Summary

C-alkyl derivatives of hydroxynaphthoquinone are produced, together with the isomeric O-ethers, by the action of γ-methyl- and γ,γ-dimethylallyl bromide on the silver salt of hydroxynaphthoquinone. Since the crotyl derivative formed in the first case is not identical with the product of rearrangement of either of the crotyl O-ethers, it can only be 2-(γ-methylallyl)-3-hydroxy-1,4-naphthoquinone. It is inferred that the acidic substance produced in the second reaction is 2-(γ,γ-dimethylallyl)-3-hydroxy-1,4-naphthoquinone. The identity of the compound with lapachol furnishes additional evidence in support of Hooker's formula for this natural coloring matter.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

THE REDUCING ACTION OF SODIUM METHYLATE

BY H. SHIPLEY FRY AND JESSIE LOUISE CAMERON[1]

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Introduction

There are numerous references in the literature relative to the reducing action of sodium methylate upon aromatic nitro compounds. The most common example is the reduction of nitrobenzene to azoxybenzene according to the equation

$$4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O \qquad (1)$$

This equation was postulated by Klinger[2] but neither he nor subsequent investigators, as far as we know, have attempted to check quantitatively the amount of azoxybenzene formed with the amount of sodium methylate oxidized to sodium formate or, in other words, to establish the stoichiometrical ratio $2(C_6H_5N)_2O:3HCOONa$ indicated in Klinger's equation.

This reaction is effected by heating a solution of nitrobenzene and sodium methylate in methyl alcohol. The sodium methylate is prepared by dissolving either sodium (Equation 2) or sodium hydroxide (Equation 3)[3] in methyl alcohol.

$$2Na + 2CH_3OH \longrightarrow 2CH_3ONa + H_2 \qquad (2)$$

$$NaOH + CH_3OH \longrightarrow CH_3ONa + H_2O \qquad (3)$$

The yield of azoxybenzene is usually between 80 and 90% of that calculated by Equation 1.

It should be noted that water is not only a product of Reaction 1, but

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[1] A synopsis of a thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Jessie Louise Cameron in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Klinger, *Ber.*, **15,** 866 (1882).

[3] Zinin, *J. prakt. Chem.*, **36,** 98 (1845).

that it is initially introduced into the reaction mixture when sodium methylate is prepared according to Reaction 3. In this connection, Lachman[4] maintains that the use of sodium methylate prepared according to either of the above methods (Equation 2 or 3) has no special influence upon the course of the reaction (Equation 1) and states that "the amount of water present is relatively without influence."

In view of the foregoing opinions, the present work was undertaken with a four-fold purpose, namely, (a) to establish by a quantitative study of the respective yields of azoxybenzene and sodium formate the stoichiometrical ratio $2(C_6H_5N)_2O:3HCOONa$, (b) to ascertain the effect of the presence of increasing molar concentrations of water, and (c) likewise of pyridine, upon the course of the reaction represented by Equation 1, and (d) to extend the senior author's explanation[5] of the oxidizing action of fused caustic alkalies upon carbon compounds to the interpretation of the mechanism of the reducing action of sodium methylate, and its concomitant oxidation to sodium formate.

A. The Yields of Azoxybenzene and Sodium Formate

After numerous experiments with various concentrations of nitrobenzene and sodium methylate in methyl alcohol solution, the following standardized method of procedure was adopted as best fitted to give conveniently comparable yields of azoxybenzene and sodium formate.

Azoxybenzene.—In each reaction conducted, 17.3 g. of thoroughly cleaned sodium (five times the molar equivalent of sodium methylate, based upon the employment of 0.05 molecular proportion of nitrobenzene, according to Equation 1) was dissolved in 150 cc. of the purest obtainable methyl alcohol, free from acetone; d^{21}, 0.7965. To the sodium methylate solution cooled to room temperature, 20.44 cc. (24.6 g., or 0.05 molecular proportion of pure nitrobenzene) was added from a buret. This homogeneous mixture was diluted with methyl alcohol to exactly 250 cc., transferred to a 500cc. roundbottomed flask, with a reflux condenser attached, and boiled for three hours over a waterbath. The reaction was then immediately stopped by adding 100 cc. of ice water. Steam distillation freed the reaction mixture from methyl alcohol and unreduced nitrobenzene. The azoxybenzene remaining in the distilling flask was separated from the strongly alkaline (with sodium hydroxide) aqueous solution of sodium formate by repeated extraction with pure benzene. Evaporation to dryness of the combined benzene extractions, previously dried with calcium chloride, furnished the yield of pure azoxybenzene melting at 36°.

Sodium Formate.—The alkaline solution of sodium formate was boiled vigorously to free it from any traces of benzene, previously used in extracting the azoxybenzene, then cooled and diluted with water to exactly 1000 cc. Aliquot portions of this solution, 10 cc. diluted to 100 cc., were used in the formate determinations according to the alkaline permanganate-oxalic acid method described by Scott.[6]

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[4] Lachman, THIS JOURNAL, **24,** 1178 (1902).

[5] (a) Fry, Schulze and Weitkamp, *ibid.,* **46,** 2268 (1924). (b) Fry and Schulze, *ibid.,* **48,** 958 (1926).

[6] Scott, "Standard Methods of Analysis," D. Van Nostrand Co., **1922,** vol. 2, p. 1054.

Two sets of experiments (I and II) involving the reduction of nitrobenzene to azoxybenzene and the oxidation of sodium methylate to formate, each performed in duplicate (a and b), were conducted. The quantitative results are embodied in Table I.

TABLE I

YIELDS OF AZOXYBENZENE AND SODIUM FORMATE

Run	Azoxybenzene Found, g.	 Calcd., g.	 Calcd., %	Sodium formate Found, g.	 Calcd., g.	 Calcd., %
Ia	17.00	19.8	85.85	8.74	10.20	85.90
Ib	17.20	19.8	86.86	8.85	10.20	86.82
IIa	17.30	19.8	87.36	8.80	10.20	86.30
IIb	17.20	19.8	86.86	8.84	10.20	86.68

The close agreement between the per cent. yields of azoxybenzene (av., 86.74) and sodium formate (av., 86.43) now establishes the stoichiometrical ratio $2(C_6H_5N)_2O:3HCOONa$ required by Equation 1, first proposed by Klinger.

These yields, obtained according to the standardized method described, will serve as a norm in the following investigations relating to the effects of water and of pyridine upon the course of the reaction.

B. The Effect of The Presence of Water

Apropos of the previously noted statement of Lachman[4] that "the amount of water present is relatively without influence" upon the course of the reaction represented by Equation 1, it should be noted that Lachman employed very concentrated solutions of sodium hydroxide in methyl alcohol to serve as the source of supply of the reducing agent, sodium methylate. Not only is water introduced into the reaction mixture in this way (see previously noted Equation 3), but it is being continuously introduced as the reaction proceeds according to Equation 1.

Preliminary to determining quantitatively the effects of increasing concentrations of water upon the extent of the reaction, it was necessary to determine the maximum quantity of water that could be introduced into the reaction mixture without throwing the nitrobenzene out of solution. Experiments to this end showed that the 250 cc. of the standardized reaction mixture could contain 54 cc. or 3 moles of water and maintain homogeneity.

This result made it convenient to study the effect upon the standardized reduction method of incorporating initially within the 250cc. reaction mixture gradually increasing molar quantities of water, namely: 0.125, 0.25, 0.50, 1.00, 1.50, 2.00, 2.50 and 3.00 moles. Each of these reductions (I–VIII) was conducted in duplicate (a and b).

Since it has been proved in the preceding section (A) that azoxybenzene and sodium formate are formed in the stoichiometrical ratio $2(C_6H_5)_2O$:-3HCOONa, it follows that the determination of the quantity of sodium formate obtained in each of the reactions will be a direct measure of the extent of the reduction of nitrobenzene to azoxybenzene.

Table II summarizes the results so obtained. It shows the molar quantities of water initially present in the reaction mixtures and the corresponding percentages of the total amounts of nitrobenzene reduced to azoxybenzene, that is, the actual per cent. yields of sodium formate equivalent to azoxybenzene formed in terms of the established Equation 1.

TABLE II

THE EFFECT OF WATER UPON THE EXTENT OF THE REDUCTION OF NITROBENZENE

Run	H_2O present, moles	Extent of reduction, %	Run	H_2O present, moles	Extent of reduction, %
Ia	0.125	71.42	Va	1.50	43.10
Ib	.125	71.08	Vb	1.50	43.21
IIa	.25	63.84	VIa	2.00	30.11
IIb	.25	63.62	VIb	2.00	29.95
IIIa	.50	60.91	VIIa	2.50	23.26
IIIb	.50	60.66	VIIb	2.50	23.20
IVa	1.00	54.81	VIIIa	3.00	19.14
IVb	1.00	54.94	VIIIb	3.00	19.07

When no water was added initially to the reaction mixture, the extent of the reduction averaged 86.58%. It is of interest to note that the maximum quantity of water formed on the completion of the reaction according to Equation 1 would be 2.4 g. The quantity actually formed was 2.0 g., an amount slightly less than 0.125 mole (2.25 g.) which was initially present in Runs Ia and Ib. This quantity decreased the extent of the reduction from 86.58 to 71.42%. Thus it is evident that small amounts of water initially present in the reaction mixture have a marked effect in decreasing the extent of the reduction. Furthermore, the above data show conclusively that increasing molar concentrations of water fairly regularly decrease the extent of the reduction of nitrobenzene to azoxybenzene and the concomitant oxidation of sodium methylate to sodium formate.

C. The Effect of Pyridine

This section presents a preliminary study of the effect of pyridine, in amounts equal to 0.125, 0.25, 0.50 and 1.00 mole, upon the reduction of nitrobenzene by sodium methylate in methyl alcohol solution, conducted according to the standardized method. The quantities of pyridine mentioned above were initially incorporated in the several reaction mixtures immediately prior to boiling for three hours. The concentrations of the nitrobenzene and sodium methylate were the same in each reaction mixture, and the total volume of each, after addition of the pyridine, was again 250 cc. Each of the reductions (I–IV) was conducted in duplicate (a and b).

Table III summarizes the results obtained. It shows the molar quantities of pyridine (purest Kahlbaum grade) initially present in the reaction mixtures and the corresponding percentages of the total amounts of nitrobenzene reduced presumably to azoxybenzene, calculated in terms of per cent. yield of sodium formate according to Equation 1.

TABLE III

THE EFFECT OF PYRIDINE UPON THE EXTENT OF THE REDUCTION OF NITROBENZENE

Run	Pyridine present, moles	Extent of reduction, %	Run	Pyridine present, moles	Extent of reduction, %
Ia	0.125	80.74	IIIa	0.50	109.70
Ib	.125	81.41	IIIb	.50	110.10
IIa	.25	89.86	IVa	1.00	115.10
IIb	.25	89.78	IVb	1.00	115.10

It was a surprise to find in Runs III and IV that the yields of sodium formate in terms of Equation 1 were, respectively, about 10 and 15% in excess of those calculated. Since the corresponding amounts of nitrobenzene were not originally present in the reaction mixture, it follows that a small fraction of the nitrobenzene underwent reduction beyond the azoxybenzene stage or, in other words, some of the azoxybenzene formed according to Equation 1 presumably suffered some further reduction to azobenzene according to Equation 4.

$$2(C_6H_5N)_2O + CH_3ONa \longrightarrow 2C_6H_5N{=}NC_6H_5 + H_2O + HCOONa \qquad (4)$$

This would account for the formation of sodium formate in amounts exceeding the calculated yield.

That azoxybenzene is partly reduced by sodium formate to azobenzene in the presence of pyridine was shown by the following experiments.

Twenty g. of azoxybenzene (Kahlbaum) was dissolved in a minimum quantity of methyl alcohol and added to sodium methylate solution, prepared as described in the standard method. To this solution was added 0.5 mole (40 cc.) of pyridine and methyl alcohol to a total volume of 250 cc. Two such reaction mixtures were boiled for three hours. The azoxybenzene, which contained some azobenzene, and the sodium formate were recovered, as previously described. The yields of sodium formate were 2.86 and 2.81% of those calculated by Equation 4.

Having thus shown that azoxybenzene in the presence of pyridine is reducible by sodium methylate to azobenzene, it next became necessary to determine the yields of both azoxybenzene and azobenzene obtained when 0.125, 0.25, 0.5 and 1.0 mole of pyridine were initially present in the previously noted reaction mixtures of nitrobenzene and sodium methylate. Furthermore, if the excess yields of sodium formate so obtained could be shown to be stoichiometrically proportional to the combined yields of azoxybenzene (Equation 1) and of azobenzene (Equation 4), then the simultaneous occurrence of the reactions represented by Equations 1 and 4 would be established.

In determining the respective percentage yields of azoxybenzene and azobenzene, the method suggested by Snowdon[7]—using the melting points of mixtures of known percentage composition of the two components—was found quite satisfactory. Since Snowdon's original article did not include the melting points of the various mixtures, such data had to be determined in this study and are embodied in Table IV.

TABLE IV

MELTING POINTS OF MIXTURES OF AZO- AND AZOXYBENZENE

Azobenzene, %	Azoxybenzene, %	M. p., °C.	Azobenzene, %	Azoxybenzene, %	M. p., °C.
0	100	35.4	60	40	48.0
10	90	29.2	70	30	55.0
20	80	25.5	80	20	59.0
30	70	27.5	90	10	62.5
40	60	35.5	100	0	66.2
50	50	42.0			

The melting points of the mixtures of azo- and azoxybenzene obtained when 0.125, 0.25, 0.5 and 1.0 mole of pyridine were used, were determined and from these the percentages of azobenzene and azoxybenzene in each reaction product were read from the graph based upon the data of Table IV. From the percentage compositions of the reaction products, the corresponding amounts of azo- and azoxybenzene contained therein were calculated. These data are recorded in Table V.

TABLE V

COMPOSITION OF AZOBENZENE-AZOXYBENZENE PRODUCT MIXTURE

Run	Pyridine, moles	Azo-azoxy mixture, g.	Azoxybenzene, %	Azobenzene, %	Azoxybenzene, g.	Azobenzene, g.
I	0.125	15.70	97.0	3.0	15.23	0.47
II	.25	17.05	95.0	5.0	16.20	.85
III	.50	20.00	93.5	6.5	18.70	1.30
IV	1.00	20.90	93.0	7.0	19.44	1.46

From the known composition of the mixtures it is possible to calculate the extent of the reduction in each run by adding the calculated amount of sodium formate equivalent to the azoxybenzene to that equivalent to the azobenzene. This sum should then equal the total yield of sodium formate found on analysis. These calculations are based upon Equations 1 and 5, respectively, in conjunction with the data in the last two columns of Table V. (Equation 5 is the summation of previously noted Equations 1 and 4.)

$$4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O \qquad (1)$$

$$2C_6H_5NO_2 + 2CH_3ONa \longrightarrow C_6H_5N{=}NC_6H_5 + 2HCOONa + 2H_2O \qquad (5)$$

These data are embodied in Table VI.

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[7] Snowdon, *J. Phys. Chem.*, **15**, 797 (1911).

TABLE VI

COMPARISON OF THE CALCULATED AND ACTUAL YIELDS OF SODIUM FORMATE

Run	HCOONa, g. $\Bumpeq$ $(C_6H_6N)_2O$ (Eq. 1)	HCOONa, g. $\Bumpeq$ $C_6H_5N=NC_6H_5$ (Eq. 5)	Total HCOONa	
			Calcd., g.	Found, g.
I	7.84	0.35	8.19	8.26
II	8.35	.64	8.99	9.18
III	9.63	.97	10.60	11.27
IV	10.01	1.09	11.10	11.74

The close agreement between the calculated and the found quantities of sodium formate (Table VI) establishes the fact that nitrobenzene is reduced by sodium methylate in the presence of pyridine, not only to azoxybenzene, the usual product of reduction, but also to azobenzene. Furthermore, as noted in Table V, increasing molar concentrations of pyridine slightly diminish the yield of azoxybenzene and increase the yield of azobenzene.

A possible explanation of this effect of pyridine will be offered after the question of the mechanism of the reducing action of sodium methylate is considered.

D. The Mechanism of the Reducing Action of Sodium Methylate

In previous papers by Fry and co-workers[5] it has been shown that the liberation of hydrogen from carbon compounds and their concomitant oxidation when their vapors were passed through fused, anhydrous, equimolecular mixtures of sodium and potassium hydroxides, conform to a general type reaction (M = Na or K): $R(H)_n + n(HOM) \longrightarrow R(OM)_n + nH_2$.

Many reactions of this general type, each involving the acidic dissociation of the caustic alkalies, have been quantitatively established. A brief review must now be given of this mechanism[8] in its relation to the quantitative oxidation of methyl alcohol to carbonate with the liberation of hydrogen in conformity with the equation $CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2$, which was assumed to involve the following steps.

$$CH_3OH + HONa \longrightarrow CH_3ONa + H_2O \qquad (a)$$
$$CH_3ONa + HONa \longrightarrow CH_2(ONa)_2 + H_2 \qquad (b)$$
$$CH_2(ONa)_2 + HONa \longrightarrow CH(ONa)_3 + H_2 \qquad (c)$$
$$CH(ONa)_3 + HONa \longrightarrow C(ONa)_4 + H_2 \qquad (d)$$
$$C(ONa)_4 + H_2O \longrightarrow Na_2CO_3 + 2NaOH \qquad (e)$$
$$\Sigma \text{ (a), (b), (c), (d), (e) } CH_3OH + 2HONa \longrightarrow Na_2CO_3 + 3H_2 \qquad (A)$$

Not only the quantitative verification of the summation reaction (Equation A), but also the subsequent proof in this Laboratory (data reserved for future paper) of the presence of sodium methylate and formate in the reaction mixture, indicate the following mechanism for the production of sodium formate and hydrogen,

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[8] Ref. 5a, p. 2272.

$$CH_3OH + HONa \longrightarrow CH_3ONa + H_2O \qquad (a)$$
$$CH_3ONa + HONa \longrightarrow CH_2(ONa)_2 + H_2 \qquad (b)$$
$$CH_2(ONa)_2 + HONa \longrightarrow CH(ONa)_3 + H_2 \qquad (c)$$
$$CH(ONa)_3 + H_2O \longrightarrow HCOONa + 2HONa \qquad (c')$$
$$\Sigma\ (a), (b), (c), (c') \quad CH_3OH + HONa \longrightarrow HCOONa + 2H_2 \qquad (B)$$

Now, since the oxidation of methyl alcohol by fused sodium hydroxide according to Equation A involves the intermediate formation of sodium methylate and orthoformate (Equations a and c), it is readily conceivable that under special conditions the hydrolysis of sodium orthoformate (Equation c′) may occur. In other words, *the interaction of methyl alcohol and sodium hydroxide may yield, according to Equation B, sodium formate and hydrogen.* The latter under certain conditions will not necessarily be evolved in the free state but may act as a reducing agent. Thus, in the reduction of nitrobenzene by sodium methylate in methyl alcohol solution, traces of water were always present, and more or less hydrolysis of sodium methylate occurred. Such a mixture may naturally be assumed to effect the reduction of nitrobenzene to azoxybenzene according to the following scheme of reactions.

$$3CH_3ONa + 3HOH \longrightarrow 3CH_3OH + 3HONa \qquad (x)$$
$$3CH_3OH + 3HONa \longrightarrow 3HCOONa + 12H \qquad (y\ or\ B)$$
$$4C_6H_5NO_2 + 12H \longrightarrow 2(C_6H_5N)_2O + 6H_2O \qquad (z)$$
$$\Sigma\ (x), (y), (z) \quad 4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O \qquad (1)$$

From the foregoing, the mechanism of the reduction of nitrobenzene by sodium methylate may be regarded as involving the hydrolysis of sodium methylate (Equation x) and oxidation of methyl alcohol to sodium formate by means of sodium hydroxide (Equation y). This reaction, previously described as Equation B, involves the acidic dissociation of sodium hydroxide, and the available hydrogen therefrom effects the reduction of the nitrobenzene (Equation z). The summation of Equations x, y and z gives the commonly accepted Equation 1.

This interpretation affords in turn an explanation not only of the effect of water (see Part B) in limiting reduction, that is, the yields of azoxybenzene, but also the opposite effect of pyridine (see Part C) in increasing the amount of reduction, even to the azobenzene stage.

Since, as previous work indicates, the oxidation of methyl alcohol or sodium methylate to formate and the concomitant production of hydrogen, the reducing agent, involves the acidic dissociation of sodium hydroxide, then it follows *that conditions which disfavor this acidic dissociation will limit the extent of reduction, while conditions which favor acidic dissociation will increase reduction.*

As the addition of water disfavors acidic dissociation of sodium hydroxide through the promotion of basic dissociation, it follows that the addition of increasing molar concentrations of water to the standard reaction mixtures likewise disfavors acidic dissociation and thereby gives limited reduction (increasingly lower yields of azoxybenzene).

On the other hand, increasing the molar concentrations of pyridine would naturally promote the acidic dissociation of sodium hydroxide because *pyridine is decidedly basic.* Furthermore, its marked property of forming salts and a great variety of unstable molecular addition compounds, lends support to the idea that it may here function as a carrier of the ions H^+ and ONa^- and thereby facilitate Reaction y, $CH_3OH + HONa \longrightarrow HCOONa + 2H$, of the previously discussed reaction mechanism.

Our grateful acknowledgments are due to Professor John Uri Lloyd, whose interest and assistance as donor of a Fellowship in Chemistry made this investigation possible.

Summary

In this study of the reducing action of sodium methylate in methyl alcohol solution, the following conclusions are noted.

1. The equation originally proposed by Klinger for the reduction of nitrobenzene by sodium methylate, $4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O$, has been quantitatively verified in a standardized method of procedure by establishing the stoichiometrical ratio $2(C_6H_5N)_2O:3HCOONa$.

2. The incorporation within the standardized reaction mixture of *increasing* molar quantities of *water* regularly *decreases* the extent of the reduction of the nitrobenzene to azoxybenzene as shown by the successively *decreased* yields of sodium formate.

3. Similar experiments with *increasing* molar quantities of *pyridine* *increased* the extent of the reduction. Both azoxy- and azobenzene are formed, the former according to the above equations, the latter according to the equation $2C_6H_5NO_2 + 2CH_3ONa \longrightarrow C_6H_5N = NC_6H_5 + 2HCOONa + 2H_2O$.

The combined yields of azoxy- and azobenzene are quantitatively proportional to the amount of sodium formate obtained.

4. In previous papers[5] the oxidation of carbon compounds by fused anhydrous caustic alkalies, accompanied by the liberation of hydrogen, was shown to conform quantitatively to a general type reaction (where $M = Na$ or K) $R(H)_n + n(HOM) \longrightarrow R(OM)_n + nH_2$, which involves the acidic dissociation of the caustic alkalies. Analogously, the mechanism of the reducing action of sodium methylate in methyl alcohol is also assumed to involve the acidic dissociation of sodium hydroxide in the equation $CH_3OH + HONa \longrightarrow HCOONa + 2H_2$. Here the hydrogen is not liberated but effects reduction of the nitrobenzene.

5. Granting the extent of the reduction to be a function of the extent of the acidic dissociation of sodium hydroxide, the effect of water in limiting

the extent of the reduction is due to its promoting basic dissociation and thereby limiting acidic dissociation. On the other hand, the effect of pyridine in increasing the extent of reduction is due to its basic properties, which promote acidic dissociation of sodium hydroxide.[9]

CINCINNATI, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 13]

THE POLYMERIZATION OF THE AMYLENES[1]

BY JAMES F. NORRIS AND JOZUA M. JOUBERT

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The object of this work was to study in detail the conditions under which the amylenes are polymerized by sulfuric acid, the mechanism of the reaction, and the structure of the resulting compounds. The investigation seemed of importance because our knowledge of the mechanism of polymerization and of the properties of the higher olefins is limited, and because of the fact that these hydrocarbons are formed in the cracking of oils and are present in commercial products. Brooks and Humphrey[2] have studied the behavior of certain olefins with sulfuric acid and have shown that the process of treating crude cracked oils with the acid does not free them from unsaturated compounds. Since the preparation of olefins can be effected from petroleum, it is possible that they may become a source of compounds of industrial importance.

The polymerization of the butylenes has been studied in some detail, but the statements in regard to the amylenes are conflicting and incomplete.

The five isomeric amylenes were prepared in pure condition and their behavior was studied with varying concentrations of sulfuric acid. The effect of the structure of the hydrocarbon was marked. There were great variations in the strength of the acid required to dissolve the hydrocarbons, in the times required for solution and for the precipitation of the polymer, and in the extent to which polymerization took place.

The isomers which have two radicals in combination with an unsaturated carbon atom reacted most readily. They did not appear to form a sulfuric acid ester when they dissolved because the tertiary alcohol was precipi-

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[9] An investigation of the effects of other basic substances upon the reducing action of sodium methylate is in progress. A preliminary note should also be made of the observation that certain carbon compounds *in aqueous solution* of sodium hydroxide are partially oxidized, in the presence of a catalyst, with concomitant liberation of hydrogen. This is evidence of acidic dissociation of sodium hydroxide in aqueous solution.

[1] From the thesis of J. M. Joubert presented, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1922.

[2] Brooks and Humphrey, THIS JOURNAL, **40**, 822 (1918).