

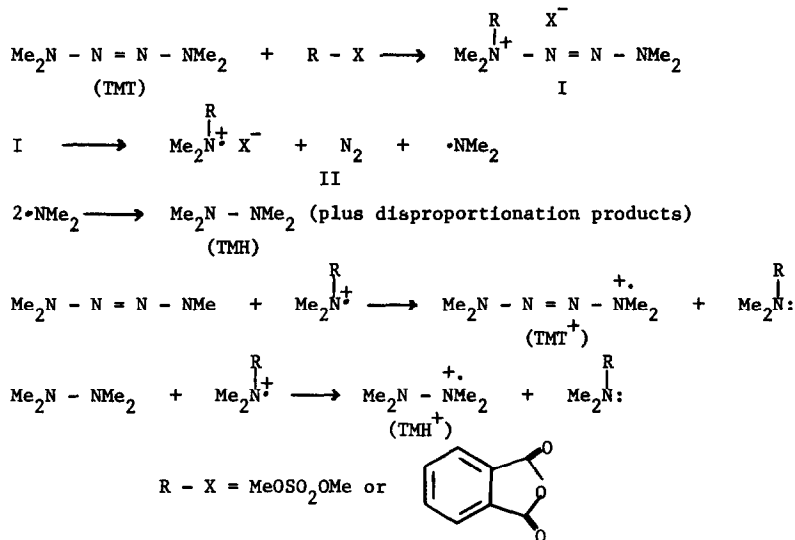
Alkylation and Acylation of Tetramethyl-2-tetrazene

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In a previous communication we reported the reaction of tetramethyl-2-tetrazene (TMT) with methyl iodide (1). The purpose of this paper is to report some interesting results of a further study. In our earlier work we noted that TMT was alkylated by methyl iodide to form the unstable pentamethyltetrazenium iodide. This salt decomposed rapidly in water to form iodine and tetramethylhydrazine (TMH), trimethylamine and nitrogen. The first two compounds then reacted to form tetramethylhydrazine radical cation ( $\text{TMH}^{\dot{+}}$ ), which was detected by esr. The iodine was formed by electron transfer from iodide to the trimethylamine radical ion. Nelsen (2) reported that when TMT was treated with anhydrides, particularly dichloromaleic anhydride,  $\text{TMH}^{\dot{+}}$  was formed. He proposed a mechanism which was consistent with his data.

When TMT was treated with phthalic anhydride in acetonitrile solution (degassed) the spectrum of the TMT radical ion ( $\text{TMT}^{\dot{+}}$ ) was observed by esr. This spectrum was described by Tolles, Moore and Thun (3). Our spectrum compared well with a computer simulated trace calculated on the basis of the hyperfine coupling constants determined by these workers. After about one half hour the spectrum of  $\text{TMH}^{\dot{+}}$  began to appear along with that of  $\text{TMT}^{\dot{+}}$ . The spectrum of  $\text{TMH}^{\dot{+}}$  has been described in detail by Nelsen (2) and by us (1,4). On standing for about one hour all the  $\text{TMT}^{\dot{+}}$  was gone and only the spectrum of  $\text{TMH}^{\dot{+}}$  was observed. On a larger scale this reaction gave a good yield of the mono-dimethylamide of phthalic acid. No radicals were formed when TMH was treated with phthalic anhydride. We propose the following set of reactions to account for the formation of both  $\text{TMH}^{\dot{+}}$  and  $\text{TMT}^{\dot{+}}$ .



In the case just discussed R - X was phthalic anhydride and hence the intermediate acylated tetrazene I was a zwitterion. We propose that I decomposes homolytically to the amidium radical ion II, nitrogen and the dimethylamino radical. The latter radical dimerizes to form tetramethylhydrazine (TMH). The radical ion II, on the other hand, undergoes an electron transfer reaction with the tetrazene to form TMT<sup>+</sup> and then with the hydrazine to form TMH<sup>+</sup>. Initially only TMT<sup>+</sup> is observed by esr because the concentration of TMH is very low but as it starts to grow the TMH<sup>+</sup> radical begins to appear.

This mechanism differs from the one proposed by Nelsen (2). His mechanism however, was based largely on the study of the reaction of TMT with dichloromaleic anhydride. We repeated some of his experiments and concur with his results.

It was of interest to carry out the reaction of TMT with methylsulfate. In our previous study (1) the intermediate trimethylaminium radical ion (II, R = CH<sub>3</sub>) oxidized the iodide counter ion to free iodine. The use of methylsulfate as the methylating agent should preclude such a reaction because the methylsulfate counter ion should be inert to further oxidation. Indeed, when degassed chloroform solutions of methylsulfate and TMT were mixed, an esr spectrum was produced which showed the presence of both TMT<sup>+</sup> and TMH<sup>+</sup>. We were never able to obtain a spectrum in which only TMT<sup>+</sup> was present, even when TMT was in large excess. This suggests that TMH is more easily oxidized than TMT and/or TMH<sup>+</sup> is more stable than TMT<sup>+</sup>. No radicals were produced when TMH was mixed with methylsulfate under identical conditions.

The same reaction scheme suggested for the phthalic anhydride reaction is proposed to account for the methylsulfate reaction.

Strong support for the feasibility of electron transfer from TMT and TMH to the trimethylaminium radical ion was provided by the consideration of the heats of formation of the species involved. Heat of combustion data and ionization potential for trimethylamine were available from the literature as was the heat of formation of TMT and  $\text{TMH}^\dagger$ . The ionization potential of TMT was determined using the Varian ion cyclotron resonance spectrometer (this instrument is particularly convenient for use in such measurements). The standard in the determination of the ionization potential of TMT was TMH, whose ionization potential is known (5). The semi-log method was used to obtain the value of the ionization potential of TMT. These data are summarized in Table I. The Table also shows the heats of formation of the radical ions calculated from the ionization potentials and the heats of formation of the neutrals by means of the following relationship:

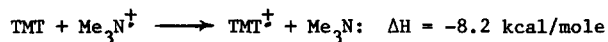
$$\Delta H_f^{\circ}(\text{A}) = \Delta H_f^{\circ}(\text{A}^\dagger) - \text{I.P.}$$

Table I

Compound	I.P.	Ref.	$\Delta H_f^{\circ}$ (Neutral)	Ref.	$\Delta H_f^{\circ}$ (Ion)
TMH	7.75 ev	5	-16.6 kcal/mole	5	196 kcal/mole
$(\text{CH}_3)_3\text{N}$	8.32 ev	6	- 5.81 kcal/mole	7	186.4 kcal/mole
TMT	7.96 ev		55 kcal/mole	8	239 kcal/mole

a) An estimate made by Dibeler, Franklin and Reese (5) using Franklin's method of group equivalents (Ind. Eng. Chem., 41, 1070 (1949)).

By substituting the appropriate heats of formation into the electron exchange reactions it is found that the electron transfer from TMT to the trimethylamine radical ion is exothermic by approximately 8.2 kcal/mole and the electron transfer from TMH to the trimethylamine radical ion is exothermic by about 12.8 kcal/mole.



In conclusion, our data support the generalized mechanism as outlined above. Nelsen's (2) mechanism, however, seems to be best for the reaction of dichloromaleic anhydride with TMT. It has been shown (9) that protonated TMT decomposes by heterolytic cleavage with no radicals being

formed in the process. Thus it appears that at least three possible mechanisms may operate depending on the nature of reagent used to coordinate one of the terminal nitrogens of TMT.

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