Branching Ratios and Vibrational Distributions in Water-Forming Reactions of OH and OD Radicals with Methyl Amines

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Supporting Information

1. Bond dissociation energies (review and discussion).

The first data for D_{298}^{0}(C-H) in trimethyl amine (TMA), dimethyl amine (DMA) and mono-methyl amine (MMA), 83.8, 86.9 and 93.9 kcal mol^{-1}, respectively, were from the appearance potential measurements27. In 1985 Grela and Colussi28 used the Arrhenius parameters from pyrolysis of N,N-dimethyl 2-phenylethylamine and 2-phenyl ethylamine to obtain D_{298}^{0}(C-H) = 85.3 kcal mol^{-1} in TMA and 87.9 kcal mol^{-1} in MMA. To calculate the Δ_{f}H_{298}^{0} of the CH_{2}N(CH_{3})_{3} and CH_{2}NH_{2} radicals they used Δ_{f}H_{298}^{0} (benzyl) = 47 kcal mol^{-1}. If the currently accepted Δ_{f}H_{298}^{0} (benzyl) = 49.6 kcal mol^{-1} is used29, their measurements would become 82.7 (TMA) and 85.3 (MMA) kcal mol^{-1}. In 1997 Wayner et al.24 reported D_{298}^{0}(C-H) = 88.9 and 92.7 kcal mol^{-1} for TMA and MMA, respectively, from photo-acoustic calorimetric measurements. Both values were higher than those from Grela and Colussi28, moreover, based on G2(MP2) calculations, the authors claimed that the influence of the CH_{3} group was not as important as previously thought, and recommended D_{298}^{0}(C-H) of: 92.4 (TMA), 92.2(DMA) and 92.7(MMA). More recent high-level MP2/aug-cc-pVTZ calculation gave nearly equal BDEs for all three amines (D_{0}(C-H) = 91.5 kcal/mol)12. Another experimental value for TMA, D_{298}^{0}(C-H) = 91 kcal mol^{-1}, was obtained by correction of photo-acoustic calorimetric measurement for solvent effect30. This latter was chosen for our calculations as the most recent experimental value which agrees with the high-level theoretical result. The same value was accepted for the D_{298}^{0}(C-H) in DMA, and 3 kcal mol^{-1} higher value was taken for the D_{298}^{0}(C-H) in MMA, taking into account the difference between the D_{298}^{0}(C-H) in TMA and MMA obtained in Refs. 24 and 28 and the “spectroscopic” calculation by Gribov et al.31. The highest HF(v,J) levels observed from the F + CH_{3}ND_{2} reaction32 suggested that D_{298}^{0}(H-CH_{2}ND_{2}) has a value similar to the 93.9 kcal mol^{-1} of Griller and Lossing27.

The experimental D(N-H) values are based mainly upon very low pressure pyrolysis studies33 of benzyllamine, N-methyl benzyllamine and N,N-dimethylbenzyllamine. Based upon the enthalpy of formation of benzyll and the measured activation energies for dissociation (plus some adjustments), the values obtained were D_{298}^{0}(H-NH_{2}) = 110±1.5, D_{298}^{0}(H-N(CH_{3})H) = 103±2.5 and D_{298}^{0}(H-N(CH_{3})_{2}) = 95±2.5 kcal mol^{-1}. After correction for Δ_{f}H_{298}^{0}(benzyl), these bond dissociation energies become 105, 98
and 90 kcal mol\(^{-1}\) for NH\(_3\), MMA and DMA, respectively. McMillen and Golden\(^{34}\) recommended 2 kcal mol\(^{-1}\) higher values, 107, 100 and 92 kcal mol\(^{-1}\), which better agreed with the existing measurements for NH\(_3\) and the appearance potential measurement of Sharma and Franklin\(^{35}\) for MMA. The 100 kcal mol\(^{-1}\) value agrees with the translational energy measurement \((D_0(H-N(CH_3)H) = 98.8 \pm 0.6\) kcal mol\(^{-1}\) \((D_{298}(H-N(CH_3)_2) = 100.2\) kcal mol\(^{-1}\))\) of Reed et al.\(^{36}\), which also agrees with the calculation of Onel et al.\(^{12}\). The choice for DMA was \(D_0(H-N(CH_3)_2) = 91.3\) kcal mol\(^{-1}\), which is 8 kcal mol\(^{-1}\) lower than that of MMA as in Ref. 33 and 1.7 kcal mol\(^{-1}\) higher than \(D_0(CH_3NHCH_2-H)\) as obtained by high-level calculation\(^{12}\). A summary of the bond dissociation energies of the amines is given in Table 1 of the manuscript. When only \(D_{298}(H-R)\) values were available, conversion to 0 K was made with the help of Kirchoff's equation, which gives \(D_0(H-R) = D_{298}(H-R) - 1.4\) kcal mol\(^{-1}\) from the assumption that the heat capacities of the product radicals are identical with those of their parent molecules.

2. Surprisal plots.

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**Figure S1.** Surprisal plots for D\(_2\)O from OD reactions with (CD\(_3\))\(_2\)NH (a) and CD\(_3\)NH\(_2\) (b). (a) The point corresponding to \(P_{1,3}(4)\) was not included in the linear fitting.
Figure S2. Surprisal plots for HOD from OH reactions with (CD$_3$)$_2$NH (a) and CD$_3$NH$_2$ (b).


The only product observed from secondary reactions was HNO in the TMA system. The intensity of HNO emission increased with NO$_2$ concentration and at [NO$_2$] ≥ 2 × 10$^{14}$ molecules cm$^{-3}$ it even exceeded the peak intensity from water, confirming reaction (2). The 2$\nu_1$-$\nu_1$ hot band was also identified by its deep minima at 2452 cm$^{-1}$, indicating excitation of two N-H stretching quanta in reaction (2). We suggest that HNO is formed via the reaction between (CH$_3$)$_2$NCH$_2$ with NO$_2$ through the six-membered complex shown in Figure S3. The complex then decomposes to HNO, CH$_2$O and CH$_3$N=CH$_2$:

\[
\text{NO}_2 + (\text{CH}_3\text{)}_2\text{NCH}_2 \rightarrow (\text{CH}_3\text{)}_2\text{NCH}_2\text{(ONO)} \rightarrow \text{CH}_3\text{N=CH}_2 + \text{CH}_2\text{O} + \text{HNO},
\]

\[\Delta H_r \approx -26 \text{ kcal mol}^{-1}\]

![Figure S3](image)

Figure S3. Intermediate complex suggested for the (CH$_3$)$_2$NCH$_2$ + NO$_2$ reaction.

The reaction enthalpy was obtained from $\Delta H_f((\text{CH}_3\text{)}_2\text{NCH}_2) = 27$ kcal mol$^{-1}$\textsuperscript{27,28} and $\Delta H_f(\text{CH}_3\text{N=CH}_2) = 11$ kcal mol$^{-1}$\textsuperscript{S1}, which is sufficient to excite two H-N stretching vibrations in HNO. The products from
OH + TMA with excess NO$_2$ were examined by Pitts et al.$^{S2}$ in a chamber study and formaldehyde was observed as a major product, which supports the mechanism suggested above.

Apparently, two methyl groups are required for this mechanism because no HNO emission was observed in the DMA system, even though the reaction would be exothermic by approximately 24 kcal mol$^{-1}$ (this enthalpy was estimated using $\Delta H_f$(CH$_3$NHCH$_2$) = 30 kcal mol$^{-1}$ and $\Delta H_f$(HN=CH$_2$) = 17 kcal mol$^{-1}$). We may assume that in this case the reaction proceeds by hydrogen abstraction from the N-atom, producing CH$_3$N=CH$_2$ and HONO, which is energetically favorable ($\Delta H_r$ = -46 kcal mol$^{-1}$). Similar mechanism can take place in the MMA system, where CH$_2$NH$_2$ + NO$_2$ yields HN=CH$_2$ and HONO.

Reactions of NO$_2$ with (CH$_3$)$_2$N and CH$_3$NH radicals from the channels (a) proceed via formation of (CH$_3$)$_2$N-NO$_2$ and CH$_3$NH-NO$_2$ adducts; at atmospheric pressure they are mostly stabilized giving nitramines, R$_1$R$_2$N-NO$_2$, with minor amounts of HONO ($\approx$20%) as reported in chamber studies.$^{16,42}$


4. Simulation of the IR spectra from the reactions of hydroxyl radicals with amines.

The least squares method requires a minimization of the value of the estimator $Q = \sum (I_{\text{exper}} - I_{\text{model}})^2$ by fitting the linear coefficients for basic emission bands. Every band is considered as a vector with $N$ elements corresponding to a number of measurements in a spectrum. For a unity resolution, $N = 700$ in one 3200-3900 cm$^{-1}$ spectrum. The estimator can be presented as $Q = \sum (s_i - \sum P_j b_{ij})^2$, where $s_i$ is the $i$-th measurement in the spectrum, $b_{ij}$ is the $i$-th element of the $j$-th basic band, and $P_j$ are the populations of the corresponding vibrational states. According to a least-squares formalism$^{S3}$, the standard deviation of the population can be estimated as $\sigma(P_j) = [(G)^{-1} Q/N]^{1/2}$, where $(G)^{-1} _{ii}$ is the diagonal element of the inverse Gram’s matrix of the basic vectors $b_i = (b_{i1}, \ldots, b_{iN})$. For example, the spectrum in Figure S4 was obtained with 12 bands (vectors) included in the simulation, giving the residual $Q = 4.36 \times 10^5$. Calculated values of $(G)^{-1} _{ii}$ for H$_2$O bands vary from 2.7 to $4.4 \times 10^6$, giving the largest magnitude of $\sigma(P_j)$ corresponding to about 5%.

**Figure S4.** H$_2$O spectrum from OH + (CH$_3$)$_3$N. Q = 4.36 × 10$^5$.

**Figure S5.** HOD spectrum from OD + (CH$_3$)$_3$N. Q = 1.41 × 10$^5$.

**Figure S6.** HO-D spectrum from OD + (CH$_3$)$_3$N. Q = 1.39 × 10$^5$. 
Figure S7. HO-D spectrum from OH + (CH$_3$)$_2$NH. Q=1.25 × 10$^5$.

Figure S8. H$_2$O spectrum from OH + (CH$_3$)$_2$NH. Q=4.55 × 10$^5$.

Figure S9. HOD spectrum from OD + (CH$_3$)$_2$NH. Q=1.21 × 10$^5$. 
Figure S10. H$_2$O spectrum from OH + CH$_3$NH$_2$. $Q = 4.47 \times 10^5$.

Figure S11. HOD spectrum from OH + CH$_3$NH$_2$. $Q = 1.41 \times 10^5$.

Figure S12. HOD spectrum from OD + (CD$_3$)$_2$NH. $Q = 7.03 \times 10^4$. 
Figure S13. HOD spectrum from OD + CD$_3$NH$_2$. Q=1.33 × 10$^5$.

Figure S14. D$_2$O spectrum from OD + (CD$_3$)$_2$NH. Q=2.42 × 10$^5$.

Figure S15. D$_2$O spectrum from OD + CD$_3$NH$_2$. Q=4.02 × 10$^5$. 
Figure S16. HO-D spectrum from OH + (CD$_3$)$_2$NH. Q=5.59 $\times$ 10$^5$.

Figure S17. HO-D spectrum from OH + CD$_3$NH$_2$. Q=1.04 $\times$ 10$^6$. 