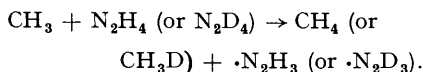


The Attack of Methyl Radicals on 1,2-Dimethylhydrazine

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HYDROGEN abstraction by methyl radical from hydrazine¹ (or tetradeuterohydrazine²) is a fast reaction; with k equal to $10^{8.41}$ cm.³ mole⁻¹ sec.⁻¹ at 150° c:

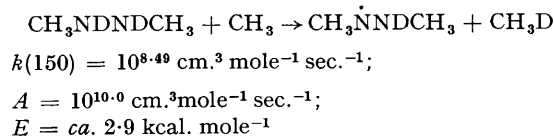
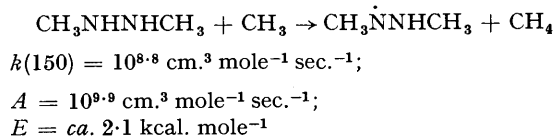


The activation energy E is 5.0 kcal. mole⁻¹ ($E = 6.4$ for N_2D_4) and the pre-exponential factor A is $10^{11.0}$ cm.³ sec.⁻¹ mole⁻¹ ($A = 10^{10.9}$ for N_2D_4). Since experiments with deuterium-labelled amines (methylamine,³ ethylamine,⁴ and dimethylamine⁵) have shown that attack on N-H (or N-D) bonds is considerably faster in these alkyl derivatives of ammonia than in ammonia itself, it is of interest to see whether the high reactivity of the hydrogen atoms in hydrazine is enhanced still further by methylation. Accordingly we have now studied the abstraction of hydrogen and deuterium from symmetrical dimethylhydrazine (SDMH) and symmetrical dimethyldideuterohydrazine (SDMH-d₂) over the temperature range 79–162° c. Azomethane has been used as the methyl-radical source and velocity constants and Arrhenius parameters determined relative to Shepp's values⁶ for the combination of methyl radicals.

Several facts stand out from the study made here. First, SDMH is markedly more reactive than hydrazine itself. At 150° there is a six-fold enhancement in reactivity (per N-H bond). This is in accord with the relationship between ammonia

and the amines where the introduction of one methyl group increased¹ the reactivity (per N-H bond) about 11 times. Secondly, the origin of the enhancement lies in the reduced activation energy—from 5.0 kcal. mole⁻¹ for hydrazine to 2.1 kcal. mole⁻¹ for SDMH—which resembles the spectacular fall from 9.8 kcal. mole⁻¹ for NH_3 to 5.7 kcal. mole⁻¹ for CH_3NH_2 . There is a simultaneous drop in A -factor in both cases—from 10^{11} cm.³ mole⁻¹ sec.⁻¹ in N_2H_4 to $10^{9.9}$ in SDMH and this somewhat offsets the effect of the fall in E . Thirdly, the experiments with SDMH-d₂ establish the superior reactivity of the amine sites: four out of every five H-atoms abstracted at 150° come from the amine groups; this corresponds to a relative reactivity (per H-atom available) of about 12.

The values found for the velocity constants (at 150°) and Arrhenius parameters for attack on the NH and CH₃ groups are as follows:



¹ P. Gray and J. C. J. Thynne, *Trans. Faraday Soc.*, 1964, **60**, 1047.

² P. Gray and A. Jones, *Chem. Comm.*, 1965, 360.

³ P. Gray and J. C. J. Thynne, *Trans. Faraday Soc.*, 1963, **59**, 2275.

⁴ P. Gray and A. Jones, *Trans. Faraday Soc.*, 1965, in the press.

⁵ P. Gray, A. Jones, and J. C. J. Thynne, *Trans. Faraday Soc.*, 1965, **61**, 474.

⁶ A. Shepp, *J. Chem. Phys.*, 1956, **24**, 939.

$\text{CH}_3\text{NDNDCH}_3 + \text{CH}_3 \rightarrow \cdot\text{CH}_2\text{NDNDCH}_3 + \text{CH}_4$
 $k(150) = \text{ca. } 10^{8.2} \text{ cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1};$
 $A = \text{ca. } 10^{11.6} \text{ cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1};$
 $E = \text{ca. } 6.6 \text{ kcal. mole}^{-1}$

Thus, isotopic substitution produces an effect on reactivity in the normal direction: H is abstracted from SDMH twice as rapidly as D from SDMH-d₂. This is a consequence of the lower activation energy ($E_D - E_H = \text{ca. } 0.8 \text{ kcal. mole}^{-1}$), since the *A*-factors are identical.

The only other work on substituted hydrazines concerns unsymmetrical dimethylhydrazine (UDMH). Gray and Thynne,⁷ describing work on the unlabelled compound, reported an overall reactivity not unlike that of hydrazine itself (see above). At 150°, $k_{\text{udmh}}/\text{cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1}$ is $10^{8.32}$; $A_{\text{dmh}}/\text{cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1}$ is $10^{11.34}$, and $E_{\text{udmh}}/\text{kcal.}$

mole^{-1} is 5.8. The similarity of UDMH to hydrazine is to be expected if attack is principally at the amine group, since the methyl groups in UDMH are not adjacent to the H-atoms abstracted and an activating influence identical with that produced on passing from NH₃ to MeNH₂ or from NH₂·NH₂ to MeNH·NH·Me is impossible. This interpretation is confirmed by recent work⁸ on monomethylhydrazine (MMH). On the basis above, MMH would be expected not to behave as a half-way stage between hydrazine and UDMH, but to be very similar to SDMH. In accord with this, Herod⁸ finds for (overall) methyl radical attack on MMH that $E_{\text{mmh}}/\text{kcal. mole}^{-1}$ is ca. 2, $A_{\text{mmh}}/\text{cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1}$ is about $10^{9.6}$ and, at 150°, k_{mmh} is $10^{8.81} \text{ cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1}$

(Received, November 3rd, 1965; Com. 696.)

⁷ P. Gray and J. C. J. Thynne, "Tenth Symposium (International) on Combustion," Combustion Institute, New York, 1965, p. 435.

⁸ A. Herod, Leeds, 1965, personal communication.