

It is seen that the intermolecular effect remains constant in the temperature range 137 – 196°C., a fact which is in agreement with theoretical predictions. Moreover, the ratio $\frac{k_1}{2k_3} = 1.036 \pm 0.003$ is in closer agreement with the results of Bigeleisen and Friedman ($1.037 \pm .002$) than the value previously reported from this laboratory. Although the magnitude of the effect is not in agreement with the predicted value of 1.021 calculated by Bigeleisen (2), the invariance of the effect with temperature is an interesting partial substantiation of theory.

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The Nitrosation of Hexamine

The aim of this work was to raise the yield of trimethylenetrinitrosamine, the nitroso analogue of RDX, from hexamine. Although it was not attained, the results may have some theoretical interest. Bachmann and Deno (1) have recently referred to part of them.

A number of variations of the original method of Mayer (2) were tried. The basic procedure was to add successively 1 mole equivalent of hexamine, then 4.8 moles sodium nitrite, to 5.5 moles hydrochloric acid, all in water solution near 0°C. With total water 31 cc. per gram hexamine, reaction time 30–60 min. followed by filtration, washing with water at 0°, and drying to constant weight at 50°, these proportions gave a 48–52% yield of trinitrosamine, m.p. 99–100° corr. or better (pure trinitrosamine, m.p. 105–107°). The yield figure is on a mole-for-mole basis. No change in this procedure gave any higher yield. All runs were made with 10.5 gm. (0.075 mole) hexamine and corresponding amounts of the other reagents.

When the reaction stood only 15 min. before working up, the product was a mixture of trinitrosamine and the less degraded dinitrosopentamethylenetetramine (m.p. pure, 207°). The dinitroso compound could be isolated readily because of its lower solubility in boiling 95% ethanol (1 gm. dissolved in about 60 cc. solvent, compared with 8 cc. for trinitrosamine). A mixture was also obtained when the amount of hydrochloric acid was reduced to 4.4 moles; Bachmann and Deno have shown that this is because of a pH effect. Simply allowing the hexamine and acid solutions to stand together for one and one-half hours or more, or allowing the aqueous hexamine solution to stand alone for about 10 days, before reaction, also gave a mixture under conditions where trinitrosamine would otherwise have been the sole product.

Doubling the nitrous acid lowered the yield to 38-40%. No effect was observed when the reaction volume was doubled, or when sodium chloride was added in an effort to salt out more product. Stirring was found to have no effect provided the reagents were once thoroughly blended at the start, by vigorous mixing for about 30 sec.

Carbon lost in the reaction could be largely accounted for as formaldehyde; the procedure used was dimedone precipitation (3). The formaldehyde found corresponded to 61-64% of the carbon originally present in the hexamine. The 48-52% yield (on mole-for-mole basis) of trinitrosamine corresponds to a further 24-26% of the original carbon. Altogether, therefore, the two products contained 85-90% of the carbon from the hexamine.

The formaldehyde found was slightly higher when the filtrate had been allowed to stand a few days first. Probably this was from decomposition of product remaining in the solution.

Nitrogen peroxide (from a commercial cylinder), added either as liquid or gas to hexamine solution, gave yields of trinitrosamine as high as 48% when 8-10 moles per mole hexamine was used. Addition of 2 to 5 moles ammonium hydroxide had no effect in dilute solution (yield was slightly lowered in concentrated solution). When 5 moles sodium hydroxide was added, the product was nearly all the dinitroso compound.

Dinitrosopentamethylenetetramine, when powdered to -200 mesh and treated with 4 moles of nitrous acid at 0-3°, was converted to trinitrosamine, m.p. 105°, in a maximum yield of 40% after 50 min. With 2 moles of nitrous acid the product was a mixture.

A point of interest in the results is that hexamine in water or dilute acid, on standing, gave a solution which would no longer give pure trinitrosamine with nitrous acid as did the fresh reagents. Instead a mixture of the two nitroso compounds was produced. The mechanism for this is still unknown.

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Wheat Straw Native Lignin*

An attempt has been made to isolate native lignin from mature wheat straw (Saunders) by extracting the finely ground material with alcohol at room temperatures and removing the water- and the ether-soluble fractions. A considerably smaller percentage of lignin was obtained in this way than has been reported as isolable from spruce (1) and aspen (2) by Brauns *et al.* and

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