actual reactive species. The conclusion was also supported by the reaction of **1** with *p*-methoxybenzoyl chloride, which resulted in the formation of 4-methyl-4′-methoxybenzophenone (52% yield).[14] These features of **1** will offer some interesting possibilities for further manipulation of 12-Sb-6 "ate" complexes,

(14) The reaction of 0.7 equiv of *p*-tolyllithium with *p*-methoxybenzoyl chloride did not give the ketone but instead yielded (4-methoxyphenyl) bis-(4-methylphenyl)carbinol (68%).

(15) Partial support of this research is acknowledged for a Grant-in-Aid for Special Project Research (No. 61225019) by the Ministry of Education, Science, and Culture of the Japanese Government.

Bimolecular Reactions of Doubly Charged Metal Ions in the Gas Phase. Formation of NbCH2^2+

Steven W. Buckner and Ben S. Freiser*

*Department of Chemistry, Purdue University
West Lafayette, Indiana 47907*

Received September 22, 1986

There has been much interest in the reactivity of gas-phase metal ions with small organic molecules as seen in the extensive literature relating to this topic.[1] This interest has, until now, exclusively involved singly charged metal ions. This trend is similar to that seen for gas-phase organic ions where there is a far greater amount of literature related to singly charged ions.[2,3]

Multiply charged metal ions have not received much attention due in part to the belief that rapid charge exchange would occur exclusively. This has, in fact, been observed for multiply charged, later transition metals.[4] In a very interesting recent paper, however, Tonkyn and Weisshaar[5] have observed clustering reactions of Ti^{2+} with methane and hydride abstraction from ethane in a flowing afterglow. This prompted us to look at some bimolecular reactions of multiply charged early transition metals with various organic molecules under low-pressure conditions in a Fourier transform mass spectrometer (FTMS). The early transition metals have relatively low second ionization potentials.

All experiments were performed on a prototype Nicolet FTMS-1000 equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. Laser desorption[6] was used to generate Nb^{2+} from a Nb target. Nb^+ was also generated in varying amounts relative to Nb^{2+} depending on experimental conditions, but it could be cleanly ejected from the cell eliminating any interference.[7] A typical reaction sequence is shown in Figure 1. A Bayard–Alpert ionization gauge was used to monitor the pressure and was calibrated for the kinetics experiments using reaction 1 with a rate constant of 1.14×10^{-9} cm^3/molecule s.[8]

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3^• \qquad (1)$$
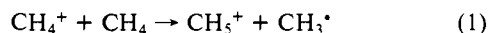
Multiply charged metal ions produced by laser desorption can have considerable excess electronic and kinetic energy.[4,9,10] In order to minimize these effects, the Nb^{2+} was trapped for 500 ms in the presence of $\sim 6 \times 10^{-7}$ torr of reagent and enough Ar to

(1) For a review of gas-phase metal ion chemistry, see: Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1986; Vol. 34, p 628.

(2) Cooks, R. G. *Collision Spectroscopy*; Plenum: New York, 1978.

(3) Koch, W.; Maquin, F.; Stahl, D.; Schwarz, H. *Chimia* **1985**, *33*, 376.

(4) Wise, M. B. Ph.D. Thesis, Purdue University, 1984.

(5) Tonkyn, R.; Weisshaar, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7128.

(6) Cody, R. B.; Burnier, R. C.; Reents, W. D., Jr.; Carlin, T. J.; McCrery, D. A.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 37.

(7) Comisarow, M. B.; Parisod, G.; Grassi, V. *Chem. Phys. Lett.* **1978**, *57*, 413.

(8) Huntress, W. T.; Laudenslager, J. B.; Pinizzotto, R. F. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *13*, 331.

(9) Cassady, C. J. Ph.D. Thesis, Purdue University, 1984.

(10) Kang, H.; Beauchamp, J. L. *J. Phys. Chem.* **1985**, *89*, 3364.

Figure 1. (A) Laser ionization of Nb foil; (B) isolation of Nb^{2+}; (C) reaction of Nb^{2+} with CH_4; (D) isolation of $NbCH_2^{2+}$.

bring the total pressure to $\sim 1 \times 10^{-5}$ torr, after which the doubly charged ions were reisolated and permitted to react.[11] Observation of a simple first-order reaction decay of Nb^{2+} for at least two half-lives suggested a predominantly ground-state population. The presence of nonthermal ions, however, cannot be completely ruled out.

Nb^{2+} (2nd IP(Nb) = 14.3 eV)[12] is observed to react via many other routes besides charge exchange, as in reactions 2 and 3 with methane (IP = 12.6 eV) (see Figure 1C). Observation of $NbCH_2^{2+}$ from methane implies $D^0(Nb^{2+}-CH_2) > 112$ kcal/mol.[13]

$$Nb^{2+} + CH_4 \xrightarrow{52\%} NbCH_2^{2+} + H_2 \qquad (2)$$

$$\xrightarrow{7\%} NbH^+ + CH_3^+ \qquad (3)$$

$$\xrightarrow{41\%} Nb^+ + CH_4^+ \qquad (4)$$
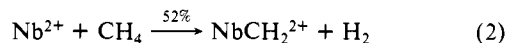
The overall reaction rate constant for reactions 2–4 is (0.95 ± 0.19) × 10^{-9} cm^3/molecule s, giving a calculated reaction efficiency of ~ 0.47.[14] This reaction is more than 2 orders of magnitude faster than the reaction of Nb^+ with methane, reaction 5, which occurs with a rate constant of (0.9 ± 0.2) × 10^{-11}

$$Nb^+ + CH_4 \rightarrow NbCH_2^+ + H_2 \qquad (5)$$
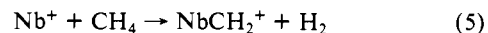
cm^3/molecule s, which gives a calculated reaction efficiency of ~ 0.008. Reaction 5 is believed to be slightly endothermic on the basis of the slow reaction rate and from photodissociation experiments.[15] The fast rate for reaction 2, however, indicates that the thermodynamic limit of $D^0(Nb^{2+}-CH_2) > 112$ kcal/mol is

(11) Ahmed, M. S.; Dunbar, R. C. *Collisional Quenching of Photo-Excited Bromobenzene Ions*; presented at the 34th Annual Conference on Mass Spectrometry and Allied Topics, Cincinnati, OH, June 8–13, 1986.

(12) 2nd IP(Nb) from: Moore, C. E. *Atomic Energy Levels as Derived From Analysis of Optical Spectra*; Office of Standard Reference Data, National Bureau of Standards: Washington, DC, 1952; Vol. 2.

(13) Supplementary thermochemical information taken from: Rosenstock, H. M.; Draxl, D.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1* **1977**, *6*.

(14) The reaction efficiency is given by $k_{obsd}/k_{Langevin}$ as in: Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1, pp 83–118.

(15) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

valid, The efficiency for reaction 2 is almost 3 times greater than the efficiency reported in the flowing afterglow studies for reaction of Ti^{2+} with methane.[5]

Reactions of $NbCH_2^{2+}$ showed this species to be a powerful proton donor. Proton-transfer experiments indicate $PA(CH_4) = 132$ kcal/mol $< PA(NbCH^+) < 142$ kcal/mol $= PA(CO)$,[16] yielding $PA(NbCH^+) = 137 \pm 7$ kcal/mol. Charge-exchange reactions indicate $IP(C_2H_4) = 10.5$ eV $<$ 2nd $IP(NbCH_2) < 10.6$ eV $= IP(i\text{-}C_4H_{10})$, yielding 2nd $IP(NbCH_2) = 10.55 \pm 0.05$ eV compared to 2nd $IP(Nb) = 14.3$ eV, These results, together with $\Delta H_f(NbCH^+) = 328 \pm 8$ kcal/mol and $\Delta H_f(NbCH_2^+) = 316 \pm 7$ kcal/mol reported earlier,[15] yield values of $\Delta H_f(NbCH_2^{2+}) = 556 \pm 11$ kcal/mol from the proton affinity experiment and $\Delta H_f(NbCH_2^{2+}) = 559 \pm 7$ kcal/mol from the charge-exchange experiment. Thus, we assign a value of $\Delta H_f(NbCH_2^{2+}) = 558 \pm 10$ kcal/mol, from which the values of $D^0(Nb^{2+}\text{–}CH_2) = 197 \pm 10$ kcal/mol and $D^0(Nb^+\text{–}CH_2^+) = 107 \pm 10$ kcal/mol are derived. For comparison, $D^0(Nb^+\text{–}CH_2) = 109 \pm 7$ kcal/mol has recently been reported.[15]

The novel reactivity of multiply charged early transition metals is now under continued investigation in our laboratory. We hope these ions can be compared to the higher oxidation state species which are observed in solution,

(16) Proton affinity values taken from: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

Preparation and Conformation of (E,E)-1,5-Cyclooctadiene[†]

Dieter Boeckh, Rolf Huisgen,* and Heinrich Nöth*

Institute für Organische and Anorganische Chemie der Universität, D-8000 München 2, FRG

Received June 27, 1986

Irradiation of CuCl-complexed (Z,Z)-1,5-cyclooctadiene and Hofmann elimination of 1,5-bis(trimethylammonio)cyclooctane diiodide furnished 1% and 2.4% of (E,E)-1,5-cyclooctadiene (1) in isomer mixtures;[1] oxidation of isolated 1 gave succinic acid. The constraint of the double bonds in 1 does not allow interconversion of the rac and meso conformations, 1a and 1b. The

1a   1b   2
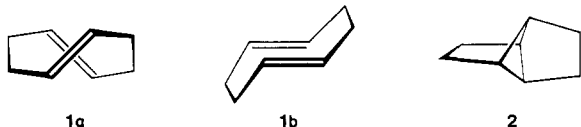
ingenious tentative assignment of 1a (δ_H 2.43, 4,88 in 2:1 ratio) by Whitesides, Goe, and Cope[1] rested on the photocyclization to 2. Force field calculations favored the twist form 1a over the chair 1b by 5.35 (MM1)[2] or 7.36 kcal mol^{-1} (Ermer–Lifson).[3a] We report a method which makes the elusive 1 available gramwise and present conclusive evidence for the twist conformation 1a.

[†] Dedicated to Professor Arthur Lüttringhaus on the occasion of his 80th birthday.
(1) Whitesides, G. M.; Goe, G. L.; Cope, A. C. *J. Am. Chem. Soc.* **1969**, *91*, 2608.
(2) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734.
(3) Ermer, O. *Aspekte von Kraftfeldrechnungen*; W. Bauer: München, 1981; (a) p 173, (b) p 127–135.

Combinations of trans addition and cis elimination have been employed to convert cis-cyclooctene into the strained trans isomer.[4] Peracid oxidation of (Z,Z)-1,5-cyclooctadiene resulted in the pure cis-diepoxide 3,[5] An attempt to convert 3 into 1 had failed.[4b]

We adapted the procedure of Bridges and Whitham[4d] and reacted 3 with 2.1 equiv of lithium diphenylphosphide in THF at 0 °C and, subsequently, with 10% H_2O_2 and acetic acid. The dihydroxy bis(diphenylphosphine oxides) 4 and 5 (78%, 77:23) were separated. The ^{13}C NMR spectra of rac 4, mp 220–222 °C,[6] and meso 5, mp 241–242 °C, confirm the C_2 or C_s symmetry; the J values suggest the assignment but are not convincing,

3   4   R = H   5
6a   R = (-)-menthoxyacetyl   7
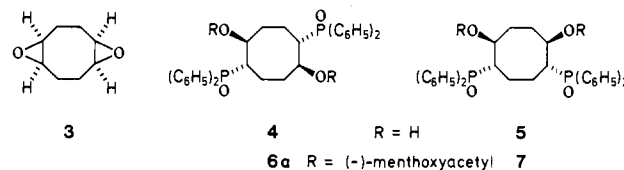
Two diastereoisomeric bis esters, 6a and 6b (only 6a illustrated), both with C_2 symmetry, are the expected products from rac 4 and 2 mol of (−)-menthoxyacetyl chloride, whereas 5 should provide one bis ester, 7, lacking symmetry. However, 6a and 6b formed 1:1 mixed crystals, mp 226–227 °C, thus thwarting the distinction from 7, mp 220–221 °C, by counting ^{13}C signals. Fortunately, HPLC[7] separated the 1:1 mixture, 6a and 6b, whereas 7 moved as a single zone.

In the base-induced cis elimination of diphenylphosphinate, rac 4 is predestined to produce the twist conformation 1a, and meso 5 is the logical precursor of 1b. Treatment of 4 with NaH in DMF at 20 °C, hydrolysis at 0 °C, and extraction with pentane furnished a solution of 35–41% of 1, *free of isomers* (GC analysis);[8] no volatile olefin emerged from 5 under the same conditions, sparing us the laborious separation of 4 and 5. We obtained 17–21% of 1 from the mixture on a 40–80-mmol scale. Its distillation as a colorless liquid is accompanied by much polymerization. The pentane solution of 1 keeps well at −78 °C and its transfer to other solvents is achieved via aqueous 0.5 M $AgNO_3$ and extraction after adding KCN at 0 °C.

Beyond the genetic relation 4 → 1a, we searched for direct evidence for the conformation of 1. According to inspection of models the "jump rope rotation"[9] should be even more barred for 1a than for (E)-cyclooctene; optical resolution would rule out 1b. We considered another approach: Cycloaddition of 2 mol of a chiral 1,3-dipole should convert rac 1a into two pairs of regioisomeric diastereomers, i.e., four bis adducts with C_2 axis each. Two regioisomeric bis adducts without symmetry are anticipated from the chair form 1b. After reaction of 1 with the azide (R)-8 as well as with the nitrile oxide (R)-9, two sharp-melting bis

8   9   10
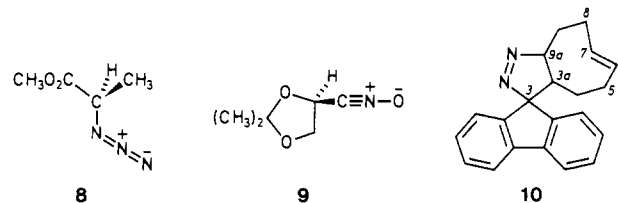
(4) (a) Corey, E. J.; Carey, F. A.; Winter R. A. E. *J. Am. Chem. Soc.* **1965**, *97*, 934. (b) Vedejs, E.; Snoble, K. A.; Fuchs, P. L. *J. Org. Chem.* **1973**, *38*, 1178. (c) Hines, J. N.; Peagram, M. J.; Thomas, E. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2332. (d) Bridges, A. J.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1974**, 142.
(5) Cope, A. C.; Fisher, B. S.; Funke, W.; McIntosh, J. M.; McKervey, M. A. *J. Org. Chem.* **1969**, *34*, 2231.
(6) Satisfactory elemental analysis and spectra were obtained for all new compounds.
(7) Silica gel, C_{18} reversed phase (Zorbax ODS of Du Pont, 25-cm analytical column), THF/H_2O 60:40, 150 bar, flow 1.2 mL/min, retention times 14.7 and 15.5 min.
(8) Packed column, 1 m, with OV17-Silicon on Varioport at 40 °C, injector 80 °C, 2 bar of He, flow 24 mL/min; retention times (min): toluene (weighed standard) 4.3, 1a 11.1. The calibration factor of (Z,Z)-cyclooctadiene/toluene was set equal with that of 1a/toluene.
(9) Marshall, J. R.; Konicek, T. R.; Flynn, K. E. *J. Am. Chem. Soc.* **1980**, *102*, 3287.