# Metastable Dissociations of $CH_3NO_2^+$ and $CD_3NO_2^+$ Ions. Isotope Effects of the Loss of a Hydroxyl Radical

Ryuichi Arakawa
College of Biomedical Technology, Osaka University, 1-1 Machikaneyama-cho, Toyonaka, Osaka 560

(Received December 21, 1988)

**Synopsis.** A large kinetic isotope effect has been observed for the metastable transitions of $CX_3NO_2^+ \rightarrow CX_2NO^+ + OX$ (X=H, D). The large effect was explained by assuming a rate-determining isomerization to an *aci*-nitromethane ion and the quantum mechanical tunneling of a hydrogen atom.

The dissociation of a nitromethane ion has been studied by a variety of experimental techniques.[1–7] The dissociation mechanism has been discussed in terms of the participation of an *aci*-nitromethane tautomer, $CH_2{=}N(OH)O^+$, and a methyl nitrite ion, $CH_3ONO^+$. In particular, isomerization to an *aci*-nitromethane ion, followed by the formation of $CH_2NO^+$ and OH, has been established by recent studies of the appearance energy and metastable-ion fragmentations using MS/MS and photoionization experiments.[6,7] On the other hand, the $NO^+$ formation from the nitromethane ion has been explained by its isomerization to the methyl nitrite ion prior to dissociation.[3,4] Moreover, it has been reported that the dissociations of the nitromethane ion at the near threshold are all competing processes.[7] However, no quantitative interpretation accounting for the metastably slow dissociations, including $CH_2NO^+$ and $NO^+$ paths, has been presented based on a usual RRKM/QET treatment.

In the system of a methyl nitrite ion, it is of much interest that the dissociation involves non-interconverting excited states or structures. The $CH_2OH^+$ formation from $CH_3ONO^+$ appears with a rate constant of $k(E) \approx 10^5\ s^{-1}$, while the rate of $NO^+$ is $k(E) \gg 10^7\ s^{-1}$.[3,4] There is no satisfactory interpretation of the slow $CH_2OH^+$ path. Recently, Ferguson[8] has suggested that a quantum mechanical tunneling for a hydrogen migration is due to the slow dissociation of $CH_2OH^+$ and has interpreted the large isotope effect of $k_H/k_D \approx 10$, measured previously by Gilman et al.[4] This suggests an alternative reaction path leading to $D_2NO^+$ for $CD_3NO_2^+$. However, more recent studies,[9,10] have excluded such a proposal.

There is a class of dissociation reactions in which ions dissociate at a rate much slower than that predicted from the RRKM/QET calculation. In such a case, the activation energy is usually less than 1 eV, so that the predicted rates are much greater than $10^7\ s^{-1}$, while the measured rates are in the $10^5\ s^{-1}$ range. To overcome this difficulty, it has been proposed that the reaction involves isomerization into sufficiently stable isomers or the existence of stable ion-dipole complexes. In addition, tunneling through a potential barrier or a rotational barrier and the participation of an anharmonic interaction potential[11] have been reported to be the origin of the metastable-ion dissociations. The reaction systems of nitromethane and methyl nitrite cations lie within the category discussed above. Below we will present an isotope effect $k_H/k_D$ for the loss of a hydroxyl radical in the nitromethane metastable dissociations. If the isomerization to the *aci*-nitromethane ion is a rate-determining step, tunneling is a probable process for explaining the slow dissociation; thus, the large isotope effect can be expected.

Figure 1 shows the metastable-ion decays for $CH_2NO^+$ and $NO^+$ as a function of the ion-storage time, as determined by the use of the ion-trapping

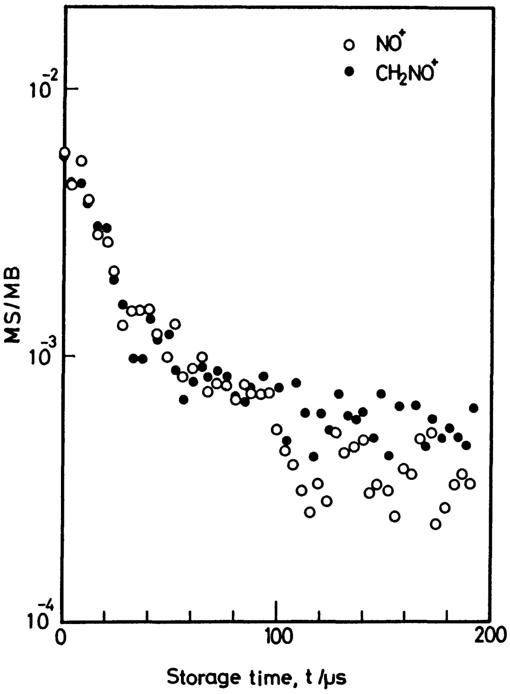

Fig. 1. Metastable-to-main-beam intensity ratio vs. the ion-storage time at the electron-impact energy of 40 eV.

Table 1. Metastable Ion (MI) and Collision-Induced Dissociation (CID) Spectra of Nitromethane Ions

| Ion | $CH_3NO_2^+$ | | $CD_3NO_2^+$ | |
|---|---|---|---|---|
| (*m/z*) | MI | CID | MI | CID |
| 15 | | 2 | | |
| 30 | 27 | 35 | 44 | 46 |
| 34 | | | | <1 |
| 44 | 26 | 4 | | |
| 46 | | 42 | 1±1 | 37 |
| 48 | | | | 2 |
| 60 | 47 | 17 | | |
| 62 | | | 55 | 14 |

technique[12] utilizing the space charge of an electron beam. It indicates that slow dissociations are measured at $\leqq 10^4$ s$^{-1}$. The two intensities are almost the same throughout the long storage time. This is consistent with the photoionization result[7] that their appearance energies are nearly equal within the limits of experimental error. The intensities of the metastable ions and of the collision-induced dissociations (CID) at the zero storage time are listed in Table 1. The CID spectra were measured at a 20% decrease in the main beam intensity by raising the He gas pressure in a collision cell. We believed that the CID components in the metastable peaks were negligible, because there was no CID peak of $NO_2^+$. For $CD_3NO_2^+$ the peak at $m/z$ 46 corresponding to $CD_2NO^+$ or $NO_2^+$ was observed with a low intensity. This peak may be $CD_2NO^+$, because no peak of $NO_2^+$ was observed for $CH_3NO_2^+$. The metastable observation is actually limited within a narrow rate range, because the present time window in the second-field-free region is between 6.8 and 10.6 $\mu$s; it corresponds to the average decay rate of $1.2\times10^5$ s$^{-1}$. Thus, the intensity ratio in Table 1 represents the relative rate constant. Consequently, the isotope effect was determined to be $k_H/k_D \approx 26$ for the hydroxyl radical loss.

The tunneling correction of the unimolecular rate constants was examined in order to explain the large experimental isotope effect. The correction is given by $k(E)=p(E)k(E_0)$, where $p(E)$ is the tunneling probability and where $k(E_0)$ is the minimum rate at the threshold energy of $E_0$. The vibrational frequencies for a reactant and a transition state were obtained by a vibrational analysis for the assumed geometries and force fields.[13] The value of $k_H/k_D$ may be independent of the influence of approximate vibrational frequencies resulting from the simple force field. Thus, the rough estimation of vibrational frequencies is sufficient to account for the present isotope effect. The isomerization to the *aci*-nitromethane ion probably involves a hydrogen migration to a oxygen atom prior to the OH loss. A four-center complex was employed as the transition state; the bond orders of C-H and H-O regarding the migrating hydrogen were assumed to be 0.5. The results of the vibrational analysis are shown in Table 2. The activation entropies, $\Delta S^*$, as calculated from a set of frequencies, are $\Delta S^*=-0.20$ (X=H) and $-0.63$ e.u.(X=D) when $T$=1000 K. In general, rearrangements, followed by molecular elimination, exhibit "tight" transition states and low(or even negative) $\Delta S^*$ values, while simple bond cleavages have "loose" transition states and high $\Delta S^*$ values.[14] For example, HCN eliminations from pyridine[15] and benzonitrile[16] cations are specified as $\Delta S^*=-2.5$ and 0.4 e.u. respectively. In recent RRKM calculations with reference to the reaction of the methyl nitrite ion to $H_2COH^+ + NO$, Baer and Hass[17] have synthesized very tight transition-state frequencies such as $-5.6$ e.u. Accordingly, the present model represents a reasonable tightness as structural isomerization. Actual RRKM calculations yielded $k(E_0)=3\times10^8$ s$^{-1}$ for $CH_3NO_2^+$, and proved that the chief origin of the large isotope effect is not the $k(E_0)$ rate, but the tunneling probability. The activation energy for $CD_2NO^+$ was estimated by applying a zero-point energy correction.

Tunneling has been investigated for neutral unimolecular reactions by Miller and his co-workers[18,19] and for metastable-ion dissociations of methane,[20] methanol,[21] and phenol[22] cations. Tunneling through a potential barrier is generally favored for a case of one-step hydrogen-bond cleavage. For isomerization to the aci-nitromethane ion, the barrier heights, as estimated relative to the reactants and the products, are 0.63 and 1.58 eV respectively.[6,7] The $p(E)$ values in Table 3 were calculated with the imaginary frequencies described in Table 2, based on Miller modification[18] using a generalized Eckart potential. The imaginary frequencies used here are nearly equal to those[18] in the isomerization of *trans*-formaldehyde to $H_2CO$. $p(E)$ depends upon imaginary frequencies and, as may be seen in Table 3, decreases more rapidly for D species than for H with a decrease in the energy. At the energy of 0.35 eV below the threshold, which represents the experimental metastable rate of $10^5$ s$^{-1}$, the ratio of tunneling probabilities is $p_H(E)/p_D(E) \approx 30$;

Table 3. The Calculated Tunneling Probabilities

| $(E-E_0)$/eV | X=H | X=D |
|---|---|---|
| 0 | $5.3\times10^{-1}$ | $5.2\times10^{-1}$ |
| −0.1 | $1.2\times10^{-1}$ | $5.4\times10^{-2}$ |
| −0.2 | $1.3\times10^{-2}$ | $2.4\times10^{-3}$ |
| −0.3 | $1.1\times10^{-3}$ | $7.3\times10^{-5}$ |
| −0.4 | $6.5\times10^{-5}$ | $1.5\times10^{-6}$ |
| −0.5 | $2.3\times10^{-6}$ | $1.5\times10^{-8}$ |

Table 2. Vibrational Frequencies for the Reaction of $CX_3NO_2^+ \rightarrow CX_2NO^+ + OX$(X=H,D) as Used in RRKM Calculations

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| a) The reactant state | | | | | | | | | | |
| X=H | 3080 | 3080 | 2960 | 1650 | 1560 | 1480 | 1330 | 1060 | 1060 | 840 |
| | 660 | 520 | 380 | 370 | 200 | | | | | |
| X=D | 2300 | 2290 | 2140 | 1640 | 1440 | 1140 | 1060 | 830 | 830 | 780 |
| | 560 | 410 | 360 | 350 | 150 | | | | | |
| b) The transition state | | | | | | | | | | |
| X=H | 3470 | 3080 | 2980 | 1720 | 1330 | 1130 | 1090 | 850 | 820 | 660 |
| | 520 | 430 | 370 | 190 | 2450$i$ | | | | | |
| X=D | 2600 | 2290 | 2150 | 1720 | 1310 | 960 | 870 | 750 | 600 | 590 |
| | 430 | 380 | 360 | 140 | 1770$i$ | | | | | |

thus, it leads to $k_H/k_D \approx 100$. This is in fair agreement with the experimental isotope effect.

Finally, tunneling correction explains the large isotope effect for the hydroxyl-radical loss, assuming that the reaction involves rate-determining isomerization to the *aci*-nitromethane ion prior to dissociation. It is not unusual that an OH or $H_2O$ loss from oxygen containing ions shows intense metastable peaks in the mass spectra in spite of a small activation energy; examples include the $H_2O$ loss from ionized ethyl acetate23) and the $CH_2OH$ loss from ionized methyl acetate.24) The reactions involving hydrogen-atom migration generally indicates a complex mechanism in the isomerization/dissociation paths.

## References

1) S. Meyerson and E. K. Fields, *Org. Mass Spectrom.*, **9**, 485 (1974).

2) Y. Niwa, S. Tajima, and T. Tsuchiya, *Int. J. Mass Spectrom. Ion Phys.*, **40**, 287 (1981).

3) J. P. Gilman, T. Hsieh, and G. G. Meisels, *J. Chem. Phys.*, **78**, 1174 (1983).

4) J. P. Gilman, T. Hsieh, and G. G. Meisels, *J. Chem. Phys.*, **78**, 3767 (1983); G. G. Meisels, T. Hsieh, and J. P. Gilman, *J. Chem. Phys.*, **73**, 4126 (1980).

5) I. K. Ogden, H. Shaw, C. J. Danby, and I. Powis, *Int. J. Mass Spectrom. Ion Phys.*, **54**, 41 (1983).

6) H. Egsgaard, L. Carlsen, and S. Elbel, *Ber. Bunsenges. Phys. Chem.*, **90**, 369 (1986).

7) C. Lifshitz, M. Rejwan, I. Levin, and T. Peres, *Int. J. Mass Spectrom. Ion Processes*, **84**, 271 (1988).

8) E. E. Ferguson, *Chem. Phys. Lett.*, **138**, 450 (1987).

9) H. Egsgaard and L. Carlsen, *Chem. Phys. Lett.*, **147**, 30 (1988).

10) M. P. Irion, A. Selinger, A. W. Castleman, Jr., E. E. Ferguson, and K. G. Weil, *Chem. Phys. Lett.*, **147**, 33 (1988).

11) J.-D. Shao, T. Baer, J. C. Morrow, and M. L. F.-Monterio, *J. Chem. Phys.*, **87**, 5242 (1987).

12) A. A. Herod and A. G. Harrison, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 415 (1970).

13) A frequency program in BEVOBIV-IV was used for the frequency calculations. L. B. Sims, G. W. Burton, and D. F. Lewis, BEVOBIV-IV, Quantum Chemistry Program exchange No. 337 (1977); C. W. Burton, L. B. Sims, J. C. Wilson, and A. Fry, *J. Am. Chem. Soc.*, **99**, 3371 (1977).

14) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, London (1972).

15) J. H. D. Eland, J. Berkowitz, H. Schulte, and R. Frey, *Int. J. Mass Spectrom. Ion Phys.*, **28**, 297 (1978).

16) H. M. Rosenstock, R. Stockbauer, and A. C. Parr, *J. Chim. Phys.*, **77**, 745 (1980).

17) T. Baer and J. R. Hass, *J. Phys. Chem.*, **90**, 451 (1986).

18) W. H. Miller, *J. Am. Chem. Soc.*, **101**, 6810 (1979).

19) Y. Osamura, H. F. Shaefer, S. K. Gray, and W. H. Miller, *J. Am. Chem. Soc.*, **103**, 1904 (1981).

20) A. J. Illies, M. F. Jarrold, and M. T. Bowers, *J. Am. Chem. Soc.*, **104**, 3587 (1982).

21) J. H. Beynon, A. E. Fontaine, and G. R. Lester, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 1 (1968).

22) C. Lifshitz, S. Gefen, and R. Arakawa, *J. Phys. Chem.*, **88**, 4242 (1984).

23) R. Arakawa, *Bull. Chem. Soc. Jpn.*, **61**, 569 (1988).

24) N. Heinrich, J. Schmidt, H. Schwarz, and Y. Apeloig, *J. Am. Chem. Soc.*, **109**, 1317 (1987); R. Arakawa, *Bull. Chem. Soc. Jpn.*, **61**, 3425 (1988).