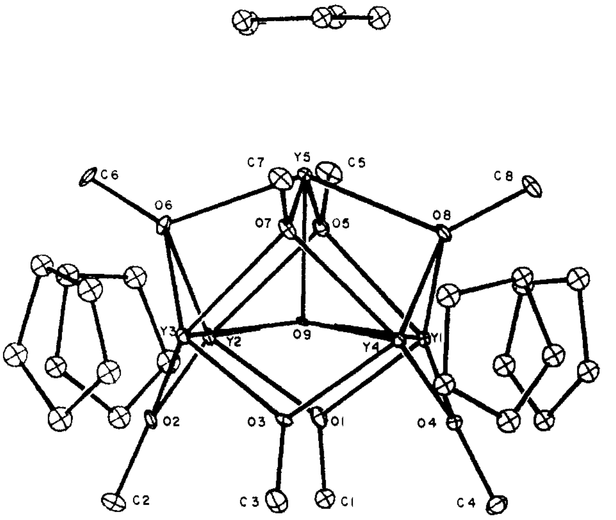

Figure 1. ORTEP drawing of the molecular structure of $(C_5H_5)_5Y_5(\mu\text{-}OCH_3)_4(\mu_3\text{-}OCH_3)_4(\mu_5\text{-}O)$. The probability ellipsoids have been reduced to 5% for clarity.

methoxide group. An oxide ligand is in the interior of the structure. Each metal interacts with five oxygen atoms and one cyclopentadienyl group for a formal coordination number of eight.

The structure is very regular. The four basal yttrium atoms are coplanar to within 0.006 Å. The four oxygen atoms associated with the μ_3-OCH_3 groups and the four oxygen atoms of the μ-OCH_3 ligands also form planes with coplanarity within 0.006 and 0.018 Å, respectively. These three planes are parallel as evidenced by the fact that the vector between the apical yttrium and the oxide ligand is perpendicular to each plane to within 0.9°. The oxide ligand in **2** is located 0.258 Å from the plane of the four basal yttrium atoms in the direction of the apical yttrium.

The Y-O distances in this pentametallic species can be compared with the 2.275 (3) and 2.290 (3) Å Y-O lengths in $[(C_5H_5)_2Y(\mu\text{-}OCH{=}CH_2)]_2$,[10] in which the yttrium atoms are also eight-coordinate. Also worth noting are distances of 2.299 (8) and 2.443 (8) Å in YVO_4[11] (eight-coordinate yttrium), 2.28 Å in Y_2O_3[12] (six-coordinate yttrium), and 2.305 Å in $UO_3 \cdot 3Y_2O_3$[13] (six-coordinate yttrium). The longest Y-O distances in **2** involve the connections of the basal yttrium atoms, Y(1)-Y(4), to the μ_3-OCH_3 groups with a range of 2.40 (2)-2.46 (2) Å (2.43 Å average). The μ_3-OCH_3 groups lie closer to apical yttrium atom, Y(5), with Y(5)-O lengths from 2.30 (2) to 2.35 (2) Å (2.33 Å average). As expected the doubly bridging distances are shorter: the eight Y(basal)-O(μ-OCH_3) distances average 2.22 Å with a 2.19 (2)-2.25 (2) Å range. The internal oxide is within 2.34 (2)-2.41 (2) Å of the basal yttrium vertices and is located 2.27 (2) Å from apical Y(5).[14]

The yttrium oxygen framework in complex **2** resembles a metal oxide lattice in which one metal vertex has been removed from the set of metals surrounding an oxide ion in an octahedral hole. As such, this soluble molecule may provide an interesting model for chemistry in a polymetallic oxide environment. From another point of view, this molecule can be compared to B_5H_9.[16] Both molecules have a square-pyramidal arrangement of trivalent element vertices with one terminal ligand each and both have four doubly bridging units around the base of the square. It remains to be determined if this is anything more than a structural coincidence.[17]

In any case, this molecule provides an interesting new example of inorganic self-assembly.[19] We find that this species appears in a variety of cyclopentadienyl yttrium alkoxide systems. The generality of such structures, the reactivity of this complex, and the origin of the oxide ligand are under investigation.

Acknowledgment. We thank the Division of Basic Energy Sciences of the Department of Energy for support of the research. We also thank the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E.).

Supplementary Material Available: Tables of crystal data, bond distances, angles, final fractional coordinates, and thermal parameters and a fully numbered ORTEP plot of **2** (8 pages); table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

---

(10) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291-1296.

(11) Baglio, J. A.; Gashurov, G. *Acta Crystallogr., Sect. B* **1968**, *B24*, 292-293.

(12) O'Connor, G. H.; Valentine, T. M. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2140-2144.

(13) Bartram, S. F. *Inorg. Chem.* **1966**, *5*, 749-754.

(14) The average Y-C(η^5) distance of 2.69 Å is within the range found for eight-coordinate yttrium organometallic species.[10,15]

(15) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291-1300.

(16) Lipscomb, W. N. *Boron Hydrides*; W. A. Benjamin: New York, 1963; and references therein.

(17) For example, is there an electronic correlation? If one ignores, for electron counting purposes, the exopolyhedral doubly bridging groups in **2** and B_5H_9, does the $(\mu_3\text{-}OR)_4O$ unit hold five $(C_5H_5Y)^{2+}$ units together in a manner analogous to the way in which the $2n + 4 = 14$ electrons hold five BH^{2+} units in a nido conformation?[18]

(18) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1-66. Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67-142.

(19) Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455-490. Ibers, J. A.; Holm, R. H. *Science (Washington, D.C.)* **1980**, *209*, 223-235.

Observation of "Intramolecular" Ion-Molecule Reactions within Ionized Hetero Clusters of Methyl Chloride-Acetone

James F. Garvey and Richard B. Bernstein*

Department of Chemistry and Biochemistry
University of California, Los Angeles, California 90024

Received April 10, 1986

Upon ionization,[1,2] large polyatomic molecules (such as halocarbons[3-5]) are usually excited and the ions undergo unimolecular decay. One might therefore expect a nascent cluster ion to fragment simply into a small ion and neutral molecular constituents, i.e., the "solvent" molecules. In contrast, as reported for methyl halide clusters,[6,7] extensive bond reformation (not merely "evaporation") can take place within the ionized clusters. This suggests that bimolecular (and possibly termolecular) reactions are occurring rapidly *within* a cluster ion. The major pathways observed can indeed be accounted for by known bimolecular ion-molecule reactions, previously studied by ICR[8-12] (and other methods).

Here we report the extension of our methyl halide cluster beam

---

(1) Mansell, P. I.; Danby, C. J.; Powis, I. *J. Chem. Soc. Faraday Trans.* **1981**, *77*, 1449.

(2) Baer, T.; DePristo, A. E.; Hermans, J. J. *J. Chem. Phys.* **1981**, *76*, 1449.

(3) Simm, I. G.; Danby, C. J. *J. Chem. Soc., Faraday Trans.* **1976**, *77*, 861.

(4) Powis, I.; Danby, C. J. *Chem. Phys. Lett.* **1979**, *65*, 390.

(5) Powis, I. *Mol. Phys.* **1980**, *34*, 311.

(6) Garvey, J. F.; Bernstein, R. B. *Chem. Phys. Lett.* **1986**, *126*, 394.

(7) Garvey, J. F.; Bernstein, R. B. *J. Phys. Chem.* **1986**, *90*, 3577.

(8) McAskill, N. A. *Aust. J. Chem.* **1970**, *23*, 2301.

(9) Herod, A. A.; Harrison, A. G.; McAskill, N. A. *Can. J. Chem.* **1971**, *49*, 2217.

(10) Beauchamp, J. L.; Holtz, D.; Woodgate, S. D.; Patt, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 2798.

(11) McMahon, T. B.; Blint, R. J.; Ridge, D. P.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 8934.

(12) Blint, R. J.; McMahon, T. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1269.

0002-7863/86/1508-6096$01.50/0

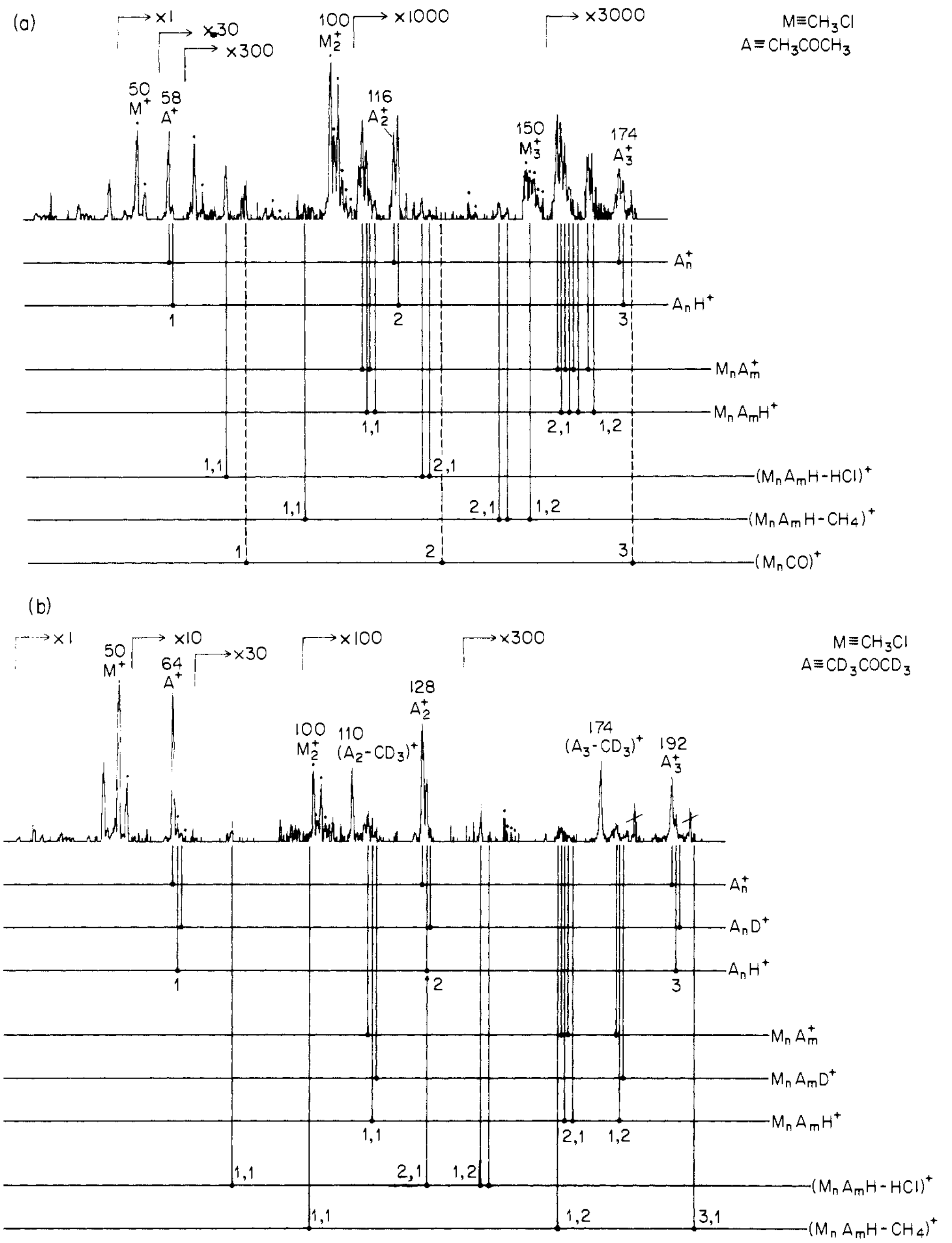

Figure 1. (a) Typical EI (70 eV) mass spectrum of a M_nA_m cluster beam (where M = CH_3Cl and A = CH_3COCH_3). Mass assignments and empirical formulas are indicated for each major ion peak. For isotopic peaks that appear together as a clump, only the most intense peak (i.e., for all-^{35}Cl isotopes) is identified. Peaks denoted by a dot are those that also appear in neat CH_3Cl expansions. The numbers n or n,m under the peaks identify the empirical formula of the ion. The first set indicates an acetone-based ion, the second set indicates hetero-cluster ions, and the third set refers to the ejection of a neutral molecule from a protonated hetero-cluster ion. Dashed lines indicate uncertain assignments. Relative sensitivity factors appear at the top of the figure. A slash mark through a peak denotes a known impurity. (b) Same as for (a), except here A = CD_3COCD_3.

Table I. Reaction Yield Ratios

n	(1) $[A_{n-1}H^+]/[A_{n-1}M^+]$	(4) $[A_{n-1}D^+]/[A_n^+]$
2	6.4	0.6
3	10.4	0.4

studies to the hetero clusters M_nA_m, where M = CH_3Cl and A = $(CH_3)_2CO$ or $(CD_3)_2CO$. From the mass spectral fragmentation patterns (Figure 1) we conclude that the most important intramolecular reaction (within the hetero-cluster cation) is the attack of an A^+ on a CH_3Cl "solvent" molecule to yield a protonated acetone cluster ion.

The apparatus has been described.[7] To generate molecular beams of heteroclusters, gaseous CH_3Cl (Matheson, >99%) at 3.7 atm is bubbled through liquid acetone (CH_3COCH_3, Mallinckrodt, >99%; CD_3COCD_3, Cambridge Isotope Labs, >99.8%). The mixed vapor is expanded through a 50-μm-diameter nozzle. The jet is skimmed and the resulting cluster beam passes through two differentially pumped chambers (total path ca. 1.3 m, $P \simeq 10^{-7}$ torr) before being ionized (70 eV electrons) and mass analyzed by a Dycor M200M quadrupole mass spectrometer.

Figure 1, parts a and b, shows typical mass spectra respectively for a hetero CH_3Cl-$(CH_3)_2CO$ and CH_3Cl-$(CD_3)_2CO$ cluster beam. Dots designate peaks previously observed[7] for neat CH_3Cl beams. We also observe the same peaks reported by Stace and Shukla[13] for ionized clusters of neat acetone, attributed to fragmentation as well as ion-molecule reactions occurring intracluster. Figure 2 summarizes our reaction scheme for the hetero clusters, which explains the origin of the several new heteroions observed.

---

[13] Stace, A. J.; Shukla, A. K. *J. Phys. Chem.* **1982**, *86*, 865.

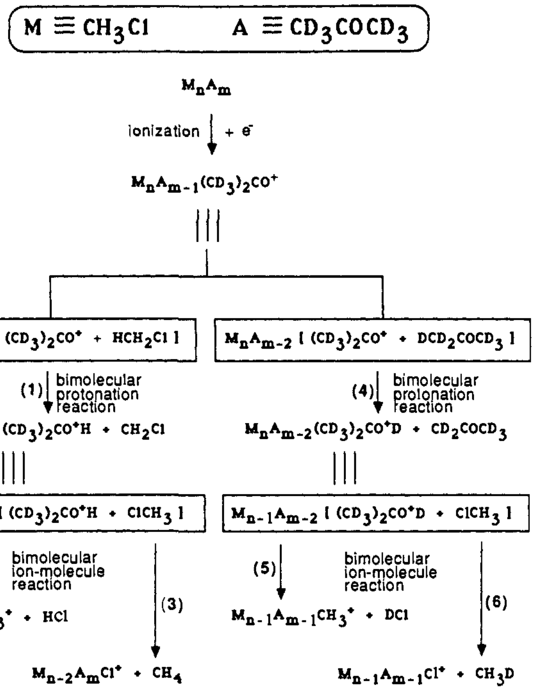

Figure 2. Overall reaction mechanism, accounting for all observed mass peaks of Figure 1b. Symbols ≡ and ||| denote equivalence of empirical formulas. Formulas in boxes serve as heuristic aids.

On the basis of the ionization potentials of the monomers (the IP of A being 1.7 eV less than that of M), we assume that it is an acetone molecule in the hetero cluster which is ionized (either directly or by very rapid intracluster charge transfer from an initially ionized CH$_3$Cl) and proceeds to react. Then there are two possible protonation reactions, (1) or (4) [either of which can be followed by further reactions,[14-19] i.e., (2) and (3) or (5) and (6)]. Which of these is the predominant protonation mechanism?

This question can be answered using hetero clusters of methyl chloride and perdeuterioacetone (Figure 1b). Defining a "reaction yield" as the ratio of the ion intensity of "product" peak to "reactant" peak,[20] we can compare processes 1 and 4, i.e., $MA_{n-1}^+ \rightarrow A_{n-1}H^+ + CH_2Cl$ with $A_n^+ \rightarrow A_{n-1}D^+ + CD_3COCD_2$ (see Table I).

We note that these reactions would yield identical ion products if CH$_3$COCH$_3$ were used, thus the utility of isotope labeling. The preferential protonation reaction is thus the attack of an acetone cation on a CH$_3$Cl solvent molecule within the cluster (preference enhanced with increasing cluster size[21]).

This propensity for H abstraction from CH$_3$Cl rather than acetone does not follow simply from the overall thermochemistry[18] but may be the result of the acetone dimer (trimer) ion being more stable than the corresponding hetero dimer (trimer) ion.

We have extended this work to other M$_n$A$_m$ systems (M = CH$_3$X with X ≡ F, Cl, and I and A = H$_2$O, CH$_3$OH, CH$_3$OCH$_3$, and CO), to be reported later.

Our observations of intramolecular ion-molecule reactions with neat[6,7] and hetero-cluster ions of increasing size have shown the profound effect that even a few solvent molecules have on the course of a reaction. Such intramolecular cluster ion reactions provide a bridge between bimolecular gas-phase reaction dynamics and solution kinetics.

Acknowledgment. This research has been supported by NSF Grant CHE83-16205, hereby gratefully acknowledged. We thank T. J. Curtiss, S. R. Gandhi, and Qixun Xu for assistance in the construction of the apparatus.

---

(14) As previously observed with neat CH$_3$Cl clusters,[7] the protonated cluster ion can undergo further rearrangement to eject HCl or CH$_4$. Such a fast, sequential ion-molecule reaction also occurs with the hetero clusters of methyl halides. In accord with ref 13, in our hetero system no ions are observed corresponding to the dehydration reaction $A_{m-1}H^+ \rightarrow A_{n-2}CH_3CCH_2^+ + H_2O$. Yet this ion product is prevalent in gas-phase ion-molecule reactions.[15] An explanation involving collisional deactivation of the excited precursor $A_{m-1}H^+$ has been proposed.[16]

(15) Munson, M. S. B. *J. Am. Chem. Soc.* **1965**, *87*, 5313.

(16) Sieck, I. W.; Ausloos, P. *Radiat. Res.* **1972**, *52*, 47.

(17) Luczynski, Z.; Wincel, H. *Int. J. Mass Spectrom.* **1972**, *56*, 3007.

(18) In the gas phase, the analogous processes are, respectively, acetone ion (A$^+$) attacking CH$_3$Cl (1) and A$^+$ attacking acetone, both yielding AH$^+$ (4). Reaction 1 is exothermic by ca. 2.8 kcal mol^{-1}, reaction 4 by ca. 5.4 kcal mol^{-1} (based upon tabulated proton affinities).[10,19] (However, their relative rates are not known.)

(19) Kebarle, P. *Annu. Rev. Phys. Chem.* **1976**, *28*, 445. See also: McMahon, T. B.; Kebarle, P. *J. Chem. Phys.* **1985**, *83*, 3919.

(20) Our work on CH$_3$F clusters[7] suggests that little or no "solvent evaporation" occurs for the cluster ions in the course of the protonation reaction. We assume this to be the case here also.

(21) Since the present data are limited to $m/z \leq 200$, Table I is limited to $n = 3$.

Electron-Transfer-Induced Dimerization of Spiro[2.4]heptadiene. A Facile Radical Cation Diels-Alder Reaction

Heinz D. Roth,* Marcia L. M. Schilling, and Christopher J. Abelt

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

Received May 27, 1986

The oxidative dimerization of diolefins resulting in cycloadducts of the [4 + 2] type (cation radical Diels-Alder reaction) has been the focus of much interest recently.[1-8] However, only limited experimental evidence is available concerning the key step of the dimerization, i.e., the addition of the radical cation to the parent olefin. Is this addition stepwise or concerted? Does the radical cation serve as the "diene" component ([3 + 2] cycloaddition) or as dienophile ([4 + 1] cycloaddition)? The observed retention of dienophile stereochemistry supports a concerted mechanism,[2] whereas the existence of a singly linked doubly allylic radical cation derived from *endo*-dicyclopentadiene[9] might be viewed as evidence for a stepwise mechanism. No experimental evidence differentiates the [3 + 2] from the [4 + 1] cycloaddition type, but orbital symmetry arguments favor the latter type.[4,5] In this paper we describe a system which provides evidence for a nonconcerted component in the cycloaddition/cycloreversion.

We have been interested in radical cations derived from cyclopropane derivatives.[10,11] The radical cation of spiro[2.4]heptadiene (M) appeared to be an interesting target. It can be generated as a short-lived intermediate by photoinduced electron transfer to strong electron acceptors.[9,11-15] During the elec-

---

(1) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718-720.

(2) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665-2667.

(3) Jones, C. R.; Allman, B. J.; Mooring, A.; Spahic, B. *J. Am. Chem. Soc.* **1983**, *105*, 652-654.

(4) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378-2382.

(5) Bellville, D. J.; Bauld, N. L.; Pabon, R.; Gardner, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 3584-3588.

(6) Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 6870-6871.

(7) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993-7994.

(8) Mlcoch, J.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 412-414.

(9) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 716-718.

(10) Haddon, R. C.; Roth, H. D. *Croat. Chim. Acta* **1984**, *57*, 1165-1176.

(11) Roth, H. D.; Schilling, M. L. M.; Schilling, F. C. *J. Am. Chem. Soc.* **1985**, *107*, 4152-4158.

(12) Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1079-1080.

0002-7863/86/1508-6098$01.50/0