

The Mechanochemical Self-Propagating Reaction between Hexachlorobenzene and Calcium Hydride

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We report on studies of the solid state reaction between hexachlorobenzene and calcium hydride carried out by high-energy ball milling. The transformation behavior depends on the intensity of the mechanical energy transferred to the reactants at the impact. At lower energy regimes, chemical conversions increase gradually as a function of the milling time and a large excess of calcium hydride was found to favor the reaction rate. Calcium hydride-chloride and benzene are formed as end products. Beyond an impact energy threshold, self-sustaining transformations were observed leading to an instantaneous transformation to hydrogen, graphite, and, depending upon the reactant molar ratio, to calcium hydride-chloride or calcium chloride. The sudden increase of the reactor-vial temperature was proportional to the hexachlorobenzene content in the reacting mixture and the total heat evolved was found to be in good agreement with the forecasted reaction enthalpies. The ignition time, i.e., the milling time at which the combustion-like event occurs, was followed as a function of the reactant composition. The incubation period rapidly decreases by increasing the calcium hydride to hexachlorobenzene molar ratio, that is, moving away from the stoichiometric composition at which calcium chloride forms predominantly. Some suggestions concerning the activation energy of the two competing end products were inferred from the mechanochemical yield which has been calculated as the ratio between the moles of reacted hexachlorobenzene divided by the total injected energy dose. Keeping the molar composition constant and modulating the shock power intensity, the self-sustaining reaction takes place only when the same dose of mechanical energy has been supplied to the reacting system, irrespective of the single impact energy. © 1997 Academic Press

INTRODUCTION

Recent works have described the mechanochemical degradation of chlorinated organic compounds by high-energy ball milling. Calcium and magnesium powders and their oxides were used as reactive substrates (1). The specific use of calcium hydride as a reducing agent allowed the dehalogenation process to be accomplished along a neater and quite straightforward path (2). In the case of chloro-

benzene, the products of the completed reaction were restricted to benzene and chloride salts. Neither the breakdown of the organic species into unwanted by-products nor the formation of toxic congeners was observed (2).

The solid-state reaction between hexachlorobenzene and CaH_2 is worthy of further interest which adds up to our initial concern in the disposal of chlorinated aromatics and environmentally related problems. In fact, a combustion-like reaction was observed, suggested by a sudden increase of the milling-vial temperature and leading to the instantaneous and complete dehalogenation of the parent organic compound. To obtain some understanding of the chemistry involved we explore here the reactivity behavior of the system under milling as a function of the $\text{CaH}_2/\text{C}_6\text{Cl}_6$ molar ratio and of the kinetic energy transferred to the milled powders on impact.

It is known that high-intensity mechanical milling can induce self-propagating combustion reactions in highly exothermic systems. Tschakarov *et al.* (3) first observed the explosive mechanochemical synthesis of metal chalcogenides from their elemental constituents. Further examples have been reported in the last few years also concerning the oxygen displacement reaction of a metal oxide with a more reactive metal partner (4), the formation of intermetallic alloys (5), the magnetite reduction by aluminum (6), and the synthesis of refractory compounds (7). To the best of our knowledge, however, no combustion-like reactions have been reported yet involving organic compounds under milling. Furthermore, the thermodynamics of the system under examination are also important owing to the competing roles of the two reaction products, calcium chloride and calcium hydride-halide, which depend on the stoichiometry of the reacting mixture.

More general questions arise concerning common aspects between chemical reactions triggered by high-intensity ball milling and other solid state processing techniques such as self-propagating high-temperature synthesis (SHS) (8) or those initiated by dynamic compression during the passage of shock waves (9). The fundamental reaction mechanisms for all of these processes remain poorly understood and

possible correlations are rarely obtainable due to the largely different conditions under which processes are run. Progress in this direction demands a precise evaluation of the processing variables. Accordingly, we focus here on the intrinsic parameters of the milling treatment, such as the kinetic energy transferred at the collision event and the impact frequency, to determine the threshold conditions required for ignition. An effort is also made to establish a relationship between the amount of energy expended and the mechanochemical yield.

EXPERIMENTAL SECTION

General Procedures

The calcium hydride (95% purity, $-4 + 40$ mesh) and hexachlorobenzene (99%) compounds were obtained from Aldrich.

The reacting powders were mixed at different $\text{CaH}_2/\text{C}_6\text{Cl}_6$ molar ratios and loaded into a special hardened steel vial, used as batch reactor, inside a glove box under a purified argon atmosphere. Constant loads of approximately 8.8 g were used and the milling treatments were carried out with a commercial 8000 Spex Mixer Mill operating at 1425 rpm corresponding to 875 cycles per min of the vial.

In the course of the experiments the temperature was continually recorded by a thin lamella-shaped Pt resistance thermometer fixed on a groove machined on the external surface of the vial. Quasi-adiabatic conditions were obtained with an insulating jacket of granulated cork. The total heat capacity of the reactor vial was determined by heating the system with a carefully measured quantity of electrical energy.

At the end of the milling treatments gaseous products were sampled from the reactor head space through leak-proof valves and analyzed by a PE 8500 GC equipped with a flame ionization detector. Part of the reacted mixtures were then removed from the vial, solubilized in *n*-pentane, and analyzed by a Fisons HRGS 5300 GC and a Finnigan TRACKER Mass Spectrometer GC/MS PE 8420.

The chemical conversion is reported as total percent organic chlorine converted to inorganic chloride.

X-ray diffraction (XRD) analysis was carried out with a Siemens D500 diffractometer equipped with a graphite monochromator in the diffracted beam. $\text{CoK}\alpha$ radiation was employed and patterns were collected stepwise over selected angular ranges until a satisfactory signal-to-noise ratio was reached. Owing to the hygroscopicity and reactivity of CaCl_2 and CaHCl salts, scans were performed under helium by using a special sample holder. The identification of the diffracting phases was accomplished by peak analysis routine on the basis of Data Index Powder Diffraction Files (10).

We warrant the reader that all handling procedures must be performed with care under a controlled environment

owing to the possibility of toxic by-products of the incomplete reaction and the very high reactivity of hydrides.

Evaluation of Impact Frequency and Energy Transfer

Full details on the experimental procedures we have developed to evaluate the collision energy and the impact frequency in milling processes are given in Refs. (11, 12).

In all but a few noted cases, milling runs were carried out with a single ball to avoid ball-ball collisions and rebound phenomena, which prevent a reliable evaluation of the frequency and intensity. To modify the energy intensity of the collision over a suitable range, balls of different size and density (tungsten-carbide or stainless steel) were chosen.

The complex action of the Spex-Mill shakes the vial along a harmonic tridimensional swing which cannot be easily reduced to a functional form. For this reason the vial course was reconstructed by acquiring the vial coordinates in a fixed reference frame step by step during a complete cycle. This was accomplished by making use of a mechanical tracking system. The vial coordinates were recorded and used as a data base for a computer program which reconstructs the actual motion of the vial, also providing its instantaneous velocity throughout the whole period T of the cycle. Assuming inelastic impact conditions, the ball moves along with the vial, then detaches from the vial end when the vial has reached the maximum velocity and begins to decelerate. The ball travels a linear trajectory at a constant speed which corresponds to the highest vial velocity. The ball impact occurs at the opposite end of the vial when the vial has passed its maximum displacement point and has already acquired speed in the opposite direction. After each collision, ball and vial move jointly up to the next detachment. Two collisions occur per cycle at $T/4$ and $3T/4$. To calculate the ball trajectory, the computer program takes into account the real inclination of the vial base as well as the transversal and longitudinal components of the acceleration at the moment of the launch. The program also calculates the flight time of the ball, the impact time, the position, and the velocity of the vial at the moment of the impact. Then the component of the vial velocity along the ball trajectory was used to get the relative ball velocity. An average parameter, v_{kin} , was obtained by taking into account possible different trajectories. From v_{kin} , the energy transferred per hit, E (Joule), was obtained as $(mv_{\text{kin}}^2)/2$, (m is the mass of the ball), whereas the shock power I (watt) has been determined by multiplying E by the number of hits per second N .

This semiempirical model has been substantiated experimentally. To detect the impact time, a method was implemented by employing a magnetic position sensor coupled with a piezoelectric transducer fixed at one end of the vial. When the vial reaches the maximum displacement points, the position sensor emits a trigger pulse with reference to which the piezoelectric device records each impact. The

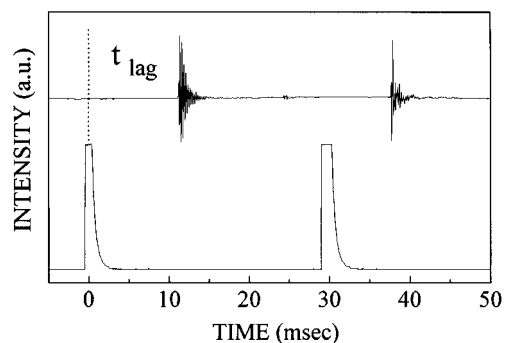


FIG. 1. (inset) Typical traces registered by a piezoelectric device (upper trace) coupled with a position sensor (low graph). The bars mark the time lag between the passage of the vial at the maximum angular position and the impact event.

piezoelectric transducer, connected with an amplifier and an analyzer, reveals each collision as an oscillation rapidly fading away to the background level. An on-line computer records both the trigger and piezoelectric signals allowing one to determine the impact time with respect to $T/2$ or T (at which the vial reaches the maximum displacement points). This can be seen in Fig. 1. Figure 2 reports a complete pattern collected over 0.3 sec by using an 8.78 g powder batch of a $\text{CaH}_2\text{-C}_6\text{Cl}_6$ mixture milled with a hardened steel ball of 12.4-mm diameter for a mass of 8.3 g. One notices that a regularly spaced impact is registered at each half cycle, timed with the trigger signal. An average of 29 hits per second was obtained and this value corresponds to twice the vial frequency of 14.6 cycles per sec.

For each milling run, one hundred time lags were averaged and entered in the computer program to determine the position and the acquired velocity of the vial at the moment of the impact. As previously remarked, the impact energy was obtained by taking into account the component along the ball trajectory. The so-obtained values are found to be in good agreement with the calculated values, with the

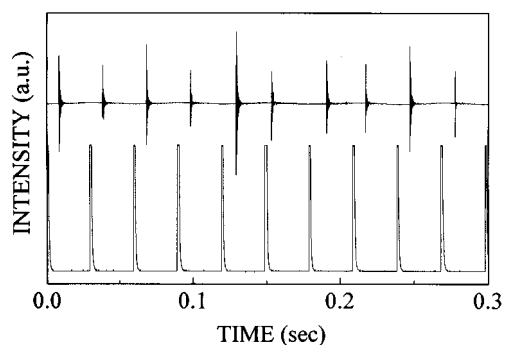


FIG. 2. Collision sequence registered by the piezoelectric probe during a milling time of 0.3 sec. Spikes in the low trace register each half period of the vial motion.

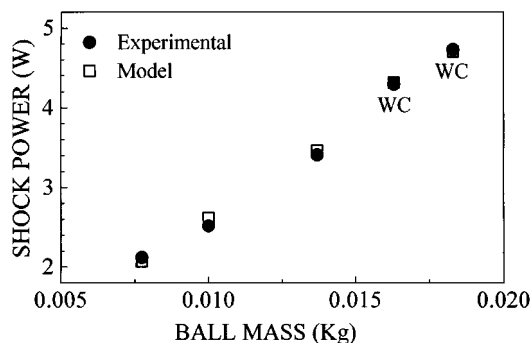
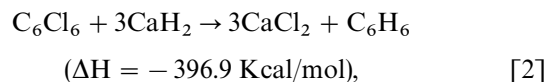
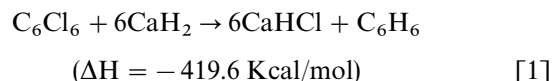


FIG. 3. Shock powers as a function of the ball masses. Full symbols refer to values obtained by averaging the time lags, whereas the open squares point out the corresponding parameter from the model. Stainless steel or tungsten carbide (WC) balls were employed.

modeling and experimental approaches supporting each other satisfactorily. Comparison is performed in Fig. 3 which reports the shock power transfer as a function of the mass of the balls we have employed in this work.

RESULTS AND DISCUSSION

Depending on the molar ratio of the reactants, the complete dehalogenation process occurs according to two possible pathways



both reactions being highly exothermic. The relevant thermodynamic data were obtained from different sources (13–15).

Initial milling trials were performed at low-impact regimes over a wide range of $\text{CaH}_2/\text{C}_6\text{Cl}_6$ molar ratios. The dehalogenation process behaved as a “normal” mechanochemical reaction, no self-sustaining transformations were observed and a spread of products began to form after a first induction period. Some results are given in Fig. 4 in which the C_6Cl_6 conversion is presented as a function of the $\text{CaH}_2/\text{C}_6\text{Cl}_6$ molar ratio for trials performed with four balls of 1 g each (in a single ball experiment an impact energy of approximately 0.02 J was measured).

Conversions have been obtained by analyzing the reacted mixtures at the end of continuous milling treatments lasting 12 hr: one notices that a large excess of calcium hydride in the mixture speeds up the transformation rate significantly. At intermediate milling times, a progressive change of the

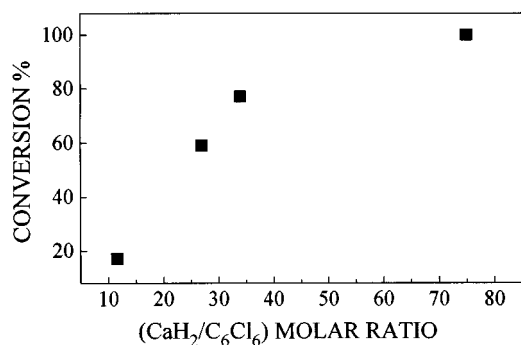


FIG. 4. Hexachlorobenzene conversion values after 12 hr milling treatments as a function of the $\text{CaH}_2/\text{C}_6\text{Cl}_6$ molar ratio in the reacting mixture.

products was observed. As shown in Fig. 5, the GC/MS analysis reveals the initial formation of a number of compounds including partially chlorinated compounds, peaks 2 to 10, biphenyl, 11, and some PCBs, 15–18. However, the progress of the mechanical treatment restricted the organic products essentially to benzene. Methane and ethane were also identified in the gaseous samples withdrawn from the vial head space. X-ray analysis of the 100% conversion powders shows the formation of CaHCl even if patterns are dominated by the diffraction peaks of CaH_2 , which is in agreement with the larger amount of CaH_2 used in the trials.

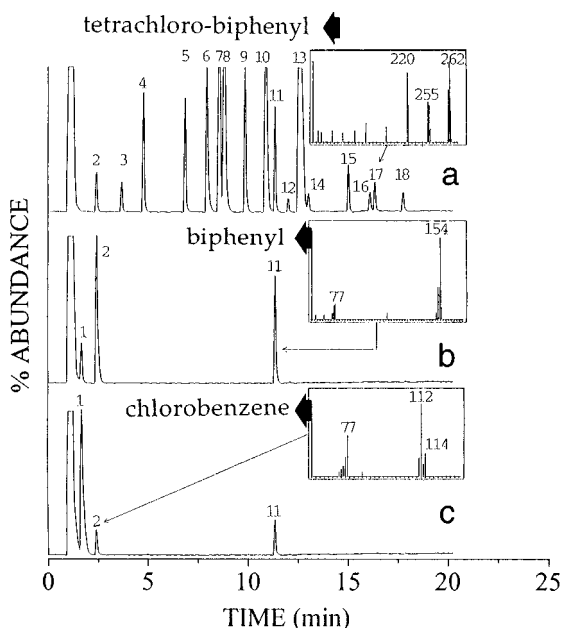


FIG. 5. Chromatograms relevant to a $\text{CaH}_2/\text{C}_6\text{Cl}_6$ mixture with a molar ratio of 75:1 reacted for 3, 6, and 9 hr (from the top). The mass spectra of the compounds pointed out by the arrows are shown in the insets. Four balls of 1 g were used.

New aspects emerged by increasing the impact energy of the milling treatment. For a given composition, an energy threshold exists beyond which a self-propagating reaction occurs. This is observed in an abrupt rise in the vial temperature and subsequently assessed by product analyses. Typical temperature traces are shown in Fig. 6.

Several concurring factors have been advanced to explain self-propagating or explosive-like behaviors under milling. Local activated states develop in the mechanically processed powder due to accumulation of structural defects, vacancies, dislocations, and intergranular boundaries. These promote diffusive events, chemical interactions, and spontaneous transformations. The continued recleaning of the available surfaces by the milling action limits diffusional influences and prevents the products from hindering further reaction. This regime has been referred to as deformation mixing (16). Similar mechanisms underlie the transformation processes observed at low-impact energy and during the precombustion periods. However, higher intensive grinding acts to increase both the defect content and the accessible reaction area by further reduction of the powder particle size. More activation sites form and a larger excess energy is accumulated in the extended network of intergranular boundaries that is consequentially available for chemical reaction. In addition to this, the local temperature increases in the immediate impact area due to the higher power of the colliding ball. It is generally maintained that the process speeds up to a critical rate above which the reaction spreads spontaneously because of the powder self-heating (17). This is due to the emission of the large reaction heat. It is worth noting that in this view the self-sustaining reaction is not intrinsically a mechanochemical reaction even if the deformation mixing appears to be the limiting stage for the thermally activated process.

This picture provides only general explanations. To acquire quantitative insights of the reaction, we explored the

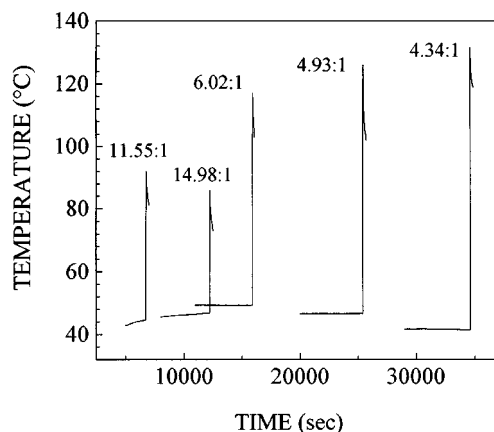


FIG. 6. Vial temperature spikes registered as a function of milling time for various reactant compositions.

TABLE 1
Mechanochemical Results at Constant Impact Energy J/hit = 0.118

CaH ₂ /C ₆ Cl ₆ Molar ratio	C ₆ Cl ₆ 10 ² Mol	<i>t</i> _{ign} (sec)	Δ <i>T</i> (K)	Δ <i>Q</i> _v (KJ/mol)	Dose KJ	Yield (Mol/MJ)	Δ <i>Q</i> _v /Σ <i>s</i> C _p (K)	Δ <i>H</i> /Σ <i>s</i> C _p ^a (K)
4.34	1.87	34625	79.6	413.7	118.1	0.158	4141	^b 4139
4.93	1.79	25420	79.5	431.6	86.7	0.206	4107	^b 3912
6.02	1.63	15910	69.9	417.0	54.3	0.300	3584	3719
9.02	1.32	12540	56.8	418.3	42.8	0.309	2858	2957
11.48	1.14	10800	50.7	432.5	36.8	0.310	2519	2520
14.98	0.96	12225	42.3	428.2	41.7	0.231	2081	2102

^a Calculated for CaHCl formation, according to reaction [1].

^b Calculated for CaCl₂ formation, according to reaction [2].

concentration range within which explosive-like phenomena occur by a first series of milling treatments carried out under a constant input energy. Strictly comparable experimental conditions were kept, with a constant powder load of 8.78 g and by using only one hardened steel ball with an average impact energy of 0.118 J. The experiments were interrupted when the sudden temperature increase was observed, or at a maximum time of 12 hr. A comprehensive view of the results is given in Table 1.

The explored compositions are reported in Fig. 7 as CaH₂ mol% and as CaH₂/C₆Cl₆ molar ratio. The latter diagram is more representative. Although stoichiometric mixtures are expected to favor self-sustaining behaviors, the combustive region found here covers only in part the stoichiometric range of 3 to 6, corresponding to the reactions. One notices that the self-propagating regime continues at the larger contents of CaH₂: the hydride excess seems to hold an essential role in steering the process, as it was previously suggested by the conversion trend at low-impact energies. Further details emerge considering the sharp vial temperature increases, Δ*T*, and the related ignition times, *t*_{ign}. As

for the former parameter, a linear trend in Fig. 8 characterizes the Δ*T* values in the whole range pointing out their direct proportionality with the amounts of C₆Cl₆ in the mixture.

The heats evolved per mole of C₆Cl₆, Δ*Q*_v, were then calculated taking into account the total heat capacity of the vial reactor system, the ball included. Adiabatic conditions were assumed based upon the short time scale of the event. The results presented in Fig. 8 compare well to the above-reported reaction enthalpies. The contribution due to the constant-volume running mode of the reaction is negligible, moreover, −11.7 Kcal/mol must be added to the quoted values since graphite and hydrogen form during the process from each molecule of benzene. Furthermore, in spite of the experimental data scatter, a trend is discernible, descending with the increase of C₆Cl₆ in the reacting mixture, which appears to be significant. It can be explained by noting that the reaction leading to CaHCl, which is expected to form at high CaH₂ content, progressively turns in favor of the less exothermic formation of CaCl₂. About 22 Kcal/mol differentiate the two transformation paths.

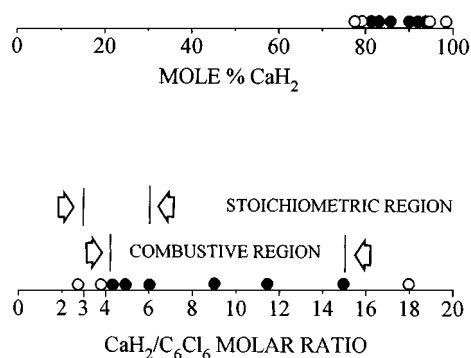


FIG. 7. CaH₂-C₆Cl₆ concentration diagram giving a survey of the explored mixtures. Compositions with a self-sustaining behavior are shown by full circles. The stoichiometric range corresponding to the quoted reactions are marked by vertical bars.

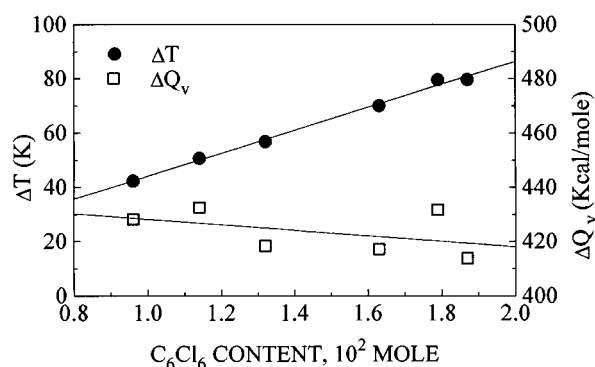


FIG. 8. Vial temperature increases, Δ*T* (full circles), and the corresponding emitted heats, Δ*Q*_v, (open squares) as a function of the C₆Cl₆ mole content.

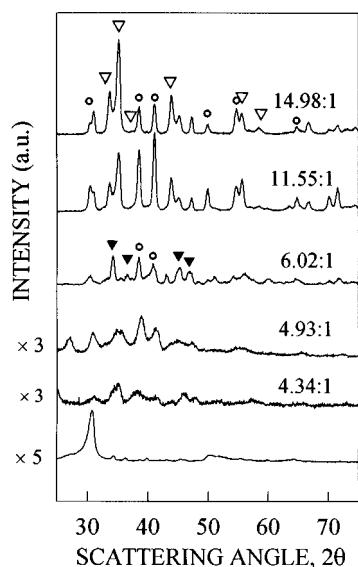


FIG. 9. CoK α X-ray diffraction patterns of the reacted mixtures. The corresponding CaH₂/C₆Cl₆ molar ratios are shown in the inside. For each compound of interest, the angular positions of the main peaks are also quoted. Open triangle, CaH₂; open circles, CaHCl; full triangles, CaCl₂.

This suggestion is substantiated by the XRD analysis. With reference to Fig. 9, disorder and particle size effects strongly broaden the peak profiles which also overlap since Bragg positions of different compounds fit in the same angular range. However, the diffraction peaks from the excess of CaH₂ (JCPDS Card 13-384) and from CaHCl (JCPDS Card 14-167) characterize the upper pattern. The peak intensities decrease progressively and are still visible for the 4.34 molar ratio mixture. Here the CaCl₂ phase (JCPDS Card 12-56) gives an important contribution to the pattern. The lowest trace is relative to the carbonaceous residue obtained by washing in *n*-pentane and filtering the reacted powder: the main peak relevant to graphite is always present along the pattern sequence. Significantly, no signals from unreacted C₆Cl₆ are observable. So a frame has been obtained coherent with the thermal findings.

Returning to the related ignition times, a well defined trend is observable in the t_{ign} data set presented in Fig. 10. Values decrease quickly inside the stoichiometric range and a weak increase is also discernible at the other extremity of the combustible region.

The ignition time is commonly correlated with the exothermic character of the reaction. Owing to the lack of required thermodynamic data in the literature, it was only possible to calculate the true adiabatic temperature for the reaction path leading to CaCl₂, hydrogen and graphite: a value of 2894 K was obtained. Nevertheless, a self-consistent reference frame was obtained for the sake of comparison, neglecting the latent heats and the temperature dependence of the heat capacity. Data were obtained as the

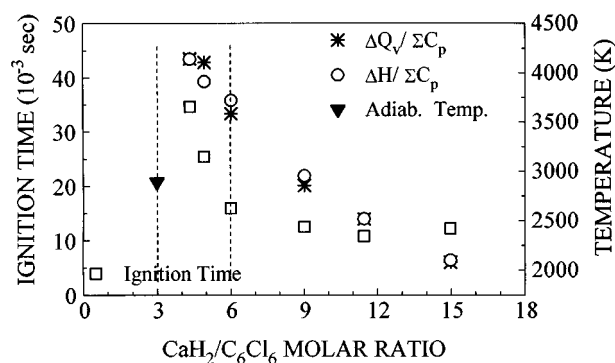


FIG. 10. The ignition time trend across the composition range (open squares). $\Delta Q_v/\Sigma C_p$ and $\Delta H/\Sigma C_p$ values are presented as star symbols and open circles, respectively, whereas the true adiabatic temperature, calculated for the complete transformation to CaCl₂, is shown as a triangle. The pertinent scale is on the right-hand side.

ratio between the heat evolved and the mean heat capacity at room temperature of the end products, including the CaH₂ excess, and are shown in Fig. 10 as $\Delta Q_v/\Sigma C_p$. We also report the $\Delta H/\Sigma C_p$ values obtained by using the quoted reaction enthalpies normalized to the actual compositions: depending on the reactant molar ratio, -431.3 or 408.5 Kcal/mol have been employed as computation input. See also Table 1. There is a good agreement between $\Delta Q_v/\Sigma C_p$ and $\Delta H/\Sigma C_p$, further supporting the reliability of the ΔQ_v experimental parameter.

The ignition time trend parallels the decrease of the $\Delta Q_v/\Sigma C_p$ values and therefore does not conform to the forecasted behavior according to which the shortest ignition times are expected for mixture compositions with highest adiabatic temperatures, which usually correspond to the exact reaction stoichiometry. For instance it has been reported that the precombustion milling periods of certain reduction reactions involving metal oxides generally decrease with increasing adiabatic temperature (17). An opposite dependence is observed here, and this behavior may be due to the excess of CaH₂ which increases the total heat capacity of the mixture, whereas not contributing to the released reaction heat. The effects of nonstoichiometric compositions on the ignition times have been studied recently by Takacs and Susol in the synthesis of Zn and Sn sulfides from elemental powders and in the reduction of magnetite in a wide range of compositions (18). They observed the shortest ignition times far from ideal compositions and our results agree well with their findings.

It has also been suggested that combustion occurs, under milling, because the critical reaction temperature is reduced to the local temperature of reactants. For the CuO/Fe reduction couple, Schaffer and McCormick followed such a decrease experimentally and argued that the ignition time is the milling time required for the critical temperature to

decrease to the powder temperature under processing (19). A similar correlation was not observed in the reduction of V_2O_5 over Mg, Al, and Ti studied more recently by Yang and McCormick (21) who also remarked that ignition times could not be associated with a critical degree of microstructural refinement. The combustion event seemed determined by the statistical probability of achieving a particular collision configuration under milling. However, the very regular behavior with which self-propagating events are observed in the present dehalogenation reaction cannot be explained by such particular structural states or by occasional local superheating due to the collision.

Being more properly related to the reaction mechanism, the mechanochemical yield of the reaction seems more pertinent to follow up this analysis. We express the mechanochemical yield as the total moles of reacted hexachlorobenzene—which, in agreement to the previous findings, corresponds to the nominal concentrations in the reacting mixtures, divided by the total energy dose D . D is obtained as the impact energy multiplied by impact frequency and by ignition time. The yield data are plotted in Fig. 11. Strictly constant values result in the central part of the combustive region, rapidly decreasing at the extremities. The drop at low CaH_2 is remarkable in that it occurs just at the molar ratio at which the hydride content is not enough to sustain the formation of the mixed hydride chloride. Stoichiometric constraints in this region require the concurrent formation of $CaCl_2$ as final compound. This behavior suggests two different reaction mechanisms which depend upon the reactant molar ratio, possibly because of different energy barriers relevant to the two competing end products. The present results concern a constant impact regime which means that the discrete amount of energy absorbed per hit is also constant. Longer milling times are therefore required to reach higher energy saturation limits. In the mixture leading to $CaHCl$, the excess energy of the system approaches the activation barrier for the reaction earlier, whereas the total

absorbed energy becomes inadequate to sustain the transformation to $CaCl_2$. It may therefore be surmised that the activation energy of the process leading to $CaCl_2$ exceeds that required for the formation of the mixed hydride chloride. It is also suggested by the fact that self-sustaining behaviors are no longer observed when the C_6Cl_6 content is increased further—within the 12 hr of the milling treatment at least.

At the other side of the combustive range, where a less rapid decrease is observed, the same transformation mechanism leading to $CaHCl$ holds. However, a large excess of CaH_2 now does not take part in the dechlorination process. The total injected power is partially consumed in this unreacted CaH_2 fraction and, accordingly, the energy dose needed to reach the energy threshold of the reaction requires longer milling times.

We now examine the results obtained in the second series of experiments. Here, the CaH_2/C_6Cl_6 molar ratio has been fixed at 11.8, corresponding to 0.0114 moles of C_6Cl_6 . The impact energy was varied by utilizing single balls of different size and mass. Results are collected in Table 2. The temperature spikes were found to be independent of the collision energy. When ΔT data are converted to the emitted heats by considering the actual heat capacity of the system (this parameter now changes because of the WC or stainless steel ball masses) ΔQ values average 426.9 Kcal/mol. This further confirms that the heat produced by the reaction depends only on the amount of hexachlorobenzene reacted.

As in the previous trials performed at constant energy intensity, the regularity of the ignition event is worth noting and a well-defined correlation exists between ignition times and the shock power. As seen in Fig. 12, a linear trend is evident, decreasing as the impact energy is increased, in spite of some dispersion. The incubation periods now depend upon the energy intensity of the milling treatment. Because of the impact energy variations across the range explored, the effects of the local temperature increases (20) cannot be disregarded. However, when the total doses are computed for each ignition time, the data spread remains

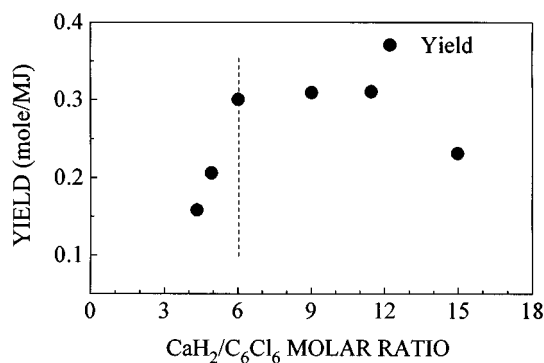


FIG. 11. Mechanochemical yield plotted as function of the CaH_2/C_6Cl_6 mole content. The broken vertical line shows the limit of CaH_2 excess in respect to the stoichiometric composition range.

TABLE 2
Mechanochemical Runs at Constant Molar Ratio

Impact energy (J)	ΔT (K)	ΔQ_v (KJ/mol)	t_{ign} (sec)	I (watt)	Dose (KJ)
0.073	52.6	437.4	12353	2.12	26.2
0.087	51.2	426.4	9851	2.51	24.7
0.118	50.7	432.5	8913	3.41	30.4
0.148	51.8	428.7	3355	4.29	14.4
0.163	49.4	409.4	3515	4.73	16.6

Note. $CaH_2/C_6Cl_6 = 11.48$; moles of $C_6Cl_6 = 0.0114$ hits/sec = 29; 8.78 g of mixture.

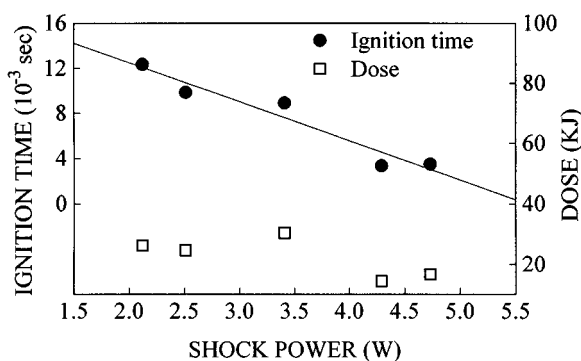


FIG. 12. Ignition times obtained at constant $\text{CaH}_2/\text{C}_6\text{Cl}_6$ molar ratio as a function of the experimentally determined shock power. The continuous line shows the best-fitted trend. The total doses are also shown in the lower part of the figure (open squares).

within a narrow range pointing out that the self-sustaining reactions take place only when a critical amount of mechanical energy has been supplied to the reacting system, irrespective of the single impact energy. From the data shown in Fig. 11, an average value for the energy dose was obtained as 22 ± 6 KJ. These results underline with some force that instantaneous states, which form under treatment, such as compositional fluctuations, structural configurations, and local temperature rises have only an ancillary role in the reaction ignition. These effects can act only when a well-defined level of mechanical energy has been transferred to the powder.

CONCLUSIONS

It seems to us that useful insights have been gained to elucidate the reactivity of hexachlorobenzene and calcium hydride under milling. The characteristic self-propagating behavior of this reaction has been defined in terms of impact energy intensity and in relation with the reactant composition. This was our primary concern owing to possible connections with new degradation routes for health threatening compounds.

The methodological approach we have followed has provided a quantitative analysis and a deeper understanding of the process. Important parameters, such as the ignition time, can give useful insights into the basic mechanism of a shock-induced reaction when correlated with the total energy dose and the mechanochemical yield.

From the results it is evident that highly reactive configurations and an intimate mixing of both reactants are necessary for the occurrence of self-sustaining phenomena.

However, the initiation mechanism occurring at the onset of the reaction requires further understanding. Local super-heatings at the collision, possibly increasing the powder temperature to the ignition level, cannot justify the regular trend with which the explosive-like events were observed (we refer in particular to the trials run at constant collision energy). In regard to this it is probably safe to say that the peculiarity of the reaction, involving the chloroorganic compounds plays an important role. It is well known that aryl radicals are formed in the reduction process of aryl chlorides. At the moment, a chain reaction mechanism seems to us (2) the simplest possible picture for the intensification of the reaction when an ideal globally mixed configuration has been achieved.

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REFERENCES

1. S. A. Rowlands, A. K. Hall, P. G. McCormick, R. Street, R. J. Hart, G. F. Ebell, and P. Donecker, *Nature* **367**, 223 (1994). Australian patent application PL6474 (1992).
2. S. Loïselle, M. Branca, G. Mulas, and G. Cocco, *Environ. Sci. Technol.* **31**, 261 (1997).
3. Chr. G. Tschakarov, G. G. Gospodinov, and Z. Bontschev, *J. Solid State Chem.* **41**, 244 (1982).
4. G. B. Schaffer and P. G. McCormick, *Appl. Phys. Lett.* **55**, 45 (1989).
5. M. Atzmon, *Phys. Rev. Lett.* **64**, 487 (1990).
6. L. Takacs, *Mater. Lett.* **13**, 119 (1992).
7. E. Ma, J. Pagan, G. Cranford, and M. Atzmon, *J. Mater. Res.* **8**, 1836 (1993).
8. Z. A. Munir and U. Ansemi-Tamburini, *Mater. Sci. Rep.* **3**, 277 (1989).
9. N. N. Thadhani, *J. Appl. Phys.* **76**, 2129 (1994).
10. JCPDS International Centre for Diffraction Data: 1601 Parke Line, Swarthmore, PA, 1987.
11. G. Cocco, G. Mulas, and L. Schiffini, *Mater. Trans. JIM* **36**, 150 (1995).
12. G. Mulas, L. Schiffini, and G. Cocco, *Mater. Sci. Forum* **225-227**, 237 (1996).
13. O. Kubaschewski, C. B. Alcock, and P. J. Spencer, *Materials Thermochemistry*, 6th Ed., Pergamon, Elmsford, NY, 1993.
14. P. Ehrlich, K. Peik, and E. Koch, *Anorg. Allgem. Chem.* **324**, 113 (1963).
15. E. S. Domalski and E. D. Hearing, *J. Phys. Chem. Ref. Data* **22**(4), 805 (1993).
16. P. Yu. Butyagin, *Sov. Sci. Rev. B Chem.* **14**, 1 (1989).
17. G. B. Schaffer and P. G. McCormick, *Mater. Sci. Forum* **88-90**, 779 (1992).
18. L. Takacs and M. A. Susol. Proc. of the 1995 International Symposium on Metastable Mechanically Alloyed and Nanocrystalline Materials, ISMANAM 1995, Quebec, July 24-28, 1995. Also, *Mater. Sci. Forum* **225-227**, 559 (1996).
19. H. Yang and P. G. McCormick, *J. Solid State Chem.* **110**, 136 (1994).
20. G. C. Koch, *Int. J. Mechanochem. Mech. Alloy.* **1**, 55 (1994).