Figure 2. Deuterium-decoupled 200-MHz proton spectra of (a) the *cis*-dideuterioethylene adduct and (b) the cis adduct to which a small amount of the trans adduct has been added.

couplings assigned for the benzonitrile oxide adduct with ethylene.[17] Figure 2a shows the relevant portion of the 200-MHz deuterium-decoupled proton spectrum of the adduct obtained from the reaction of *cis*-dideuterioethylene with *p*-nitrobenzonitrile oxide.

The small impurity peaks are due to the presence of the d_1 adduct, which was prepared from monodeuterioethylene for comparison, and not to the trans-d_2 adduct. The CH_2 resonances of the d_1 adduct appear downfield of CHD resonances of the d_2

adduct, a consequence of a normal upfield shift of proton resonances caused by a vicinal deuterium.[18] Mass spectrometry confirmed that this sample contained 9% d_1. Addition of some of the trans adduct to the cis compound produces the spectrum shown in Figure 2b. This spectrum shows that there is no detectable trans product in the cis adduct. We estimate that as little as 2%, perhaps even 1%, of the trans product could have been detected if it were present in the cis adduct.

These experiments establish that the reaction of **1** with **2** is ≥98% stereospecific. If a diradical intermediate were formed, the barrier to rotation about bond **a** would have to be at least 2.3 kcal/mol higher than the barrier to cyclization. Since the rotational barrier of bond **a** is most likely ≤0.4 kcal/mol, i.e., that expected for a normal primary radical, there can be no barrier to cyclization for the predominant cycloaddition pathway. The most reasonable mechanism for this 1,3-dipolar cycloaddition is the concerted one. Although we have found no evidence for a competing stepwise mechanism, our experiments do not exclude the possibility that a slower stepwise mechanism occurs at a rate that is more than 10 times slower that the rate of the concerted reaction.[19] While these results confirm the concerted mechanism for this 1,3-dipolar cycloaddition, calculations[5] indicate that the concerted transition state is asynchronous, with somewhat more CC than CO bonding in the single transition state separating reactants from products.[20]

(17) Sustmann, R.; Huisgen, R.; Huber, H., *Chem. Ber.* **1967**, *100*, 1802.

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(19) For example, if the stepwise reaction gave only 27% stereochemical crossover, then 2% of the trans adduct would be formed overall from the cis reactant if the concerted reaction were 13 times faster than the stepwise. Competing concerted and stepwise mechanisms have been postulated for various Diels-Alder reactions. See, for example: Bartlett, P. D.; Mallet, J. J.-B. *J. Am. Chem. Soc.* **1976**, *98*, 143 and references therein.

(20) This conclusion is consistent with Harcourt's valence-bond treatment of 1,3-dipolar cycloadditions. Harcourt suggested that the cyclo-diradical is actually the transition state for concerted cycloaddition: Harcourt, R. D.; Little, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 41 and references therein.

Ionic Multimers from Heterocyclic Compounds. Clusters or Polymers?

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Recently, we discovered that high-pressure ion/molecule reactions of cyclic oligomers of methylenenitramine ($-CH_2NNO_2-$) and formaldehyde ($-CH_2O-$) give rise to a series of ionic multimers, $[(CH_2NNO_2)_nH]^+$ and $[(CH_2O)_nH]^+$, which can be many times the molecular weight of the oligomeric unit. Our first published report on this subject[1] described ion abundance distributions of two series of ionic multimers $[(CH_2NNO_2)_nH]^+$ generated by ion/molecule reactions of two methylenenitramine oligomers, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), the cyclic trimer, where $n = 1$–15, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) the cyclic tetramer, where $n = 1$–56. Enhancements in the ion abundance distributions were observed at n values corresponding to integral molecular units, but some intermediate enhancements also were observed for the HMX

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(1) Campana, J. E.; Doyle, R. J., Jr. *J. Chem. Soc., Chem. Commun.* **1985**, 45-46.
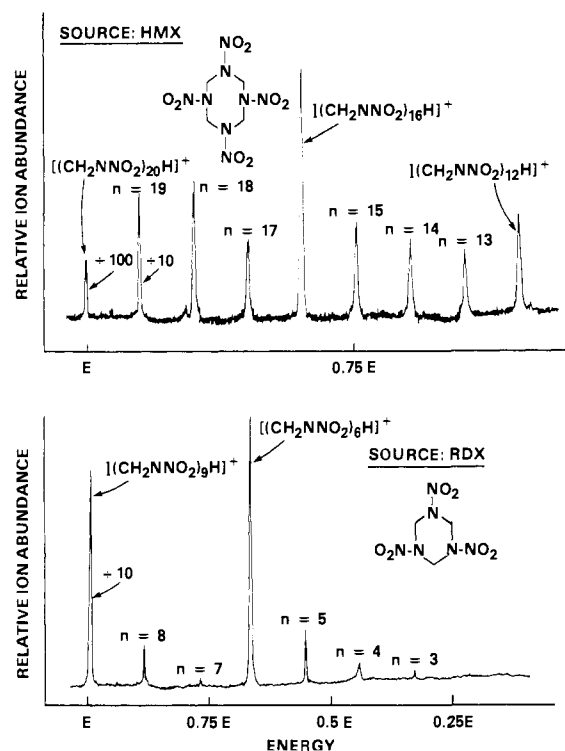
Figure 1. Mass-analyzed ion kinetic energy spectrometry (MIKES) collision-induced dissociation (CID) spectra of the ionic methylene-nitramine multimers $[(CH_2NNO_2)_{20}H]^+$ and $[(CH_2NNO_2)_9H]^+$ generated from HMX and RDX. The most abundant fragment corresponds to loss of a molecular entity (HMX or RDX), and losses of $(CH_2NNO_2)_n$ are observed.

Figure 2. Ion abundance distributions of the series of ionic multimers generated by ion/molecule reactions of trioxane or tetroxocane. Ion abundance enhancements are observed at multimers corresponding to integral molecular units.

species. The ion abundance distributions of the multimeric series generated from RDX and HMX were different; and, in fact, the distributions could be related to their known solid-state properties of intermolecular orientation and intermolecular forces. The origin of one multimer, the protonated RDX dimer, was studied in detail.[2,3] By isotope labeling studies we established that the protonated dimer was formed in the gas phase and not by direct evaporation from the solid.[2] A second study used Fourier transform ion cyclotron resonance mass spectrometry double-resonance techniques to elucidate three primary reactions that lead to the formation of the protonated dimer.[3] Each reaction step involves the RDX molecule as a reactant and methylene-nitramine as a product. The results of these two studies indicate that ring integrity is preserved during the gas-phase formation of the protonated dimer of RDX.

A question remains, what is the nature of the bonding in the ionic multimers—are they cluster ions or polymeric ions? We have used collision spectroscopy techniques[4,5] to understand the bonding in both the RDX[2] and HMX[6] ionic multimers. Figure 1 shows the mass-analyzed ion kinetic energy spectrometry (MIKES) collision-induced dissociation (CID) spectra of two multimeric ions generated from HMX and RDX. The most abundant fragment ion observed in either spectrum is the loss of a moiety corresponding to a molecular unit—HMX or RDX. This analytical technique requires known standards for structure identification, the spectra cannot always be interpreted empirically, and there are no stable methylenenitramine polymers that can be used for comparison.

In this paper, we report the MIKES/CID spectra of the ionic multimers generated from the cyclic oligomers of formaldehyde
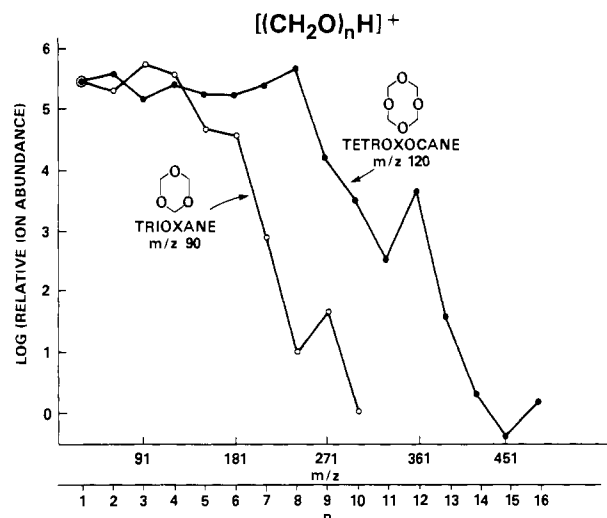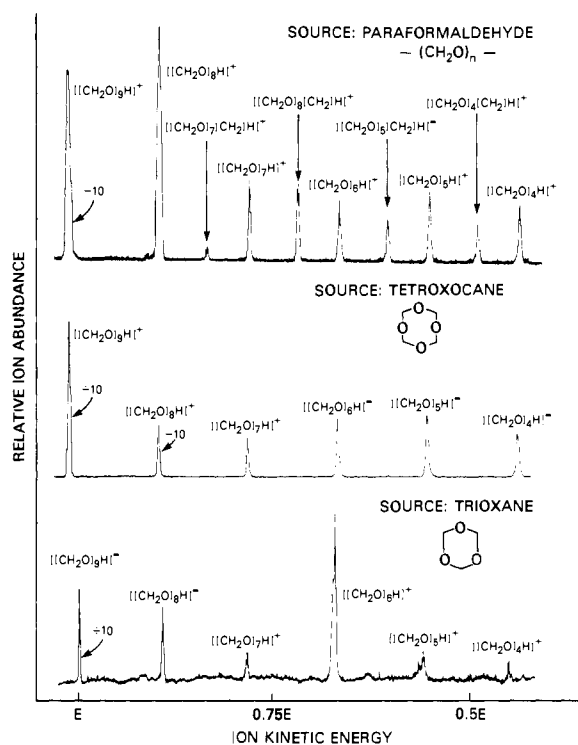
Figure 3. MIKES/CID spectra of the ionic multimers $[(CH_2O)_9H]^+$ generated from (a) paraformaldehyde, (b) tetroxocane, and (c) trioxane. This figure shows that the polymeric ions from paraformaldehyde fragment at every bond of the $-/-CH_2-/-O-/-$ backbone. In contrast, the multimeric ions from the cyclic oligomers fragment primarily by loss of only monomeric units, CH_2O. (For example, the percentage of the $[(CH_2O)_5(CH_2)H]^+$ intermediate fragment relative to the $n = 6$ cluster is 77% from the paraformaldehyde precursor, about 1% from the tetroxocane precursor, and is not observed from the trioxane precursor.)

and for comparison the MIKES/CID spectra of the corresponding linear formaldehyde polymeric ions generated from paraformaldehyde $[-(CH_2O)_n-]$. The results of these studies also bear on the bonding in the ionic methylenenitramine multimers.

Figure 2 shows the ion abundance distributions of the series of multimeric ions of general formula $[(CH_2O)_nH]^+$, generated by ion/molecule reactions (~ 1 torr) of 1,3,5-trioxane (trioxane) and 1,3,5,7-tetroxocane (tetroxocane). As with the methylene-nitramines, ion abundance enhancements are observed at n values corresponding to an integral number of molecular species. Figure

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3 compares the MIKES/CID spectra of the $[(CH_2O)_9H]^+$ species generated by ion/molecule reactions of paraformaldehyde (heated at 200 °C) and those isomeric ions generated by ion/molecule reactions of trioxane and tetroxocane. Clearly, significant differences are observed in the figure. In particular, the MIKES/CID spectrum of the ionic polymer standard shows bond cleavages at every bond in the backbone, whereas the corresponding species generated from the cyclic oligomers show a series of fragment ions corresponding primarily to loss of monomeric units, CH_2O. These significant spectral differences are indicative of structural differences between the two ionic multimers.

We contend from the results of our MIKES/CID studies on the methylenenitramines[2,6] and the present study that the ionic multimers, generated by gas-phase ion/molecule reactions of the heterocyclic compounds, are indeed cluster ions and not linear polymeric ions. The MIKES/CID results shown here on the methylenenitramines (Figure 1) also show a series of fragment ions corresponding to loss of the monomer, CH_2NNO_2, but no consecutive cleavages of the backbone ($-CH_2-/-NNO_2-/-CH_2-$) are observed. We have discussed the strong intermolecular forces that exist between the paired molecules in the protonated RDX dimer,[2] which must preclude dissociation of the protonated dimers into the molecular entities. This also indicates that at least the dimers are not simple proton-bound dimers, otherwise they would fragment easily into molecular units such as those proton-bound dimers reported in studies by Cooks and co-workers.[7] Consequently, the resulting cluster ions must be composed of intact molecules of the heterocycles, and the intermediate clusters contain monomeric subunits. These cluster ions are held together by rather complex cohesive forces that govern the fragmentation pathways.

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Alkyl Migration or Carbonyl Migration? Ab Initio MO Study of Reaction Mechanism for Carbonyl Insertion of Pd Complex

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Carbonyl insertion reaction is an important elementary reaction of catalytic processes.[1] One of the most interesting questions concerning this reaction is whether the reaction takes place via alkyl group migration or carbonyl migration.[1,2] It has been proposed recently that the agostic interaction could assist the alkyl group migration.[3] Although some experimental and theoretical studies have appeared to elucidate the mechanism,[4,5] the structure

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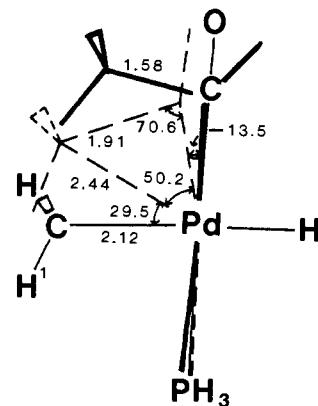

Figure 1. Optimized geometries (in Å and deg) of Pd(CH$_3$)(H)(CO)-(PH$_3$), the transition state, and Pd(COCH$_3$)(H)(PH$_3$). The position of the Pd atom and the direction of the PdH bond are fixed. The illustrated positions of atoms are those in Pd(CH$_3$)(H)(CO)(PH$_3$). The positions shown by the broken lines and the thick solid lines are those at the transition state and in Pd(COCH$_3$)(H)(PH$_3$), respectively. For clarity, only essential geometrical parameters are shown.

Table I. Relative Energy (kcal/mol) for Pd(CH$_3$)(H)(CO)(PH$_3$) → Pd(COCH$_3$)(H)(PH$_3$)

method	reactant	transition state	product
RHF	0.0	25.8	19.1
MP2	0.0	13.5	8.8

of transition state, which could give direct evidence on the reaction mechanism, has never been determined.

In this paper we report the optimized transition-state structure for the carbonyl insertion reaction of Pd(CH$_3$)(H)(CO)(PH$_3$) (1) and show that the reaction takes place via methyl migration. This system has been chosen as a model of an intermediate considered to exist in the experimentally studied reaction of *trans*-Pd-(CH$_3$)$_2$(PR$_3$)$_2$ and CO.[4d] We used for the geometry optimization the energy gradient technique at the restricted Hartree–Fock (RHF) level with the relativistic effective core potential approximation.[6] A smaller basis set (valence double ζ except for PH$_3$) was used for structure optimization and a larger basis set (all valence double-ζ) and the second-order Møller-Plesset perturbation method (MP2) were used for energy calculations at the RHF optimized geometries.[7]

The structures of 1, the product (Pd(COCH$_3$)(H)(PH$_3$)), and the transition state between them are shown in Figure 1 and their relative energies are in Table I. During the course of reaction, the structure of the H$_3$PPdH fragment remains nearly unchanged, the angle PPdH being about 90°. The methyl group, with its pseudo C$_3$ axis kept nearly horizontal, moves up halfway toward the carbonyl group at the transition state and proceeds further to form a CC bond with the carbonyl group in the product. At the transition state the carbonyl group moves slightly toward the methyl group as if to facilitate its migration. This result indicates

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