIC ACIDS OBTAINED BY CARBONATION OF SODIUM NAPHTHALENE AS FORMED

| Solvent | Carbonation temp., °C. | Yields crude acid fractions, % calculated on sodium basis 1,4-acids | 1,2-acids | Resin-like acids | Total acids |
|---|---|---|---|---|---|
| Dimethyl glycol ether | 28–38 | 21 | 2 | 16 | 39 |
| | 28–32 | 18 | 9 | 24 | 51 |
| | −5 | 32 | 10 | 34 | 76 |
| Dimethyl ether | −40 to −55 | 39 | Not measured | | |
| Dimethyl ether | −50 to −63 | 52 | 33 | -- | 85 |

**Action of Heat on Crystalline Acid Fractions.**—Small amounts of the crystalline acid fractions were heated at 200° for one hour in a stream of dry nitrogen and the carbon dioxide and water evolved were accurately measured. The results are shown below.

| | 1,4-Acid fraction Wt., g. | Milli-moles | Molar ratio | 1,2-Acid fraction Wt., g. | Milli-moles | Molar ratio |
|---|---|---|---|---|---|---|
| Acid sample | 1.6249 | 7.45 | 1.00 | 1.2152 | 5.57 | 1.00 |
| Water produced | 0.0106 | 0.59 | 0.08 | 0.0874 | 4.85 | 0.87 |
| Carbon dioxide produced | .0085 | .19 | .03 | .0324 | .74 | .01 |

The results show that on heating at 200°, the 1,2-acid fraction gives up approximately one mole of water per mole, whereas the 1,4-acid fraction does not. Duplicate experiments at 250° gave approximately identical results.

### Ferricyanide Oxidation of Dihydronaphthalene Dicarboxylic Acids

**A. 1,4-Acid Fraction—Preparation of alpha-Naphthoic Acid.**—A solution containing 21.8 g. of crude, 1,4-acids, 40 g. of potassium hydroxide, 66 g. of potassium ferricyanide and 400 cc. of water was heated on a steam-bath for six hours. On working up the reaction mixture an 81% yield of crude alpha-naphthoic acid melting at 163° was obtained. The purified acid had a neutralization equivalent of 170 (calculated value = 172) and melted at 162.5 to 163.5°. It was identified by a mixed melting point with a sample of pure alpha-naphthoic acid purchased from the Eastman Kodak Co.

**B. 1,2-Acid Fraction—Preparation of beta-Naphthoic Acid.**—A solution containing 618 g. of the 1,2-acid, 875 g. of sodium hydroxide, 1980 g. of potassium ferricyanide, and 8 liters of water was heated on the steam bath for six hours. Sodium beta-naphthoate crystallized from the reaction mixture and was filtered off. Acidification of the mother liquor gave alpha-naphthoic acid. A yield of 63% beta-naphthoic and 12% alpha-naphthoic acid was obtained. The purified beta-naphthoic acid melted at 183–185° and was identified by a mixed melting point with a known sample of beta-naphthoic acid prepared by hydrolysis of beta-naphthonitrile purchased from the Eastman Kodak Co.

More highly purified samples of the 1,2-naphthalene acid gave yields of beta-naphthoic acid over 80%.

### Bromine Oxidation of 1,4-Dihydronaphthalene Dicarboxylic Acid—Preparation of Naphthalene-1,4-dicarboxylic Acid

Eighty grams of the 1,4-acid fraction was oxidized in 420 cc. of boiling glacial acetic acid by the gradual addition of 20.2 cc. of bromine dissolved in a little glacial acetic acid. On cooling the reaction mixture 1,4-naphthalic acid crystallized out. This product was obtained in 89% yield. Its neutralization equivalent was 108 and it did not melt at a temperature below 290°.

*Anal.* Calcd. for $C_{12}H_8O_4$: C, 66.63; H, 3.73. Found: C, 66.59; H, 4.20.

The methyl ester of this product melted at 66.5° and had a saponification equivalent of 121 (calculated value, 122). A rough molecular weight determination gave the value 226, which is in approximate agreement with the theoretical value of 244.

*Anal.* Calcd. for $C_{14}H_{14}O_4$: C, 68.82; H, 4.95. Found: C,68.95; H, 5.09.

These data for the acid and its ester are in good agreement with the values reported by Bradbook and Linstead[6] for naphthalene-1,4-dicarboxylic acid.

**Reaction of Crude 1,2-Acid with Bromine.**—When the crude 1,2-acid was treated with bromine in glacial acetic acid employing the same procedure as that described above, the main products of the reaction were a brominated crystalline acid and a black tar. The bromo acid melted at 227° with evolution of hydrogen bromide and changed to tar. Its neutralization equivalent was 175. Analysis showed it to contain 38.3% combined bromine. The product is probably an unstable bromine addition compound of the original 1,2-acid. Such an acid would have the formula $C_{10}H_8Br_2(COOH)_2$, would contain 42.3% bromine, and would have a neutralization equivalent of 189. The low values observed for the product are probably due to partial decomposition with loss of hydrogen bromide. Yields of naphthalene-1,4-dicarboxylic acid varying from 10 to 20% according to the purity of the 1,2-acid were also obtained. This shows that the crude 1,2-acid definitely contains 1,4-acid as an impurity. The alpha-naphthoic acid obtained by oxidizing crude 1,2-acids with ferricyanide is produced by the oxidation of this 1,4-acid.

## Summary

High yields of a mixture of isomeric dihydronaphthalene dicarboxylic acids have been obtained by carbonation of sodium naphthalene.

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(6) Bradbook and Linstead, *J. Chem. Soc.*, 1740 (1936).

These acids have been identified as dihydronaphthalene-1,4-dicarboxylic acid and an acid having adjacent carboxyl groups, one of which is in the 2-position. The latter acid is probably dihydronaphthalene-1,2-dicarboxylic acid.

A new procedure for converting dihydroaromatic dicarboxylic acids to monocarboxylic aromatic acids by oxidation with alkaline ferricyanide is described.

Naphthalene-1,4-dicarboxylic acid has been prepared in high yield by the oxidation of the dihydronaphthalene-1,4-dicarboxylic acid with bromine in glacial acetic acid.

NIAGARA FALLS, N. Y. RECEIVED DECEMBER 7, 1937

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

# The Thermal Decomposition of Alicyclic Compounds. I. The Decomposition of Cyclohexene and Some Simpler Hydrocarbons

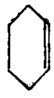
BY F. O. RICE, P. M. RUOFF[1] AND EDWARD L. RODOWSKAS

## 1. Introduction

In contrast to the thermal decomposition of open chain paraffin hydrocarbons to which the free radical chain mechanism may be applied successfully,[2] consideration of the decomposition of cyclic compounds indicates that an entirely different mechanism may be involved since a rupture of the ring does not cause the immediate formation of two radicals.

This difference in behavior may be ascribed to a fundamental difference between open chain and ring compounds; both may be regarded as being built up of small unsaturated molecules joined together by the opening of double or triple bonds; in ring compounds the two free valences are joined to form the ring and, thus, when a cyclic compound is ruptured, it can fall apart into its constituent molecules;[3] on the other hand, when an open chain compound is ruptured, the two free radicals fly apart and cannot undergo internal rearrangement into molecules.

Therefore, when a molecule such as cyclohexene is thermally decomposed, a primary rupture of a C–C bond may be postulated according to the equation



$$\longrightarrow -CH_2CH_2CH_2CH=CHCH_2- \qquad (1)$$

This particular rupture of a C–C bond rather than one of the two alternative scissions[4] has been selected because a resonating radical is formed which may also be written in the form

$$-CH_2-CH_2-CH_2-\overset{|}{C}H-CH=CH_2 \qquad (2)$$

but since neither of these forms represents the true formula, it is preferable to represent it as

$$-CH_2-CH_2-CH_2-CH=CH=CH_2 \qquad (3)$$

It seems reasonable to assume that the formation of this resonating radical will lower the activation energy required, and, therefore, the primary C–C rupture would be expected to occur in the beta-position to the double bond rather than at some other position which would not yield a resonating radical. It is, of course, possible that the intermediate radical, $-CH_2CH_2CH_2CH=CH=CH_2$, may have no appreciable stability so that the decomposition into ethylene and butadiene may occur in a single elementary act.[5]

The primary formation, then, of the radical (3) may be followed by a simple electronic rearrangement to give ethylene and butadiene according to the equation

$$-CH_2-CH_2-CH_2-CH=CH=CH_2 \longrightarrow CH_2=CH_2 + CH_2=CH-CH=CH_2 \qquad (4)$$

Since this decomposition of the radical (3) probably requires only a relatively small activation energy and involves nothing more than a change in electronic configuration, the reaction represented by equation (4) may be assumed to predominate and any attack of the radical (3) on the substrate such as

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[1] Hormel Foundation Fellow, 1934–1938.

[2] (a) Rice, THIS JOURNAL, 53, 1959 (1931); (b) Rice and Rice, "The Aliphatic Free Radicals," the Johns Hopkins Press, Baltimore, Md., 1935; (c) Frey, *Ind. Eng. Chem.*, 26, 200 (1934).

[3] See ref. 2b, Chapter XIII.

[4] Presumably the rupture of a C–H or a C=C bond may be omitted from consideration, since they are far stronger than the C–C bond.

[5] For a discussion of resonance see Pauling and Sherman, *J. Chem. Phys.*, 1, 606 (1933); Ingold, *Chem. Rev.*, 15, 225 (1934); see also Harkness, Kistiakowsky and Mears, *J. Chem. Phys.*, 5, 682 (1937), who have proposed resonating free radicals for the association of dienes.