

Articles

Size- and Charge-State-Dependent Reactivity of Azidoacetonitrile with Anionic and Cationic Rhodium Clusters Rh_n^{\pm}

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Gas-phase reactions of anionic and cationic rhodium clusters with azidoacetonitrile are studied by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry under near-thermal conditions. All anionic and large cationic clusters react by adding $[C_2, N_2]$ in consecutive steps, either by forming interstitial carbides and nitrides or by adding two CN groups to the cluster surface. Small cationic clusters behave differently, with the unimolecular decomposition of the azide determining the reactivity. Saturation is identified via the size-dependent efficiency of consecutive reaction steps. The present results are the first study of organic azides on transition metal clusters. The observed selectivity of the reaction is in contrast to the high exothermicity of any reaction with azide species. The cationic cluster reactivity shows a gradual transition from gas-phase to surface-like behavior with increasing cluster size.

Introduction

Hydrazoic acid, or hydrogen azide, HN_3 , was first prepared in 1890 by the oxidation of aqueous hydrazine by nitrous acid,¹ while phenyl azide was discovered as early as 1864.² Since then, azide chemistry was extensively studied, and countless derivatives were synthesized.³ The N_3 group as well as several other groups with large electron affinities, such as CN or OCN, behave in many of their compounds similar to halogens and are often referred to as pseudohalogens.⁴ Their compounds are often ionic, and the N_3^- anion is, similar to the isoelectronic CO_2 molecule and other 16 valence electron species, linear and centrosymmetric. In biochemistry, N_3^- acts as an enzyme inhibitor by coordinating to a metal center.^{5,6} In covalent compounds the N_3 unit may deviate somewhat from linearity, and in general the lengths of the two $N=N$ bonds are different.

Most of the azide compounds react strongly exothermically and are often quite explosive.³

Due to their interesting properties, organic azides played a not insignificant role in the development of modern physical chemistry. Ramsperger tested the newly developed unimolecular reaction rate theory on the thermal decomposition of hydrazoic acid and methyl azide,⁷ and Pauling developed the adjacent charge rule for resonant Lewis valence structures, among other molecules, on methyl azide.^{8,9}

The azides have nowadays a considerable importance in industry and technology both as chemical intermediates and as end products and are used in numerous applications. Lead azide is the most common primary explosive used in detonators,^{10,11} while sodium azide is the most frequently used propellant in automobile air bags.^{12,13} Also organic, covalent azides have found applications in photoresists,¹⁴ vulcanization,¹⁵ and poly-

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mer coupling.¹⁶ Increasingly, they are also used in chemical vapor deposition for generating nitride films.^{17–19}

Obviously, the use of azides as propellants, fuses, and detonators, as well as sources of atoms in semiconductor processing, makes the question of the mechanisms and pathways of their decomposition particularly important. Starting from Ramsperger's work, thermal decomposition of azides has been studied for more than 70 years.^{7,20–24} The availability of modern experimental techniques for the spectroscopy of transient species, like photoelectron spectroscopy²⁵ and matrix isolation,²⁶ has recently renewed the interest in these species.^{27–32} Also the wide distribution of computational chemistry packages in the past decade has left its mark in the azide literature.^{33–39} The Curtius rearrangement (reaction 1) is the well-established decomposition pathway of alkyl azides by nitrogen elimination to form an alkyleneimine:³³



Recent studies also report formation of the methyl-*nitrene* diradical upon photodissociation of methyl

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azide.^{40,41} Together with the multiconfigurational self-consistent-field calculations by Arenas et al.,^{36–38} there is experimental as well as theoretical evidence that the alkyleneimine is a stable intermediate in the decomposition of alkyl azides.

In striking contrast to the large body of work in the gas and condensed phase, studies of the decomposition of organic azides on surfaces, as well as their gas-phase ion chemistry, are rare to not available. While the adsorption of hydrazoic acid on semiconductors was studied as a possible precursor for nitride formation,^{42–44} to the best of our knowledge azidoacetic acid is the only organic azide so far studied in a surface apparatus.⁴⁵ Oliveira et al.⁴⁶ have investigated the N_3CH_2COOH , $N_3CH_2COCH_3$, and $N_3CH_2CH_2OH$ compounds by mass spectrometry. For each of them they detected only a weak parent cation peak, but their spectra indicated that for each of the compounds the dominant fragment corresponds to the loss of a mass of 56 amu, presumably the N_3CH_2 entity. Another common feature is a strong signal at a nominal mass of 28 amu. Unfortunately the resolution of the instrument used in their study was not sufficient to differentiate between the N_2^+ and CH_2N^+ fragments with the same nominal mass. Recent high-resolution measurements by Duarte et al.⁴⁷ indicate that the $m/z = 28$ peak is due to CH_2N^+ ions in the EI impact spectra of aliphatic α -carbonyl azides.

Most azides readily decompose, especially if the activation barrier is lowered by the presence of a suitable catalyst. Transition metals are known to be useful catalysts for many reactions involving unsaturated compounds. One of the difficulties of studies on bulk solids is that the adsorbed species can move around on the surface, and their decomposition may be the result of a complex sequence of a number of reactions. Furthermore, detailed diagnostics of such processes is usually quite difficult. On the other hand, studies of reactions on surfaces of small ionic metal clusters in the gas phase offer a convenient, much more tractable alternative.^{49–52} Since in this case the products are the result of a single bimolecular collision, where the exact masses and elemental compositions of both of the reactants and of their products are known, very unambiguous statements can often be made about the occurring reactions. Additional insight into their course and mechanisms can be gained by observing the reactivity trends as a function of cluster size and charge state.^{53–55}

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In the present article we investigate the reactions and surface-activated decomposition of one simple representative of aliphatic covalent azides with the help of Fourier transform ion cyclotron resonance mass spectrometry. We report here the reactions of the azide of acetonitrile, N_3CH_2CN , on the surface of rhodium clusters as a function of their size and charge state.

Experimental Section

Most of the relevant experimental details were described in our previous publications,⁵⁶ and so only a brief outline of the experiment will be given here. The ionic Rh_n clusters with about $n = 1-20$ are produced in an external source chamber by laser vaporization of rhodium metal with a frequency-doubled Nd:YAG laser (Continuum SureliteII) operated at a repetition rate of 10 Hz and an energy of typically 10 mJ per 5 ns laser pulse. A sufficient number of both positively and negatively charged ions are formed without need for post-ionization.⁵³ The clusters, either anions or cations, are then transferred through several stages of differential pumping into the high vacuum of the FT-mass spectrometer and trapped in the ICR cell, where they are exposed to a steady pressure of typically 8.0×10^{-9} mbar of the azidoacetonitrile reactant. Rhodium has only one isotope, which is favorable for mass spectrometric studies.

Preliminary experiments with size-selected clusters have shown that under the conditions of our experiment, similar to previous studies,⁵³ no breakage of rhodium–rhodium bonds takes place, and in the course of the chemical reactions no rhodium atoms are lost from the clusters. This made it possible in the subsequent experiment to dispense entirely with mass selection and investigate the reaction of the entire broad cluster distribution at the same time. By varying the delay between trapping of the ions and acquisition of the mass spectrum, the reaction kinetics is followed over a total period of 20 s. Relative rate constants are obtained by fitting the normalized data with pseudo-first-order kinetics, with an accuracy of typically 10%. The absolute pressure of azidoacetonitrile inside the ICR cell cannot be determined due to the lack of published rate constants for ion–molecule reactions with azidoacetonitrile which would be necessary for calibration. Therefore, no absolute rate constants are given. The relative rate constants in this publication refer to an uncalibrated azidoacetonitrile pressure of 8.0×10^{-9} mbar. The absence of rhodium–rhodium bond cleavage is again substantiated by the exponential decay of the parent ion. Loss of intensity to smaller clusters would inevitably lead to a significant curvature of the parent ion intensity in a semi-logarithmic plot, which is not observed.

The compound studied here, azidoacetonitrile (N_3CH_2CN), was prepared by methods described in the literature.⁵⁷ To avoid its decomposition, it was kept at dry ice temperature, and prior to experiment it was degassed by three freeze–pump–thaw cycles. During the experiment the sample was maintained at room temperature and shielded from light to prevent photolysis.

Safe Handling Instructions. Azidoacetonitrile may decompose rapidly and spontaneously. Decomposition products include hydrogen cyanide (HCN) and are toxic. If possible,

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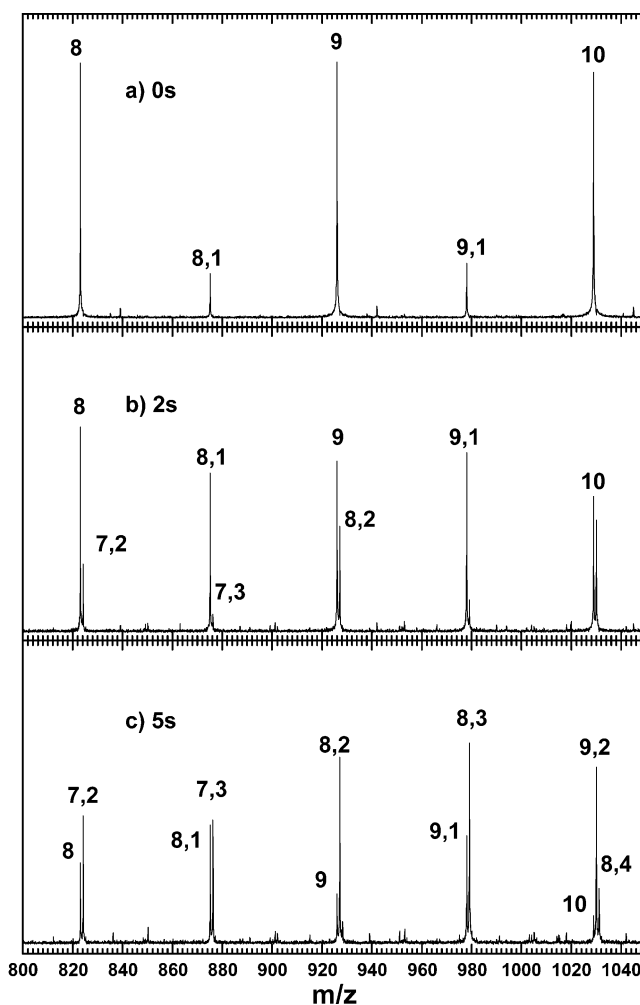


Figure 1. Mass spectra showing the neighborhood of the Rh_8^- cluster and of its reaction products at the nominal time $t = 0$ (a) and after reaction delays of 2 s (b) and 5 s (c). The numbers denote the cluster size n ; numbers after the comma refer to the number of consecutive reaction steps. The only reaction products correspond to the sequential addition of a mass of 52 amu to the Rh_n^- cluster, $Rh_nC_{2m}N_{2m}^-$.

prepare and handle only small quantities, and ensure adequate protection. Dispose properly.

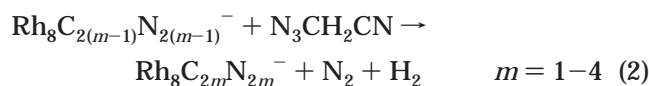
Results and Discussion

After establishing firmly that the Rh_n^\pm clusters always react as an unbreakable unit, we have carried out the reactions for the entire cluster distribution, without mass selection. This has, besides the fact that in a single experiment the reactivity data are obtained for a number of cluster sizes simultaneously, also the obvious advantage that all of them are investigated under exactly identical conditions. Overall we have investigated the reactions of azidoacetonitrile with both negatively and positively charged clusters of rhodium, Rh_n^+ , $n = 1-16$, and Rh_n^- , $n = 3-16$. Monomer and dimer anions are not produced in sufficient quantities in our ion source.

Reactions of Anionic Clusters. Typical data from an experiment involving the larger clusters are exemplified by Figure 1, showing part of the mass spectra in the neighborhood of the Rh_8^- cluster and of its reaction products. Figure 1a shows the mass spectrum right after

cluster accumulation at a nominal time $t = 0$, while the spectra after reaction delays of 2 and 5 s, respectively, are presented in Figures 1b and 1c. It should be noted that since the rhodium clusters are accumulated over typically 20 laser pulses, and since the azidoacetonitrile reactant is present in the mass spectrometer continuously, the reactions actually take place already during the accumulation time of 2 s. Due to this, the zero nominal time corresponds actually to a nonzero reaction delay, and this is reflected in the fact that even the spectrum in Figure 1a, corresponding to time $t = 0$, already clearly shows the presence of reaction products.

The reactions occurring in the trap are relatively simple, and the only products correspond to the addition of a mass of 52 amu to the Rh_8^- cluster, or in other words to a loss of a mass of 30 amu from the gaseous $\text{N}_3\text{CH}_2\text{CN}$ reactant, which has a nominal mass of 82 amu:



The products of the reaction with azidoacetonitrile thus correspond to $\text{Rh}_8\text{C}_{2m}\text{N}_{2m}^-$, with N_2 and H_2 "evaporating" from the cluster in each step. Naturally, mass spectra do not give any direct information about the departing neutral reactants and cannot directly distinguish between the loss of discrete N_2 and H_2 molecules, or that of an N atom together with an NH_2 radical, or perhaps even of the neutral diazene N_2H_2 . Formation of the latter, however, would require quite complicated rearrangements, and its heat of formation at 220 kJ/mol⁵⁸ lies significantly above the elemental dimers. For mechanistic and thermochemical reasons, we assume that N_2 and H_2 molecules are evaporated.

At first sight the evaporation of both the H atoms from the CH_2 entity, and on the other hand the retention of one of the nitrogen atoms from the azide N_3 group, might seem surprising. It becomes, however, quite reasonable if one considers that rhodium and its neighbors in the periodic table are characterized by large affinities to nitrogen as well as carbon, with which they form very stable and refractory, so-called interstitial carbides and nitrides,⁵⁹ but on the other hand are relatively unreactive towards hydrogen. Furthermore one has to consider that the azides involved are actually metastable with respect to the loss of molecular N_2 . Calculations for methyl azide suggest that roughly 200 kJ/mol is released upon N_2 elimination.³³ Overall, the reaction with the cluster surface, which may result in the formation of very strong metal-carbon or metal-nitrogen bonds, is undoubtedly highly exothermic, and the reactive cluster intermediate formed in its course must therefore be extremely hot. This high temperature must then result in the evaporation of the comparatively weakly bound hydrogen atoms, probably in the form of molecular H_2 . As an alternative to the formation of interstitial carbides and nitrides, CN groups with their

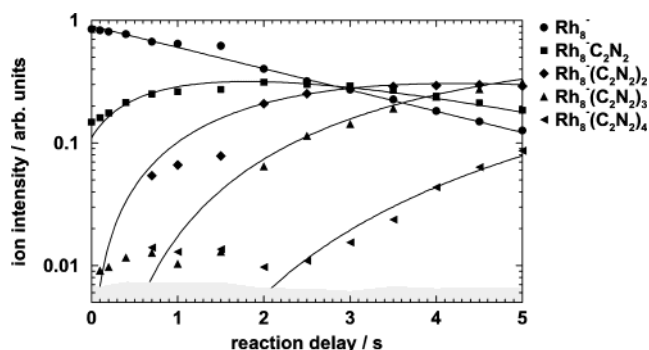


Figure 2. Time profile for the reaction of Rh_8^- with $\text{N}_3\text{CH}_2\text{CN}$. The first three reaction steps proceed efficiently, while the fourth $\text{N}_3\text{CH}_2\text{CN}$ molecule reacts significantly more slowly, suggesting that a certain kind of saturation is achieved. The gray shaded area denotes the noise level. The parent ion decay is linear in the semilogarithmic scale of the figure, indicating the absence of rhodium-rhodium bond cleavage.

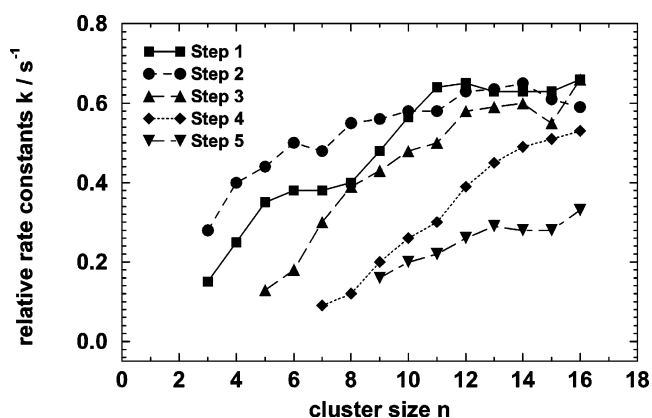


Figure 3. Relative rate constants assuming pseudo-first-order kinetics of reaction of rhodium anions Rh_n^- , $n = 3-16$, with azidoacetonitrile $\text{N}_3\text{CH}_2\text{CN}$. All anionic clusters react subsequently by evaporation of N_2 and addition of $[\text{2C},\text{2N}]$ to the cluster surface. The number of efficient reaction steps increases with cluster size, which indicates that the cluster is gradually saturated with either interstitial carbides and nitrides or CN groups on its surface.

thermochemically favorable triple bond may be attached to the surface.

In a typical experiment, spectra similar to those exemplified in Figure 1 were actually measured at 14 different delays ranging from nominally $t = 0$ up to $t = 5$ s. Relative intensities of reactant and product ions are extracted from these data and normalized, as displayed in Figure 2. Numerical fits assuming pseudo-first-order reaction kinetics yield the appropriate reaction rate constants. The problem noted above, that is, the fact that the nominal $t = 0$ corresponds actually to nonzero reaction time, can easily be compensated by assuming a nonzero starting intensity of the products.

Figure 2 illustrates that the first three reaction steps proceed efficiently, while the fourth $\text{N}_3\text{CH}_2\text{CN}$ molecule reacts significantly more slowly, as can also be seen in the relative rate constants displayed in Figure 3. The numeric fit is made somewhat more difficult by the fact that the products of neighboring cluster sizes overlap, because two reaction steps add a nominal mass of 104, while the mass of a rhodium atom is 103. The upcoming

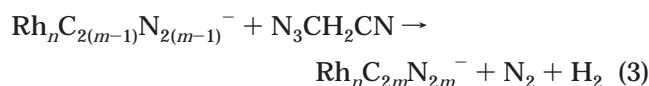
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secondary product of Rh_n^- overlaps with the base of the still intense unreacted clusters Rh_{n+1}^- , and its intensity is not determined correctly by the data acquisition software. This problem is resolved by ignoring the unreliable intensities in the fit.

The fourth $\text{N}_3\text{CH}_2\text{CN}$ molecule obviously faces some difficulty in finding a reactive site on the cluster, indicating that a certain kind of saturation is reached. This is in line with our interpretation of the formation of interstitial carbides and nitrides. As soon as most of the interstitial sites are taken, the cluster ceases to react. The same argument, however, applies to the surface covered with CN groups.

A similar kinetic evaluation of the data was undertaken for all clusters Rh_n^- , $n = 3-16$, and the rate constants of up to five consecutive steps are summarized in Figure 3. All anionic clusters react sequentially by evaporation of N_2 and H_2 and addition of $[\text{C}_2, \text{N}_2]$ to the cluster surface:



In other words, in each consecutive step an additional $\text{N}_3\text{CH}_2\text{CN}$ reactant molecule is decomposed on the cluster, with two additional carbon and two additional nitrogen atoms being incorporated into the product and presumably one N_2 and one H_2 molecule escaping from the cluster. In general, the number of such steps (3), that is, the maximum value of m , depends on the cluster size and increases with the number of rhodium atoms, from $m = 2$ for the smallest clusters studied, $n = 3, 4$, to $m = 7$ observed for $n = 13$. The larger the cluster, the more efficient the later reaction steps and the larger the maximum number of steps. This behavior clearly indicates that the reaction proceeds at an intact part of the rhodium cluster surface. We tentatively conclude this to be the genuine behavior of a rhodium surface in the reaction with azidoacetonitrile.

Reactions of Cationic Clusters. For cationic clusters, the picture is considerably more complex, since a number of competing reactions occur, which are characteristic for certain cluster sizes or size regimes. Reaction kinetics were again analyzed for reaction times of up to 5 s. Since competing reaction pathways are present, the precursors of secondary products were not always identified unambiguously. We therefore concentrated on a clear assignment of the primary products, and the results are summarized in the rate constant plot of Figure 4.

Reaction 4 is the equivalent of reaction 3. It is the dominant reaction pathway for most clusters, and its branching ratio increases with increasing cluster size. Starting at $n = 3$, where it is barely observed, it becomes the dominant pathway at $n = 5$, with the rate constant quickly increasing until it reaches a constant value at $n = 13$, where it also becomes the only remaining reaction:



In an intermediate size region, $n = 5-12$, another process typical of surfaces is observed, formation of the pure carbide cations Rh_nC_2^+ , which corresponds to the

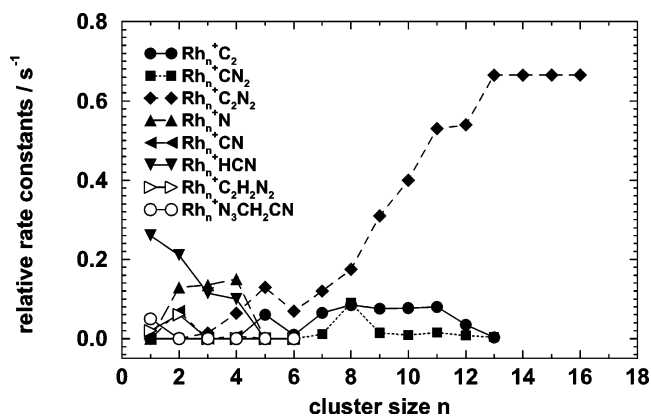
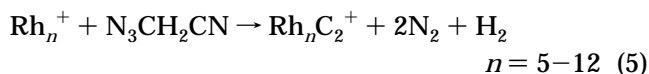


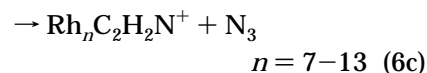
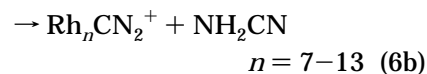
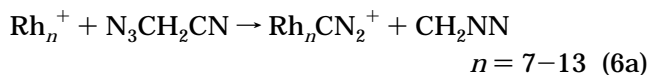
Figure 4. Relative rate constants assuming pseudo-first-order kinetics of the reaction of rhodium cations Rh_n^+ , $n = 1-16$, with azidoacetonitrile $\text{N}_3\text{CH}_2\text{CN}$. For smaller clusters, the gas-phase reactivity of $\text{N}_3\text{CH}_2\text{CN}$ is responsible for the observed reaction pattern, while larger clusters show reactivity similar to the anions, which is probably characteristic of a rhodium surface.

evaporation of H_2 as well as of two N_2 molecules from the reactive complex according to eq 5:



In this intermediate size regime, the reaction enthalpy heats the cluster sufficiently to prevent formation of the nitride and to enable the presumably energetically less favorable evaporation of a second N_2 molecule.

Even slower and less abundant were reactions corresponding to the loss of a nominal mass 42, resulting in the Rh_nCN_2^+ or $\text{Rh}_n\text{C}_2\text{H}_2\text{N}^+$ species. These were observed for $n = 7-13$, with a pronounced maximum at $n = 8$. Unfortunately, the mass resolution of our 4.7 T instrument is not sufficient in this mass region at this pressure to reliably distinguish between the two possible elemental compositions of the product cluster. However, looking at the possible neutral products and the overall reaction pattern, one can identify three chemically reasonable possibilities, loss of a diazomethane (6a), cyanamide (6b), or the azide radical N_3 (6c):



Among these three possibilities, formation of the azide radical (6c) is unlikely, first of all because radical formation is in general less favorable than formation of closed shell neutrals as in reactions 6a,b, and the heat of formation of N_3 at 414 kJ/mol is substantially higher than the corresponding values of 215 kJ/mol for diazomethane, CH_2NN , or 134 kJ/mol for cyanamide, NH_2CN .⁵⁸ In addition, the hydrogen atoms do not remain on the cluster in the parallel reaction pathways 4 and 5, and a common pattern with respect to hydrogen incorporation seems reasonable. Arguing for or against

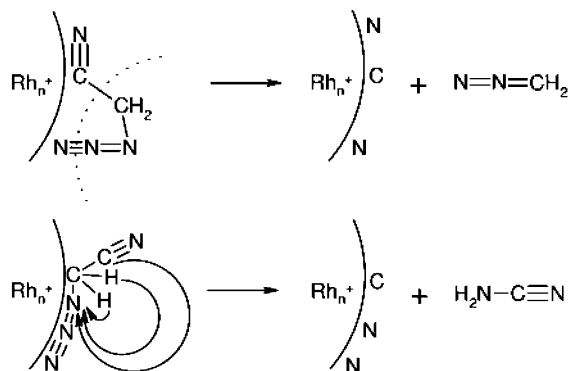


Figure 5. Possible routes to the formation of Rh_nCNN^+ . The azide group is destroyed upon adsorption of azidoacetonitrile on the cluster, leading to formation of diazomethane (a) or cyanamide (b). Mechanistically speaking the formation of diazomethane (a) is much more likely because it does not require rearrangements of C–N bonds, in contrast to cyanamide (b). Thermochemically, (b) is favored by 81 kJ/mol over (a), the difference between the heat of formation of diazomethane and cyanamide.

6a vs 6b is much less straightforward. Mechanistically, formation of diazomethane seems much more likely, since it does not require rearrangement of C–N bonds, in contrast to cyanamide, as illustrated in Figure 5. Thermochemically, however, reaction 6b is favored by 81 kJ/mol over 6a, the difference between the heat of formation of diazomethane and of cyanamide.⁵⁸ The preferred occurrence of the reaction for $n = 8$, however, indicates a mechanistic origin, and it is quite intriguing to imagine that the initial adsorbent structure in Figure 5a is most likely realized in a relatively compact cluster structure with “sharp” edges. The complex rearrangement and survival of the CN group required in Figure 5b must be considered unlikely, since the triple bond will interact predominantly with the cluster surface. Under these circumstances, an intact abstraction after recombination with a newly formed NH₂ group is hard to imagine.

Overall, the subsidiary reactions 5 and 6 are of decreasing importance with increasing cluster size, so that essentially only the dominant primary reaction 4 is detected for $n \geq 13$. Two possible interpretations can be offered for this trend. One contributing factor may be that the probability of the two remaining N atoms approaching each other on the cluster surface close enough in order to recombine and form molecular N₂ is reduced with the increase of its size.

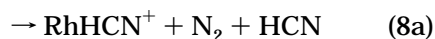
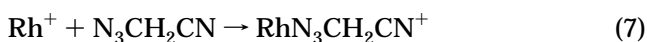
More important, however, is probably the effect of the available energy.⁵⁰ The reaction of the metal cluster according to eq 4 can be viewed as a metal-catalyzed, exothermic decomposition of the metastable azide compound with the loss of molecular N₂, followed by reaction of the remaining NCH₂CN entity with the metal cluster, which results in the elimination of both hydrogen atoms in the form of molecular H₂. A large amount of energy will be deposited in the reaction product. This energy will consist of several contributions: the initial kinetic energy of the reactants, the adsorption energy of the unsaturated compound on the metal cluster surface, the enthalpy of the N₃CH₂CN reactant decomposition with N₂ and H₂ elimination, and finally of the enthalpy of the product ion formation. Overall, this large energy will be statistically distributed among the internal vibra-

tional modes of the resulting product and will raise its effective temperature to a very high value.

Apparently the temperature may remain high enough so that even the evaporation of the remaining two nitrogen atoms as an N₂ molecule can take place, reaction 5. The overall amount of energy deposited will undoubtedly, in particular for the larger clusters, not depend very strongly on the specific value of n . On the other hand, the number of internal vibrational modes and low-lying electronic states, over which this energy can be distributed, will increase linearly with n , and consequently the effective cluster temperature must decrease with size. The net result of these effects will be the decrease in the effective temperature of the product cluster, which is then reflected in the suppression of the minor, presumably less exothermic side reactions for clusters $n \geq 13$.

In contrast to these presumably surface-like reactions (4–6), an almost completely different chemistry is observed for the smallest clusters, $n \leq 4$. This is undoubtedly due to the fact that when the number of rhodium atoms becomes too small, enough Rh–C and Rh–N bonds cannot form, and the stable interstitial carbide or nitride structure cannot develop. The exothermicity of the reaction of the azidoacetonitrile with the cluster decreases, so that the dehydrogenation reaction may not proceed to completion, and products with residual hydrogen appear.

Starting with the simple, monatomic rhodium cation, its observed reactions are described by eqs 7, 8a, and 9a.



The simple adduct of Rh⁺ with azidoacetonitrile according to reaction 7 is apparently sufficiently long-lived so that it can be stabilized, either radiatively or collisionally. This stabilization is obviously facilitated by the presence of unsaturated bonds in the azide and nitrile groups.

Obviously stabilization of the complex is not the most probable outcome of the reaction, since the major product observed is an ion with the RhHCN⁺ composition, according to reaction 8a. The time-resolved profile of the product ion with RhH₂C₂N₂⁺ composition suggests that it is at least partially a primary product formed according to reaction 9a. Two other ions are observed corresponding to Rh⁺HCN(N₃CH₂CN) and Rh⁺(HCN)₃, which are clearly the products of secondary reactions, as confirmed by their time-resolved intensity profiles.

Reactions 8a and 9a can easily be rationalized with the help of the Curtius rearrangement, reaction 1. As illustrated in Figure 6a, the standard Curtius rearrangement leads to formation of NHCHCN, which may be stabilized on Rh⁺, while N₂ evaporates. Unlike most other organic azides, however, azidoacetonitrile offers the possibility that the Curtius rearrangement proceeds in the wrong direction, with the H atom attacking the nitrile carbon instead of the imine nitrogen. In this case, two HCN molecules are formed, together with N₂. One of the HCN stays attached to the Rh⁺, the stabilization

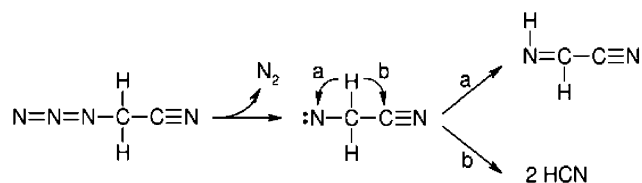
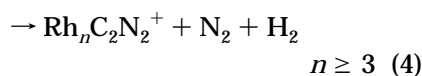
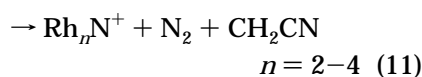
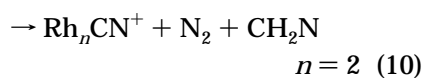
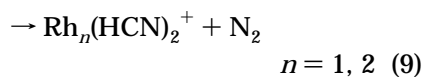
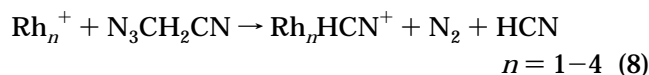


Figure 6. The Curtius rearrangement may proceed in two directions for the unimolecular decomposition of azidoacetonitrile. Standard Curtius rearrangement leads to formation of NHCHCN (a), which may be stabilized on Rh^+ , while N_2 evaporates. If an H atom attacks the nitrile carbon (b) instead of the imine nitrogen, two HCN molecules are formed, together with N_2 . During the process, one of the HCN attaches to the Rh^+ , the stabilization being helped by the evaporation of two neutral molecules.

being helped by evaporation of two neutral molecules. In summary, the reactivity of Rh^+ with $\text{N}_3\text{CH}_2\text{CN}$ can be rationalized by the unimolecular decomposition pathways of azidoacetonitrile illustrated in Figure 6.

In contrast with Rh^+ , no complexes of Rh_n^+ with undecomposed azidoacetonitrile are observed for any cluster with $n \geq 2$. One can understand this observation in terms of an exothermic decomposition of the azidoacetonitrile on the rhodium metal, which is incomplete only in the case of the monatomic cation. The reactions of the small clusters in the intermediate range of $2 \leq n \leq 4$ can be described by the following set of equations, and the approximate relative yields are summarized in Table 1:



While for the larger clusters there is no analogue of reaction 7, for the $n = 2$ dimer both the analogue reactions 8 and 9 occur. Besides, two new reactions, 10 and 11, are observed, with nominal masses of 26 and 14, respectively, remaining on the cluster. As already discussed, the corresponding gaseous products can be inferred only indirectly from the reaction stoichiometry and thermochemistry. Also the $n = 3$ and 4 clusters yield major products according to reactions 8 and 11, but the reactions 9 and 10 are not observed. They are replaced by the "large cluster" reaction 4, which is, as

discussed above, the dominant reaction for all the clusters with $n \geq 5$.

In the case of reactions 10, the product $\text{Rh}_2\text{C}_2\text{H}_2^+$ with the same nominal mass can be ruled out on the basis of the mass difference of 26.001 to the Rh_2^+ ion, which compares favorably with the 26.003 amu expected for CN, and is in heavy disagreement with the 26.016 amu expected for C_2H_2 . Reaction 10 can be seen as reaction 8 proceeding somewhat further, with the formation of a bridged $[\text{RhCNRh}]^+$ structure, and the second HCN taking the remaining H atom away.

Again, the product of reaction 11 is unambiguously assigned as Rh_nN^+ on the basis of the measurement of the mass difference to the bare Rh_n^+ cluster. The reaction can be rationalized with a CH_2CN radical leaving the collision complex in the first step. The azide radical decomposes, yielding Rh_2N^+ and an N_2 molecule.

The analysis of consecutive reactions for larger cationic clusters is less unambiguous than for the anionic clusters and is obviously complicated by the occurrence of the reactions 5 and 6. The presence of parallel processes makes the reaction scheme more complex and dilutes the signal among more product ions. Despite these difficulties, one can clearly say that the dominant reactions are again the cationic analogues of reaction 3, with major products being the $\text{Rh}_n\text{C}_{2m}\text{N}_{2m}^+$ cation clusters.

Comparison of Cationic and Anionic Clusters.

The variation of the rates of the primary reactions as a function of the rhodium cluster size n , as well as of their charge, is summarized graphically in Figure 7. For the anions the reaction rates increase almost monotonically with the cluster size n and then level off above about $n = 11-13$. In contrast, there is a minimum of the observed reactivity of the cations for $n = 6$, which is explained by two overlapping processes: With increasing n , the rates of reactions 7-11, which are dominated by the gas-phase dissociation behavior of the azidoacetonitrile molecule, are decreasing. At the same time, the rates of the surface-driven reactions 4-6 are increasing. The slope of this rate increase is, however, faster for the cations than for the anions, so that just about at the point where the rates level off, the difference between the anions and cations essentially disappears. Above about $n > 12$ the reaction rates become almost size independent, and within the accuracy of the measurement, basically the same for anions and cations. The fundamental difference between cations and anions lies in the observation that the small cationic clusters are able to induce the unimolecular decomposition of azidoacetonitrile, presumably by offering thermochemically favorable positively charged rhodium compounds as potential products.

Several local deviations from the overall trends can be found in the data, but in the absence of any knowledge of the rhodium cluster structure, nothing more can be done than to note them in passing. Clearly

Table 1. Branching Ratios in Percent of $\text{Rh}_n^+ + \text{N}_3\text{CH}_2\text{CN} \rightarrow \text{Products}$, $n = 1-4$

n	$\text{Rh}_n\text{N}_3\text{CH}_2\text{CN}^+$ (7)	Rh_nHCN^+ (8)	$\text{Rh}_n\text{H}_2\text{C}_2\text{N}_2^+$ (9)	Rh_nCN^+ (10)	Rh_nN^+ (11)	$\text{Rh}_n\text{C}_2\text{N}_2^+$ (4)
1	15	75	10			
2		35	15	15	35	
3		35			60	5
4		30			50	15

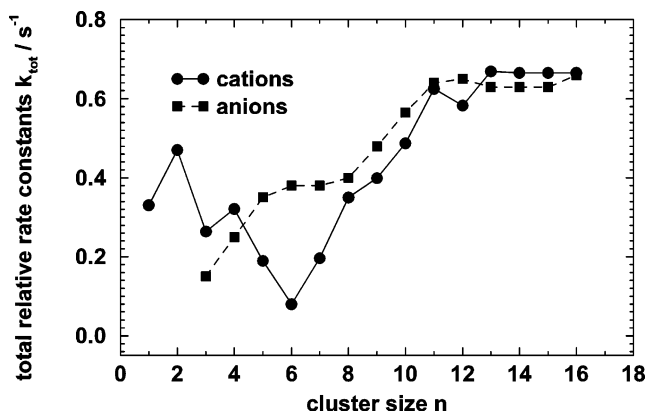


Figure 7. Total relative rate constants of the primary reactions of rhodium clusters with azidoacetonitrile as a function of their charge and size n . For the anions (squares) the reaction rates increase almost monotonically with the cluster size n , and then level off around $n = 11$ – 13 . In contrast, there is a minimum of the observed reactivity of the cations (circles) for $n = 6$, due to the fact that by increasing n the rates for unimolecular decomposition of azidoacetonitrile are decreasing and at the same time the rates of the surface-driven reaction are increasing. Above $n > 12$ the reaction rates become almost size independent. Starting with $n = 8$, the rates for anions and cations become the same.

visible is the somewhat lower overall reactivity of the $n = 6$ cation cluster, which reacts distinctly slower than either $n = 5$ or $n = 7$.

Another interesting observation is that the subsidiary reactions 5 and 6 do not occur for the anionic clusters, which react exclusively according to reaction 3. Following the arguments made above for larger cationic clusters, this might reflect a somewhat lower exothermicity of the reaction for the small anions, and consequently lower effective temperature of the products formed.

One general conclusion that can be made, for the reactions of both anions and cations, is that for $n \geq 5$ no product clusters containing hydrogen are clearly identified and that the "evaporation" of hydrogen from the clusters is in all cases complete. As noted previously, this can be understood on the basis of the general reluctance of rhodium and nearby metals to form bonds with hydrogen. Another observation perhaps worth

repeating is that, again in agreement with our previous work, in no case do we observe rhodium atom loss and breakage of metal–metal bonds, even in the reaction with the high-energy species azidoacetonitrile.

Conclusions

Reactions of anionic and large cationic rhodium clusters with azidoacetonitrile lead to the uptake of $[2C,2N]$ into the cluster, either as interstitial carbides and nitrides or as CN groups, accompanied by full dehydrogenation and evaporation of neutral N_2 in consecutive steps. The reaction stops presumably when the cluster surface is saturated with the reaction products. The monomer Rh^+ reacts more or less as a spectator, with the azidoacetonitrile undergoing unimolecular reactions, whose products are stabilized as complexes with Rh^+ . In the size region from two to five atoms, this unimolecular type of reaction becomes less important and ceases to occur with $n = 5$, while formation of the surface-typical reaction products $Rh_nC_xN_y^+$ starts at $n = 2$ and becomes the dominant reaction at $n = 3$. The cationic clusters illustrate the gradual transition from metal ion gas-phase chemistry to surface-like behavior. The reactivity of both cationic and anionic clusters shows that in the gas phase the high-energy species azidoacetonitrile undergoes clean and defined reactions. The results suggest that azidoacetonitrile can be used to generate a stoichiometrically well-defined 1:1 carbide-nitride film or a film consisting of CN groups on a rhodium surface. Surface science experiments to test this prediction are highly desirable.

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Note Added after ASAP: On the fifth page, the heat of formation of diazomethane was incorrectly given as 25 kJ/mol in the version posted on March 26, 2004. The correct value of 215 kJ/mol appears in the version posted on April 5, 2004.

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