the exception of illinium and thulium and concluded that samarium was the only one of the group whose radioactivity persisted after purification.[8] As thulium is classified in the first group, it also may possess radioactive properties of a magnitude comparable with that of samarium. Hence, a study of the radioactivity of thulium preparations is well worth investigating.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY,
NEW YORK CITY

RECEIVED JULY 16, 1935

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[8] G. von Hevesy and M. Pahl, *Nature*, **131**, 434 (1933); *ibid.*, *Z. physik. Chem.*, **A169**, 147 (1934).

COMMUNICATIONS TO THE EDITOR

ATTEMPTED PREPARATION OF VANILLOYLFORMIC ACID

Sir:

In an attempt to repeat the oxidation of apocyanin to vanilloylformic acid with nitrobenzene in alkaline solution as described by H. O. Mottern [THIS JOURNAL, **56**, 2107 (1934)] no action whatever was observable under the conditions described by the author. Nitrobenzene was recovered quantitatively from the reaction mixture and neither aniline nor azobenzene was detectable by qualitative means.

Difficulty was also experienced in repeating the author's description of the preparation of apocyanin by means of the Fries reaction. The aluminum chloride double compound with guaiacol acetate is quite solid at the temperatures described (0–5°). Before a third of the required amount of aluminum chloride has been added, the mass is so hard as to be impenetrable to a stirring rod, making it impossible to incorporate the balance. The apocyanin used was prepared by the method for low temperature Fries isomerizations described by Baltzly and Bass [*ibid.*, **55**, 4293 (1933)] which differs from the authors in the use of nitrobenzene as a solvent.

FARMINGDALE, L. I. W. E. BARCH

RECEIVED MARCH 12, 1935

NOTE BY THE EDITOR

After the receipt of this Communication a repetition of the oxidation of apocyanin to vanilloylformic acid with nitrobenzene in alkaline solution as described by H. O. Mottern was attempted by a member of the Editorial Board and independently by the Director of Research of a firm manufacturing vanillin on a large scale. Both were unsuccessful; their concordant conclusion is expressed by the latter's statement: "The synthesis of vanillin cannot be carried out following the disclosures of the paper published in THIS JOURNAL, 1934, page 2107."

OCTOBER 10, 1935 ARTHUR B. LAMB, *Editor*

THERMAL DECOMPOSITION OF $CrO_4 \cdot 3NH_3$

Sir:

Some unusual observations recently made in this Laboratory, and which we hope to study in greater detail, should prove of considerable general interest. While attempting the preparation of the tetroxide of chromium, CrO_4, by deammonating $CrO_4 \cdot 3NH_3$ (I) [made according to Riesenfeld, *Ber.*, **38**, 4070 (1905)], the following was noted. (1) Compound (I) loses practically no ammonia upon standing for four months over concentrated sulfuric acid *in vacuo* and at room temperature. (2) If the pressure in a tube containing some (I) is reduced to less than 1 mm. and the tube, still attached to the vacuum line, is immersed in a bath whose temperature may be controlled, a vigorous reaction ensues at 120 ± 10°. Particles of (I) become incandescent and dart about in spectacular fashion. The action is reminiscent of the thermal decomposition of ammonium dichromate and also of certain models that have been constructed to portray molecular motion in gases. (3) The solid residue of the above mentioned decomposition of (I) is composed of microscopic, elongated square prisms of black $CrO_3 \cdot NH_3$ (II). Analysis of (II) for ammonia was made by distilling into standard acid and for chromium by forming lead chromate. The results for samples of (II) obtained from two different experiments are:

Cr found		NH_3 found	
44.50%	Run 1	14.45%	Run 1
44.39		14.47	
44.47	Run 2	14.49	Run 2
Mean 44.46		Mean 14.47	

Cr calcd., 44.44 NH_3 calcd., 14.55

This compound has not been reported previously and unlike the parent substance gives no test for the peroxide group. (4) The presence of small amounts of impurities has a marked influence upon the rate of decomposition of (I), in some cases increasing it to the point of explosive violence (danger!). In some of our experiments (I) was purposely left impure and may have contained ammonium chromate, dichromate or perchromate. (5) The reaction does not proceed under the conditions mentioned in (2) if carried out in the dark or near-dark. Radiation, in or near the visible, is apparently essential to start the reaction. (6) If the starting pressure in the tube be approximately 1 cm., (I) decomposes in the same scintillating manner as under (2) but the product gives the peroxide test and its composition is variable (37–38% Cr, 21–22% NH_3), lying between that of (I) and (II). It probably consists of a mixture of the latter two. (7) The density of (II) is 2.073 g./cc. at 23.5°. It is practically insoluble in carbon tetrachloride, stable in air under ordinary conditions, and hydrolyzed in water. It detonates in the neighborhood of 200° in the atmosphere, leaving Cr_2O_3.

It is interesting to note that (II) may be formulated as a partial dehydration product of ammonium dichromate: $(NH_4)_2Cr_2O_7 = 2CrO_3{\cdot}NH_3 + H_2O$, and that neither ammonium dichromate nor chromate shows any sign of reaction under the conditions mentioned in (2).

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RECEIVED JULY 30, 1935

THE PHOTOLYTIC AND THERMAL DECOMPOSITION PRODUCTS OF AZOMETHANE. THERMAL REACTION RATES IN QUARTZ, 260 TO 290°

Sir:

Pressure readings at room temperature, −78.5 and −183° at various stages of decomposition of *initially pure azomethane* show that (1) upon complete decomposition the pressure is approximately double the initial pressure of azomethane; (2) the ratio of the pressure increase at room temperature to the pressure of "permanent" gases formed by the reaction however, diminishes from a value of at least two, in the initial stages, to unity at complete decomposition. A plausible assumption to explain these facts is that the products include, with nitrogen, other "permanent" gases consisting largely of methane. This tentative conclusion is being tested by chemical analysis.

The above observations hold for both photochemical decomposition at 30° and for thermal decomposition at 300°. The course of the thermal reaction at 300° was unaffected by mercury vapor at a pressure of 100 mm. approximately, when this was intentionally introduced.

The thermal reaction rates in quartz fit the unimolecular formula, like Ramsperger's, but our rate constants are roughly half as great as his. The decomposition in Pyrex is being investigated.

The ten-degree temperature coefficient from the dark reaction rates at 260, 270, 280 and 290° is 2.9, in agreement with that of Ramsperger, and apparently affected but little by the presence of mercury vapor.

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RECEIVED SEPTEMBER 25, 1935

SEPARATION OF GUANIDINE AND METHYLGUANIDINE BY MEANS OF BETA-NAPHTHALENESULFONYL CHLORIDE

Sir:

In a study of the relation of simple and substituted guanidines to health and disease, occasion came to separate guanidine from methylguanidine. Finding the benzenesulfonyl derivatives, prepared by Ackermann [*Z. physiol. Chem.*, **47**, 366 (1906); **48**, 382 (1906)] unsuitable for the differential precipitation of these guanidines, recourse was had to beta-naphthalenesulfonyl chloride, which was found to give hitherto undescribed derivatives of guanidine and methylguanidine, suitable for the separation of these substances from each other and from other closely related compounds.

Experimental. Di-(β-naphthalenesulfonyl)-guanidine.—To one mol. of guanidine carbonate (1.5 g.) dissolved in 10 cc. of water was added 1.0

cc. of 5 *N* sodium hydroxide. Beta-naphthalenesulfonyl chloride, somewhat in excess of 2 mols. (4.5 g.), was dissolved in 10 cc. of ether, the two solutions were mixed and shaken thoroughly in a separatory funnel. After standing for five minutes, the heavy white precipitate was filtered off and washed with alcohol and ether. The yield was 4.4 g. or 93%. Upon crystallization from hot water, slightly acidified with hydrochloric acid, long, saber-shaped crystals separate rapidly. Similarly shaped but slightly shorter crystals are deposited from hot 95% alcohol. Both sets of crystals melted at 204–206° (uncorrected) apparently without decomposition. After cooling they can be melted again over a broader range, 200–206°. Hydrolysis by 20% hydrochloric acid yields beta-naphthalenesulfonic acid and free guanidine. *Analysis.* Calcd. for $C_{21}H_{17}N_3O_4S_2$: N, 9.56; S, 14.59. Found: N, 9.34; S, 14.47. The desiccator-dried sample contained two moles of water of crystallization, easily removed by heating at 105° in an oven. At 24° 100 cc. of water dissolves 9.0 mg.

Beta - naphthalenesulfonylmethylguanidine.—The procedure used for the guanidine compound yielded no insoluble complex with methylguanidine. A precipitate was obtained with higher alkalinity and a longer period of shaking. One mole of methylguanidine hydrochloride (110 mg.) was dissolved in water and added to a solution of 1 mol. of beta-naphthalenesulfonyl chloride (230 mg.) dissolved in 10 cc. of ether. The mixed solutions were shaken in a separatory funnel after the addition of 2.5 cc. of 5 *N* sodium hydroxide. Shaking was repeated at intervals of five minutes, for half an hour, and the mixture was then allowed to stand overnight. The white crystalline precipitate was removed, washed with alcohol and ether, and dried in a desiccator. The yield was 171 mg. or 65%. Upon crystallization from hot water, slightly acidified with hydrochloric acid, long, slightly curved, branching needles separated rapidly. Similarly shaped crystals are deposited from alcohol. The compound has a greater solubility in alcohol than the guanidine derivative; melting point, 101–102° (uncorrected). *Analysis.* Calcd. for $C_{12}H_{13}N_3O_2S$: N, 15.97; S, 12.18. Found: N, 15.19; S, 12.02. At 24° 100 cc. of water will dissolve 21 mg. Hydrolysis by 20% hydrochloric acid yields beta-naphthalenesulfonic acid and free methylguanidine.

Guanidine yields a di-acylated product whereas the methylguanidine derivative is mono-acylated.

Attempts to prepare insoluble beta-naphthalenesulfonyl derivatives of creatine, creatinine, glycocyamine and glycocyamidine were unsuccessful.

Fifty mg. each of the hydrochlorides of guanidine and methylguanidine were dissolved in 5 cc. of water. With use of beta-naphthalenesulfonyl chloride and a little alkali, the first precipitate was the guanidine complex, rather pure. With increase in alkali, a mixture was obtained readily fractionated and with more alkali and longer standing, the approximately pure methylguanidine complex was obtained. From the original mixture 90% of the guanidine was recovered and with no further attention to maximal yields 45% of the methylguanidine.

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