Decomposition of Pentamethyltetrazenium Iodide in Water

By W. H. BRUNING, C. J. MICHEJDA, and D. ROMANS
(Department of Chemistry, University of Nebraska, Lincoln, Nebraska)

THE reaction of 2-tetrazenes with methyl iodide was first investigated by Wieland and Fressel.[1] We re-investigated the reaction within the framework of a study of amino-radicals because it was possible that a free-radical mechanism was involved.

Tetramethyl-2-tetrazene[2] was treated with one equiv. of methyl iodide at 0°, without solvent. The crystalline product was pentamethyltetrazenium iodide (I), described recently by Mackay and Waters.[3] This material decomposed slowly at room temperature, with evolution of nitrogen (identified by mass spectrometry). It decomposed rapidly in water at 0° to produce a brown solution, whose colour faded after one or two minutes. The brown solution gave a strong positive starch test for iodine. When the decomposition was carried out in aqueous thiosulphate, no colour appeared, again indicating the presence of molecular iodine in the unquenched reaction. The products of the quenched reaction were analyzed by g.l.c. Tetramethylhydrazine was formed in approximately 65% yield, the other principal product being trimethylamine.[4]

The aqueous decomposition solution of the methiodide (I) was found to be strongly paramagnetic. The e.s.r. spectrum[5] contained 15 equally spaced major splittings; each of the lines exhibited further fine structure. An identical spectrum was obtained when authentic tetramethylhydrazine[6] was dissolved in water saturated with iodine. On the basis of relative intensity measurements within the groups of lines the spectrum can be interpreted as being due to two equivalent nitrogens, $a_N = 13{\cdot}5 \pm 0{\cdot}1$ gauss, and twelve equivalent protons, $a_H = 12{\cdot}7 \pm 0{\cdot}1$ gauss. According to this analysis not all the lines were observed experimentally; the two outer lines were lost in the noise and some of the small splittings were lost because of the large differences in the relative intensities within the groups.

The data presented above can best be accounted for by the tentative mechanism opposite.

It is dangerous to extend this mechanism to solvents other than water. When the methiodide (I) was dissolved in acetonitrile, evolution of nitrogen occurred but no iodine was formed and no paramagentic species was produced. The principal product of this decomposition was pentamethylhydrazinium iodide.

$$\mathrm{I^-\,Me_3\overset{+}{N}{-}N{=}N{-}N{-}Me_2} \xrightarrow{\mathrm{H_2O}}$$

(I)

$$\mathrm{Me_3\overset{+}{N}{\cdot}\,I^- + N_2 + {\cdot}NMe_2}$$

$$\mathrm{Me_3\overset{+}{N}{\cdot}\,I^- \rightarrow Me_3N{:} + I{\cdot} \xrightarrow{I\cdot} I_2}$$

$$2\,{\cdot}\mathrm{NMe_2} \rightarrow$$

$$\mathrm{Me_2N{-}NMe_2}\ \text{or}\ \mathrm{Me_2N{-}H + CH_2{=}N{-}Me}$$

$$\mathrm{Me_2N{-}NMe_2 + I_2 \rightarrow Me_2\overset{+\cdot}{N}{-}NMe_2}$$

(*Received, October 21st,* 1966; *Com.* 840.)

---

[1] H. Wieland and H. Fressel, *Annalen*, 1912, **392**, 133.

[2] J. S. Watson, *J. Chem. Soc.*, 1956, 3677.

[3] D. Mackay and W. A. Waters, *J. Chem. Soc.* (*C*), 1966, 813.

[4] It was difficult to get a quantitative estimate of this product under our conditions, but its yield was at least equal to that of tetramethylhydrazine.

[5] The complete analysis of the spectrum, together with some interesting solvent effects, will be published elsewhere. The spectra were obtained with a JEOLCO 3BSX e.s.r. spectrometer employing 100 kc./sec. field modulation.

[6] R. T. Beltrami and E. R. Bisell, *J. Amer. Chem. Soc.*, 1957, **78**, 2467.