The Attack of Methyl Radicals on 1,2-Dimethylhydrazine

By PETER GRAY and A. JONES

(*Physical Chemistry Department, The University, Leeds,* 2)

HYDROGEN abstraction by methyl radical from hydrazine[1] (or tetradeuterohydrazine[2]) is a fast reaction; with k equal to $10^{8\cdot41}$ cm.^{3} mole^{-1} sec.$^{-1}$ at 150° C:

$$CH_3 + N_2H_4 \text{ (or } N_2D_4) \rightarrow CH_4 \text{ (or } CH_3D) + \cdot N_2H_3 \text{ (or } \cdot N_2D_3).$$

The activation energy E is 5·0 kcal. mole^{-1} (E = 6·4 for N_2D_4) and the pre-exponential factor A is $10^{11\cdot0}$ cm.^{3} sec.$^{-1}$ mole^{-1} ($A = 10^{10\cdot9}$ for N_2D_4). Since experiments with deuterium-labelled amines (methylamine,[3] ethylamine,[4] and dimethylamine[5]) 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-d_2) 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 values[6] 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 increased[1] 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 $10^{9\cdot9}$ in SDMH and this somewhat offsets the effect of the fall in E. Thirdly, the experiments with SDMH-d_2 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 CH_3 groups are as follows:

$$CH_3NHNHCH_3 + CH_3 \rightarrow CH_3\dot{N}NHCH_3 + CH_4$$

$k(150) = 10^{8\cdot8}$ cm.^{3} mole^{-1} sec.$^{-1}$;

$A = 10^{9\cdot9}$ cm.^{3} mole^{-1} sec.$^{-1}$;
E = *ca.* 2·1 kcal. mole^{-1}

$$CH_3NDNDCH_3 + CH_3 \rightarrow CH_3\dot{N}NDCH_3 + CH_3D$$

$k(150) = 10^{8\cdot49}$ cm.^{3} mole^{-1} sec.$^{-1}$;

$A = 10^{10\cdot0}$ cm.^{3}mole^{-1} sec.$^{-1}$;
E = *ca.* 2·9 kcal. mole^{-1}

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[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.

$CH_3NDNDCH_3 + CH_3 \rightarrow \cdot CH_2NDNDCH_3 + CH_4$
$k(150) = ca.\ 10^{8\cdot2}$ cm.^{3} mole^{-1} sec.$^{-1}$;
$A = ca.\ 10^{11\cdot6}$ cm.^{3} mole^{-1} sec.$^{-1}$;
$E = ca.$ 6·6 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-d_2. This is a consequence of the lower activation energy ($E_D - E_H = ca.$ 0·8 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_{udmh}/cm^3 mole^{-1} sec.$^{-1}$ is $10^{8\cdot32}$; A_{dmh}/cm.^{3} mole^{-1} sec.$^{-1}$ is $10^{11\cdot34}$, and E_{udmh}/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 NH_3 to $MeNH_2$ or from $NH_2{\cdot}NH_2$ to MeNH·NH·Me is impossible. This interpretation is confirmed by recent work[8] 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, Herod[8] finds for (overall) methyl radical attack on MMH that E_{mmh}/kcal. mole^{-1} is *ca.* 2, A_{mmh}/cm.^{3} mole^{-1} sec.$^{-1}$ is about $10^{9\cdot6}$ and, at 150°, k_{mmh} is $10^{8\cdot81}$ cm.^{3} mole^{-1} sec.$^{-1}$

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[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.