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DECOMPOSITION OF TETRAMETHYL-2-TETRAZENE:
REACTIVITY OF THE DIMETHYLAMINO RADICAL

by
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A DISSERTATION

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In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy
Department of Chemistry

Under the Supervision of Professor C. J. Michejda

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TITLE

Decomposition of Tetramethyl-2-Tetrazene:

Reactivity of the Dimethylamino Radical

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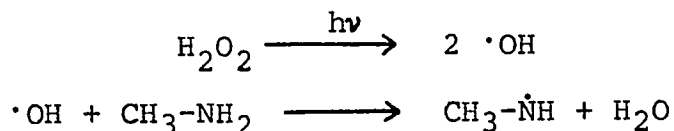
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INTRODUCTION

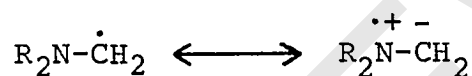
Dialkylamino radicals and their reactions have not been well-characterized. Hadley and Volman¹ have reported an esr study of methylamino and dimethylamino radicals produced from the 1849 Å irradiation of the corresponding amines at 77°K. Homolytic N-H bond cleavage was postulated as the primary photochemical process.



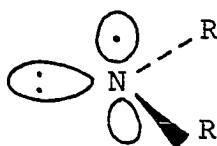
The esr spectra, although poorly resolved, could be simulated if the coupling constants to nitrogen and all hydrogens were taken as 32 gauss. That the observed radicals were amino rather than alkyl was substantiated by the irradiation of deuterated compounds, e. g., the amines and the N-deuterated amines gave the same spectra. These spectra could also be produced from the amine and hydroxyl radicals.



The above reaction would not be predicted since Bridger and Russell² have shown that amino groups cause a 31- to 40-fold increase in the rate of hydrogen abstraction from the α -carbon relative to the alkane. Hydrogen abstraction from aromatic amino nitrogen is only 1.3 times faster than abstraction from the corresponding hydrocarbon. Polar resonance contributions are thought to stabilize α -amino-alkyl radicals.



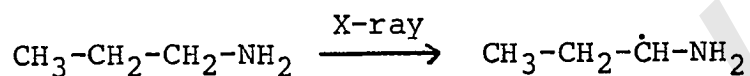
Danen and Kensler⁶⁵ have recently observed esr spectra of some simple dialkylamino radicals. The radicals were produced by irradiating ten percent solutions of the corresponding tetrazenes within the esr cavity. The coupling constants to nitrogen were all about 14 gauss--less than one-half the value reported by Hadley and Volman.¹ The magnitude of these nitrogen coupling constants suggests that the unpaired electron resides in an orbital which is essentially 2p since the interaction of the nucleus with an electron in a p orbital is smaller than that with an electron in an s orbital. Intermediate neglect of differential



overlap calculations on the dimethylamino radical predict a

nitrogen coupling constant of 14.80 gauss; the observed coupling constant was 14.78 gauss.

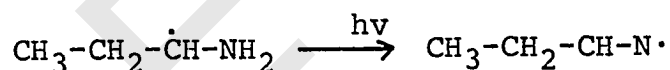
When a series of alkylamines were subjected to X-irradiation,⁵⁵ the α -aminoalkyl radicals were produced according to the following equation.



The esr spectra gave the following coupling constants:

$a_{\text{H}\alpha} = 14.6$, $a_{\text{H}\beta} = 16.4$, $a_{\text{HN}} = 4.8$, and $a_{\text{N}} = 4.8$ gauss.

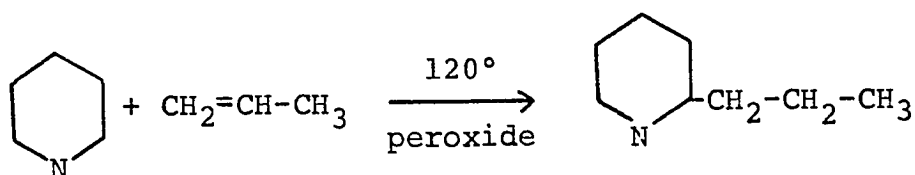
About one-third of the electron density was delocalized to nitrogen. Subsequent photolysis⁵⁶ of the α -aminoalkyl radical, which had a half-life of several hours in an adamantane matrix, gave the corresponding alkylimino radical,



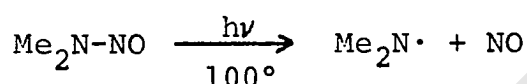
which had the following coupling constants: $a_{\text{N}} = 9.5$,

$a_{\text{H}\alpha} = 78.5$, and $a_{\text{H}\beta} = 2.77$ gauss. The deuterated amine gave an identical esr spectrum for the alkylimino radical.

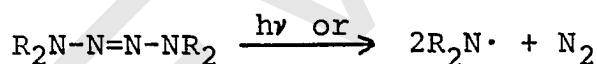
The di-*t*-butyl peroxide initiated addition of amines to terminal olefins⁵⁷ gave the adduct which resulted from attack of the α -aminoalkyl radical on the olefin.



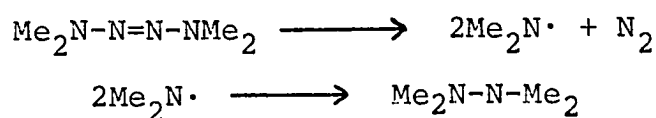
Dialkylamino radicals have been postulated as intermediates in the photolysis of dialkyl nitrosamines.⁵⁸ Thus, the photolysis of dimethylnitrosamine gave almost exclusively nitric oxide and dimethylamine as volatile products. The formation of the amine will be discussed later.



The most common and straightforward method of generating dialkyl amino radicals is the thermal or photochemical decomposition of the corresponding tetraalkyl-2-tetrazene since tetrazenes are easily synthesized and there are no other reactive products produced during the



decomposition. The dimethylamino radical has apparently been trapped as a violet-colored material at -196° by passing dilute vapors of tetramethyl-2-tetrazene (TMT) over a tungsten filament at 1300° then quickly condensing the products at liquid nitrogen temperature.³ When the violet material was warmed to -160° it irreversibly changed to a white solid, identified as tetramethylhydrazine. The

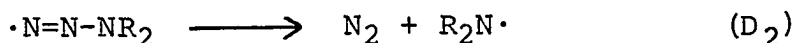
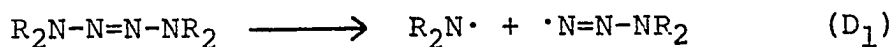


same results were obtained when TMT vapors were photolyzed and then quickly cooled.

Gowenlock and co-workers⁴ have made a thorough kinetic study of the gas-phase thermal decomposition of TMT and tetraethyl-2-tetrazene (TET) in a flow system. The first-order rate constants were independent of carrier gas and presence of nitric oxide although the corresponding nitrosamines were formed confirming the presence of the radical.



The fact that the rate constants were insensitive to the presence of nitric oxide demonstrated that the reaction was irreversible. The rapid formation of the nitrosamine would have increased the observed rate if the reaction were reversible. The kinetic results gave the following activation parameters: $E_a = 36.1 \pm 1.0$ Kcal and $\log A = 14.4 \pm 0.5$ (193-266°) for TMT; $E_a = 33.0 \pm 2.0$ Kcal and $\log A = 13.7 \pm 0.9$ (198-235°) for TET. It was suggested that azoalkanes and tetrazenes decompose by a common thermochemical mode, viz., in three fragments, since the sum of the bond dissociation energies representing the one-step process is lower than that for a single bond cleavage; i.e., $D_1 + D_2 < D_1$.



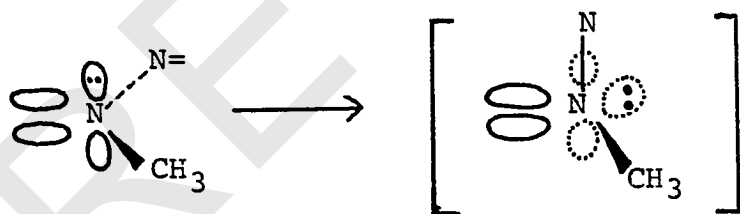
There is some evidence for a two-fragment cleavage of TMT at low temperatures. Snowden and Davidson⁶⁶ observed the principal TMT absorption at $273^\circ\text{m}\mu$ in a hydrocarbon glass at 77°K . After the sample was irradiated, this absorption band disappeared. Upon warming the band reappeared at twenty percent of its original intensity. They postulated that some of the radicals produced by photolysis recombined as the temperature increased. The author has found



that during the thermolysis of TMT some minor product(s), which absorbed at the same wavelength as TMT, were formed. This fact rendered uv methods unsuitable for kinetics and could account for the above result obtained by Snowden.

Several workers have examined the static system decomposition of tetrazenes. Watson and Waring⁵ report $E_a = 31.9 \pm 3.0$ Kcal and $\log A = 11.4 \pm 1.65$ (125.5 – 147.5°) for TMT. Also Good and Thynne⁶ report $E_a = 34.6$ Kcal and $\log A = 13.83$ (127 – 175°) for TMT. The latter values, obtained over a larger temperature range, are probably more trustworthy and are also closer to those of Gowenlock.⁴

Until recently kinetic studies of the solution decomposition of tetrazenes have been scant. In a study of the thermal decomposition of 1,4-dimethyl-1,4-diphenyl-2-tetrazene and seven symmetrically substituted analogs Nelsen and Heath⁷ have shown that the rate of decomposition in cumene (110 and 125°) has a moderately large substituent effect with $\rho = -0.93$, i.e., the decomposition rates are faster with electron releasing substituents. From the activation parameters it can be seen that it is the ΔS^\ddagger term rather than ΔH^\ddagger which controls the rate of decomposition. This is interpreted as reflecting the relative difficulty in attaining the conformation for maximum stability of the ensuing anilino radical. Thus for *p*-methoxy and *p*-carbethoxy the ΔH^\ddagger values are 33 and 31 Kcal respectively but the

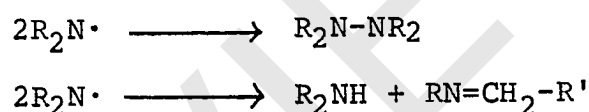


ΔS^\ddagger values are 15 and -3 eu, respectively.

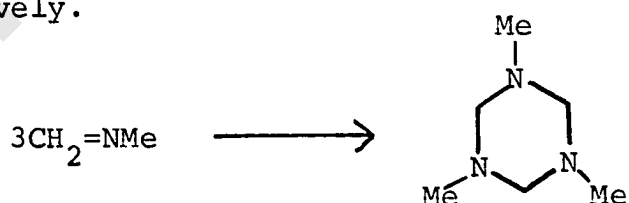
Dialkylamino radicals can be produced by the pyrolysis of tetraalkylhydrazines at higher temperatures. Westphal and Eucken⁸ reported E_a values of 40- and 27 Kcal for the gas phase thermal decomposition of tetrapropyl- and tetraethylhydrazine respectively at 230-250°. The E_a value of 27 Kcal/mole for tetrapropyl-hydrazine seems somewhat low. Clearly, these values do not reflect the relative

stabilities of the radicals formed in the decomposition. These E_a values can be compared to the E_a value of 30 ± 1.5 Kcal for the decomposition of tetraphenylhydrazine in *o*-dichlorobenzene at 75-100°. ⁹ The high temperature necessary for reaction in the case of the alkylhydrazines make them undesirable as amino radical precursors.

In the absence of other reactive species dialkyl-amino radicals preferentially undergo recombination and disproportionation. Thus, pyrolysis of TMT in a flow

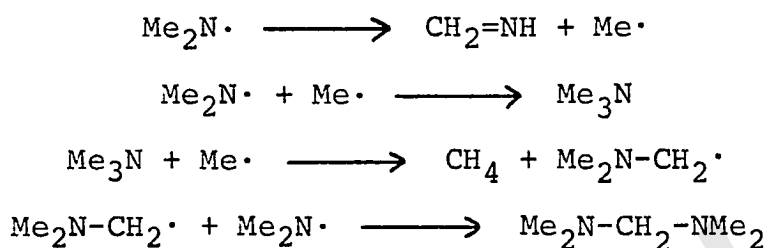


system at 300° yields 41% tetramethylhydrazine (TMH) and 44% dimethylamine; and photolysis of the liquid gives 32% TMH and 45% dimethylamine. ¹⁰ The imine is not isolated but some of it trimerizes, e.g., the pyrolysis and photolysis experiments mentioned above produced 3.6- and 4.5% of the trimer respectively.

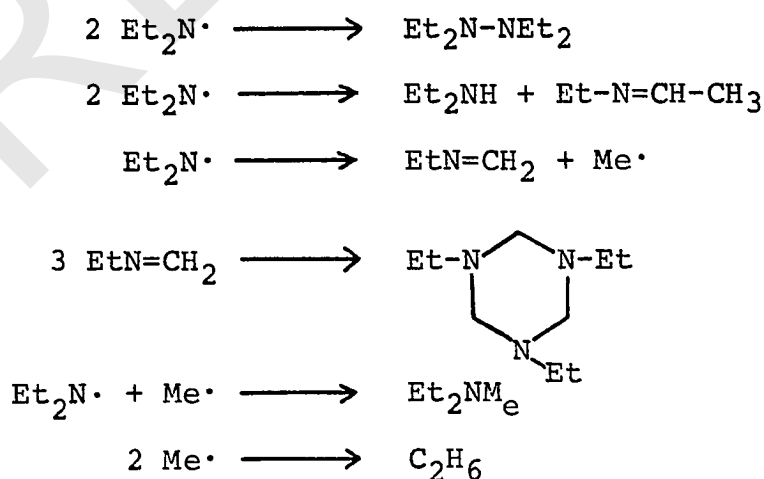


The pyrolysis of TMT above 255° resulted in small amounts of trimethylamine and tetramethylmethylenediamine as well as tetramethylhydrazine. ⁴ The following pathway involving the participation of methyl radical has been

suggested⁵⁹ to account for these products.

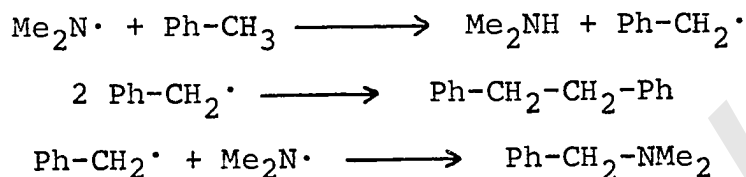


When tetraethyl-2-tetrazene was pyrolyzed at 254° in a flow system,⁴ the product mixture was more complex than that obtained from TMT. The following product ratios (based on tetramethylhydrazine) were obtained. Tetramethylhydrazine, 1; diethylamine, 3.8; ethylethylideneamine, 2.5; diethylmethylaniline, 1.8; ethane, 0.3; and 1,3,5-triethylhexahydro-s-triazine, trace. Again a mechanism involving the methyl radical was postulated.



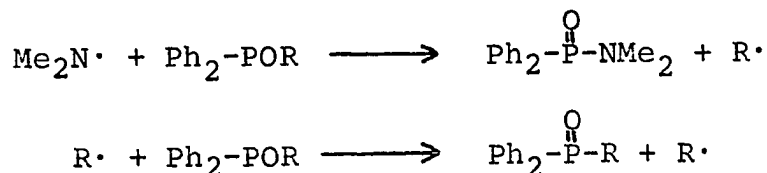
Dialkylamino radicals have been found to be weak

dehydrogenating agents, e.g., the photolysis of 4M TMT in boiling toluene¹¹ results in a 60% yield of dimethylamine but only 28% bibenzyl and 3% N,N-dimethylbenzylamine.



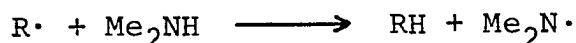
Thus, only about half of the dimethylamine results from hydrogen abstraction by the dimethylamino radical from toluene. The remaining dimethylamine probably results from the hydrogen abstraction from TMT. The above work was expanded by Johnston, Williams, and Williams¹² to include a series of arylalkyl amino radicals. About one-fourth to one-tenth of the amine was produced by hydrogen abstraction from cumene. No abstraction was observed with diphenylamino radical.

R. S. Davidson¹³ has reported the oxidation of methyl- and ethyldiphenylphosphinite by dimethylamino radical derived from the photolysis of TMT in benzene to give 40.5 and 55% respectively of N,N-dimethyldiphenyl-



phosphinic amide. The corresponding alkyldiphenylphosphine

oxides are also formed. The latter reaction can be suppressed by the addition of dimethylamine to the reaction mixture and is taken as evidence for the following step in the reaction mechanism:



Dimethylamino radicals from the photolysis of TMT will displace an alkyl radical from a boron center¹⁴ resulting in the corresponding aminoborane. This process is also



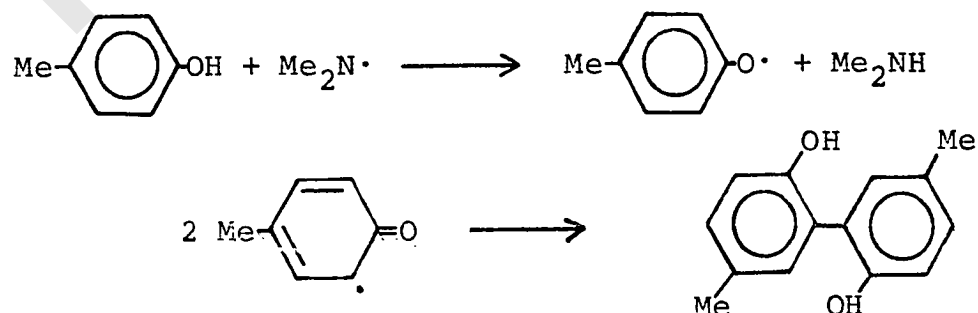
involved in the reaction of N-chloramines with alkylboranes. The reaction is a radical chain process; the propagation step is postulated to be chlorine atom abstraction from the chloramine by the alkyl radical.



Erusalimsky and co-workers¹⁵ have shown that 0.324 mole% 1,4-dimethyl-1,4-diphenyl-2-tetrazene effectively initiates the polymerization of styrene at 85° and also noted the complete absence of dimethylamine when 0.8 mole% TMT was decomposed in α-methylstyrene at 145°. These results were taken as evidence for the addition of

amino radicals to olefins. Cowley and Waters¹⁶ also decomposed TMT in α -methylstyrene and claimed 42-45% of the dimethylamino radicals added to the olefin. However, Neale and co-workers¹⁷ have pointed out that the products were not characterized and could have been products of allylic abstraction followed by recombination. Cowley and Waters¹⁶ also decomposed 5% TMT in 1-nonene yielding 72% dimethylamine and a hydrocarbon mixture which contains both terminal and non-terminal double bonds. The olefin isomerization was thought to result from allylic hydrogen abstraction by the dimethylamino radical.

That dialkylamino radicals do not undergo addition to aromatic systems has been demonstrated by Jacobson, Johnston and Williams.⁶⁰ These workers decomposed TMT in a variety of aromatic substrates including naphthalene, phenanthrene, and *p*-cresol; but no addition products could be isolated. The isolation of small amounts of 2,2'-dihydroxy-5,5'-biphenyl from the decomposition of TMT in *p*-cresol was noted and explained as hydrogen abstraction by the dimethylamino radical from *p*-cresol.



EXPERIMENTAL

All melting points and boiling points are uncorrected. Ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer; the ir spectra were obtained with Perkin-Elmer Models 237 and 621 instruments. The nmr spectra were recorded on Varian A-60 and A-60-D spectrometers; the glpc analyses were performed on Varian Aerograph Models A90-P3 and 1520 gas chromatographs. Mass spectra were determined on a Perkin-Elmer Hitachi RMU-6D spectrometer; esr spectra were recorded on a JEOLCO 3BSX spectrometer employing 100 KHz field modulation.

Benzene (Mallinckrodt, analytical reagent), toluene (Baker, reagent), and cyclohexane (Matheson) were heated at reflux over sodium ribbon and distilled.

Cumene (Eastman) was washed with conc. sulfuric acid, 10% sodium bicarbonate, and then water. After drying (MgSO_4) it was distilled from calcium hydride and the distillate was stored over sodium.

Nitrobenzene (Baker) was passed through a column of alumina, recrystallized twice from 95% ethanol, and after most of the solvent was removed in vacuo the residue was passed over another column of alumina to remove traces of