



Synthesis and thermal stability of mercury diacetylide $\text{Hg}(\text{C}\equiv\text{CH})_2$



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ABSTRACT

Mercury diacetylide was synthesized and studied by FT-IR spectroscopy, both in the mid and far infrared, and electronic absorption spectroscopy. The spectral data are consistent with the structure $\text{H}-\text{C}\equiv\text{C}-\text{Hg}-\text{C}\equiv\text{C}-\text{H}$. Mercury diacetylide is insoluble in common solvents but shows a minimal solubility in ethanol and tetradecane. The thermal stability of mercury diacetylide was studied by thermogravimetry (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). In an open crucible under nitrogen, mercury diacetylide undergoes an exothermal and explosive decomposition releasing 725.6 J/g with an onset temperature of about 250 °C and a peak temperature of 287 °C. The decomposition occurs at a higher temperature in a sealed crucible (onset 326 °C and peak 337 °C). Using the TGA-FT-IR analytical technique it has been found that the deflagration of mercury diacetylide produces elemental carbon, elemental mercury and acetylene. The enthalpy of formation of mercury diacetylide has been determined for the first time. The explosive parameters of mercury diacetylide have been compared with those of other common explosives showing that it is a dangerous and powerful explosive.

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1. Introduction

Copper and silver acetylides are useful compounds in organic synthesis and this has ensured a constant interest in these compounds [1]. Furthermore, the chemical structure of copper and silver acetylides was deeply investigated because the air oxidation of these compounds leads a solid state coupling of the acetylide moieties forming polyynes chains [2–5]. The synthesis of a polyynic mixture with the submerged carbon arc technique [6] has given direct access to polyynic chains having more than 16 carbon atoms [7] and this has led to the synthesis and structural characterization of copper and silver polyynides [8–10]. Particularly interesting, in terms of the hazard in handling copper and silver acetylides and polyynides, is the work of Cataldo and Casari which has been dedicated to the thermal stability and explosiveness of these compounds [7].

In contrast to copper and silver acetylides, there is very little knowledge about mercury diacetylide and the potential risks in handling such a compound. The literature reports on mercury diacetylide are limited to very old works done without any spectral and thermal analysis. For example, in a work dated 1894, Plimpton and Travers [11] report on the formation of mercury(II) acetylide and describe this compound as having a behavior almost similar

to that of silver and copper acetylides, even in its instability and explosiveness. Another work [12] mentioned by Frad [13] and Aylett [14] distinguishes between mercurous and mercuric acetylide. The former was obtained as a white precipitate by passing acetylene into an aqueous suspension of mercurous acetate, but was too unstable and decomposed during the recovery. On the other hand mercuric acetylide (afterwards referred as mercury diacetylide) was quite easily accessible, for example by passing acetylene into alkaline solutions of K_2HgI_4 or $\text{K}_2\text{Hg}(\text{CN})_4$ [13,14]. Nesmejanov [15] rationalized the reactivity of acetylene and alkynes with mercury compounds pointing out that alkaline conditions are necessary to ensure the formation of mercury acetylide, otherwise other products ranging from organomercury chlorovinyl derivatives to aldehydes are formed.

Mercury diacetylide is described as a whitish powder, insoluble in common solvents and with a density of 5.3 g/cm^3 , that explodes violently by rapid heating or under mechanical shock [14]. The present work is dedicated to the study of mercury diacetylide and particular attention is dedicated to its thermal stability and explosive decomposition.

The renewed attention to mercury diacetylide is due to the fact that mercury and organomercury compounds are widespread in the environment [16]. Some oil and gas streams from refineries and petrochemical production do contain mercury and mercury compounds along with acetylene and alkynes [17]. In addition, mercury catalysts are still used in the industrial synthesis of vinylchloride and acetaldehyde from acetylene. Consequently, there is

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still the possibility of mercury diacetylide or mercury alkynides formation under given process conditions. Therefore, there is the need to know better the safety and the explosive properties posed by these organomercury compounds.

A number of mercury aryl- and alkylacetylides have been well studied since they were employed for the isolation and identification of alkynes before the advent of the spectroscopy for the same purposes [18–23]. Mercury alkynides have also been used to synthesize other organomercury compounds and to study the relative reaction kinetics [24–27]. There are also reports about the hazards in handling such compounds [28]. For example, the bis(alkynyl) mercurial (*i*-Pr–C≡C)₂Hg was found to be easily explosive [28] and the hazard in handling copper and silver acetylides was assessed very recently [7,29].

It is important to underline that the research on transition metal acetylides is flourishing as demonstrated by the very recent review on homoleptic acetylides [30], which also include mercury-based derivatives. The interest in complex metal acetylides resides in the potential application of these species as luminescent materials or as molecular components in microelectronics [31–34]. Thus, assessing the potential hazard in handling metal alkynides is very important as a necessary step in any application. In the present work we are focusing on the simplest mercury alkynide: mercury diacetylide.

2. Experimental

HgI₂ and HgCl₂ were purchased from Sigma–Aldrich and used as received. All the other reagents and solvents were analytical grade materials obtained from Sigma–Aldrich or from Fluka. The FT-IR spectra were recorded on a Nicolet 6700 spectrometer from Thermo-Scientific. The mid infrared spectra were recorded in the transmittance mode with the samples embedded in a KBr pellet or in the reflectance mode using a ZnSe crystal and a horizontal attenuated total reflectance attachment. The far infrared spectra were obtained on the same spectrometer using the samples in CsI pellets. The thermogravimetric analysis of the samples was performed on a Linseis TGA model L-81 + DTA at a heating rate of 10 °C/min under a nitrogen flow (20 L/h). The combined TGA–FT-IR analysis was performed by connecting the TGA apparatus with a transfer line to the FT-IR gas cell of 10 cm path length and equipped with BaF₂ windows. The differential scanning calorimetry (DSC) study was performed on a Mettler-Toledo DSC-1 Star System. Different heating rates were used, as stated in the text, and the samples were heated under a nitrogen flow of 3 L/h using either a conventional aluminum pan with a hole or completely sealed medium pressure stainless steel crucibles. In both cases the sample size was 5 mg.

2.1. Synthesis of mercury diacetylide Hg(C≡C–H)₂ from HgI₂

Mercury diiodide (HgI₂, 760 mg) was suspended by magnetic stirring in 40 ml of distilled water and then potassium iodide (KI, 2.5 g) and potassium hydroxide (KOH, 186 mg) were added simultaneously under stirring. There was a gradual dissolution of HgI₂, which otherwise is insoluble. Once the solution was homogeneous, it was transferred into a gas washing bottle and acetylene was bubbled with continuous magnetic stirring. Mercury diacetylide started to precipitate immediately as soon as acetylene was passed into the solution. The precipitate was whitish-yellow and could be collected by filtration through filter paper, grade “Analitica A”. Once the filtration was completed, the filtrate was washed twice with distilled water and then dried in air. The total yield was 380 mg. About 20 mg of the wet mercury diacetylide were transferred with a spatula into a small agate mortar to dry overnight

at room temperature. The yellow–white powder obtained the next day was used for further characterization by infrared spectroscopy and DSC thermal analysis.

2.2. Synthesis of mercury diacetylide Hg(C≡C–H)₂ from HgCl₂

Mercury dichloride (HgCl₂, 650 mg) was completely dissolved by stirring in 35 ml of distilled water inside a gas washing bottle. The pH of the resulting solution was 4.5. The passage of a stream of acetylene did not produce any precipitate. 4.5 g of KI were then added in one shot. The precipitation of red HgI₂ was briefly observed before it dissolved quickly in the excess KI, yielding a transparent and homogeneous solution. The pH of this solution was 7.0, neutral. A stream of acetylene was then passed through this solution, but once again no precipitate formation was observed. 50 mg of sodium hydroxide (NaOH) were then dissolved into the solution and acetylene was again passed through the solution, yielding an abundant precipitate of mercury diacetylide. The precipitate was collected and washed as described in the previous Section 2.1; the diacetylide yield was about 410 mg.

3. Results and discussion

3.1. Properties, infrared and UV spectra of mercury acetylide

As mentioned in the introduction, mercury diacetylide was reported in the old literature at the end of the 19th and at the beginning of the 20th century. We have selected the most effective experimental conditions which are known to produce mercury diacetylide. These conditions require the use of complex mercury salts, such as HgI₄²⁻ and Hg(CN)₄²⁻, in a weakly alkaline medium [13–15]. The passage of acetylene through such solutions causes the formation of a white–yellow precipitate described as (–Hg–C≡C–)_x by Aylett [14], suggesting a polymeric nature to this compound, which is reported to be insoluble in any common solvent, has a density of 5.3 g/ml and is explosive.

In Section 2.1 we have produced a whitish precipitate by passing acetylene through an alkaline solution of K₂HgI₂ and in Section 2.2 it was shown that a mercury diacetylide precipitate occurs only when NaOH was added to the solution (basic conditions). Neither passing acetylene through a slightly acidic solution of HgCl₂ nor through a derived solution of K₂HgI₂ prepared by adding KI in excess to HgCl₂ resulted in Hg diacetylide.

The chemical structure of mercury diacetylide can be easily understood from its FT-IR spectrum, reported in Fig. 1. The spectrum shows a very sharp and clear acetylenic H–C≡C– stretching at 3280 cm⁻¹, while the bending of the same moiety occurs at 670 and 637 cm⁻¹. On the other hand the triple bond stretching is located at 2013 cm⁻¹.

Concerning the C–Hg–C bond stretching, literature [35] reports the asymmetric stretching of the linear molecule dimethylmercury at 538 cm⁻¹, the symmetric stretching at 515 cm⁻¹ and the bending at 160 cm⁻¹. In the case of diethylmercury, the asymmetric C–Hg–C stretching occurs at 515 cm⁻¹, the symmetric at 488 cm⁻¹ and the skeletal bending Hg–C=C at 267 cm⁻¹, while the C–Hg–C bending appears at 140 cm⁻¹. The C–Hg–C bond stretching in divinylmercury H₂C=CH–Hg–HC=CH₂ occurs at 541 and 513 cm⁻¹. Since for the elements P and Ge the passage from the divinyl derivatives to the diethynyl derivatives implies a shift to lower wavenumbers of the carbon–metal stretching band by Δν = 70 to 80 cm⁻¹ [35], the asymmetric C–Hg–C bond stretching in mercury diacetylide is expected at 464 cm⁻¹ and the symmetric stretching at 435 cm⁻¹, as indeed is seen in Fig. 1. The other three bands in the far infrared portion of the spectrum of Fig. 1 are

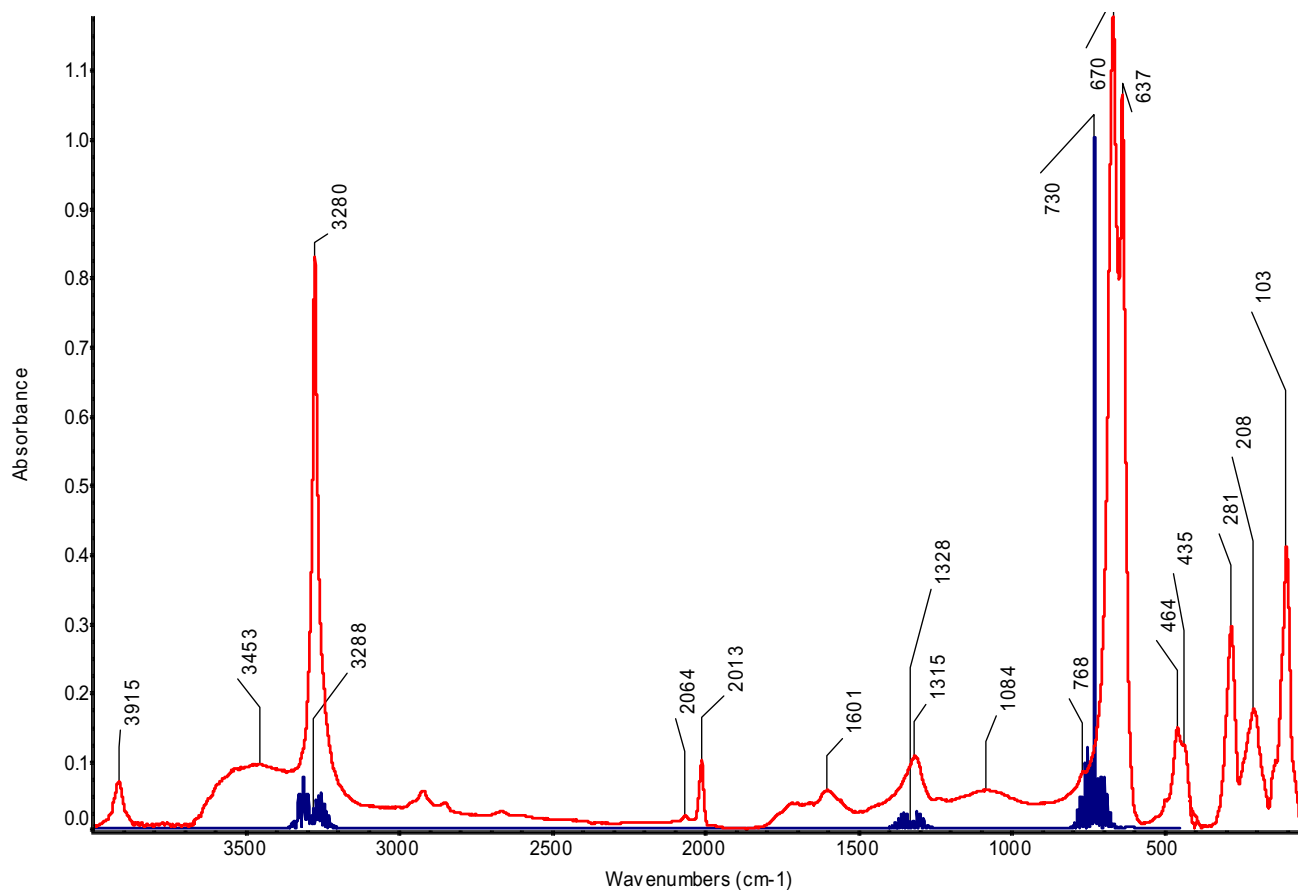


Fig. 1. FT-IR spectrum of mercury diacetylide (red line). The spectrum is dominated by the $\text{C}\equiv\text{C-H}$ stretching at 3280 cm^{-1} and the $\text{C}\equiv\text{C-H}$ bending mode at 670 and 637 cm^{-1} . Other important infrared bands are at 2013 cm^{-1} due to the triple bond stretching and, in the far infrared at 464 and 435 cm^{-1} due to the C-Hg-C stretching and at 281 , 208 and 103 cm^{-1} due to the C-Hg-C and $\text{Hg-C}\equiv\text{C}$ bending modes. The blue line shows the gas phase spectrum of pure acetylene as a reference. The position of the $\text{C}\equiv\text{C-H}$ stretching band of acetylene is almost identical to that of mercury diacetylide. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

certainly assignable to the $\text{Hg-C}\equiv\text{C}$ bending at 281 cm^{-1} and to the C-Hg-C bending at 208 and 103 cm^{-1} .

All these spectral data are completely in line with the expected chemical structure:



However, mercury diacetylide is insoluble in common solvents and, as will be shown in the following sections, it is neither fusible before decomposition nor volatile. For example, prolonged shaking of mercury diacetylide in benzene (15 mg in 4 ml) does not lead to any dissolution. Only sonication in an ultrasonic bath causes the formation of a milky dispersion of mercury diacetylide in benzene. The suspension gradually separates a white precipitate of mercury diacetylide without any decomposition. Similar results are observed when mercury diacetylide is sonicated for 15 min in tetradecane, toluene or anhydrous ethanol. The mercury diacetylide is finely dispersed by ultrasonic treatment in these solvents, giving a milky-white suspension which on standing releases as a precipitate the whitish and fluffy insoluble diacetylide. However, as soon as the tetradecane solvent is filtered from the acetylide suspension, it displays the electronic absorption spectrum shown in Fig. 2 and is characterized by an absorption maximum at 204 nm and a series of weak shoulders at 220 , 234 and 266 nm ; a similar spectrum is observed also in ethanol. This implies that a very small fraction of mercury diacetylide dissolves in these solvents.

To explain the insolubility and the lack of volatility of mercury acetylide it is necessary to invoke a π interaction between the acetylenic groups and the mercury atom in a homoleptic interaction [30]. Cataldo and Casari have already proposed such an interaction to explain the insolubility of silver and copper acetylides, and especially polyynides [7]. Evidently this interaction is the reason for the insolubility also observed in the case of mercury diacetylide.

In addition, there is evidence concerning an unusual aggregation of certain mercury alkynides in the solid state [36,37]. In such systems the Hg-Hg distances were found in the range $0.37\text{--}0.40\text{ nm}$, possibly indicating weak mercuriophilic interactions, but the main driving force for clustering appears to be the interactions between the Hg atoms and the $\text{C}\equiv\text{C}$ bonds of adjacent molecules [36,37]. In this context it is important to look at the position of $\nu_{\text{C}\equiv\text{C}}$ in the spectrum of Fig. 1. The main band is located at 2013 cm^{-1} while the free acetylenic group band should occur at 2111 cm^{-1} [35]. The shift $\Delta\nu \approx 100\text{ cm}^{-1}$ is due to the π interaction between the acetylenic group and the Hg atoms of adjacent molecules [35].

In the older literature, mercury diacetylide is reported as a monohydrated compound.



Indeed, the FT-IR spectrum of Fig. 1 also shows a relatively weak and broad stretching band for water at about 3453 cm^{-1} . This infrared band cannot be removed even after prolonged heating at

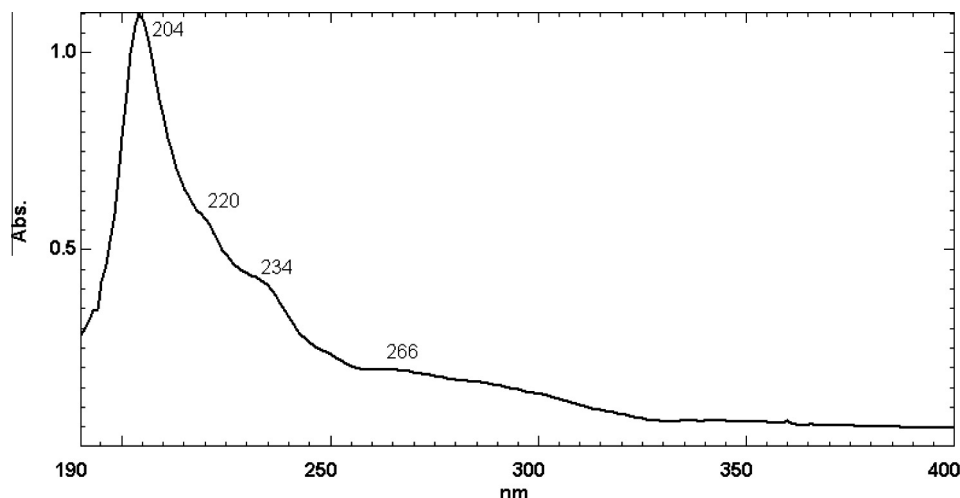


Fig. 2. Electronic absorption spectrum of the minimal fraction of $\text{Hg}(\text{C}\equiv\text{CH})_2$ soluble in tetradecane. The spectrum resembles that of diacetylene, see text for further discussion.

70 °C for 7 h. Therefore the relatively weak band at 3453 cm^{-1} is compatible with a small amount of water trapped in $\text{Hg}(\text{C}\equiv\text{CH})_2$, but the amount of water is not necessarily in an equimolar ratio with the diacetylide, as will be shown in the following section.

$\text{Hg}(\text{C}\equiv\text{CH})_2$ is considerably more stable in air and even in humid air than the copper and silver diacetylides. The latter two undergo slow changes on aging in air due to a solid state coupling reaction of the acetylenic moieties [2–5]. This phenomenon does not occur at all in the case of $\text{Hg}(\text{C}\equiv\text{CH})_2$, which seems to be indefinitely stable in air at room temperature, provided that it is not exposed to intense light or direct sunlight. In the latter case a distinctive yellowing of $\text{Hg}(\text{C}\equiv\text{CH})_2$ was observed, confirming the photosensitivity of this compound.

Turning back to the electronic absorption spectrum of $\text{Hg}(\text{C}\equiv\text{CH})_2$ in tetradecane, reported in Fig. 2, it is worth noting that it resembles the spectrum of diacetylene $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$. In fact diacetylene shows four bands at 214, 224, 234 and 246 nm [38] which should be compared with the bands at 204, 220, 234 and 266 nm in the case of mercury diacetylide. This implies that the Hg atom between the acetylenic groups does not interrupt the π conjugation, otherwise only the isolated acetylenic transitions, which occur below 190 nm, should be observed. Since the insertion of an Hg atom between two phenyl groups does not alter much both the UV spectrum and the molar extinction coefficients of the absorption bands [24], assuming that the same phenomenon occurs in the case of mercury diacetylide, then we can estimate the concentration of $\text{Hg}(\text{C}\equiv\text{CH})_2$ in tetradecane and in ethanol using an $\epsilon \approx 300\text{ L cm}^{-1}\text{ mol}^{-1}$ [38,39]. The solubility of $\text{Hg}(\text{C}\equiv\text{CH})_2$ is estimated to be about $3.5 \times 10^{-3}\text{ mol/l}$ in tetradecane and about double that value in ethanol.

3.2. Thermogravimetric analysis of mercury acetylide and TGA–FT-IR analysis

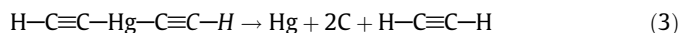
When mercury diacetylide is heated under a nitrogen flow in a thermobalance it does not show any transition or any measurable weight loss up to 250 °C. As stated in the previous section, the amount of trapped water detected by FT-IR should be very small since was not possible to quantify it by thermogravimetric analysis (TGA). Fig. 3 shows the first derivative of the TGA, the DTG, which indicated the explosive weight loss of the mercury diacetylide sample at 253.4 °C. At that temperature the maximum decomposition rate of the sample has been reached. Moreover, the differential thermal analysis (DTA) trace, also shown in Fig. 3, demonstrates

that the decomposition process of mercury diacetylide is exothermal and the decomposition onset occurs at 250.5 °C. Indeed, the explosive decomposition of mercury diacetylide was so violent that a distinct detonation was heard, accompanied by the shattering of the quartz arm of the balance and breaking of the platinum crucible filled with only 40 mg of mercury diacetylide.

During the thermogravimetric measurement, the TGA was connected to an infrared gas cell of 10 cm path equipped with two BaF_2 windows. All the gases released by the mercury diacetylide sample during the decomposition were passed into the gas cell and a series of infrared spectra of the gas phase were recorded during the decomposition, and these are reported in Fig. 4. It is evident that acetylene was produced during the decomposition of mercury diacetylide. Acetylene was easily recognized from the strong infrared absorption band at 730 cm^{-1} . The bottom of Fig. 4 shows the reference spectrum of acetylene, while the other spectra of Fig. 4 were recorded at different temperatures to follow the thermal decomposition of mercury diacetylide.

The release of acetylene is first evident at 150 °C, a much lower temperature than that of the explosion onset recorded with the DTA at 250.5 °C. Fig. 5 reports the amount of acetylene released by the mercury diacetylide decomposition, as measured from the area below the peak at 730 cm^{-1} of the spectra of Fig. 4. As pointed out, acetylene release starts at 150 °C, grows almost linearly with temperature up to 250 °C when it reaches a maximum, which coincides with the explosion. Afterwards there is a rapid drop in the acetylene concentration in the gas phase.

The explosion of mercury diacetylide produces acetylene and leaves behind a heavy dark carbon soot containing elemental mercury. Therefore, the thermal decomposition of mercury acetylide under inert atmosphere can be represented by the following reaction:



Since we now know the decomposition reaction of mercury diacetylide under an inert atmosphere, we can now measure the decomposition heat and then derive the enthalpy of formation.

3.3. Differential scanning calorimetric (DSC) study on mercury diacetylide

The thermal behavior of mercury diacetylide was studied also with the DSC, both in a conventional punched aluminium pan and in a sealed medium pressure stainless steel crucible. A heating

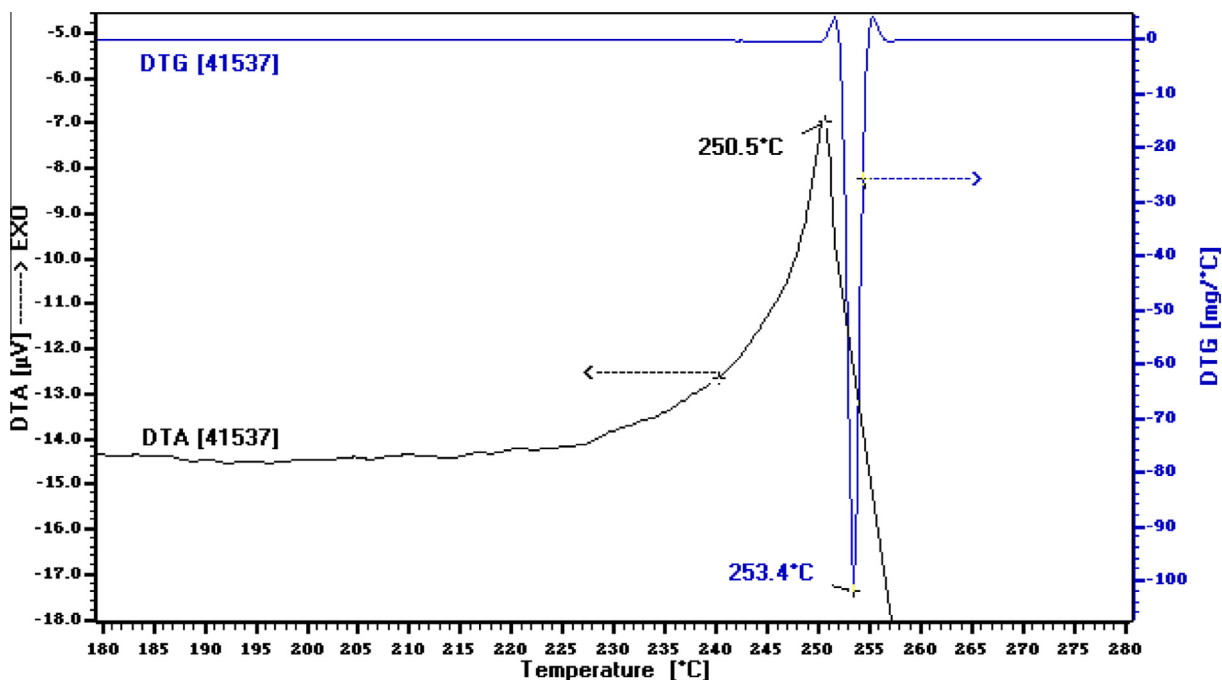


Fig. 3. Differential thermal analysis (DTA, black line) and first derivative of the thermogravimetry (DTG, blue line) of mercury diacetylide measured under a N_2 flow. The DTA shows the exothermal peak when the onset of the explosion occurred at 250°C , while the DTG shows the explosive weight loss of the sample. The maximum decomposition rate occurred at 253.4°C .

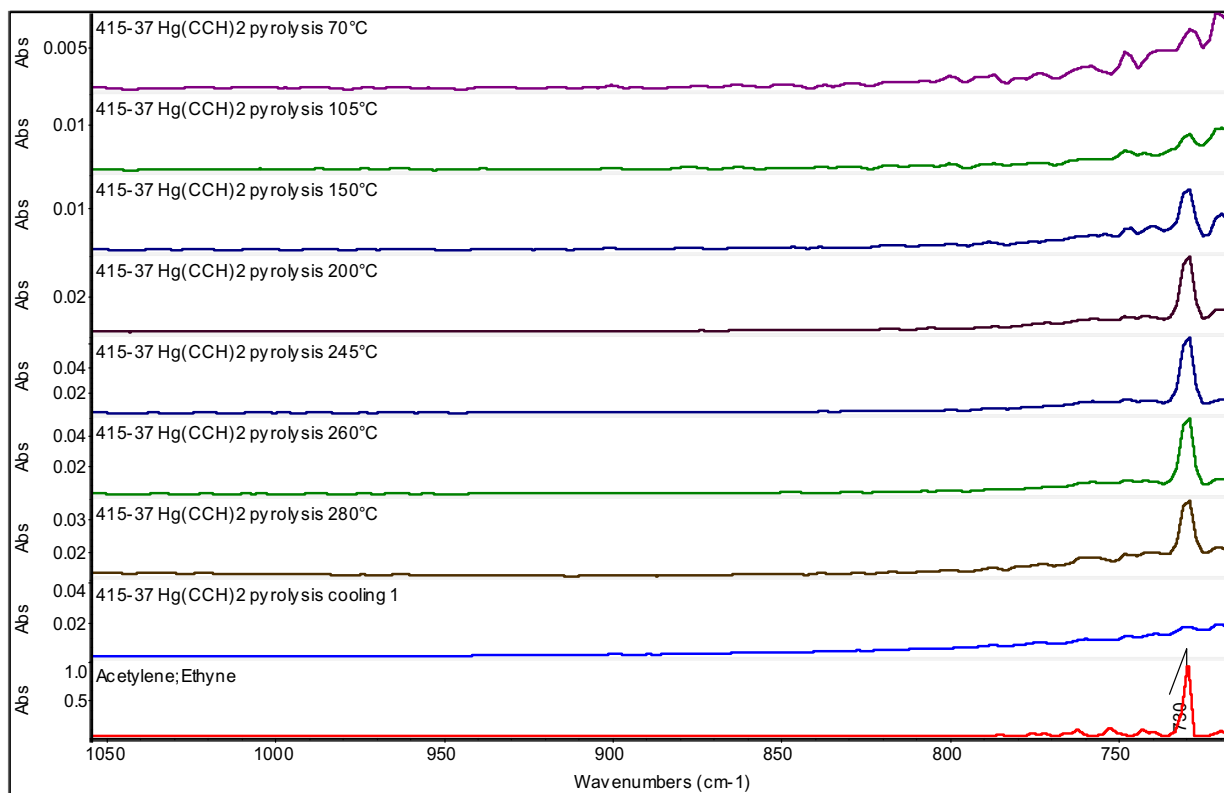


Fig. 4. Gas phase FT-IR spectra collected during the mercury diacetylide decomposition of the TGA under a N_2 flow. The peak at 730 cm^{-1} is due to acetylene, as shown by the reference spectrum reported at the bottom of the figure. The amount of acetylene released as function of temperature is reported in Fig. 5. The spectra shown were taken respectively (from top to bottom) at 70 , 105 , 150 , 200 , 245 , 260 and 280°C , and in the cooling phase after the explosion.

rate of $10^\circ\text{C}/\text{min}$ was applied to the samples and all measurements were made under a nitrogen flow. Fig. 6 shows the DSC traces of the two $\text{Hg}(\text{C}\equiv\text{CH})_2$ samples, heated in an open and sealed cruci-

ble respectively. In the case of the sample heated in the punched crucible, no thermal transitions are observed up to 200°C , which could suggest water evaporation, melting of the sample or

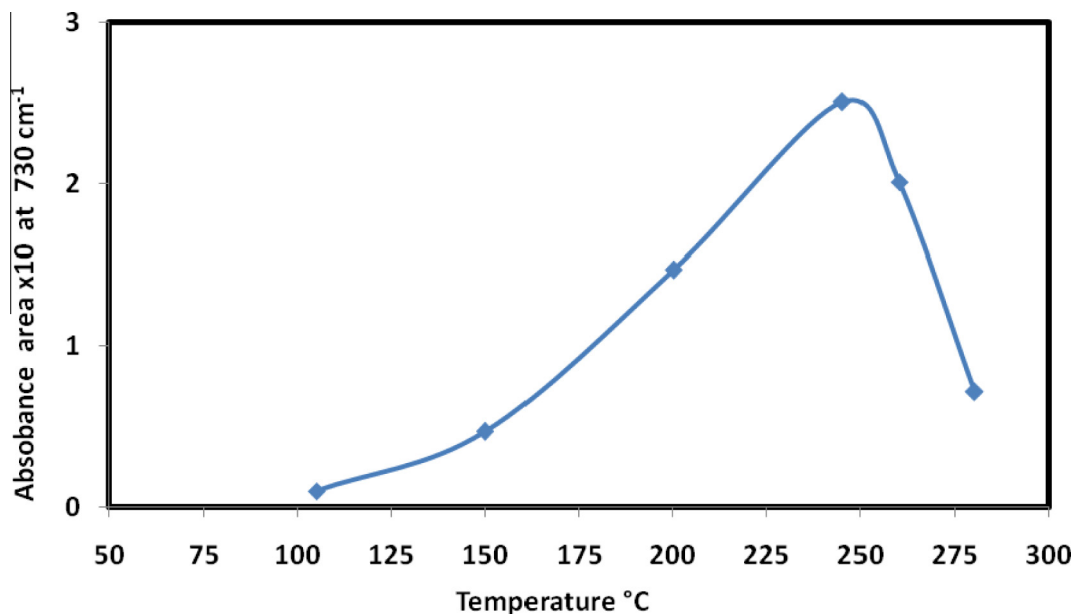


Fig. 5. Amount of acetylene released during the thermal decomposition of mercury diacetylide as measured with the TGA–FT-IR analytical technique. The amount of acetylene was evaluated from the area of the peak at 730 cm^{-1} from the spectra shown in Fig. 4. The absorbance area was measured using the Omnic software of the Nicolet 6700 spectrometer.

sublimation. Above $200\text{ }^{\circ}\text{C}$ the decomposition of $\text{Hg}(\text{C}\equiv\text{CH})_2$ starts and the decomposition onset was found at $245\text{ }^{\circ}\text{C}$, in comparison to $250\text{ }^{\circ}\text{C}$ measured with the TGA–DTA in Section 3.2. The decomposition peak occurs at $287\text{ }^{\circ}\text{C}$, thus it is at a slightly higher temperature than that measured in the TGA–DTA. The broadened shape of the decomposition peak suggests a deflagration of the sample rather than a sharp detonation. The total heat released in the thermal decomposition is impressive: 727.1 J/g . Fig. 6 also shows that the $\text{Hg}(\text{C}\equiv\text{CH})_2$ sample heated in the sealed crucible to the decomposition point releases virtually the same amount of heat: 724.2 J/g , but in this case the release of heat occurs in a sharp peak, suggesting a detonation of the sample inside the crucible. Indeed the crucible was found to be deformed, but not broken, after the measurement. Because the $\text{Hg}(\text{C}\equiv\text{CH})_2$ sample was heated in a sealed crucible under pressure, it remained stable above $300\text{ }^{\circ}\text{C}$. In fact the decomposition onset this time was found at $326\text{ }^{\circ}\text{C}$, while the explosion peak was at $337.4\text{ }^{\circ}\text{C}$.

With the DSC of Fig. 6 we have measured the heat released by reaction (3), which corresponds to an average value of 725.6 J/g . Since the molecular weight of $\text{Hg}(\text{C}\equiv\text{CH})_2$ is 250.63 Dalton , the heat released from reaction (3) is $725.3 \times 250.63 = 181.78\text{ kJ/mol}$. Since we know that the standard enthalpy of formation of acetylene is $+226.75\text{ kJ/mol}$ [40], the free energy of formation of $\text{Hg}(\text{C}\equiv\text{CH})_2$ is:

$$\Delta H_{R(3)} = [\Delta H^{\circ}_{f(\text{H}-\text{C}\equiv\text{C}-\text{H})} + \Delta H^{\circ}_{f(\text{Hg})} + \Delta H^{\circ}_{f(\text{C})}] - [\Delta H^{\circ}_{f(\text{Hg}(\text{C}\equiv\text{C}-\text{H})_2)}] \quad (4)$$

and by substituting with values we have:

$$-181.78 = 226.75 + 0 + 0 - [\Delta H^{\circ}_{f(\text{Hg}(\text{C}\equiv\text{C}-\text{H})_2)}] \quad (5)$$

so that

$$\Delta H^{\circ}_{f(\text{Hg}(\text{C}\equiv\text{C}-\text{H})_2)} = +408.5\text{ kJ/mol} \quad (6)$$

Consequently, from the average bond dissociation energy of divinylmercury [39] we have calculated $\Delta H_f = +363\text{ kJ/mol}$ for $\text{Hg}(\text{CH}=\text{CH}_2)_2$ in the gas phase, while the enthalpy of formation of diphenylmercury in the gas phase is $+392\text{ kJ/mol}$ [41]. As another reference, the enthalpy of formation of the explosive mercury fulminate $\text{Hg}(\text{NCO})_2$ is $+941.56\text{ kJ/mol}$ [42,43].

Table 1 summarizes the decomposition temperature and heat of the other explosive acetylides recently studied [7]: dicopper acetylide (Cu_2C_2) and disilver acetylide (Ag_2C_2) in comparison to mercury diacetylide. From Table 1 it is evident that Cu_2C_2 decomposes at the lowest temperature, only $126.7\text{ }^{\circ}\text{C}$, but the decomposition heat released in terms of kJ/mol is surprisingly coincident with the decomposition heat released by $\text{Hg}(\text{C}\equiv\text{CH})_2$: 185 kJ/mol for Cu_2C_2 against 181.8 kJ/mol for $\text{Hg}(\text{C}\equiv\text{CH})_2$. In terms of decomposition temperature, Ag_2C_2 is in the middle between dicopper acetylide and mercury diacetylide: $169\text{ }^{\circ}\text{C}$. However the decomposition heat released by Ag_2C_2 is ≈ 1.41 times the heat released in the deflagration of $\text{Hg}(\text{C}\equiv\text{CH})_2$ and Cu_2C_2 .

A useful value for the estimation of the hazard potential of an explosive compound is the maximum (adiabatic) temperature increase, which is given by the following equation [44]:

$$\Delta T_{\text{adiabatic}} = Q_{\text{expl}}/C_p \quad (7)$$

where Q_{expl} is the heat released during the confined explosion inside the stainless steel crucible and C_p is the mean heat capacity of the reaction contents, which is about 1.5 J/g for organic compounds but only 0.14 J/g for elemental mercury [45]. Then, for mercury diacetylide, $5183\text{ K} > \Delta T_{\text{adiabatic}} > 484\text{ K}$, which corresponds to a hazard potential of “very high” [45].

The activation energy of decomposition of $\text{Hg}(\text{C}\equiv\text{CH})_2$ can be measured by DSC in a sealed crucible using different heating rates [43,44]. As shown in Table 2, the decomposition temperature peak is affected by the heating rate and is shifted to higher temperatures for higher heating rates. The data in Table 2 can be elaborated according to the Ozawa equation [45]:

$$(2.15\text{Log}\beta)(1/T_{\text{peak}})^{-1} = -E^{\#}/R \quad (8)$$

or according to the Kissinger equation [45]:

$$[2.303\text{Log}(\beta/T^2)](1/T_{\text{peak}})^{-1} = -E^{\#}/R \quad (9)$$

This yields an activation energy for the thermal decomposition of $\text{Hg}(\text{C}\equiv\text{CH})_2$ of 153 kJ/mol .

Again, in comparison, it is interesting to note here that the activation energy for the decomposition of mercury fulminate is

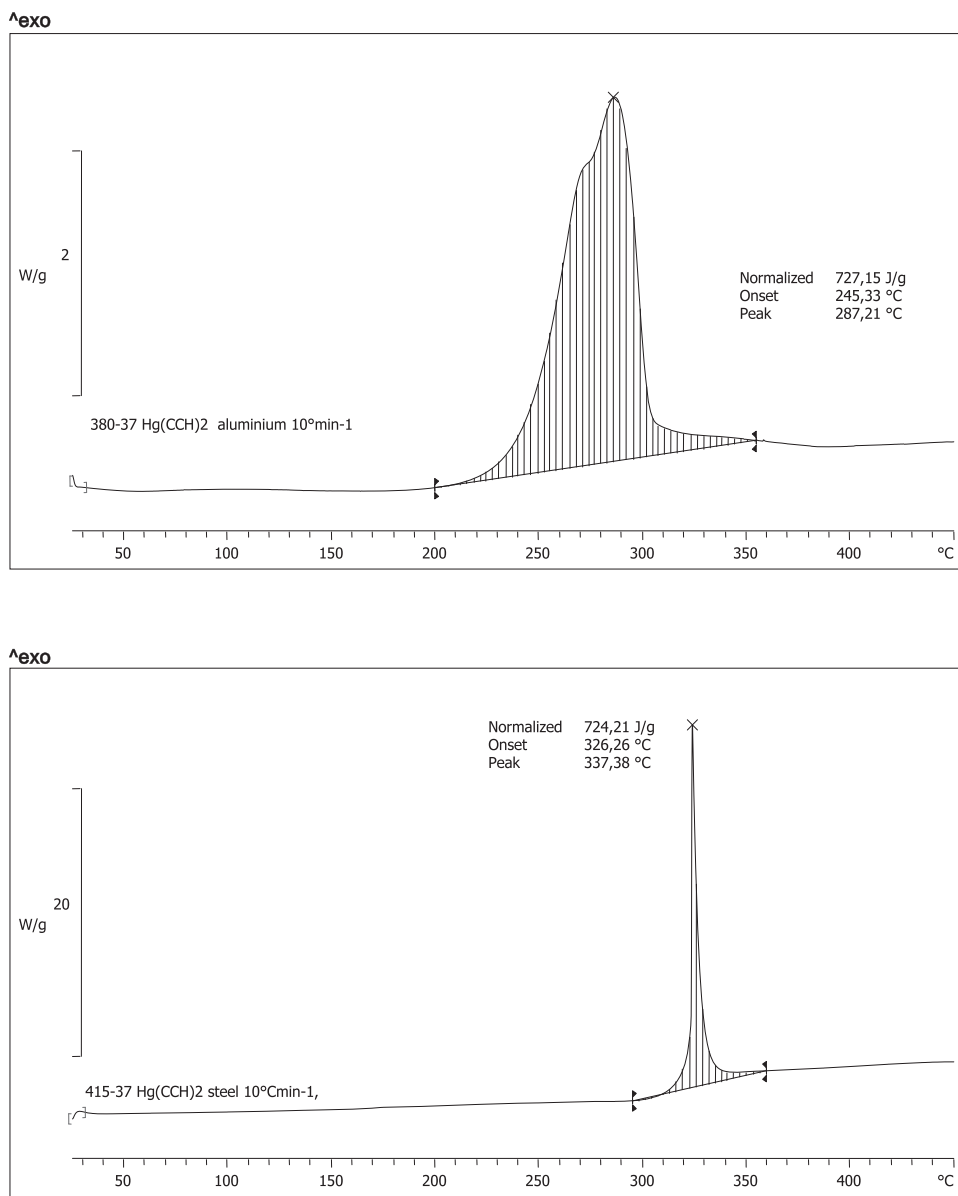


Fig. 6. Differential scanning calorimetric (DSC) measurement of mercury diacetylide. Both the DSC traces were recorded at a heating rate of 10 °C/min under a N₂ flow. The DSC trace in the upper figure was obtained for a sample heated in an aluminium crucible with a hole in the cap. The decomposition onset starts at 245 °C and the peak is reached at 287 °C. The DSC trace in the lower figure was obtained for a sample heated in a sealed, medium pressure, steel crucible. The use of a sealed crucible retards the decomposition onset, which occurs at 326 °C, while the decomposition peak is at 337 °C. However, in both cases the normalized heat released in the decomposition is comparable: 727 J/g in the upper figure and 724 J/g in the lower figure.

Table 1
Key decomposition properties of acetylides.

	Dec. T (°C)	Dec. heat (J/g)	Molecular weight (Dalton)	Dec. heat (kJ/mol)	Refs.
Cu ₂ C ₂	127	1225.2	151.11	185.1	[7]
Ag ₂ C ₂	169	1070.4	239.76	256.6	[7]
Hg(C≡CH) ₂	287	725.6	250.63	181.9	this work

Table 2
E[#] For Hg(C≡CH)₂ decomposition.

Heating rate (°C/min)	Peak dec. temp. (°C)	E [#] (kJ/mol) Ozawa equation	E [#] (kJ/mol) Kissinger equation
5	320.45	152.9	153.6
10	337.38	152.9	153.6
20	347.30	152.9	153.6
40	360.69	152.9	153.6

105 kJ/mol, while it is 167 kJ/mol for silver azide and 160 kJ/mol for lead azide [41]. Mercury fulminate is reported to be much more sensitive to impact and friction detonation than silver and lead azide due to its lower activation energy for the decomposition reaction [41].

The detonation velocity and the detonation pressure are other parameters which can be easily estimated using the Kamlet and Jacobs equations [46,47] once the heat released during the thermal decomposition of Hg(C≡CH)₂ is known.

Table 3
Detonation velocity and pressure of Hg(C≡CH)₂.

	Density (g/cm ³)	Detonation velocity (mm/s)	Detonation pressure (kbar)
Mercury fulminate	3.3	4.5	n.a.
Lead azide	3.8	4.5	n.a.
TNT	1.6	6.8	190
RDX	1.8	8.8	338
HMX	1.9	9.1	390
HNB	2.0	9.4	406
CL-20	2.0	9.4	420
ONC	2.1	10.1	500
Hg(C≡CH) ₂	5.3	10.5	760

Note: All the data in the table are from Refs. [42] and [47], with the exclusion of the data on Hg(C≡CH)₂ which are the result of the present work. TNT = trinitrotoluene; RDX = cyclotrimethylenetrinitramine; HMX = cyclotetramethylenetetranitramine; HNB = hexanitrobenzene; CL-20 = hexanitrohexaazaisowurtzitan; ONC = octanitrocubane.

$$\text{Detonation velocity [mm/ms]} = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho_0) \quad (10)$$

$$\text{Detonation pressure [kbar]} = 15.58\rho_0^2NM^{1/2}Q^{1/2} \quad (11)$$

where N = moles of detonation gases per gram of explosive, M = average molecular weight of these gases, Q = chemical energy of the detonation [cal/g], and ρ_0 = density of the explosive [g/cm³].

Using the decomposition reaction data (3), the value of $N = 0.0159$ and $M = 68.64$, assuming that at the explosion temperature elemental mercury is in the gaseous state together with acetylene and carbon vapor. Using a density of 5.3 g/cm³ for Hg(C≡CH)₂ and the decomposition heat of 725.6 J/g = 173.4 cal/g, and substituting in Eqs. (10) and (11), the detonation velocity and detonation pressure of mercury diacetylide are obtained and reported in Table 3 in comparison to a series of common and less common explosives taken from Ref. [47].

The results are impressive: Hg(C≡CH)₂ seems to outperform all the other explosives both in terms of detonation velocity and detonation pressure. However, these results must be taken only as a rough estimate since the Kamlet and Jacobs equations are optimized only for explosives of the type CHNO, thus for molecules not containing metals or other types of heteroatoms.

4. Conclusions

The chemical structure of mercury diacetylide was studied by FT-IR spectroscopy in the mid and far infrared, as well as by electronic absorption spectroscopy. All the spectral data are consistent with the structure H-C≡C-Hg-C≡C-H. The polymeric structure (-Hg-C≡C-)_x proposed by Aylett [14], on the grounds of its insolubility, can be ruled out on the basis of the strong infrared stretching band at 3280 cm⁻¹ (see Fig. 1). Such a band should be absent or extremely weak in the case of a polymeric structure. Furthermore, mercury diacetylide is indeed insoluble but it shows a minimal solubility, for instance in tetradecane and ethanol, and this has permitted us to record the electronic absorption spectrum of mercury diacetylide and to make an estimation of its solubility.

Remarkably, the electronic absorption spectrum of mercury diacetylide resembles that of diacetylene, suggesting that the mercury atom inserted between the two acetylenic moieties does not interrupt the π resonance occurring between the two groups. The insolubility of mercury diacetylide as well as the lack of volatility and the absence of a melting point until its decomposition onset at 250 °C is explained in terms of π interactions between the Hg

atoms and the C≡C bonds of the adjacent Hg(C≡C-H)₂ molecules, leading to a homoleptic structure [30] similar to that suggested for the dicopper and disilver acetylides [7].

It is confirmed that Hg(C≡C-H)₂ undergoes an explosive and exothermal deflagration when heated either in an open aluminium crucible or in a sealed stainless steel crucible under a nitrogen flow. The thermal decomposition of Hg(C≡C-H)₂ releases 725.6 J/g with an onset temperature of about 250 °C and a peak temperature of 287 °C. The decomposition occurs at a higher temperature in a sealed crucible (onset 326 °C and peak 337 °C). As shown in Table 1, the amount of heat released in the explosive decomposition of Hg(C≡C-H)₂, 181.9 kJ/mol, is the same as that released by the explosive decomposition of dicopper acetylide (Cu₂C₂).

Using the TGA-FT-IR analytical technique it has been determined that the thermal decomposition of Hg(C≡C-H)₂ occurs under N₂ according to reaction (3), with the formation of elemental carbon, elemental mercury and acetylene. Through reaction (3) and the amount of heat produced in the deflagration of mercury diacetylide it was possible to calculate, for the first time, the enthalpy of formation of mercury diacetylide: ΔH_f Hg(C≡C-H)₂ = +408.5 kJ/mol. The activation energy for the thermal decomposition of mercury diacetylide was ascertained to be about 153 kJ/mol, a value comparable to that of silver and lead azides. Such a relatively high activation energy makes mercury diacetylide relatively insensitive to friction and shock-induced explosion, as in the case of the mentioned azides.

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