The Journal of Physical Chemistry A

© Copyright 1999 by the American Chemical Society VOLUME 103, NUMBER 48, DECEMBER 2, 1999

LETTERS

Novel Rare Gas Ions BXe^+, BKr^+, and BAr^+ Formed in a Halogen/Rare Gas Exchange Reaction

Jere T. Koskinen and R. Graham Cooks*

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

Received: August 31, 1999; In Final Form: October 19, 1999

Singly charged rare gas borynium ions were prepared for the first time by making use of mass-selected ion/molecule reactions in a triple-quadrupole mass spectrometer. Halogen for rare-gas exchange reactions leading to the formation of the novel species BAr^+, BKr^+, and BXe^+ were carried out by allowing the radical cation $BBr^{+\bullet}$ to react with neutral rare gas atoms in the second quadrupole under conditions typically used for collision-induced dissociation (CID) in tandem mass spectrometry experiments. The ions formed contain the bonds B−Ar, B−Kr, and B−Xe, the lengths of which were calculated at the B3-LYP/LANL2DZ level of theory to be 2.590, 2.635, and 2.713 Å, respectively. Natural bond orbital (NBO) population analysis revealed that the bond order increases with increasing size of the rare gas atom: $Ar < Kr < Xe$. The reactions leading to the formation of the singly charged boron cations of Ar, Kr, and Xe are endothermic by 50.1, 45.8, and 38.7 kcal/mol, respectively. The energy required to drive these reactions is supplied by the collision energy. The BX^+ products formed are 7.2, 11.5, and 18.5 kcal/mol more stable than the separated B^+ ion and the neutral rare gas X atom (= Ar, Kr, Xe, respectively).

Introduction

Exciting chemistry of the rare gases has emerged since the discovery of the first such compound in 1962 by Bartlett,[1] which was reported to be $Xe^+[PtF6]^-$, but later shown to be a mixture of $XeF^+[PtF_6]^-$ and $XeF^+[Pt_2F_{11}]^-$.[2] Most known rare gas compounds contain either Xe−O or Xe−F bonds.[3] Examples of these include an unusually strong Xe−O bond in $XeNO_3^+$,[4] and Xe−F bond in XeF^+;[5] Xe−Cl, Xe−N, and Xe−C bonds are also known to exist, representative examples being $XeCl_2$,[6] $FXeN(SO_2F)_2$,[7] and $Xe(CF_3)_2$.[8] Turner and Pimentel reported a study on KrF_2, the first krypton compound in 1963,[9] while Kr−O[10] and Kr−N[11] bonds in neutral compounds have subsequently been found to exist. The first and, so far, only tentative example of the Xe−B bond was reported in $FXe{-}BF_2$ in 1979 by Goetschel and Loos.[12]

Recent additions to rare gas chemistry include such species as H−Xe−SH (the first reported Xe−S bond),[13] as well as the charge-transfer molecules H−Xe−Cl, H−Xe−Br, H−Xe−I, H−Kr−Cl, H−Xe−H, H−Xe−D, D−Xe−D, H−Xe−CN, H−Xe−NC, and H−Kr−CN,[14−17] the preparations of which made extensive use of the matrix isolation technique[18−20] and the synthetic utility of low-temperature solid Xe and Kr matrixes.[21] Typical classes of species formed by the rare gases are weakly bound van der Waals complexes[22,23] and clathrates.[24] For example, laser fluorescence spectroscopy has been used to study the excited states of the neutral van der Waals complexes BNe, BAr, and BKr.[25]

Studies on isolated ions have expanded the scope of rare gas chemistry. Protonated rare gases XH^+ are well-known.[26−28] The corresponding Rydberg molecules XH^*,[29] rare gas cluster ions X_n^+,[30] and other species such as F_3SiXe^+ [31] have been reported. Pyykkö predicted chemical bonds between Au^+ and the rare

---

* Author to whom correspondence should be addressed. Phone: 765-494-5263. Fax: 765-494-0239. E-mail: cooks@purdue.edu.

10.1021/jp993091z CCC: $18.00

gases, and the existence of the neutral analogues PdXe and PtXe.[32] The former prediction was confirmed by Schröder, Schwarz, and Pyykkö in 1998.[33] A recent zero energy kinetic energy (ZEKE) electron spectroscopy study on the anionic species $KrBr^-$, $XeBr^-$, and $KrCl^-$ reported accurate electron affinities for these systems.[34] Other ionic rare gas compounds studied include the cationic species BHe^{n+}, BNe^{n+} and BAr^{n+}.[35−38] Nevertheless, most studies on these systems have either been completely theoretical or have involved high-energy collisions,[39] high temperatures or high pressures, or other unusual systems such as cryogenic plasmas.

There are, however also results on rare gas ions in controlled experimental systems. Early studies on collisions of electronically excited neutral particles with atoms or molecules yielded, by Penning ionization, previously unknown ions such as $NeAr^+$, ArN_2^+, ArI^+, and CH_4Xe^+, $C_2H_2Hg^+$, and N_2Hg^+.[40−44] Herman and Cermák reported on reactions of mixtures of rare gases with alkali metal vapors occurring in the ionization chamber of a Nier type mass spectrometer as early as 1963.[44] They observed the following product ions: $HeLi^+$, NeK^+, $ArLi^+$, $ArNa^+$, ArK^+, $ArCs^+$, and $KrNa^+$. Other mass spectrometric studies on rare gas compounds include electron impact (EI) ionization of rare gas van der Waals molecules, such as Ar_2, Kr_2, ArKr, HeXe, NeXe, and ArXe,[45] the latter two of which yielded doubly charged diatomic molecules ($NeXe^{2+}$ and $ArXe^{2+}$). Similar studies on the rare gas excimers ArKr and NeXe have also been reported.[46] Recent studies include work from this laboratory on collisions of $Xe^{+\bullet}$ ions with fluorinated self-assembled monolayers, in which $XeCF_2^+$, $XeCF^+$, and XeF^+ are observed as products,[5,47] and a study by Schwarz and co-workers, in which they report on bonding in xenon halide species.[48]

Neutral compounds and ions derived from the rare gases are finding novel uses as, for example, propulsion media of rockets used in space research,[49] and it is clear that we are only beginning to discover the full potential of rare gas chemistry as a whole. New areas of application for rare gases may also include biological systems. For instance, the case of Xe is of special interest given its strong anesthetic and analgesic activity.[50−52]

Methods

Tandem Mass Spectrometry. BBr_3 (Aldrich Chemical, Milwaukee, WI) was introduced via a Granville-Phillips leak valve into the ionization source of a Finnigan TSQ 700 (Finnigan MAT, San Jose, CA) equipped with an ion volume for chemical ionization (CI). The reagent underwent self-CI at 2−3 mTorr pressure at 25−70 eV electron energy, and formed $BBr_3^{+\bullet}$, BBr_2^+, $BBr^{+\bullet}$, and B^+ ions. Each of these was mass selected in turn and allowed to react in turn with He (UN 1046, Airco, Murray Hill, NJ), Ne (Airco, Murray Hill, NJ), Ar (UN 1006, Airco, Murray Hill, NJ), Kr (grade 4.7-Research, UN 1056, Airco, Murray Hill, NJ), and Xe (grade 3.5, UN 2036, Airco, Murray Hill, NJ) neutral gases in the second quadrupole (Q2). The collision energies in Q2 were varied between 0 and 15 eV (laboratory frame of reference) in each experiment at nominal pressures corresponding to 15−85% attenuation of the primary ion beam as specified. The product ions formed in Q2 were mass analyzed by scanning Q3.

Quantum Chemical Calculations. The structures, total energies, and vibrational frequencies were calculated quantum chemically for the species BX^+ (X = He, Ne, Ar, Kr, and Xe) at the B3-LYP/LANL2DZ level, except for the lighter species containing B and He only, for which the calculations were done at the B3-LYP/6-311G(d,p) level. (The selected levels of theory are regarded as sufficient to give reasonable estimates for the structures and energies needed for this study.) The *Gaussian 94* (Revision B.1) software package[53] was used with the default settings as installed on a Cray C94 supercomputer (Center for Scientific Computing, Espoo, Finland). Natural population analysis (NPA) was performed to estimate bonding between the boron atom and each of the rare gases in the BX^+ species. To explore the energetics of the reaction leading to the formation of these novel species, the pertinent calculations were also performed for $Br^\bullet$, $BBr^{+\bullet}$, and B^+.

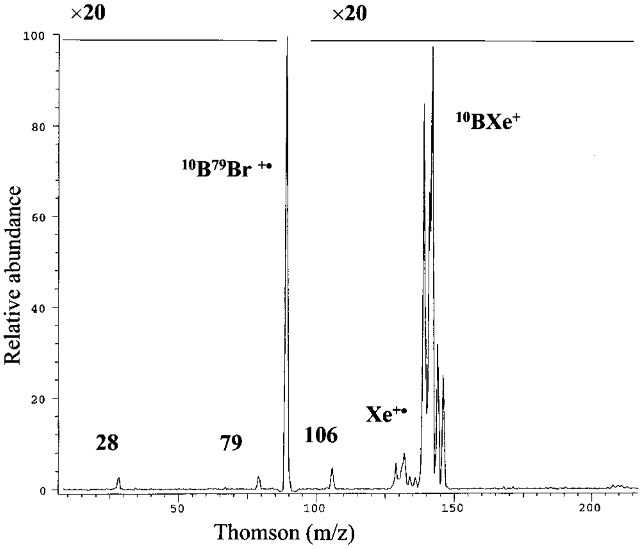

Figure 1. Product ion tandem mass spectrum indicating the formation of BXe^+ when $^{10}B^{79}Br^{+\bullet}$ ion (*m/z* 89) was mass selected in Q1 and allowed to react with Xe (approximately 15% attenuation of primary ion beam at 0.4 mTorr pressure) in Q2 at 4 eV collision energy (nominal laboratory frame energy). The ions between *m/z* 139 and 146 are various isotopomers of BXe^+. The ion at *m/z* 106 is most likely $BBr(OH)^+$ (small amounts of oxygen and water are dissolved into the liquid reagent BBr_3 from the atmosphere during sample preparation). The isotopomer corresponding to *m/z* 146 is produced in almost 5% relative abundance under the conditions used.

Results and Discussion

Tandem mass spectrometry (MS/MS) is a powerful tool in the study of gas-phase ion/molecule reactions,[54] one in which mass-selected ions are allowed to react with other species under carefully controlled conditions. In this study, $BBr_3^{+\bullet}$, BBr_2^+, $BBr^{+\bullet}$, and B^+ were mass selected and were allowed to react with neutral rare gas atoms. With He and Ne, respectively, no products other than those arising from collision-induced dissociation (CID) were observed. In contrast, Ar, Kr, and Xe yielded BX^+ (X = Ar, Kr, Xe) when $BBr^{+\bullet}$ was allowed to react with each of the neutral gases:

$$BBr^{+\bullet} + X \rightarrow Br^\bullet + BX^+ \qquad (1)$$

The identity of these ions was confirmed by the isotopic patterns of the rare gases exhibited by the product ions, and also by performing experiments in which $^{10}B^{79}Br^{+\bullet}$, $^{10}B^{81}Br^{+\bullet}$, $^{11}B^{79}Br^{+\bullet}$, and $^{11}B^{81}Br^{+\bullet}$ were mass selected in turn. Figures 1 and 2 show the mass spectra of the products formed in these halogen/rare gas exchange reactions for Xe and Ar, respectively. Similar results were observed for Kr. On the basis of these data, it is clear that novel products BXe^+, BKr^+, and BAr^+ were formed. $BBr_3^{+\bullet}$, BBr_2^+, and B^+ were not observed to react under the same conditions as $BBr^{+\bullet}$ to yield rare gas products except for the ions generated by simple charge exchange.

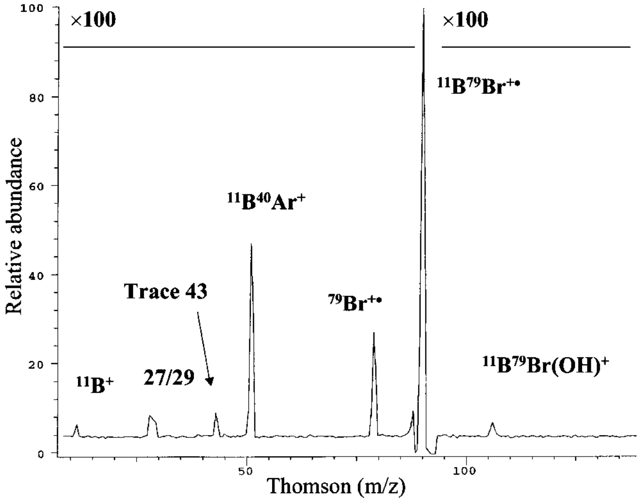

Figure 2. Product ion tandem mass spectrum indicating the formation of BAr^+. The mass selected ion $^{11}B^{79}Br^{+\bullet}$ yielded $^{11}B^{40}Ar^+$ upon reaction with Ar (approximately 85% attenuation at 0.95 mTorr) at 9 eV nominal collision energy.

TABLE 1: Results of Quantum Chemical Calculations: B3-LYP/LANL2DZ Structures, NBO Analysis, Reaction Enthalpies (Reaction 1)

	bond length B−X (Å)	Δ*H* (kcal/mol)
$BBr^{+\bullet}$	1.823	
He (basis set 6-311G(d,p))	2.636	79.8
Ne	2.451	54.9
Ar	2.590	50.1
Kr	2.635	45.8
Xe	2.713	38.7
$BrBXe^+$	1.848 (B−Br) 2.845 (B−Xe)	

NBO charges in BX^+	X	B
BHe^+	0.049 He $1s^{1.95}$	0.998 B [He] $2s^{2.00}$
BNe^+	0.029 Ne [He] $2s^{2.00}$ $2p^{5.97}$	0.971 B [He] $2s^{2.00}$ $2p^{0.03}$
BAr^+	0.103 Ar [Ne] $3s^{2.00}$ $3p^{3.98}$ $4p^{1.92}$	0.897 B [He] $2s^{2.00}$ $2p^{0.10}$
BKr^+	0.167 Kr [Ar] $4s^{2.00}$ $4p^{3.97}$ $5p^{1.87}$	0.833 B [He] $2s^{2.00}$ $2p^{0.17}$
BXe^+	0.272 Xe [Kr] $5s^{1.99}$ $5p^{5.74}$	0.728 B [He] $2s^{2.00}$ $2p^{0.27}$

The most favorable laboratory frame collision energy for the formation of BXe^+ was found to be approximately 4−7 eV, and those for BKr^+ and BAr^+ were 8−10 eV and 9−11 eV, respectively. These nominal collision energies reflect the endothermicities of the reactions (see Table 1). When higher pressures were used collisional relaxation was a likely process. However, even when the pressure was increased so that the main beam was attennuated by 85%, the yield of BAr^+ was an order of magnitude less than that of BXe^+. Typical yields of product ions, as judged simply from the product ion abundances, were 0.2%, 0.4%, and 10% of the mass selected $BBr^{+\bullet}$ reagent ion (base peak) for BAr^+, BKr^+, and BXe^+, respectively (see Figures 1 and 2). This trend reflects the increasing collision cross-sections down the group in the periodic table.

The calculated (B3-LYP) structures have bond lengths (see Table 1) that are shorter than the sums of the van der Waals radii[55] of the species in question. This implies bonding which is stronger than dispersive van der Waals bonding. Results of natural bond orbital (NBO) population analysis (Table 1) show that the bond in BXe^+ corresponds to the transfer of approximately 0.27 units of electron charge to boron. The reaction energetics calculated from the quantum chemical data show that for BX^+ the ionic species are 18.5 kcal/mol, 11.5 kcal/mol, 7.2, 3.6, and 0.4 kcal/mol more stable than the separated species B^+ and X for X = Xe, Kr, Ar, Ne, and He, respectively. On the other hand, the overall reaction 1 is always endothermic (38.7 kcal/mol, 45.8 kcal/mol, 50.1 kcal/mol for Xe, Kr, and Ar, respectively). The energy needed to drive the reactions is provided by the collision energy, hence the cross section displays the nonzero energy maximum already noted. The trend in endothermicity also conforms to the experimentally observed trend of product yield with increasing collision energies for BXe^+, BKr^+, and BAr^+.

The ground state of the assumed transition species in eq 1 $[X{-}B{-}Br]^{+\bullet}$ was calculated to be 50.1 kcal mol^{-1} lower in energy than the reagents and 15.4 kcal mol^{-1} lower than the products in the case of Xe. This is contrary to the experimental observation, according to which it is necessary to supply energy in Q2 to cause the reactions to take place. Consequently, these reactions must proceed via excited species although the states involved have not been identified. Interesting insights to the dynamics of heavy + light-heavy (HLH) atom transfer dynamics have been provided by the theoretical calculations of Amaee et al.[56] They found that reactant rotational energy promotes this type of reaction, and that the products are formed in highly excited rotational states. As can be seen from the NBO data on the atomic charges of the BX^+ species, these can be regarded as systems where the electron cloud of the rare gas atom solvates a B^+ ion. Thus, it is intuitively clear that the more polarizable this electron cloud, the more stable the BX^+ species formed.

In conclusion, BXe^+, BKr^+, and BAr^+ have been generated experimentally in stoichiometrically one-to-one halogen/rare gas atom transfer reactions and observed under carefully controlled experimental conditions for the first time. The reaction by which they are thought to form is endothermic, and the energy required to drive the reaction is supplied by the collision energy. This work provides direct experimental evidence of BAr^+, BKr^+, and BXe^+ produced in controlled mass-selected ion/molecule reactions with the neutral rare gas atoms, the reactivity and subsequent product yields of which correlate with increasing polarizability and size of the rare gas electron cloud (He < Ne < Ar < Kr < Xe).

Considering the widespread use of the rare gases as collision gases in MS/MS experiments[57] and other forms of mass and collisional spectroscopy, it is of interest to note that these neutral gases are quite capable of reacting under the conditions typically used.

Acknowledgment. This work was supported by the Foundation of Neste Corporation (Espoo, Finland) and the National Science Foundation (CHE9732670).

References and Notes

(1) Bartlett, N. *Proc. Chem. Soc.* **1962**, 218.
(2) Sladky, F. O.; Bulliner, P. A.; Bartlett, N. *J. Chem. Soc. A* **1969**, 2179.
(3) Malm, J. G.; Selig, H.; Jortner, J.; Rice, S. A. *Chem. Rev.* **1965**, *65*, 199.
(4) Bernardi, F.; Cacace, F.; de Petris, G.; Pepi, F.; Rossi, I. *J. Phys. Chem. A* **1998**, *102*, 5831.
(5) Feng, B.; Shen, J.; Grill, V.; Evans, C.; Cooks, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 8189.
(6) Nelson, L. Y.; Pimentel, G. C. *Inorg. Chem.* **1967**, *6*, 1758.
(7) LeBlond, R. D.; DesMarteau, D. D. *J. Chem. Soc. Chem. Commun.* **1974**, 555.
(8) Turbini, L. J.; Aikman, R. E.; Lagow, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5833.
(9) Turner, J. J.; Pimentel, G. C. *Science* **1963**, *140*, 975.

(10) Sanders, J. C. P.; Schrobilgen, G. J. *J. Chem. Soc. Chem. Commun.* **1989**, 1576.

(11) Schrobilgen, G. J. *J. Chem. Soc. Chem. Commun.* **1988**, 863.

(12) Goetschel, C. T.; Loos, K. R. *J. Am. Chem. Soc.* **1972**, *94*, 3018.

(13) Pettersson, M.; Lundell, J.; Khriachtchev, L.; Isoniemi, E.; Räsänen, M. *J. Am. Chem. Soc.* **1998**, *120*, 7979.

(14) Pettersson, M.; Lundell, J.; Räsänen, M. *J. Chem. Phys.* **1995**, *102*, 6423.

(15) Pettersson, M.; Lundell, J.; Räsänen, M. *J. Chem. Phys.* **1995**, *103*, 205.

(16) Pettersson, M.; Lundell, J.; Kriachtchev, L.; Räsänen, M. *J. Chem. Phys.* **1998**, *109*, 618.

(17) Pettersson, M.; Nieminen, J.; Khriachtchev, L.; Räsänen, M. *J. Chem. Phys.* **1997**, *107*, 8423.

(18) Whittle, E.; Dows, D. A. *J. Chem. Phys.* **1954**, *22*, 1943.

(19) Norman, I.; Porter, G. *Nature* **1954**, *174*, 508.

(20) Andrews, L.; Moskovits, M. *Chemistry and Physics of Matrix Isolated Species*; Elsevier: Amsterdam, 1989.

(21) Howard, W. F.; Andrews, L. *J. Am. Chem. Soc.* **1974**, *96*, 7864.

(22) Tao, F.-M.; Klemperer, W. *J. Chem. Phys.* **1994**, *101*, 1129.

(23) Williams, J.; Rohrbacher, A.; Djahandideh, D.; Janda, K.; Jamka, A.; Tao, F.-M.; Halberstadt, N. *Mol. Phys.* **1997**, *91*, 573.

(24) Greenwood, N. N.; Earnshaw, A. E. *Chemistry of the Elements*; Pergamon Press: Oxford, 1994; pp 1047−1048.

(25) Dagdigian, P. J.; Yang, X.; Hwang, E. *ACS Symp. Ser.* **1997**, *678 (Highly Excited Molecules)*, 122.

(26) Johns, J. W. C. *J. Mol. Spectrosc.* **1984**, *106*, 124.

(27) Ram, R. S.; Bernath, P. F.; Brault, J. W. *J. Mol. Spectrosc.* **1985**, *113*, 451.

(28) Rogers, S. A.; Brazier, C. R.; Bernath, P. F. *J. Chem. Phys.* **1987**, *87*, 159.

(29) Dabrowski, I.; Sadovskii, D. A. *J. Chem. Phys.* **1997**, *107*, 8874.

(30) Last, I.; George, T. F. *Cluster Ions*; Ng, C. Y., Baer, T., Powis, I., Eds.; Wiley: 1993.

(31) Cipollini, R.; Grandinetti, F. *J. Chem. Soc. Chem. Commun.* **1995**, 773.

(32) Pyykkö, P. *J. Am. Chem. Soc.* **1995**, *117*, 2067.

(33) Schröder, D.; Schwarz, H.; Pyykkö, P. *Inorg. Chem.* **1998**, *37*, 624.

(34) Yourshaw, I.; Lenzer, T.; Reiser, G,; Neumark, D. M. *J. Chem. Phys.* **1998**, *109*, 5247.

(35) Wong, M. W.; Radom, L. *J. Phys. Chem.* **1989**, *93*, 6303.

(36) Cai, X.; Meng, L.; Zheng, S. *Huaxue Wuli Xuebao* **1991**, *4*, 338.

(37) Wong, M. W.; Radom, L. *J. Phys. Chem.* **1990**, *94*, 638.

(38) Liebman, J. F.; Allen, L. C. *Inorg. Chem.* **1972**, *11*, 1143.

(39) Shimakura, N.; Suzuki, S.; Murakami, Y.; Gu, J. P.; Hirsch, G.; Buenker, R. J.; Kimura, M.; Shimamura, I. *Jpn. Phys. Scr.* **1996**, *T62*, 39.

(40) Fuchs, R.; Kaul, W. *Z. Naturforsch.* **1960**, *15a*, 108.

(41) Kaul, W.; Fuchs, R. *Z. Naturforsch.* **1960**, *15a*, 326.

(42) Henglein, A.; Muccini, G. A. *Angew. Chem.* **1960**, *72*, 630.

(43) Field, F. H.; Franklin, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 4509.

(44) Herman, Z.; Cermak, V. *Nature* **1963**, *199*, 588.

(45) Stephan, K.; Helm, H.; Maerck, T. D. *Contrib.−Symp. At. Surf. Phys.* **1980**, 123.

(46) Lipson, R. H.; Dimov, S. S.; Hu, X. K.; Mao, D. M. *Can. AIP Conf. Proc.* **1997**, *388 (Resonance Ionization Spectroscopy)*, 31.

(47) Riederer, D. E.; Miller, S. A., Jr.; Ast, T.; Cooks, R. G. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 938.

(48) Schröder, D.; Harvey, J. N.; Aschi, M.; Schwarz, H. *J. Chem. Phys.* **1998**, *108*, 8446.

(49) Jaroff, L. *Flying with Ion Power*, *Time* 1998; Vol. 152, p 52.

(50) Ferrari, A.; Erdmann, W.; Del Tacca, M.; Formichi, B.; Volta, C. A.; Bissolotti, G.; Giunta, F. *ACP-Appl. Cardiopul. P.* **1998**, *7*, 153.

(51) Miyazaki, Y.; Adachi, T.; Utsumi, J.; Shichino, T.; Segawa, H. *Anesth. Analg.* **1999**, *88*, 893.

(52) Hecker, K.; Reyle-Hahn, M.; Tenbrinck, R.; Beckers, S.; Rossaint, R. *Brit. J. Anaesth.* **1999**, *82*, A305.

(53) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R. ; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision B.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(54) Shukla, A. K.; Futrell, J. H. *Mass Spectrom. Rev.* **1993**, *12*, 211.

(55) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(56) Amaee, B.; Connor, J. N. L.; Whitehead, J. C. *Faraday Discuss. Chem. Soc.* **1987**, *84*, 387.

(57) Hayes, R. N.; Gross, M. L. *Methods in Enzymol., 193 (Mass Spectrom.)*; McCloskey, J. A., Ed.; Academic Press: San Diego, CA, 1990; Chapter 6.