



Branching Ratios of Aliphatic Amines + OH Gas-Phase Reactions: A Variational Transition-State Theory Study

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Abstract: A theoretical study on the mechanism of the OH + aliphatic amines reactions is presented. Geometry optimization and frequencies calculations have been performed at the BHandHLYP/6-311++G(2d,2p) level of theory for all stationary points. Energy values have been improved by single-point calculations at the above geometries using CCSD(T) and the same basis set. All the possible hydrogen abstraction channels have been modeled, involving the rupture of C–H and N–H bonds. It was found that as the temperature decreases the contributions of the channels involving NH sites to the overall reaction also decrease, suggesting that for upper layers in the troposphere these channels become less important. Their percentage contributions to the overall reaction, at 298 K, were found to be about 20%, 2%, and 48% for methylamine, ethylamine, and dimethylamine, respectively.

Introduction

Aliphatic amines play an important role in the context of atmospheric and environmental sciences due to their potential role as precursors of HCN and particularly N₂O, which is both an important greenhouse gas¹ and the main source of stratospheric NO_x.^{2,3} The products of the degradation of (CH₃)₂NH can also lead to the production of carcinogenic nitrosamines in the polluted environment.⁴ In contrast to ammonia (NH₃), alkylamines rapidly react with the major initiator of trace gas oxidation in the troposphere: the OH radical. However, there is scarce data available on the reactions between OH and alkylamines.

There are only two experimental studies on each of the amines studied in the present work. They are methylamine (CH₃NH₂),^{5,6} ethylamine (CH₃CH₂NH₂),^{6,7} and dimethylamine [(CH₃)₂NH].^{6,7} It has been suggested that the lack of data is caused, to some extent, by experimental problems that arise from mixing amines and suitable OH precursors, which are often acidic gases that form aerosols in the presence of the basic amines.⁶ Accordingly, in ref 6 the

kinetics of some OH + amine reactions has been investigated, at room temperature, using a novel two-photon OH source that overcomes these problems. On the other hand, no theoretical studies have been reported on these systems.

The reactions of the OH radical with amines are thought to proceed via hydrogen atom abstraction from either C–H or N–H bonds. However, the available information on the branching ratios of these reactions is even more limited. Actually there is scarce information on branching ratios for Volatile Organic Compounds (VOCs) reactions in general. However it has been established that branching ratios between different products in multichannel reactions are as important as the overall rate of reaction, in terms of practical applications and in the understanding of the fundamental mechanisms of chemical reactions.^{8,9} In the case of amines there is only one previous study on this subject,⁴ dating from 1979. In that work the H abstraction from the NH group was estimated to contribute by (37 ± 5)% to the overall rate constant of dimethylamine. For the other studied amines there are no previous reports on their branching ratios. Based on the C–H and N–H bond strengths (Table 1), the reactions are assumed to occur by H abstractions, mainly from the C–H sites.¹⁰ This would explain the slight increase in the

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Table 1. C–H and N–H Bond Strengths in the Studied Amines (kcal/mol)

	C–H	N–H
CH ₃ NH ₂	93.3 ± 2 ^a	100.0 ± 2.5 ^a
CH ₃ CH ₂ NH ₂	CH ₂ 90.1 ^b	98.7 ^b
	CH ₃ 99.0 ^b	
(CH ₃) ₂ NH	87 ± 2 ^a	91.5 ± 2 ^a

^a From ref 11. ^b From ref. 12.

rate coefficient of OH + C₂H₅NH₂ reaction, compared to that of CH₃NH₂. For (CH₃)₂NH the N–H bond is weaker and closer in energy to the C–H bond. Accordingly, the enhanced reactivity of this amine, compared to CH₃NH₂ and C₂H₅NH₂, is assumed to be caused by a larger contribution of N–H path to the overall rate coefficient.

The principal aim of this work is to model the different reactive pathways of the OH reactions with the above-mentioned amines and to estimate the proportion of their contribution to the overall reactions.

Computational Details

Full geometry optimizations were performed with the Gaussian 03¹³ program using the 6-311++G(2d,2p) basis set and the BHandHLYP hybrid HF-density functional, as implemented in Gaussian 03.¹⁴ The energies of all the stationary points were improved by single point calculations using CCSD(T)¹⁵ method and the same basis set mentioned above. Based on our previous experience,¹⁶ the use of the CCSD(T)/BHandHLYP approach properly describes the energetic and kinetics features of VOCs + OH hydrogen abstraction reactions. In addition, for this kind of reactions it has been proved that the differences in geometries between several DFT methods compared to CCSD and QCISD are minimal for BHandHLYP.¹⁷ Unrestricted calculations were used for open shell systems. Frequency calculations were carried out for all the stationary points at the DFT level of theory, and local minima and transition states were identified by the number of imaginary frequencies (NIMAG = 0 or 1, respectively). Intrinsic Reaction Coordinate (IRC)¹⁸ calculations were carried out at the BHandHLYP/6-311G++(2d,2p) level of theory to confirm that the transition states structures connect the proper reactants and products. The paths have been computed by following the Gonzalez-Schlegel steepest descent path,¹⁹ in mass-weighted internal coordinates. Fifty points were modeled on each side of the saddle points, with a gradient step size of 0.02 amu^{1/2}bohr. Thermodynamic corrections to the energy at 298.15 K were included in the determination of the activation energies and of the heats of reaction, which have been reported in terms of Gibbs free energies.

Rate coefficients were calculated using the Canonical Variational Theory (CVT),^{20–26} as implemented in The Rate program at Computational Science and Engineering Online Web site (www.cseo.net).²⁷ For H abstractions from the methyl group in ethyl amine the Conventional Transition State Theory (TST)^{28,29} was used since the corresponding reaction barrier is high enough to avoid significant recrossing effects. The Minimum-Energy Paths (MEP)³⁰ were obtained from IRC calculations at the BHandHLYP/

Table 2. Classical Potential Energies of Reaction (ΔE) and Barriers (ΔE^\ddagger) and Gibbs Free Energies of Reaction (ΔG) and Barriers (ΔG^\ddagger) at 298.15 K^a

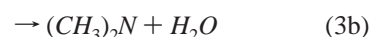
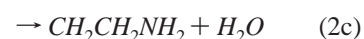
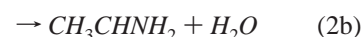
	ΔE^\ddagger	ΔE	ΔG^\ddagger	ΔG	<i>L</i>
(1a)	0.97	−17.00	7.00	−19.08	0.27
(1b)	0.36	−23.19	6.73	−24.48	0.14
(2a)	0.95	−16.99	6.93	−19.01	0.27
(2b)	−0.79	−24.01	5.89	−25.51	0.10
(2c)	5.51	−14.29	10.79	−16.35	0.43
(3a)	−2.23	−22.43	3.76	−25.16	0.12
(3b)	−0.73	−23.86	5.98	−25.19	0.13

^a All in kcal/mol.

6-311G++(2d,2p) level of theory. Force constants, harmonic vibrational frequencies, and normal-mode vectors for the 3N-7 degrees of freedom that are orthogonal to the reaction path were computed at selected points along the IRC, for which the energies were improved by CCSD(T) single point calculations.

Results and Discussion

All the possible reactive channels of the OH hydrogen abstraction reactions from the studied amines have been modeled:



Energies and Geometries. The calculated classical potential energies of reaction (ΔE), the reaction free energies at 298.15 K (ΔG), the classical potential energy barriers (ΔE^\ddagger), and the Gibbs free energy barriers at 298.15 K (ΔG^\ddagger) for all the studied channels are reported in Table 2. All the reactions were found to be exergonic ($\Delta G < 0$) with products more than 16 kcal/mol more stable than the corresponding reactants. A relationship is expected between the calculated classical potential energies of reaction and the strength of the broken bonds. Comparing values in Tables 1 and 2 it can be observed that for the N–H bonds the weakest is that of dimethylamine (DMA), which also correspond to the largest ΔE , while the N–H bond strengths in ethylamine (EA) and methylamine (MA) are of similar magnitude and so are the corresponding classical potential energies of reaction. The same trend is also observed for C–H bonds. In addition, comparing reaction channels that involves different kind of bonds for the same amine it can be seen that the difference in experimentally determined bond strengths for channels (1a) and (1b), (2a) and (2b), and (3a) and (3b) are 6.7 ± 4.5 ,¹¹ 8.6 (error not reported),¹² and 4.5 ± 4 kcal/mol,¹¹ respectively, while the calculated differences

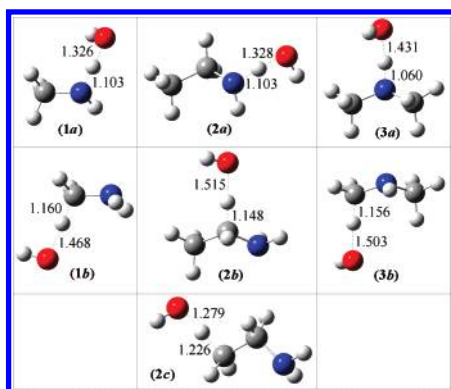


Figure 1. Fully optimized geometries of the transition states.

in ΔE are about 6.7, 7.0, and 1.5 kcal mol, i.e., there is a good agreement between both kind of results. The highest calculated barrier corresponds to path (2c), which is a logical finding since it corresponds to the only H abstraction from a primary carbon that is not next to an amino group, i.e., this is an alkane-like methyl site. Comparing channels 1b and 2c, which involve primary $-\text{CH}_3$ groups, $\Delta E^\ddagger(2c)$ is larger than $\Delta E^\ddagger(1b)$ by about 4.2 kcal/mol, which is in agreement with the 5.7 kcal/mol difference between the corresponding bond strengths. This is also in line with the fact that the amino group activates H abstractions from carbon sites directly bonded to it, i.e., alpha sites.

The L parameters for all the studied channels have also been included in Table 2. The L parameter denotes if a transition state structure is reactant-like ($L < 1$) or product-like ($L > 1$) and also quantifies the corresponding trend. Therefore, according to the Hammond postulate,³¹ there must be a direct relationship between the L value and the heat of reaction of a specific path. The L parameters were calculated for each reaction channel, following refs 32 and 33 as

$$L(N-H) = \frac{\delta r(N-H)}{\delta r(H-O)} \quad (1)$$

and

$$L(C-H) = \frac{\delta r(C-H)}{\delta r(H-O)} \quad (2)$$

where $\delta r(N-H)$ and $\delta r(C-H)$ represent the variation in the breaking bond distance between transition states and reactants; while $\delta r(H-O)$ stands for the variation in the forming bond distance between transition states and products.

According to the L parameters in Table 2, all the transition states structures are reactant-like. The relationships between L and ΔE or ΔG are well accomplished. The lowest (highest) value of L actually corresponds to the most (less) negative energy of reaction, while L values of similar magnitudes correspond to comparable energy values. It seems worthwhile to point out that these are qualitative criteria and when there are very small differences between two L (or energy) values the strict order might change. The transition states (TS) structures and the main bond distances in their fully optimized geometries are shown in Figure 1. From all the TS involved in H abstractions from N-H sites the earliest one (most reactant-like) is that corresponding to channel (3a)

with and the largest H-O distance: $r(N-H)=1.06$ and $r(H-O)=1.43$ Å, respectively. This is an indication of the higher reactivity of the N-H site in DMA compared to MA and EA. On the other hand, the TS with the lowest L , from all those involved in H abstractions from C-H sites, is that corresponding to channel (2b) with $r(C-H)=1.15$ Å, indicating that EA has the highest reactive C-H site among all the modeled ones. At this point, and based on the previous analysis, it is possible to hypothesize that DMA would have the largest contribution of the H abstractions from N-H to the overall reaction, while EA should have the lowest one, within the studied set of amines. This is in line with chemical intuition which indicates that the amine with secondary nitrogen (carbon) would have the most reactive N-H (C-H) site.

Minimum Energy Paths. Intrinsic reaction coordinate calculations (IRC) were performed at the BHandHLYP/6-311++G(2d,2p) level of theory in order to obtain the minimum energy paths (MEP) for the studied channels of reaction. The calculations were carried out starting from the fully optimized saddle-point geometries and then moving downhill along the reactant and product sides, in mass-weighted internal coordinates. Neither reorientation nor symmetry were used to construct the IRC. An even gradient step size of $0.02 \text{ amu}^{1/2} \text{ bohr}$ was used, and fifty points were calculated in each direction. The reaction coordinate s is defined as the signed distance from the saddle point (where $s < 0$ refers to the reactants' side and $s > 0$ refers to the products' side). As a reasonable compromise between speed and accuracy, and based on the curvature of the surface, five points on each side of the saddle point were chosen to construct the MEP. Their energies were improved by single-point calculations at the CCSD(T)/6-311++G(2d,2p) level of theory, and they were used in conjunction with gradients and frequencies computed at the BHandHLYP/6-311++G(2d,2p) level.

The adiabatic minimum energy potential surfaces were obtained within the B//A approach,³⁴ which has become common in the study of polyatomic systems because it is relatively inexpensive from a computational point of view and it usually reproduces correctly the main features of the reaction path. It consists of geometry optimizations at a given level (A) followed by single point calculations, without optimization, at a higher level (B). The MEP obtained using this technique presents a maximum that is shifted toward the reactants valley by about -0.2 bohr with respect to the maximum at the A level of calculation. Espinosa-Garcia and Corchado³⁵ argue that, when the MEP is constructed using the B//A technique, the energy maximum is artificially located away from the saddle point corresponding to the level of optimization (A). This shift, that is simply a numerical effect, could be mistaken with a variational effect and mislead the kinetic calculations. Consequently, we have corrected the position of the maxima as suggested by these authors. The calculated MEPs corresponding to abstractions from C-H sites are almost barrierless processes, while those corresponding to N-H abstractions show barriers that are still low but noticeable. When reaction profiles involve low and broad classical barriers, it causes large variational effects (see

Table 3. Calculated Overall Rate Coefficients (k , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for Amines + OH Reactions, within the Temperature Range 290–310 K, and Experimental Values at 298 K^a

T (K)	k_{MA}	k_{EA}	k_{DMA}
290	4.86×10^{-12}	1.18×10^{-11}	5.21×10^{-11}
292	4.95×10^{-12}	1.19×10^{-11}	5.23×10^{-11}
294	5.03×10^{-12}	1.19×10^{-11}	5.25×10^{-11}
296	5.11×10^{-12}	1.19×10^{-11}	5.20×10^{-11}
298.15	5.20×10^{-12}	1.19×10^{-11}	5.17×10^{-11}
300	5.28×10^{-12}	1.19×10^{-11}	5.15×10^{-11}
302	5.37×10^{-12}	1.19×10^{-11}	5.12×10^{-11}
304	5.45×10^{-12}	1.19×10^{-11}	5.10×10^{-11}
306	5.54×10^{-12}	1.19×10^{-11}	5.07×10^{-11}
308	5.63×10^{-12}	1.20×10^{-11}	5.05×10^{-11}
310	5.72×10^{-12}	1.20×10^{-11}	5.03×10^{-11}
exp ^{5,7}	2.20×10^{-11}	2.77×10^{-11}	6.54×10^{-11}
exp ⁶	1.73×10^{-11}	2.37×10^{-11}	6.49×10^{-11}

^a MA = methylamine, EA = ethylamine, DMA = dimethylamine.

ref 36 for more details). In these cases, the recrossing problem is essential, and variational transition state theory is needed to obtain reliable values of the rate constants (k). Accordingly the CVT approach has been used to compute the rate constant corresponding to all channels but the (2c). In this particular case the reaction barrier (ΔE^\ddagger) is high enough (Table 2) to avoid substantial recrossing effects and the conventional transition state theory, which can be considered as an upper limit of CVT, is adequate to compute k . In addition the (2c) is a minor path that hardly contributes to the overall reaction of ethylamine.

Kinetics and Branching Ratios. The rate coefficients have been calculated within the temperature range 290–310 K (Table 3), to obtain kinetic parameters corresponding to the 298 K vicinity. We have assumed that neither mixing nor crossover between different pathways occurs and that the overall rate constant (k) corresponding to each amine + OH can be calculated as the sum of the rate coefficients of each path:

$$k_{MA} = k_{(1a)} + k_{(1b)} \quad (4)$$

$$k_{EA} = k_{(2a)} + k_{(2b)} + k_{(2c)} \quad (5)$$

$$k_{DMA} = k_{(3a)} + k_{(3b)} \quad (6)$$

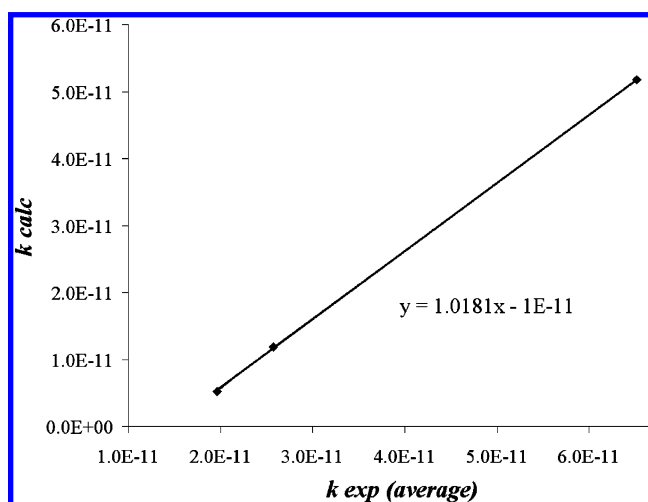
Tunneling corrections were significant only for channel 2c, with transmission coefficients (κ) ranging from 5.17 at 290 K to 4.16 at 310 K. For all the other channels tunneling corrections were found to be negligible, even at the lowest temperature. This is a logical finding since their adiabatic barriers (ΔE^\ddagger) are negative or close to zero. The branching ratios of the different reaction channels, which represent the percent of their contribution to the overall reaction, have been calculated for each amine as

$$\Gamma_{a,b \text{ or } c} = \frac{k_{a,b \text{ or } c}}{k_{\text{overall}}} \times 100 \quad (7)$$

The values of the rate constants and branching ratios for the studied temperature range are reported in Tables 3 and 4.

Table 4. Calculated Branching Ratios (Γ) within the Temperature Range 290–310 K

T (K)	MA		EA			DMA	
	Γ_{1a}	Γ_{1b}	Γ_{2a}	Γ_{2b}	Γ_{2c}	Γ_{3a}	Γ_{3b}
290	20.3	79.7	1.5	98.2	0.3	51.2	48.8
292	20.3	79.7	1.5	98.2	0.3	51.0	49.0
294	20.3	79.7	1.5	98.1	0.4	50.8	49.2
296	20.3	79.7	1.5	98.1	0.4	48.7	51.3
298.15	20.3	79.7	1.9	97.7	0.4	48.4	51.6
300	20.3	79.7	1.9	97.7	0.4	48.0	52.0
302	20.3	79.7	1.9	97.7	0.4	47.7	52.3
304	20.4	79.6	1.9	97.7	0.4	47.3	52.7
306	20.4	79.6	2.0	97.6	0.4	47.0	53.0
308	20.4	79.6	2.0	97.6	0.4	46.6	53.4
310	20.4	79.6	2.0	97.6	0.4	46.3	53.7

^a MA = methylamine, EA = ethylamine, DMA = dimethylamine.**Figure 2.** Correlation between calculated and average experimental values of k_{298} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

The calculated rate coefficients agree well with the previously reported experimental values, differing by less than 1 order of magnitude and following the same tendency. The largest discrepancy was found for methylamine with a calculated value that is about one-third of the experimental one. The good correlation between calculated and the average experimental values of the overall rate constants is shown in Figure 2. This good agreement supports the reliability of the present calculations. However the calculated values are more in line with bond dissociation energies than the experimental ones, see Table 1. The ratio between the experimental rate coefficients of ethylamine/methyl amine is only 1.3. This has no precedent in other VOCs + OH reactions when H abstractions from $-\text{CH}_3$ and $-\text{CH}_2-$ are compared. This could be rationalized only if H abstractions mainly occur from NH sites, which is not the case. On the other hand, the ratio of the calculated rate coefficients is 2.3, which is more in line with the equivalent ratio ethanol/methanol which is 3.3 and for which the H abstraction from the OH group is expected to contribute to a very low extent to the overall reaction. Within the studied temperature range the variations of k with temperature are quite small suggesting that activation energies around 298 K should be close to zero. The largest variation was found for MA. The Arrhenius

equation best fitting the calculated data for the studied amines in the 290–310 K temperature range are

$$k_{\text{overall}}^{\text{MA}} = 5.89 \times 10^{-11} e^{-757/RT}$$

$$k_{\text{overall}}^{\text{EA}} = 1.39 \times 10^{-11} e^{-49/RT}$$

$$k_{\text{overall}}^{\text{DMA}} = 2.72 \times 10^{-11} e^{200/RT}$$

According to these equations the Arrhenius activation energies are 1.43, 0.09, and -0.38 kcal/mol for the OH reaction with methylamine, ethylamine, and dimethylamine, respectively. The only experimental values available are (-0.46 ± 0.3) ,⁵ (-0.38 ± 0.3) ,⁷ and (-0.49 ± 0.3) .⁷ For DMA the calculated value is within the error range of the experimental determination. However for MA and EA the calculated Arrhenius activation energies are higher than the experimental ones, with the largest discrepancy for MA, for which it seems to be overestimated. That the experimental activation energy of MA is lower than that corresponding to EA seems to be difficult to rationalize. The calculated values are in agreement with the expected trend, based on the structure reactivity relationship, i.e., the abstraction from a secondary carbon should be energetically more favored than from a primary one, in a similar way to what occurs when comparing ethanol and methanol: 0.14 kcal/mol and 0.72 kcal/mol, respectively. The same applies for secondary and primary amino group when DMA and MA are compared, moreover the activation effect of $\text{CH}_3\text{-NH-}$ group should be larger than that of $\text{NH}_2\text{-}$ group, in a similar way that the activation energy, according to recommended values, for dimethyl ether (0.43 kcal/mol) is lower than for methanol (0.72 kcal/mol). Accordingly, both channels in DMA are expected to be activated with respect to the equivalent channels in MA, i.e., the activation energy of the overall reaction is expected to be lower. Our results are also in agreement with the bond dissociation energies experimentally determined (Table 1) and with the assumption that activation energies should correlate with bond dissociation energies, except when different channels have different tunneling corrections which is not the case. Since in the last decades not only the calculation resources but also the experimental techniques have evolved, new experiments dealing with Arrhenius parameters for aliphatic amines + OH reactions would be desirable.

As it can be seen from the values in Table 4, abstractions from the $-\text{CH}$ sites make the largest contribution to the overall rate constant, with the exception of dimethylamine at temperatures below 294 K. In all the cases the increase in temperature also increases the contribution of N-H sites abstractions. Therefore moving upward in the troposphere, which implies a lowering in temperatures, the abstraction reactions from NH sites are expected to become less and less important. For ethylamine, in particular, even at room temperature the contribution of 2a channel to the overall rate constant is less than 2%. Accordingly, it could be expected that the OH reactions with secondary amines mainly occur by H abstraction from CH sites, especially from those involving secondary carbons. On the other hand, being that DMA is the only secondary amine from all the modeled ones

it seems logical that it shows the largest contribution of H abstractions from N-H sites to the overall rate constant. At 298 K the calculations predict that about 48% of the reaction would involve the NH site. The only experimental report⁴ on branching ratios propose that $(37 \pm 5)\%$ of the $\text{DMA} + \text{OH}$ reaction takes place through this channel. Taking into account that this determination dates from 1979 and the error inherent to electronic calculations, there is good agreement between these two values. Accordingly, it seems reasonable to assume that the branching ratios proposed here for the first time are reliable enough to describe the product distribution expected for MA and EA.

Conclusion

Different channels have been modeled for the $\text{OH} +$ aliphatic amines reactions, involving the rupture of C-H and N-H bonds. According to our results, for ethylamine the only channel that significantly contributes to the overall reaction is that involving abstractions from the secondary carbon. For methylamine and dimethylamine a mixture of products is expected. For the first one the H abstraction take place mainly from the $-\text{CH}_3$ group, while for the second one products involving abstractions from NH and CH sites are expected to be formed in similar proportions. Even though the reaction was studied in a relative short interval of temperatures, around 298 K, and within this interval the rate constants change smoothly with temperature, it seems that as the temperature decreases the contributions of the channels involving NH sites to the overall reaction also decrease. This finding suggests that for upper layers in the troposphere these channels become less important. Their percentage contributions to the overall reaction, at 298 K, were found to be about 20%, 2%, and 48% for methylamine, ethylamine, and dimethylamine, respectively.

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