2. The melting points of pure 1-nitro-anthraquinone and of pure 1-amino-anthraquinone were found to be considerably higher than the values given in the literature.

3. The properties and reactions of 1-hydroxylamino-anthraquinone are described.

PRINCETON, NEW JERSEY

THE DECOMPOSITION OF AMINES IN THE VAPOR STAGE

BY FRED W. UPSON AND LILA SANDS[1]

This paper presents the results of experiments on the decomposition of amines in the vapor stage in the presence of kaolin.

Experimental

Description of the Apparatus.—The reaction chamber consisted of a silica tube drawn out to a capillary of about 1 mm. internal diameter at one end, heated in an electric furnace controllable within a range of 10°. Temperature readings were made by means of a base-metal thermocouple and a millivolt meter. The tube was packed with kaolin in pieces about 18 mm. long and 3 mm. in diameter.

The sample of amine was contained in a sealed tube, with a side arm carrying a glass stopcock, by means of which union with the capillary of the silica tube was made. The products of decomposition on leaving the tube passed first through a U-tube surrounded by a freezing mixture, then through a wash-bottle containing standard acid, and finally gaseous products were collected in a container over mercury. Connections were of sealed glass wherever possible. By means of a side tube fitted with glass stopcocks the whole apparatus could be evacuated to about 4 mm. pressure. The sample of amine was admitted to the reaction tube by opening the stopcock on the side-arm tube, the last traces being expelled by gentle heating.

Ethyl Amine.—The decomposition of ethyl amine was carried out at three different temperatures, 500°, 700° and 1000°. Except at the highest temperature, gaseous, liquid and solid products appeared. The gaseous products consisted of saturated and unsaturated hydrocarbons, nitrogen and hydrogen. In the analysis of the gas mixture unsaturated hydrocarbons were absorbed in bromine water; hydrogen and saturated hydrocarbons were determined by burning in a combustion pipet. Hydrogen was determined in a separate sample by burning over palladium black at 60°.

The results of one experiment are given in the first line of the table. These are fairly representative of the results in several different experiments carried out at 700°. The gas mixture was shown to consist of ethane and ethylene with small amounts of hydrogen and nitrogen. Ammonia was found in the wash-bottle. The products in the U-tube proved the most interesting. A substance in the form of white cubical crystals always collected here. This was proved to be ammonium cyanide. In addition an oily liquid designated in the table as "Residue in the U-tube" always collected and this was probably acetonitrile since a larger amount of this substance, collected in a special experiment, was treated in the usual manner for the hydrolysis of a nitrile, and gave evidence of the formation of acetic acid.

TABLE I

PRODUCTS OF DECOMPOSITION

Percentage of products based on weight of amine, decomposed

Amine	Temperature °C.	NH₂ in wash-bottle %	NH₂ in U-tube %	HCN in wash-bottle %	HCN in U-tube %	Residue in U-tube %	Ethylene %	Propylene %	Carbon in furnace %	Carbon as sat. gas %	H₂ as sat. gas %	H₂ as free gas %	N₂ as free gas %	Amine in wash-bottle %	Total %
Ethyl Amine	700	13.3	6.4	0.5	6.4	22.6	7.2	0.0	6.5	17.4	4.2	2.9	1.0	0.0	88.4
	500	15.9	5.1	0.0	0.0	28.3	14.8	0.0	1.0	4.3	1.0	1.9	2.6	10.2	84.9
	1000	0.0	0.0	0.0	0.0	Tr.	Tr.	0.0	5.6	26.9	6.0	5.3	33.2	0.0	77.0
Propyl Amine	700	9.3	4.3	1.7	4.9	15.9	3.0	6.4	7.2	14.5	3.4	2.9	4.6	0.0	78.3

Sabatier and Gaudion[2] have carried out similar experiments in the presence of nickel. They found that benzyl amine over nickel at 300–350° gave benzonitrile, ammonia and toluene. Isopropyl amine gave the corresponding nitrile, isopentane and ammonia. Methyl aniline[3] gave aniline, carbon, methane, benzene and ammonia. These results are very similar to ours. In the presence of nickel, however, the decomposition occurs at a lower temperature. Sabatier and Gaudion obtained results at 350° which parallel ours at 700°.

In the second line of Table I are given the results of an experiment with ethyl amine carried out with the furnace at a temperature of 500°.

A comparison of the results obtained at the two temperatures shows that at the temperature of 500°, no hydrogen cyanide is produced, a larger amount of ammonia is formed and the gaseous products contain relatively larger amounts of unsaturated hydrocarbons. At this temperature also

[2] Sabatier and Gaudion, Compt. rend., 165, 224 (1917).
[3] Sabatier and Gaudion, ibid., 165, 309 (1917).

unchanged amine appears. The product which collected in the U-tube consisted in part of unchanged amine and in part of an oily substance which was probably the nitrile but which was not identified.

In the third line are given the percentages of the various products obtained when ethyl amine is passed through the tube at a temperature of 1000°. These are gaseous. The nitrogen appears exclusively as free nitrogen, as does much of the hydrogen also. No ammonia is formed. Of special interest is the fact that saturated hydrocarbons appear with only traces of the unsaturated. Calculations based upon the results of analysis and upon the density of the gas showed that it consisted largely of *butane*.

In the last line of the table are given the results of an experiment on the decomposition of propyl amine at a temperature of 700°. The decomposition of propyl amine proceeds in a manner similar to that of ethyl amine. Crystalline ammonium cyanide collected in the cooled U-tube, as did also a small amount of oily liquid which was probably ethyl cyanide. Calculations based upon the results of analysis and upon the density indicated that the unsaturated gas was a mixture of *propylene* and *ethylene* and the saturated gases were *propane* and *ethane*.

In every experiment which was carried out free carbon in small amounts deposited on the kaolin. In addition, small amounts of a black, resinous substance always collected near the exit from the silica tube. This explains in part the fact that quantitative results were not obtained in the experiments here recorded.

Theoretical Discussion

Nef[4] has carried out extensive investigations on the dissociation reactions of alcohols, alkyl halides and related compounds at elevated temperatures. He came to the conclusion that the primary dissociation of these substances yields water or halogen hydride respectively and methylene or a homolog and not an olefin. When an olefin results on dissociation of an alcohol or alkyl halide it must be formed, according to Nef through subsequent rearrangement of the methylene derivative: $RCH_2CH_2X \longrightarrow RCH_2CH = + HX$; $RCH_2CH = \longrightarrow RCH \rightleftharpoons CH_2$.

Nef has further shown[5] that the concept of methylene dissociation as an intermediate stage in the reactions of alcohols and alkyl halides offers an adequate interpretation of the mechanism of these reactions both from a qualitative and a quantitative point of view. According to the theory, methylene or a homolog results through primary dissociation of the alcohol or halide as above indicated. The bivalent carbon group is very reactive. When no other substance is present in the system with which it may unite, rearrangement to an olefin ensues. When free hydrogen is present as in the Würtz reaction, a saturated hydrocarbon is formed: $R_3CH_2CH =$

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[4] Nef, *Ann.*, **309**, 126 (1899).

[5] Nef, *ibid.*, **318**, 1, 37 (1901); **298**, 315 (1897).

+ 2H + RCH_2CH_2. In the presence of an alcohol, as in the ordinary ether reaction, the methylene derivative unites with alcohol to form the ether: $RCH_2CH= + HOR \longrightarrow RCH_2CH_2OR$. In the presence of oxygen an aldehyde results: $RCH_3CH= + O \longrightarrow RCO_2CHO$. The applications of the theory are fully discussed by Nef.

Denis[6] and later Evans and Day[6] have made use of this theory to explain the results of the oxidation of ethyl alcohol in alkaline solution.

The results of our experiments may be explained at least from a qualitative point of view by means of the theory of methylene dissociation. In the case of ethyl amine for example, the primary dissociation yields ethylidene and ammonia: $CH_3CH_2NH_2 \longrightarrow CH_3CH= + NH_3$. Ethylene results by rearrangement of the ethylidene. At 700° and 500° there is some dissociation of ammonium into its elements, giving free hydrogen. This latter reacting with ethylidene gives ethane: $CH_3CH= + 2H \longrightarrow CH_3CH_3$. Acetonitrile must have been formed by the following dissociation: $CH_3CH_2NH_2 \longrightarrow CH_3C=N + 4H$. The acetonitrile on further dissociation gave methylene and hydrogen cyanide: $CH_3CN \longrightarrow H_2C= + HCN$. Any methylene thus formed must have combined with itself to give ethylene, as proved by Nef.

Interaction of hydrogen cyanide with ammonia accounts for the formation of ammonium cyanide in the cooled U-tube. Butane was the chief hydrocarbon formed at 1000°. This must have been formed by the union of 2 ethylidene radicals and 2 atoms of hydrogen as in the Würtz reaction: $2CH_3CH= + 2H \longrightarrow C_4H_{10}$.

In the reaction with propyl amine at 700°, the formation of ethane, ethylene, propane and propylene was indicated from the results of analysis of the hydrocarbon gas mixture. These can all be accounted for as follows.

Primary dissociation of propyl amine gives propylidene which in the presence of hydrogen becomes propane or on rearrangement gives propylene: $CH_3CH_2CH_2NH_2 \longrightarrow CH_3CH_2CH= + NH_3$. The following dissociation accounts for the formation of ethyl cyanide: $CH_3CHCH_2NH_2 \longrightarrow CH_3CH_2CN + 4H$. The cyanide on dissociation yields ethylidene and hydrogen cyanide: $CH_3CH_2CN \longrightarrow CH_2CH= + HCN$. The ethylidene must obviously have been the source of the ethane and ethylene in this experiment.

It appears, then, that the formation of *butane* from ethyl amine at 1000°, and the formation of *ethane* and *ethylene* as well as propane and propylene from propyl amine, can be accounted for only on the basis of the theory of methylene dissociation, as above indicated.

Summary

Ethylene amine decomposed by passing over kaolin at 500° gives

[6] Denis, *Am. Chem. J.*, **38**, 363 (1907). Evans and Day, THIS JOURNAL, **41**, 1207 (1919).

chiefly ammonia, hydrogen cyanide, ethylene, and a substance which is probably acetonitrile, together with smaller quantities of hydrogen and nitrogen. At 700° it gives more ethylene, less carbon and no hydrogen cyanide.

At 1000° the chief products are the elements, although traces of ethylene and probably acetonitrile were found.

Propylene at 700° gives chiefly a nitrile, ammonia, carbon and hydrocarbons, together with smaller quantities of hydrocyanic acid and the elements.

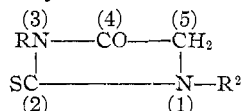The modes of formation of the decomposition products are discussed.

LINCOLN, NEBRASKA

THE REACTIONS OF THE FORMAMIDINES.
X. THE THIO-IMIDAZOLONES

BY F. B. DAINS, RUTH THOMPSON AND W. F. ASENDORF[1]

Previous investigations have shown that compounds containing methylene hydrogen, $>CH_2$, reacted with the substituted formamidines, yielding derivatives as follows: $\frac{X}{Y}\!\!>\!\!CH_2 + RHNHCHNR = \frac{X}{Y}\!\!>\!\!C = CHNHR$

$+ RNH_2$. This was found to be true not only in the case of the acetylacetone and aceto-acetic ester type but also with certain ring compounds, such as the pyrazolones, isoxazolones and the thiazolidones.[2] The study of this general reaction has been now extended to the thio-imidazolones, which contain the same methylene grouping, and it has been found that the methylene hydrogen in these derivatives can be replaced with equal ease, giving the 5-amino-methylene-thio-imidazolones.[3] Thus

$$
\begin{array}{ccc}
(3) & (4) & (5) \\
RN\!\!-\!\!-\!\!-\!\!CO\!\!-\!\!-\!\!-\!\!CH_2 \\
| & & | \\
SC\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!N\!\!-\!\!R^2 \\
(2) & & (1)
\end{array}
$$

These compounds showed a close analogy to the corresponding aldehyde substitution products investigated by Wheeler, and Johnson, and their co-workers, not only in their general properties, but also in the ability of the monosubstituted imidazolones to form thio-ethers.[4]

[2] Ber., 35, 2509 (1902). THIS JOURNAL, 31, 1148 (1909); 35, 959, 970 (1913); 38, 1841 (1916); 40, 562 (1918); 43, 613, 1200 (1921).

[3] The numbering of the ring is that used in Chemical Abstracts. In some of the literature these imidazoles are regarded as 5-keto derivatives.

[4] (a) Wheeler and Brautlecht, Am. Chem. J., 45, 447 (1911). (b) Johnson and Nicolet, THIS JOURNAL, 33, 1978 (1911).