

Direct Experimental Observations of Metastability in the (Dideuterio) Methyloxonium Radical

Asit B. Raksit and Richard F. Porter*

Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14853, U.S.A.

We report the first experimental evidence for metastability in the methyloxonium radical when the oxygen is bound to two deuterium atoms; optimal conditions for generating the radical by neutralized ion beam techniques are described.

With the development of neutralized ion beam techniques¹ many hypervalent radicals generally thought to be inaccessible experimentally can now be observed directly. In this communication we report the first experimental evidence for metastability in the methyloxonium radical when the oxygen atom is bound to two deuterium atoms. In our experiment² a fast beam (6 keV) of methyloxonium ions is neutralized by electron transfer from sodium or potassium vapour. The resulting neutral beam with dissociation fragments is then analysed by observation of its charge-stripped mass spectra and its expanded width due to dissociative scattering (beam profile). Primary ions were generated by chemical ionization of gas mixtures containing 5% of methanol in a series of carrier gases (N₂, CD₄, Ar, or D₂).

In Figure 1 we show mass spectra of products obtained when a series of isotopically substituted methyloxonium ions was neutralized by charge transfer from potassium atoms. A parent peak on reionization was observed only when CD₃OD₂⁺ or CH₃OD₂⁺ was the initial precursor ion but neither of these was observed when sodium was used for electron donor. The remaining spectral features which were observed with either K or Na as electron donor can be

attributed to radical decomposition products, CH₃OH + H and CH₃ + H₂O and their collisionally ionized fragments.

The abundance of CD₃OD₂ relative to CD₃OD increased sharply as the ion source pressure was increased (Figure 2). This effect may be explained by the necessity of reducing the precursor ion's internal energy by collisional relaxation prior to neutralization. Nitrogen was found to be a more effective quencher than CD₄ for this purpose. The dissociation products of CD₃OD₂ were the only molecular species observed at our highest source pressures when Ar or D₂ was used as carrier gas.

Neutral beam scattering profiles for CD₃OD₂ (Figure 3) show composite behaviour further indicating competing dissociative processes. By applying the appropriate kinematic relationships¹ we obtain a reasonable energy analysis by attributing the inner scattering edge (θ_1) to CD₃OD and the outer edge (θ_2) to CD₃.[†] This analysis indicates that CD₃OD₂

[†] D atoms which scatter to large laboratory angles and carry only a small fraction of the initial beam energy are not detected. Owing to its lower mass CD₃ scatters farther than D₂O.

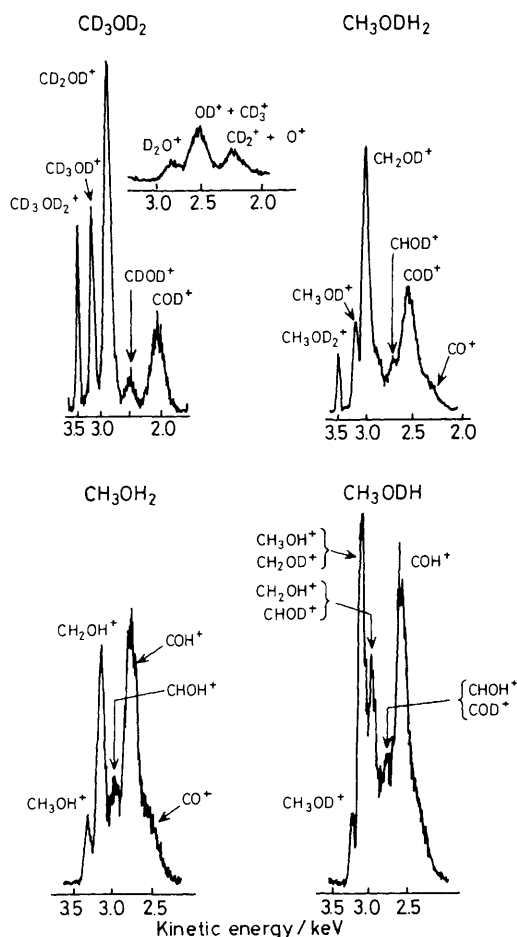


Figure 1. Mass spectra of reionized neutrals following electron transfer from K atoms to isotopically labeled methyloxonium ions. Initial ion energy 6 keV, reionization chamber at -2.5 keV; parent ions appear at 3.5 keV. For CD_3OD_2 the lower mass range (insert) was obtained with the reionization chamber at earth potential. Charge stripping gas, NO_2 . The leading peaks following the parent ions are due to methanol and its ion fragments.

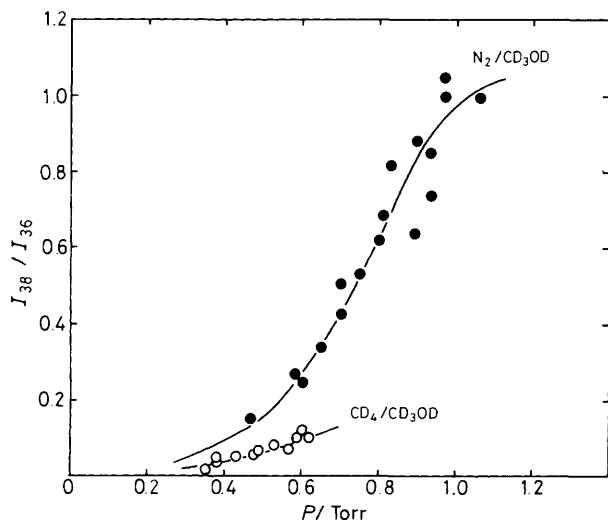


Figure 2. Effect of ion source pressure on the relative abundance of CD_3OD_2 as monitored by the intensity ratio of CD_3OD_2^+ to CD_3OD^+ for two source gases containing CD_3OD .

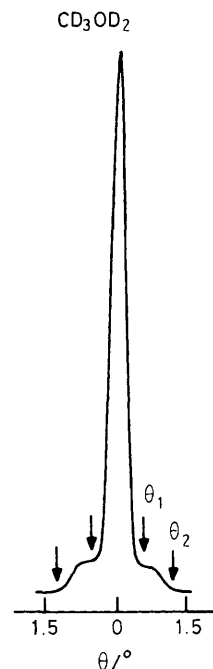


Figure 3. Neutral beam scattering profiles for CD_3OD_2 showing two dissociative processes with maximum scattering angles at θ_1 and θ_2 .

fragments exothermally to $\text{CD}_3\text{OD} + \text{D}$ and to $\text{CD}_3 + \text{D}_2\text{O}$ by 0.6 ± 0.2 and 1.7 ± 0.1 eV, respectively.

In our apparatus a CD_3OD_2 molecule travels about 10 cm from its point of formation to its point of reionization. This places a lower limit of $0.4 \mu\text{s}$ on its dissociative lifetime. The metastable species is most probably in its ground electronic state since excited Rydberg levels which can decay by radiative or predissociative processes are not expected to survive for a period greater than 10^{-7} s, the minimum time scale for observation in our experiment. Our results indicate that, although the radical is thermodynamically unstable, it is formed on a potential surface with a small potential barrier that is more readily penetrated by H atoms than D atoms. A shallow minimum on the ground potential surface of H_3O has been calculated theoretically³ but only the fully deuterated species has been observed as a metastable species.⁵ Since metastable CD_3OD_2 is formed more efficiently by electron transfer from K than from Na, energy resonance considerations suggest that its ionization potential is closer to that of K (4.3 eV) than to that of Na (5.1 eV). Our results further indicate that the barriers for the association reactions to form CD_3OD_2 from $\text{CD}_3\text{OD} + \text{D}$ or from $\text{CD}_3 + \text{D}_2\text{O}$ are too high to expect that the radical could be isolated from these reactions in a low temperature matrix.

We are grateful to the National Science Foundation for support through the Materials Science Center at Cornell University and a grant.

Received, 12th August 1986; Com. 1153

References

- 1 G. I. Gellene and R. F. Porter, *Acc. Chem. Res.*, 1983, **16**, 200.
- 2 G. I. Gellene and R. F. Porter, *Int. J. Mass Spectrom. Ion Proc.*, 1985, **64**, 55.
- 3 K. S. E. Niblaeus, B. O. Roos, and P. E. M. Siegbahn, *Chem. Phys.*, 1977, **25**, 207, and references therein.
- 4 G. I. Gellene and R. F. Porter, *J. Chem. Phys.*, 1984, **81**, 5570.