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On the Track of Reaction Mechanisms: Characterization and Reactivity of Metal Atom Dimers

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1.1
Introduction

The matrix-isolation technique is now well established as a valuable method to retain and characterize reaction intermediates [1]. In this chapter, it will be shown how this method can be used to characterize metal atom dimers and to shed light on their special reactivity. An understanding of the bond properties and reactivities of these metal atom dimers is a first step toward an understanding of the physical and chemical properties of metal atom clusters. Because of their high reactivity, metal atom clusters are widely used for catalytic processes. In addition, larger clusters with a diameter in the nm range (ideally 1–2 nm) exhibit quantum-size effects, which make their use in single-electron devices attractive. In spite of these wide-ranging applications, detailed information about the structures and electronic properties of metal atom clusters is sparse. There are not only experimental difficulties. Quantum chemical calculations become extremely difficult and expensive, even in the case of the metal atom dimers. Multi-reference methods have to be applied and inner-core correlation has to be taken into account. Often DFT methods fail or are not really reliable.

Although clusters are generally more reactive than metal atoms or ideal defect-free surfaces, first results show that there are large differences between clusters that consist of different numbers of atoms. In some cases, the maximum reactivity of an Mₙ particle (where M denotes a metal atom and n ≥ 1) seems to be reached at the stage of the metal atom dimer. Thus, gas-phase studies revealed that Rh₂⁺ brings about a spontaneous dehydrogenation reaction with CH₄, while Rh⁺ ions and Rhₙ⁺ clusters (n ≥ 3) do not induce spontaneous reaction [2]. In the same vein, Pt₂⁺, but not Pt⁺ ions or Ptₙ⁺ clusters, were found to react with NH₃ to give the dehydrogenation product [Pt₂NH]⁺ [3].

After a brief description of the matrix-isolation technique, the results which have led to a detailed characterization of Ga₂ and Ti₂ will be reported. Thereafter, the reactions between Ga₂ and H₂ and between Ti₂ and N₂ are discussed. These two model reactions underline impressively the high reactivity of metal atom dimers.
1.2 Principle and Realization of the Matrix-Isolation Experiment

In the matrix-isolation experiment, the two reactants are isolated in a host material, which generally consists of a frozen inert gas (e.g. argon) to minimize chemical interactions between the host and the isolated reactants (Fig. 1.1). The temperature is kept very low (at a few Kelvin). At these temperatures, even small reaction barriers (of a few kJ mol\(^{-1}\)) cannot easily be surmounted \((kT=0.08\text{ kJ mol}^{-1}\) at 10 K), if tunnelling processes can be neglected. Therefore, reaction intermediates that cannot survive under other conditions can be generated, trapped, and observed. Indeed, one of the great advantages of the matrix-isolation method is that the reaction intermediates can be retained for several hours or even days and therefore can be identified and characterized at leisure by applying standard laboratory techniques.

The identification and characterization of possible intermediates and reaction products usually relies on spectroscopic methods. Vibrational spectroscopy is certainly the most widely applied method, combining as it does the advantages of high sensitivity and the provision of information that can not only be used to identify the species, but also to determine some important properties such as symmetry and more detailed structural information, force constants, and, in some cases, dissociation energies (see below). To allow for a better analysis of the data, the experiments have to be repeated with as many isotopomers as possible. These isotopomers usually have to be synthesized especially for this purpose. The experimental results are often accompanied by quantum chemical calculations, which allow for a further characterization. Absorption spectroscopy with radiation energy sufficiently high to excite electrons within the species isolated in the matrix provides valuable information about possible photochemistry and may be used to analyze the properties of excited states. Thus, if the spectra are vibrationally resolved, the frequency and important structural information can be obtained for some excited states of the species under investigation. Fluorescence spectroscopy can also be extremely informative, although this technique can only be applied in certain cases. Finally, radicals might be studied by means of EPR spectroscopy (see ref. [1] for more information on possible methods of interrogation).
Fig. 1.2 illustrates the preparation of a matrix in a typical matrix experiment. In the studies discussed herein, one of the reactants is emitted from a metal evaporator. For example, gallium vapor can be generated by resistively heating the metal in a BN cell, or an alumina tube containing a carbon cell, to a temperature of 900–1000°C. An element like titanium, for which higher temperatures are necessary, may be evaporated by directly heating a pure metal wire (to 1600–1700°C in the case of titanium). The amount of deposited metal can be monitored with the aid of a microbalance. The other reactant is admixed to the matrix gas. The matrix is deposited onto a metal block (e.g., Cu or Rh-plated Cu) kept at a low temperature (10 K in general), generally by means of a closed-cycle refrigerator. UV/Vis spectra give useful information about the metal atom to metal atom dimer ratio in the matrix.

1.3 Characterization of Metal Atom Dimers

Metal atom dimers in a matrix can be characterized by means of absorption (e.g. UV/Vis), resonance-Raman, and/or fluorescence spectroscopy. In some cases, the resonance-Raman spectra reveal not only the $\nu(M-M)$ stretching fundamental, but also several overtones. These overtones can be used to estimate the dissociation energy, which is an important parameter in describing the metal–metal bond. It is also of importance for the understanding of reaction mechanisms, since the metal–metal bond is often ruptured in the course of the reaction. Thus, the energy required for the rupture of the metal–metal bond has to be compensated by the formation of other bonds if the reaction is to proceed spontaneously. In the following, the results obtained for Ti$_2$ and Ga$_2$ from matrix-isolation experiments and quantum chemical calculations are discussed. These two metal atom dimers were chosen exemplarily because, as detailed below, they show remarkably high reactivities.

Ti$_2$ Fig. 1.3 shows the resonance-Raman spectra obtained for Ti$_2$ measured with the $\lambda = 514.532$ nm line of an Ar$^+$ ion laser [4]. Some regions of the spectrum are
covered by fluorescence signals, which for the most part belong to Ti atoms. Nevertheless, in the regions free from fluorescence signals, a series of overtones can be measured, which exhibit an isotopic splitting. The results can be used to estimate the dissociation energy on the basis of a LeRoy–Bernstein–Lam analysis [5]. In this analysis, the potential near the dissociation limit is assumed to be a quadrupole-quadrupole-type interaction between two Ti atoms in their $^3F$ electronic ground state. One then interpolates between the formulas derived for the vibrational level energies near the dissociation limit (resulting from a WKB treatment) and those that are closer to the bottom of the potential-energy curve. The analysis yields a dissociation energy ($D_e$ value) of 113.9 kJ mol$^{-1}$ [4].

Additional valuable information is provided by absorption measurements. Fig. 1.4 shows the absorption spectrum of Ti$_2$ in the region between 4000 and 6500 cm$^{-1}$ [6]. Two series of bands are visible, which can be assigned to excitations into different vibrational levels of the $^13\Pi_u$ and the $^13\Phi_u$ states. The relative intensities of the bands in each series can be used to estimate the difference $\Delta r_e$ in the bond distances between the excited state and the ground state on the basis of a Franck–Condon analysis. To this end, Morse-type functions were assumed for each state. The analysis resulted in $\Delta r_e$ values of 9 pm for the $^13\Pi_u \leftrightarrow ^3\Delta_g$ and of 10 pm for the $^13\Phi_u \leftrightarrow ^3\Delta_g$ transition. Thus, the Ti–Ti bond length is found to increase in both electronically excited states relative to the ground state.

Experimental information was also obtained for the next higher $^23\Pi_u$ and $^23\Phi_u$ states. In these states, the Ti–Ti bond is even longer. Tab. 1.1 includes $\Delta r_e$,
the harmonic frequencies $\omega_e$, and the excitation energies $T_e$ for all states for which detailed experimental information is available. Tab. 1.1 also compares the experimentally derived values with those predicted by high-level quantum chemical calculations (MRCI method).

**Ga$_2$** Again, resonance-Raman spectroscopy proves to be extremely useful to obtain information about the ground state of the dimer. The resonance-Raman spectrum of Ga$_2$ is displayed in Fig. 1.5 [7]. The $\nu$(Ga–Ga) stretching fundamental occurs at 176.5 cm$^{-1}$. Three additional signals in the spectrum can be assigned to the first, second and third overtones. The signals show an isotopic
Fig. 1.5  Resonance Raman spectrum of Ga₂, obtained with the 514.532 nm line of an Ar⁺ ion laser.

<table>
<thead>
<tr>
<th>Ga₂</th>
<th>CASSCF/SVP</th>
<th>MP2/TZVPP</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>³Πₜₜ</td>
<td>d(Ga–Ga)</td>
<td>276.3</td>
<td>271.4</td>
</tr>
<tr>
<td></td>
<td>ω(Ga–Ga)</td>
<td>161</td>
<td>178</td>
</tr>
<tr>
<td>³Σ⁺</td>
<td>ΔE</td>
<td>7.1</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>d(Ga–Ga)</td>
<td>251.0</td>
<td>247.1</td>
</tr>
<tr>
<td></td>
<td>ω(Ga–Ga)</td>
<td>204</td>
<td>222</td>
</tr>
<tr>
<td>¹Σ⁺</td>
<td>ΔE</td>
<td>19.0</td>
<td>41.5</td>
</tr>
<tr>
<td></td>
<td>d(Ga–Ga)</td>
<td>309.3</td>
<td>300.3</td>
</tr>
<tr>
<td></td>
<td>ω(Ga–Ga)</td>
<td>121</td>
<td>146</td>
</tr>
<tr>
<td>³Πₜₜ</td>
<td>ΔE</td>
<td>46.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>d(Ga–Ga)</td>
<td>278.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ω(Ga–Ga)</td>
<td>154</td>
<td></td>
</tr>
<tr>
<td>¹Δₜₜ</td>
<td>ΔE</td>
<td>56.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>d(Ga–Ga)</td>
<td>258.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ω(Ga–Ga)</td>
<td>170</td>
<td></td>
</tr>
</tbody>
</table>
splitting that is in pleasing agreement with the pattern expected for Ga$_2$ (see inset in Fig. 1.5) in its three isotopic forms $^{69}$Ga$^{69}$Ga, $^{69}$Ga$^{71}$Ga, and $^{71}$Ga$^{71}$Ga. The dissociation energy of Ga$_2$ can be estimated to be ca. 130 kJ mol$^{-1}$.

Unfortunately, it has hitherto not been possible to obtain detailed information about excited states of Ga$_2$ with energies close to the ground state. Calculations indicate that a $^3\Sigma_g^-$ state has an energy which is only ca. 7 kJ mol$^{-1}$ higher than that of the $^3\Pi_u$ ground state. Several singlet states are also predicted to be close by in energy (see Tab. 1.2) [10]. It will be shown below that these excited states play a significant role in relation to the reactivity of Ga$_2$.

1.4 Reactivity of Metal Atom Dimers and Comparison with the Reactivity of Single Metal Atoms

In the following, two examples are discussed which should underline the strikingly high reactivity of metal atom dimers, namely the reaction of Ga$_2$ with H$_2$ and the reaction of Ti$_2$ with N$_2$. Both reactions proceed spontaneously with the metal atom dimers in their ground electronic states.

1.4.1 The Reaction Between Ga$_2$ and H$_2$

Ga atoms in their electronic ground state ($^2\text{P}$) do not react with dihydrogen. A reaction can only be brought about by photoactivation of the Ga atoms ($^2\text{S} \rightarrow ^2\text{P}$ excitation), thereby leading to the bent radical GaH$_2$ [8, 9]. This result is at first glance surprising, since transition metal atoms are known to react spontaneously with H$_2$ only after one of the d electrons has been excited into an empty p orbital. On this basis, it has been argued that the attractive interaction between the half-filled p orbital and the $\sigma^*$ orbitals at the dihydrogen initiates the reaction. A correlation diagram shows, however, that the ground state of the Ga···H$_2$ system (with a large separation between Ga and H$_2$) correlates with an excited state of the product GaH$_2$. Therefore, the thermal reaction is subject to a massive reconfiguration barrier [10]. In fact, a radical mechanism is favored, which leads first to GaH and H atoms, and these combine in the second step to give the GaH$_2$ radical. Thus, although the overall reaction is slightly endothermic (by 16 kJ mol$^{-1}$ according to MP2/TZVPP), [10] photolysis is needed for the reaction to take place.

For the reaction between Ga$_2$ and H$_2$, one might also assume at first glance a significant barrier, since the reaction is formally spin-forbidden (Ga$_2$ exhibits a triplet ground electronic state and Ga$_2$H$_2$ a singlet one). However, spin-orbit coupling is significant and provides a means by which the system can change its multiplicity from triplet to singlet. The experiments show that Ga$_2$ reacts spontaneously with H$_2$ to give the cyclic, $D_{2h}$ symmetric Ga($\mu$-H)$_2$Ga molecule (see Fig. 1.6) [10]. Calculations indicate that the reaction proceeds via excited states of Ga$_2$. Thus, in the early stage of the approach between the two reactants, the $^3\Pi_u$ and $^3\Sigma_g^-$ type states
of Ga₂ mix. At the point of intersystem crossing from triplet to singlet state, a \(^1\Lambda_\text{g}\) type state is adopted. As a consequence, the Ga–Ga distance first shortens from 276 to 255 pm. The relevant excited states have energies which are relatively close to that of the ground state. Therefore, the barrier to reaction is relatively low. The experiments give additional information about the reaction mechanism. Thus, the reaction proceeds spontaneously with H₂, but not with D₂. In the case of D₂, the matrix has to be kept for several hours in the dark or irradiated with IR light to complete the reaction (see Fig. 1.7). This isotopic effect indicates that the barrier to reaction is of the order of the zero-point energy difference between H₂ and D₂, viz. ca. 30 kJ mol\(^{-1}\). This value is slightly lower than the calculated estimate (ca. 50 kJ mol\(^{-1}\)). Nevertheless, both experiment and theory agree in that Ga₂ is much more reactive toward H₂ than a single Ga atom.

It is worth mentioning that Ga(μ-H)\(_2\)Ga can be converted into two other isomeric forms when the molecule is selectively photolyzed (see Fig. 1.8).
of these isomers, direct Ga–Ga bonds exist. One of the isomers is the \textit{trans}-bent species HGa–GaH. Analysis of the spectra obtained for this molecule in combination with quantum chemical calculations clearly shows that the Ga–Ga bond is most adequately described as a relatively weak donor–acceptor interaction between two GaH diatomics. According to quantum chemical calculations, the energy for fragmentation of HGa–GaH into two non-relaxed GaH units with singlet electronic state amounts to no more than 57 kJ mol\(^{-1}\) \[11\]. This again shows that the Ga–Ga bond is weak. At 262.0 pm, the calculated Ga–Ga bond distance is relatively long. Meanwhile, there are structural data (from X-ray diffraction analyses) available for some derivatives Ar\textit{GaGaAr} (e.g., with Ar being 2,6-Dipp\textsubscript{2}C\textsubscript{6}H\textsubscript{3}, Dipp=2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) \[12, 13\]. These data confirm the analysis made for HGaGaH. Like HGaGaH, the derivatives exhibit a \textit{trans}-bent structure. The Ga–Ga bond distance in Ar\textit{GaGaAr} amounts to 262.68(7) pm. The results also indicate that the Ga–Ga bond in the dianion [HGaGaH]\textsuperscript{2–} cannot be adequately described as a triple bond and thus the properties differ to a large extent from those found for HCCH. This is also reflected in the different structures (\textit{trans}-bent in the case of [HGaGaH]\textsuperscript{2–} vs. linear for HCCH). The crystal structures of derivatives [RGaGaR]\textsuperscript{2–} (e.g., R being 2,6-(2,6-iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) \[14\] were determined and the Ga–Ga distance was found to be short (231.9 pm). However, this short distance does not necessarily imply the presence of a triple bond. An analysis indicates that the Na\textsuperscript{+} cations are engaged in the bonding \[15, 16\]. At the same time, the Na\textsuperscript{+} ion interacts with the aromatic rings on the ligands. That the Ga–Ga bond length has to be taken with caution as a criterion for the bond order also becomes evident if the values determined for typical Ga–Ga single bonds are compared. Thus, in Ga\textsubscript{2}[Ga\textsubscript{2}I\textsubscript{6}], the Ga–Ga bond length is 238.7(5) pm \[17\]. At the other extreme, a value of 254.1(1) pm was determined in the case of Ga\textsubscript{2}(Trip\textsubscript{4}) (Trip=2,4,6-iPr\textsubscript{3}C\textsubscript{6}H\textsubscript{2}) \[18\] and also for Ga\textsubscript{2}[CH(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{4} \[19\].
In contrast to HGaGaH, the lighter homologue HBBH is a linear molecule with a triplet electronic ground state (see Fig. 1.9). The molecule has been characterized in matrix by IR [20] and EPR [21] spectroscopies, and has also been the subject of theoretical work [22]. The results show that, as anticipated, the triplet state arises from the presence of two degenerate π-orbitals, which are each occupied by one electron. The B–B bond is strong (in line with a formal bond order of 2) and the calculated B–B distance amounts to 150.7 pm. Fragmentation of HBBH into two geometrically non-relaxed HB units with singlet electronic states requires ca. 450 kJ mol–1 [CCSD(T) estimate] [11]. Nevertheless, the dimerization of the molecule to give B₄H₄ in its tetrahedral global energy minimum structure is predicted to be highly exothermic [ca. –482 kJ mol–1 according to CCSD(T) calculations] [23].

Recently, it has been shown that Ga₂ reacts spontaneously not only with H₂, but also with SiH₄ [24]. Interestingly, the product formed in this reaction is HGa(μ-SiH₃)Ga, featuring a terminal Ga–H bond and the SiH₃ group in a bridging position.

1.4.2
The Reaction Between Ti₂ and N₂

According to matrix experiments, Ti atoms in their electronic ground state do not engage in a complex with dinitrogen. Ti₂ dimers, however, undergo spontaneous reaction with N₂. In the course of this reaction, which proceeds without
a significant barrier, four Ti–N bonds are formed at the expense of the strong NN triple bond, leading to a cyclic Ti(μ-N)₂Ti molecule (see Fig. 1.10) [25]. The spectra indicate that the product features no direct N–N interaction. The ground state of Ti(μ-N)₂Ti is a singlet state, but a triplet state is of very similar energy. It was possible to detect some vibrationally resolved excitations around 9000 cm⁻¹ attributable to this species [25]. This reaction is especially interesting since solid Ti has been shown to react at higher temperatures with molecular nitrogen to first give compounds which contain N atoms dissolved in solid titanium (TiN₀.₂₀ intercalation compound), with the h.c.p. structure of α-Ti. Finally, with increasing concentration of nitrogen and at ca. 900 °C, a defect NaCl structure is adopted. Thus, in the course of this reaction, the NN bond of dinitrogen has to be ruptured. Ti₂N₂ might be a possible intermediate on the way to these solid phases. A goal of future studies should be the estimation of the reaction enthalpy of Ti₂N₂ formation. This value could then be used to calculate the enthalpy difference between Ti₂N₂ and solid titanium nitride. Solid titanium nitride coatings are of interest as protection layers and as semiconductors.

The isodesmic reaction 2 TiCl₄+Si₂N₂ → 2 SiCl₄+Ti₃N₂ can be used to estimate the standard enthalpy of formation for Ti₂N₂. This reaction was calculated to be exothermic by −194 kJ mol⁻¹. First, the enthalpy of formation for Si₂N₂ has to be estimated. The enthalpy for the reaction 2Si(g)+N₂(g) → Si₂N₂(g) was calculated to be ca. −650 kJ mol⁻¹ [26]. With values of +450 kJ mol⁻¹ for the standard enthalpy of formation for Si(g) [27], the standard enthalpy of formation of Si₂N₂ amounts to ca. +250 kJ mol⁻¹. With this value, the standard enthalpy of formation of Ti₂N₂(g) can be estimated to be of the order of −49 kJ mol⁻¹ (with values of −763.2 and −662.8 kJ mol⁻¹ for the standard enthalpies of formation of TiCl₄ and SiCl₄, respectively [27]). Considering a value of 945.4 kJ mol⁻¹ for the standard enthalpy of formation of two single N atoms, this value demonstrates the high affinity of titanium for nitrogen.

![Diagram](image-url)

**Fig. 1.10** The reaction between Ti₂ and N₂ leads to the cyclic Ti(μ-N)₂Ti molecule, which might be an intermediate on the way to solid nitrides of titanium.
It also implies that the reaction between Ti$_2$(g) (for which the enthalpy of formation is ca. +827 kJ mol$^{-1}$) and N$_2$ has to be highly exothermic (standard reaction enthalpy ca. –876 kJ mol$^{-1}$). The enthalpy of formation of solid TiN was determined to be –337.7 kJ mol$^{-1}$. Thus, the enthalpy for the reaction 2 Ti(s)+N$_2$ $\rightarrow$ 2 TiN(s) amounts to –675.4 kJ mol$^{-1}$. This value is smaller than the –876 kJ mol$^{-1}$ estimated for the enthalpy of formation of Ti$_2$N$_2$(g) from Ti$_2$(g) and N$_2$. These considerations do not prove, but support the view that the barrier for the formation of solid TiN from solid Ti and N$_2$ is caused by the thermal energy required to form “Ti$_2$” or other small clusters from solid Ti. According to these calculations, Ti$_2$N$_2$ could very well be an intermediate on the way to solid titanium nitride.

\section*{1.5 Concluding Remarks}

The examples discussed herein demonstrate impressively how reactive metal atom dimers are. Electronically excited states with energies close to the ground state are often responsible for these high reactivities (as shown explicitly for the reaction between Ga$_2$ and H$_2$) \cite{10}. Therefore, an understanding of the reaction mechanisms requires knowledge of the properties of the ground state and the excited states of these species. A detailed characterization can only be achieved through a combination of experimental and quantum chemical results. However, calculations are extremely difficult and multi-reference methods have to be applied. Inner-core correlation effects have to be rigorously included. As regards experiments, absorption and Raman spectroscopies have been shown to provide useful information on the matrix-isolated species.

The aims of future studies include the characterization of metal atom trimers and other small clusters and the analysis of their reactivity. The clusters can be generated by diffusion of metal atoms or dimers into the matrix upon annealing. Many new fascinating results are expected to emerge from these studies. They might prove to be valuable for possible applications in materials science and catalytic processes.

\section*{References}


References
