

Methyl nitrene: Thermochemistry and kinetics of its rearrangement to methyleneimine

Rita Kakkar* & Vibha Walia

Department of Chemistry, University of Delhi, Delhi 110 007

Received 13 July 1990; accepted 7 December 1990

The thermal unimolecular isomerisation of methyl nitrene to methyleneimine has been studied, and the macroscopic thermodynamic and kinetic properties have been calculated using the vibrational frequencies and rotational constants evaluated theoretically. The high pressure rate constants have been calculated and the fall-off behaviour has been studied using the calculated reactant and transition state properties. Kinetic isotope effects on the reaction have also been studied. The effects of fluorine substitution on the thermochemical and kinetic parameters have also been investigated.

In our previous paper¹ on the isomerisation reaction of methyl nitrene, we had reported our calculations on the ground state potential energy surface for the reaction, and also reported the singlet and triplet state structures for the reactants, transition states and products, and the effect of fluorine as a substituent. In this paper, calculations of partition functions and thermodynamic properties derivable from the potential energy surfaces are presented.

Method of Calculation

We have used the optimized reactant, transition state and product structures from our earlier work¹ for all our calculations. The vibrational frequencies, calculated previously for confirming the transition state structures reported in our previous paper, and the calculated rotational constants were used in the calculation of partition functions and thermodynamic properties².

In these calculations, we have neglected the effects of rotation-vibration coupling, anharmonicity and centrifugal distortion. Since the molecules considered are rigid, no internal rotation has been considered.

The quantum statistical Rice-Ramsperger-Kassel-Marcus (RRKM) theory^{3,4} was used to calculate the high pressure rate constants (k_∞) and the fall-off behaviour was also studied. Forst's approximation to $k(E)$ (see Eq. 1) was used in the calculations

$$k(E) = \frac{\alpha G^*(E - E_0)}{h N(E)} \quad \dots (1)$$

where α is the reaction path degeneracy,

$G^*(E - E_0)$ is the integrated density of states for the transition state at energy $E - E_0$ (E_0 is the activation energy for the reaction) and $N(E)$ is the density of states for the reactant. Both $G^*(E - E_0)$ and $N(E)$ were calculated by the method of steepest descents⁵. Hence k_∞ is given by Eq. (2)

$$k_\infty = \alpha \frac{kT Q^*}{h Q} \exp(-E_0/RT) \quad \dots (2)$$

where Q^* and Q are, respectively, the partition functions for the transition state and reactant.

The unimolecular rate constant, k_{uni} is given by⁴ Eq. (3)

$$k_{\text{uni}} = \frac{1}{Q} \int_{E_0}^{\infty} \frac{k(E)N(E)}{1 + k(E)/\lambda Zp} \exp(-E/RT) dE \quad \dots (3)$$

Simpson's rule was used for the integration, with integration steps of 0.25 kcal/mol. The collisional deactivation efficiency (λ) was taken as 1, and Z , the collision frequency was calculated using a collision diameter of 4 Å.

The deuterium kinetic isotope effects on the reactions were also investigated. All calculations were carried out at various temperatures upto 298.15 K. Similar calculations were performed for the fluorine substituted compounds.

Results and Discussion

The calculated thermodynamic properties at 1 atmosphere pressure and 298.15 K for the singlet state stationary points of the three systems, viz. CH_3N , CH_2FN and CHF_2N , are given in Table 1. For the systems CH_3N , CH_2FN and CHF_2N , the en-

Table 1 – Calculated thermodynamic properties at 1 atmosphere pressure and 298.15 K for singlet states of CH₃N, CH₂FN and CHF₂N

System	Partition function (Q) × 10 ⁻³⁷	Absolute entropy (S) (cal K ⁻¹ mol ⁻¹)
CH ₃ N		
Reactant	0.7085	68.06
Transition State	0.6281	67.73
Product	0.5225	67.34
CH ₂ FN		
Reactant	7.074	73.05
Transition State	6.521	72.67
Product	5.920	72.54
CHF ₂ N		
Reactant	41.27	77.20
Transition State	38.72	76.78
Product	40.45	77.17

Table 2 – Calculated thermodynamic properties at 1 atmosphere pressure and 298.15 K for triplet states of CH₃N, CH₂FN and CHF₂N

System	Partition function (Q) × 10 ⁻³⁷	Absolute entropy (S) (cal K ⁻¹ mol ⁻¹)
CH ₃ N		
Reactant	0.2424	65.87
Transition State	0.2118	67.89
Product	0.6260	68.02
CH ₂ FN		
Reactant	7.849	73.22
Transition State	7.127	72.99
Product	7.631	73.66
CHF ₂ N		
Reactant	40.51	77.04
Transition State	46.00	77.68
Product	50.40	78.24

properties of reaction have small negative values (-0.72 , -0.51 and -0.03 cal K⁻¹ mol⁻¹, respectively) and the activation entropies are also small and negative (-0.33 , -0.38 and -0.42 cal K⁻¹ mol⁻¹) respectively. This is to be expected as, the reactions being highly exothermic, the transition states resemble the reactants (according to Hammond's postulate⁶) and have similar vibrational frequencies. The only difference is that, in the transition state, one vibrational frequency for motion along the reaction coordinate becomes translational, and hence the vibrational contribution to the entropy decreases. The imaginary frequencies are 830, 838 and 802 cm⁻¹, respectively, for the transition states corresponding to the three reactions, and this accounts for a decrease of approximately 0.20 cal K⁻¹ mol⁻¹ in the vibrational contribution to the entropy.

The small negative entropies of reaction can also be explained on the basis that, in the product imines, the C–N bond has double bond character and this leads to an increase in the ν_{CN} mode, which in turn decreases its contribution to the vibrational entropy. In addition, the product is planar and has a lower rotational entropy.

In Table 2 are presented the thermodynamic properties for the triplet states. Here the situation is very different. For CH₃N, both the entropies of reaction and the activation entropy are larger (2.15 and 2.02 cal K⁻¹ mol⁻¹, respectively). In this case, the increase is mainly due to an increase in the rotational contribution to the entropy. The reactant molecule has C_{3v} symmetry, and hence a symmetry factor of 3, which reduces its entropy.

Secondly, in contrast to singlet imines, triplet imines have nonplanar C_s geometries¹. This suggests that they may have biradical character. An investigation of the highest occupied molecular orbitals in triplet CH₂NH indicates that the ³A" state has a singly occupied a" orbital mainly (86.4%) on nitrogen, and a singly occupied a' orbital mainly (85.3%) on carbon. This biradical character accounts for the longer C–N bonds in triplet imines as compared to those in singlet imines, and the nonplanar CH₂ group in triplet imines. Both these factors lead to an increase in the entropy, and hence the entropy of reaction is positive.

Similarly, the transition states have biradical character with one electron localized on the nitrogen (89%), and the other electron shared equally by carbon and nitrogen. Hence, these reactions have loose biradical transition states, which account for the low vibrational frequencies in the transition states. Consequently, the vibrational contribution to the entropy is increased, leading to a positive entropy of activation.

For fluorine substituted compounds, too, the situation is similar. The only difference is that, in these cases, the reactants also have C_s geometry, and there is no contribution from the symmetry factor. Hence, although the entropies of reaction are again positive, the magnitudes are small.

We have performed RRKM calculations on the reactions. The calculated k_{∞} values at various temperatures upto 298.15 K for all the reactions studied are given in Table 3. It is evident that, at low temperatures, e.g. 4 K, the rearrangement does not take

Table 3 – Calculated high pressure rate constants (k_{∞}) at different temperatures (K)

System	k_{∞} at temp (K)				
	4	77	100	200	298.15
Singlet state					
CH ₃ N	0.0	2.55×10^{-4}	1.81×10	6.33×10^6	1.04×10^9
CH ₂ FN	0.0	3.99×10^{-3}	1.39×10	1.43×10^7	1.51×10^9
CHF ₂ N	0.0	9.74×10	2.85×10^4	4.56×10^8	1.02×10^{10}
Triplet state					
CH ₃ N	0.0	0.0	0.0	0.0	2.22×10^{-23}
CH ₂ FN	0.0	0.0	0.0	0.0	7.45×10^{-24}
CHF ₂ N	0.0	0.0	0.0	0.0	2.33×10^{-25}

 Table 4 – Calculated high pressure Arrhenius parameters, A_{∞} and E_{∞}

System	$A_{\infty} \times 10^{13}$ (s ⁻¹)	E_{∞} (kcal mol ⁻¹)
Singlet state		
CH ₃ N	2.909	5.7522
CH ₂ FN	1.940	5.3180
CHF ₂ N	0.967	3.6932
Triplet state		
CH ₃ N	9.824	52.375
CH ₂ FN	2.014	48.737
CHF ₂ N	1.428	49.086

 Table 5 – Calculated $\log(p_{1/2})$ values for singlet rearrangements at various temperatures (K)

System	$\log p_{1/2}$ (torr)			
	77	100	200	298.15
CH ₃ N	3.56	4.26	4.67	5.03
CH ₂ FN	3.93	4.08	4.55	4.89
CHF ₂ N	3.89	4.04	4.50	4.80

place, and even the singlet state of CH₃N may be isolated. It has been experimentally established that alkylnitrenes cannot be observed⁷ at 77 K, but are stable at 4 K (see ref. 8). Also, the rate of reaction increases with fluorine substitution. For the triplet states, even at 298.15 K, the reaction rate is very low. Accordingly, we did not calculate fall-off curves for the triplet reaction.

The high pressure Arrhenius frequency factor, A_{∞} and the activation energy, E_{∞} , are given in Table 4. Both A_{∞} and E_{∞} decrease with increase in fluorine substitution, and A_{∞} factors are typical of reactions involving rearrangements of carbenes.

The calculated $\log(k_{\text{uni}}/k_{\infty})$ values were subjected to polynomial fits with respect to $\log(p)$ and the resultant equations solved for $p_{1/2}$. The calculated

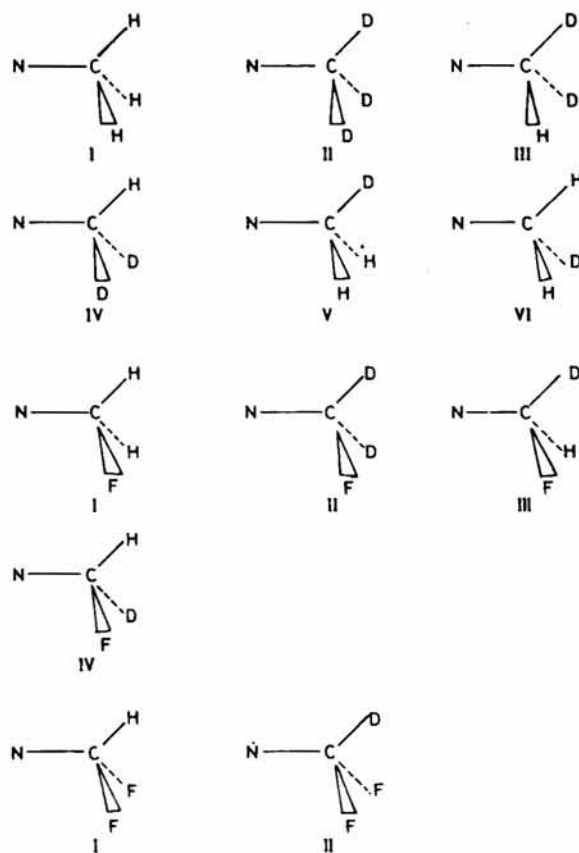


Fig. 1 – Structures of methylnitrene and substituted methylnitrenes.

$\log(p_{1/2}/\text{torr.})$ values for the various systems are reported in Table 5. The transition pressures, $p_{1/2}$, are an indication of the pressure below which the unimolecular rate constants k_{uni} begin to decline. The data in Table 5 indicate that the $p_{1/2}$ values are all in the range of 10^3 - 10^5 torr, and, as expected, increase with temperature. These values are quite high, and is indicative of the low activation energies of the reactions. There is a slight decrease in $p_{1/2}$ with increasing fluorine substitution.

We next calculated the deuterium kinetic isotope effects: Figure 1 shows the various deuterium labelled compounds used in our study. The effect on k_{∞} is given by Eq. (4)

$$\frac{k_{\infty H}}{k_{\infty D}} = \frac{Q_H^*/Q_H}{Q_D^*/Q_D} \exp[(E_{0D} - E_{0H})/RT] \quad \dots (4)$$

where Q_H and Q_H^* are, respectively, the partition functions of the reactant and transition states of the unlabelled compound, and Q_D and Q_D^* are those of the deuterium labelled isotopomers. E_{0H} and E_{0D} are, respectively, the zero-point energies of the un-

labelled and labelled isotopomers. The calculated values of $k_{\infty H}/k_{\infty D}$ are greater than unity for isotopomers II, III and V of methylnitrene, i.e., the isotopomers II, III and V exhibit large normal isotope effects. However, for the other two isotopomers, viz. I and IV, the ratio is close to unity. This difference in isotope effects arises from the fact that the former (II, III and V) exhibit primary isotope effects, while the latter (I and IV) exhibit only secondary isotope effects.

Below the transition pressure, the reactions become bimolecular, and the low pressure limiting ratios were calculated from the formula (5)

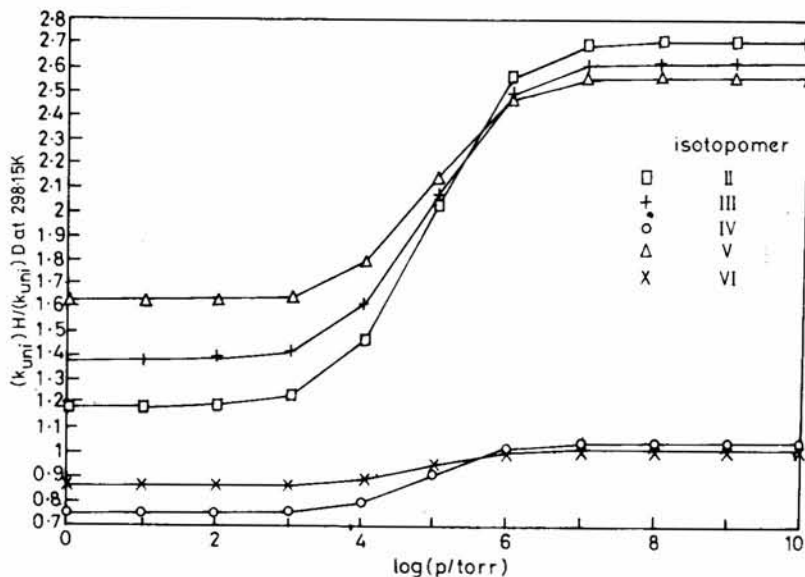


Fig. 2—Isotopic rate ratios for the deuterium labelled isotopomers of CH_3N .

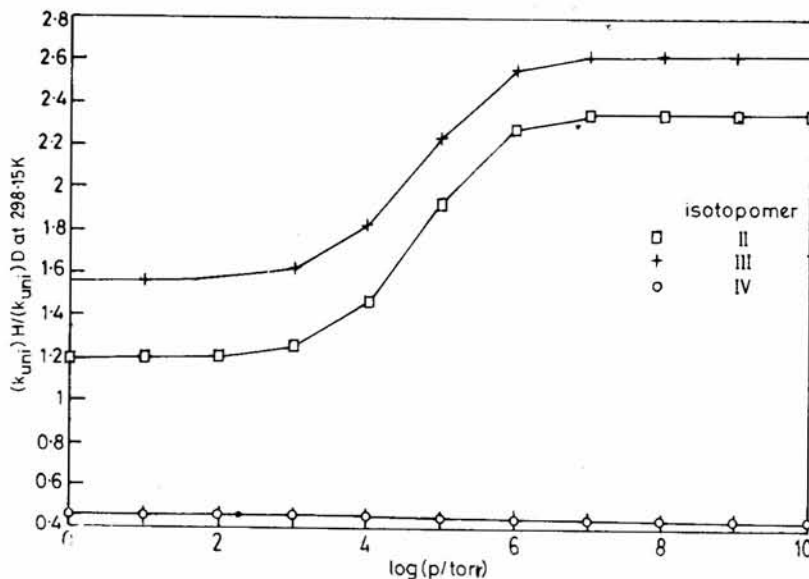


Fig. 3—Isotopic rate ratios for the deuterium labelled isotopomers of CH_2FN .

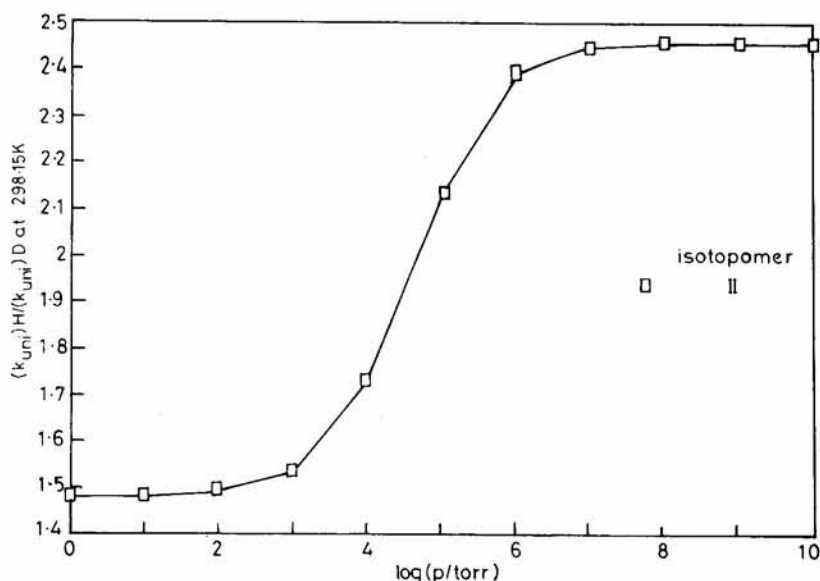


Fig. 4—Isotopic rate ratios for the deuterium labelled isotopomers of CHF₂N.

$$\frac{(k_{\text{bim}})_{\text{H}}}{(k_{\text{bim}})_{\text{D}}} = \frac{Q_{\text{H}}^*/Q_{\text{H}}}{Q_{\text{D}}^*/Q_{\text{D}}} \exp \left[\frac{(E_{0\text{D}} - E_{0\text{H}})}{RT} \right] \quad \dots (5)$$

where $Q^* = Q \exp(-E_0/RT)$

For the primary isotope effect, the ratio is greater than unity, but the isotopomers IV and VI exhibit inverse isotope effects. The ratios $(k_{\text{uni}})_{\text{H}} / (k_{\text{uni}})_{\text{D}}$ for methylnitrene are plotted against $\log(p/\text{torr})$ in Fig. 2, where the above effects are apparent. The primary isotope effect is maximum for isotopomer II, while isotopomers III and V also exhibit large primary isotope effects. The three curves cross at $\log(p/\text{torr})$ values between 5 and 6. Hence, the ratio $(k_{\text{bim}})_{\text{H}} / (k_{\text{bim}})_{\text{D}}$ is least for isotopomer II, but the ratio $k_{\infty\text{H}} / k_{\infty\text{D}}$ is maximum for this isotopomer.

For CH₂FN, the curves are given in Fig. 3. Here isotopomers II and III exhibit primary isotope effects, while isotopomer IV exhibits only a secondary isotope effect. For the isotopomers II and III, the curves are similar to those obtained for isotopomers II, III and V of methylnitrene, but now there is no crossing of the two curves. For isotopomer V, there is a large inverse secondary isotope effect at all pressures [$(k_{\text{uni}})_{\text{H}} / (k_{\text{uni}})_{\text{D}} \approx 0.45$].

The only deuterated CHF₂N exhibits a normal primary isotope effect similar to the first two molecules. The curve is plotted in Fig. 4.

Conclusions

The thermodynamic parameters involved in the thermal unimolecular rearrangement of methylni-

trene show that the activation entropies and entropies of reaction are small in magnitude and can be explained satisfactorily on the basis of the calculated transition state structures.

For the singlet states, based on the deuterium isotope effect, we have been able to predict that the primary isotope effects are normal, whereas there are inverse secondary isotope effects on the reactions.

Since it is difficult to experimentally obtain the low pressure bimolecular rate constants, particularly for reactions involving nitrenes and carbenes, the theoretical RRKM calculations should be useful for predicting $p_{1/2}$ values, etc.

Acknowledgement

The authors thank the staff of the Delhi University Computer Centre for their cooperation.

References

- 1 Walia V & Kakkar R, *Indian J Chem*, 29B (1990) 1007.
- 2 Fowler R H & Guggenheim E A, *Statistical thermodynamics*, (Cambridge University Press) 1939.
- 3 Robinson P J & Holbrook K A, *Unimolecular reactions*, (Wiley, London) 1972.
- 4 Forst W, *Theory of unimolecular reactions* (Academic Press, New York) 1973.
- 5 Forst W, *J phys Chem*, 76 (1972) 342.
- 6 Hammond G S, *J Am chem Soc*, 77 (1955) 334.
- 7 Smolinsky G, Wasserman E & Yager W A, *J Am chem Soc*, 84 (1962) 3220.
- 8 Wasserman E, Smolinsky G & Yager W A, *J Am chem Soc*, 86 (1964) 3166.