Results for the analysis of organically combined sulfur and phosphorus are given.

NEW YORK CITY

RECEIVED MAY 5, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY AND OF THE OHIO STATE UNIVERSITY]

Saponification of Diarylnitrosamines and Attempts to Prepare a Salt of Aquo-ammononitrous Acid

BY W. CONARD FERNELIUS AND GEORGE W. WATT

In accordance with Franklin's ammonia system of compounds, the substance represented by the formula H_2NNO may be regarded as an aquo-ammononitrous acid.[1] The nitrosamines, then, are esters of this acid and should yield salts upon saponification: $R_2NNO + 2KNH_2 \longrightarrow R_2NK + KHNNO + NH_3$.

The present study has shown that potassium amide in liquid ammonia solution reacts readily and completely with the aromatic nitrosamines to form not a salt of aquo-ammononitrous acid, but rather nitrogen gas and potassium hydroxide, possible decomposition products of an extremely unstable salt, KHNNO: $R_2NNO + 2KNH_2 \longrightarrow R_2NK + KOH + N_2 + NH_3$. This reaction has been found to take place quantitatively in liquid ammonia solution with both diphenylnitrosamine and di-*p*-tolylnitrosamine and with a number of basic amides. No direct evidence was found for the formation of the salt KHNNO as an intermediate product. Attempts to saponify diphenylnitrosamine dissolved in toluene with solid sodium amide gave low yields of nitrogen and tarry products. Although fused hydroxides effect a saponification of the nitrosamines,[2] it was found that diphenylnitrosamine is not saponified by alcoholic potassium hydroxide.

A brief study of the reactions of methylphenylnitrosamine and dibenzylnitrosamine with potassium amide in liquid ammonia solution has shown that these nitrosamines do not react in a manner similar to diphenylnitrosamine and di-*p*-tolylnitrosamine, since no nitrogen is liberated and there is no evidence of the formation of the metal salts of the parent amines.

Experimental

In carrying out the liquid ammonia reactions described in this paper, the familiar technique of Franklin and his co-workers[3] was employed. Gases evolved during a reaction were collected in the manner described by Bergstrom.[4]

Preparation of Materials.—The diphenylnitrosamine used in these experiments, an

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(1) Franklin, "Liquid Ammonia as a Solvent and the Ammonia System of Compounds," A. C. S. Monograph, in press. *Cf.* Fernelius and Johnson, *J. Chem. Ed.*, **7**, 1854 (1930).

(2) Bamberger, *Ber.*, **27**, 1179 (1894); *cf.* **33**, 1957 (1900).

(3) For references see Schurman and Fernelius, THIS JOURNAL, **52**, 2427 (1930).

(4) Bergstrom, *ibid.*, **47**, 2320 (1925); *cf.* Johnson and Fernelius, *J. Chem. Ed.*, **6**, 449 (1929).

Eastman Kodak Co. product, was recrystallized several times from ethanol: m. p. 66.5°; soluble in liquid ammonia at room temperature, much less soluble at −33°. Di-*p*-tolylnitrosamine was prepared from di-*p*-tolylamine by the method of Lehne[5] and purified by recrystallization from petroleum ether: light yellow monoclinic crystals slightly soluble in liquid ammonia at room temperature, m. p. 102–103°, corr. (Lehne reported 100–101°, and Cosack 103°).[6] Di-*p*-tolylamine was prepared by refluxing equimolecular quantities of *p*-toluidine and *p*-toluidine hydrochloride,[7] and purified by distillation under reduced pressure followed by recrystallization from methanol, m. p. 79°. Dibenzylnitrosamine was prepared by the method described by Curtius and Franzen[8] and, after recrystallization from ethanol, the yellow crystals melted at 61°. Methylphenylnitrosamine was prepared from methylaniline[9] and purified by distillation under reduced pressure: b. p. 114° (9.0 mm.).

The Saponification of Diphenylnitrosamine.—The description of a typical experiment will best serve to describe the course of the reaction. Diphenylnitrosamine was sealed in one leg of an ammonia tube and potassium metal (slightly in excess of two equivalents) and an oxidized iron wire catalyst in the other leg. Ammonia was then distilled into the tube. Following the conversion of the metal to the amide, the last traces of hydrogen were swept from the tube and a small quantity of the solution of potassium amide poured into the solution of diphenylnitrosamine. Immediately the color of the latter solution became a darker yellow and a flocculent precipitate formed, accompanied by a brisk effervescence. Small portions of the amide solution were added until there was no further evidence of reaction. In the case of the other amides which are insoluble in liquid ammonia, the solution of the nitrosamine was poured onto the amide.

The data relative to the volumes of gas (nitrogen) liberated in the reaction of diphenylnitrosamine with the amides used are contained in Table I. Calculations are based on the reaction: $(C_6H_5)_2NNO + 2KNH_2 \longrightarrow (C_6H_5)_2NK + KOH + N_2 + NH_3$. A portion of each gas volume was mixed with oxygen and subjected to combustion. In no case was more than a trace of combustible gas found to be present.

TABLE I

SAMPLE, 1.0000 G. CALCD. GAS EVOLVED, 113.1 CC.

Expt.	Amide	Gas evolved Obs.
2	KNH_2	110.4
3	KNH_2	110.5
4	$NaNH_2$	115.5
7	$LiNH_2$	114.5
8	KNH_2	116.0
9	$Ca(NH_2)_2$	115.8

TABLE II

ANALYSIS OF POTASSIUM HYDROXIDE

Expt.	Sample, g.	K_2SO_4, g.	K found, % 69.68 calcd.
1	0.0541	0.0826	68.4
8	.0639	.0999	70.1
10	.0482	.0734	68.9
11	.0477	.0730	69.2

The precipitates from the potassium amide reactions were washed several times to free them of ammonia-soluble material and subjected to analysis. The analyses for potassium are given in Table II. Analysis for nitrogen (Kjeldahl) of aliquots from these samples showed that only traces were present, 0.1% being the maximum value found.

Due to the insolubility of the other metal amides used, similar analyses for the reactions in which they were used could not be made.

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(5) Lehne, *Ber.*, **13**, 1544 (1880).

(6) Cosack, *ibid.*, **13**, 1092 (1880).

(7) De Laire, Girard and Chapoteaut, *Ann.*, **140**, 346 (1866).

(8) Curtius and Franzen, *Ber.*, **34**, 557 (1901).

(9) Hepp, *ibid.*, **10**, 328 (1877).

The ammonia-soluble residues remaining consisted of the excess of potassium amide and of a yellow crystalline solid (potassium diphenylamide). Upon hydrolysis these residues yielded distinctly alkaline solutions and insoluble white crystalline solids which after several recrystallizations from ether melted at 53°, and gave a mixed melting point with pure diphenylamine (m. p. 54°) of 53.5°. The residues from amides other than potassium gave identical results.

The Saponification of Di-*p*-tolylnitrosamine.—In a manner identical with that described above, the reactions between di-*p*-tolylnitrosamine and the amides of potassium and sodium were studied. Except for complications arising from the slight solubility of the *p*-tolyl compound, the reactions are identical with those of diphenylnitrosamine. The results are tabulated in Tables III and IV.

TABLE III

Expt.	Sample, g.	Amide	Gas evolved, cc. Obs.	Calcd.
1	1.5700	KNH_2	159.7	155.5
2	0.5000	KNH_2	49.8	49.5
3	0.5000	$NaNH_2$	49.6	49.5

TABLE IV

Expt.	Sample, g.	K_2SO_4, g.	K found, % Calcd. 69.68
1	0.0079	0.0120	67.1
2	0.0059	0.0090	68.3

Upon hydrolysis, the ammonia-soluble material from these reactions gave a white crystalline solid which after recrystallization from ether melted at 78°, and on mixing with pure di-*p*-tolylamine (m. p. 79°) melted at 79°.

Attempted Saponification of Other Nitrosamines.—Dibenzylnitrosamine, soluble in liquid ammonia at room temperature, was treated with potassium amide in a manner similar to that previously described for diphenylnitrosamine. A white precipitate formed momentarily but proved to be soluble in excess liquid ammonia. Similarly, a liquid ammonia solution of methylphenylnitrosamine was treated with potassium amide. An orange colored precipitate was formed, which after being washed several times ignited when exposed to the air. In both of these cases potassium hydroxide and nitrogen did not appear among the reaction products. These reactions are being further investigated.

Saponifications in Toluene Solution.—Weighed samples of diphenylnitrosamine and of dibenzylnitrosamine were dissolved in toluene and refluxed with solid sodium amide in an atmosphere of ammonia until there was no further evidence of reaction. In addition to the formation of an insoluble gas, tarry products were deposited during these reactions. Data from typical experiments are given in Table V. It is to be noted that nitrogen gas is liberated in the reaction between dibenzylnitrosamine and sodium amide in toluene solution whereas no insoluble gaseous products were formed in the reaction of this nitrosamine with potassium amide in liquid ammonia solution.

TABLE V

Nitrosamine	Sample, g.	N_2 found, cc.	N calcd., cc.
$(C_6H_5CH_2)_2N.NO$	1.0000	69.5	99.1
$(C_6H_5)_2N.NO$	1.0000	51.2	113.1

Due to the presence of the excess sodium amide, no data could be secured relative to the formation of potassium hydroxide in these reactions.

Attempted Saponification in Alcohol.—Three grams of diphenylnitrosamine was refluxed for four hours with 3.4 g. of potassium hydroxide dissolved in 150 cc. of absolute alcohol. The color of the solution changed from a yellow to a light orange. The alcohol was evaporated and the product washed with water: weight 2.9 g.; m. p. 60–63°; mixed m. p. with original $(C_6H_5)_2NNO$ (66.5°) 62–64°; m. p. after recrystallization from alcohol, 66.5°.

Summary

1. Diphenylnitrosamine in liquid ammonia solution reacts with the amides of lithium, sodium, potassium and calcium in accordance with the equation $R_2NNO + 2MNH_2 \longrightarrow R_2NM + MOH + N_2 + NH_3$.

2. Di-*p*-tolylnitrosamine reacts similarly with sodium and potassium amides.

3. Dibenzylnitrosamine and methylphenylnitrosamine do not react with potassium amide in accordance with the above equation.

COLUMBUS, OHIO
RECEIVED MAY 6, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MINNESOTA AND NORTHWESTERN UNIVERSITY]

Vapor Pressure and Boiling Point of Pure Methylacetylene*

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Methylacetylene was required by one of us (G. B. H.) for a study of its condensation in the presence of alpha particles. A sample of the gas prepared and purified in the usual way by distilling to a constant vapor pressure at a fixed temperature gave vapor pressures much lower than those reported by Maass and Wright[1] or calculated from their data using the equation given in the International Critical Tables.[2]

$$\text{Log}\,P_{\text{mm.}} = (0.05223/T) \times 21{,}372 \times 7.429$$

The logarithms of the pressures plotted against the reciprocal of the absolute temperatures gave a straight line which by extrapolation gave a boiling point of approximately −23°. This value agreed with the boiling point of −23.5° reported by Lespieau and Chavanne[2a] rather than that of −27.5° obtained by Maass and Wright. A second sample was prepared and gave similar results.

Meinert and Hurd[3] then reported a boiling point of −23° for pure methylacetylene. Davis, Crandall and Higbee[4] noted that the boiling point was higher than −27.5° and listed it as −20 to −18°. In an effort to obtain a purer product and a sample which could not contain acetylene, sodium acetylide was methylated by the action of methyl sulfate according to the method of Meinert and Hurd. About 10 cc. of product obtained by this method was distilled through a Davis column.[5] A fraction boiling between −22 and −25° was collected which when distilled a second time boiled at −23°. After distilling twice from a container maintained at the

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* Manuscript originally received October 1, 1930.

(1) Maass and Wright, THIS JOURNAL, **43**, 1101 (1921).

(2) International Critical Tables, Vol. III, p. 217 (1928).

(2a) Lespieau and Chavanne, *Compt. rend.*, **140**, 1035 (1905).

(3) Meinert and Hurd, THIS JOURNAL, **52**, 4544 (1930).

(4) Davis, Crandall and Higbee, *Ind. Eng. Chem., Anal. Ed.*, **3**, 109 (1931).

(5) Davis, *ibid.*, **1**, 61–64 (1929).