Mechanochemical Reaction of DDT with Calcium Oxide

ANNEGRET K. HALL,†
JACK M. HARROWFIELD,*,‡
REINHOLD J. HART,‡ AND
PAUL G. MCCORMICK†

Department of Mechanical and Materials Engineering and Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6907, Australia

Evidence is presented that, in the mechanochemical destruction of DDT [2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane] by ball milling in the presence of calcium oxide, a complex series of reactions occurs along the pathway to a product that appears to be essentially graphitic, though aromatic chloro and hydroxy substituents are retained to some degree. The production of the various intermediates can be understood in terms of processes initiated at both CaO and steel (of the milling device) surfaces. With the exception of DDE [2,2-bis(4-chlorophenyl)-1,1-dichloroethene], most of these intermediates attain maximum concentrations corresponding to <1 mol % of the original DDT and have been characterized only by their mass spectra. In the case of dichlorotolane [bis(4-chlorophenyl)ethyne], however, yields are sufficient for it to be isolated chromatographically as a pure, crystalline solid and characterized further by NMR spectroscopy. After 12 h of milling, no organic materials volatile enough to be detected by conventional GC/MS procedures are present, but the black, graphitic residue does retain some chlorine that is only slowly removed by extended milling.

Introduction

Chemistry occurring at surfaces under impact has long been studied and has numerous practical applications. The field is commonly referred to as "tribochemistry" or "mechanochemistry" (*1*), the latter term reflecting the fact that mechanical agitation of a material within a mill is a standard procedure. Since high energy impact between surfaces of, for example, stainless steel balls can produce transient temperature rises of large magnitude [and even the generation of triboplasmas (*1*)], it is unsurprising that such agitation can produce marked chemical activation, resulting not only in reactions between the mill charge components but also in reactions with the mill surfaces. Remarkably, this form of activation has not been widely exploited in other than relatively simple reactions, and a great range of chemistry remains open to exploration (*1*−*6*). We have recently given a preliminary report on the potential application of ball-milling mechanochemistry in the destruction of toxic wastes (*7*), specifically organochlorines, by reaction with various metal powders and one example of a metal oxide (CaO), this work being performed in parallel with studies of the use of ball-milling for the synthesis of reactive metal alkyls such as Grignard reagents (*8*). In seeking to find less expensive reagents than metal powders for use in organochlorine destruction, we have examined the behavior of a variety of metal oxides known to be effective in related reactions (*3*) and now provide detailed results on the use of calcium oxide, seemingly one of the better reagents for the destruction of DDT [2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane] in particular. There is a very long history of the use of CaO in the destruction of organic matter (*9*), and recent work has demonstrated several advantageous features of the use of CaO in the destruction of some simple chlorinated hydrocarbons, of particular significance being the fact that ultrafine CaO, such as might be produced by ball-milling, is a very effective destructive adsorbent (*10*).

The environmental ubiquity of trace levels of DDT because of its formerly extensive use as an effective pesticide is well known (*11, 12*) as are both chemical and biochemical pathways to its degradation and destruction (*13*−*15*). Thus, in the presence of a strong base like CaO, DDT is expected to rapidly undergo formal elimination of HCl to produce DDE [2,2-bis(4-chlorophenyl)-1,1-dichloroethene] and $CaCl_2$. Any reaction that DDT may undergo with a metal surface is more obscure, although there is the general expectation that any halocarbon may undergo at least initial oxidative addition to a metal (*16*). A complex suite of reactions might then be expected to ensue (*16*), and consequently, we anticipated the necessity for the use of a sophisticated analytical technique such as GC/MS in the characterization of the mechanochemical reaction of DDT and CaO. It is possible to speculate broadly on the nature of the overall reaction between these two materials, but here it is perhaps only worthy of note that if organic chlorine removal were considered formally as a series of HCl elimination steps, the other reaction product would have to be a highly unsaturated hydrocarbon:

$$2C_{14}H_9Cl_5 + 5CaO \rightarrow C_{28}H_8 + 5CaCl_2 + 5H_2O$$

Since mechanochemical activation is known to be effective in initiating alkene polymerization (*6*), such an intermediate could give rise to involatile, high molecular weight products. Although there is indeed evidence that the final product of DDT milling in the presence of CaO is a high molecular weight carbonaceous material, we show herein that the

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* Corresponding author telephone: (61) (9) 380 3170; Fax: (61) (9) 380 1116; e-mail address: jmh@chem.uwa.edu.au.

† Department of Mechanical and Materials Engineering.

‡ Department of Chemistry.

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chemistry leading to this and the actual nature of the solid are considerably more complex than the above equation would imply.

Materials and Methods

Chemicals. Reagent-grade DDT (Aldrich, 98% 4,4-isomer) and CaO (Ajax Chemicals) were used as received. Some investigations were made on various samples of commercial DDT preparations (solids and solutions) obtained through the (Government) Chemistry Centre of Western Australia. Some preparations of CaO were made by thermal decomposition (900 °C) of $CaCO_3$ and $Ca(OH)_2$. Pentadeuteriochlorobenzene (Cambridge Isotope Laboratories, 99.8% D) was used to prepare partly deuterated DDT by the method described by Ginsburg (*17*). [The deuteration was only partial due to the use of the normal form of $Cl_3CCH(OH)_2$ (TCI Chemicals, Japan) as a reactant and some degree of exchange occurring during the H_2SO_4-catalyzed reaction; ^1H NMR spectroscopy indicating that the DDT product contained ~1 aromatic proton and 7 aromatic deuterons.]

Milling Procedure. Using glovebox procedures under argon, mixtures of CaO and DDT were loaded together with hardened steel balls into a steel vial, and the vial then sealed. Typically, 10 12-mm-diameter grinding balls were used, and the ratio of ball mass to powder mass was fixed at 10:1. For all experiments presently reported, the mass ratio of CaO:DDT was 7:1. The mixtures were mechanically milled for various times using a SPEX 8000 mixer mill.

Thermogravimetry. Thermogravimetric (TG) and differential thermal analysis (DTA) measurements were performed on a Rigaku instrument.

Chromatography. Thin-layer and column chromatography experiments were conducted under conventional normal-phase condition on silica. GC/MS conditions are described below.

Elemental Microanalysis. C, H and organic Cl analyses were performed by the Australian National University Microanalytical Service, Canberra. Also, some C and H analyses were performed by the Chemistry Centre of Western Australia, Perth.

Total Inorganic Chlorine Titration (TICT). Chloride released during the destruction process was determined by potentiometric titration using a Radiometer pH Meter (PHM92) equipped with an Hg/Hg_2SO_4 reference electrode and a silver billet sensor electrode. For an analysis, between 0.25 and 0.5 g of milled sample was weighed under dry argon, then exposed to the normal atmosphere for 12 h to allow residual CaO to slowly hydrate. A mixture of water (8 mL) and concentrated HNO_3 (2 mL) was then added and the mixture stirred for 15 min before the insoluble material was filtered out and washed carefully with water (30 mL). The combined filtrate plus washings was titrated with standard 0.1 mol L^{-1} $AgNO_3$. Analytical results were unaffected if the weighed sample was not firstly exposed to the air but the reaction with the aqueous HNO_3 was somewhat more violent.

GC/MS Analysis for Organic Reactant and Products. Milled powder (~100 mg) was mixed with hexane (4.5 mL), acetone (0.5 mL), and ~5 mol L^{-1} HCl (0.5 mL) and sonicated for 15−20 min. The organic layer was separated off, and 1-μL samples were used for column injection. The chromatographic system consisted of a Hewlett-Packard 5890 Series II GC and 5970 mass-selective detector (EI ionization, mass range 33−800 amu) on a 30-m DB-5 capillary column (0.25 mm i.d., 1 μm film), He carrier, and splitless injection with temperature programming 45−330 °C. Quantitative determinations of DDT, DDE, and DDD [1,1-dichloro-2,2-bis(4-chlorophenyl)ethane], both 4,4′- and 2,4′-isomers for each, were based on calibration with certified reference standards from the National Physical Laboratory, Teddington, U.K. The amounts of various other volatile materials detected were estimated semiquantitatively by assuming, for a given number of chlorine substituents, a similar detector response to these standards. Both the Wiley and NIST (NBS 75K) Mass Spectrometry Databases were used in searches for compound identification.

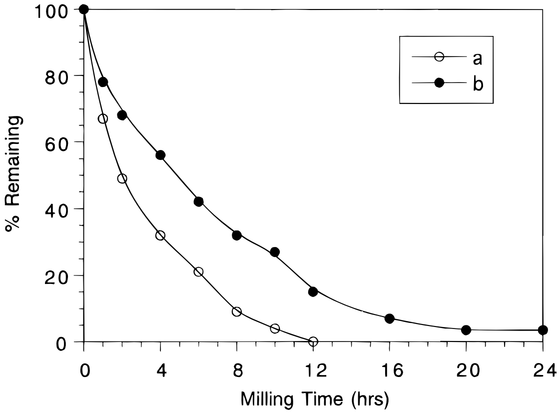

FIGURE 1. Residual organic chlorine as a function of time of milling, estimated. (a) from total organochlorines detectable by GCMS; (b) by difference from measurement of released ionic chloride.

Spectroscopic Measurements. Infrared spectra were recorded on a Digilab FTS 45 spectrometer, and nuclear magnetic resonance spectra (^1H and ^{13}C, both solution and solid state) were recorded on a Bruker AM300 instrument.

Results and Discussion

Several hundred milling experiments have been conducted to investigate the wide variety of factors that were anticipated to be possible influences upon the process of DDT destruction in the presence of CaO and then to systematically evaluate those factors that did prove to be significant. Reported below are essentially observations on the chemistry of the destruction process and a partial rationalization of its nature. Much of this is necessarily qualitative. A detailed description and analysis of physical factors that determine the efficiency of destruction will be given in subsequent publications.

Characterization of Final Reaction Products. After a period of approximately 12 h milling under ambient conditions, the CaO/DDT mixture appeared as a grayish powder, seemingly unreactive when exposed to the normal atmosphere, although still displaying the properties expected (exothermic reaction with both water and acids) due to the presence of excess CaO. Extraction of the powder with hexane/acetone/aqueous HCl revealed no significant levels of organic materials detectable by GC/MS. Extraction with aqueous acid left an amorphous black powder, graphitic in appearance but analyzing for significant levels of both hydrogen and chlorine, the latter consistent with the fact that free chloride determined on the acidic aqueous extract corresponded to less than 100% of the chlorine present in the original DDT. In fact, sampling throughout the period of milling showed that the chlorine measured as chloride ion was always less than the level expected on the basis of the chlorine content of residual organochlorines detectable (and quantified) by GC/MS (Figure 1). Although

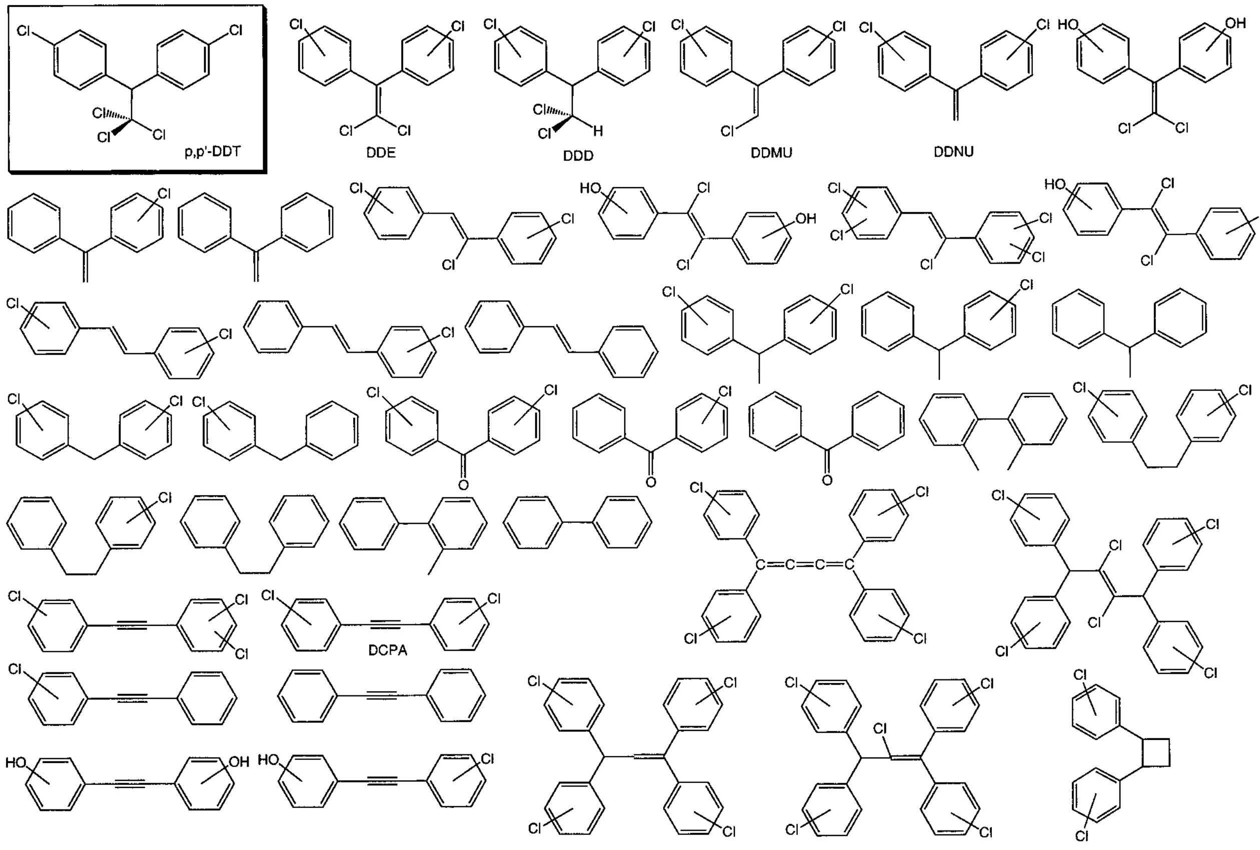

FIGURE 2. Proposed structures for intermediates detected during mechanochemical destruction of DDT in the presence of CaO.

TABLE 1

Microanalytical Data for Insoluble Products of Extended Milling of DDT with CaO

sample	%C	%H	%Cl	%O
12 h product, washed dilute HNO_3, water, ether	74.4	3.5	6.3	15.8[a]
12 h product, washed dilute HCl, water	75.4, 73.9	4.7, 3.4	9.8, 8.1	10.1,[a] 14.6[a]
24 h product, washed dilute HCl, water	74.0, 77.3	4.0, 3.6	2.8, 1.8	19.2,[a] 17.3[a]
$C_{14}H_{10}O_3$[b]	74.33	4.46	0	21.22
$C_{14}H_9ClO_2$[b]	68.72	3.71	14.49	13.08
$C_{14}H_8Cl_2O$[b]	63.90	3.06	26.95	6.08
$C_{42}H_{30}O_6$[b]	79.98	4.79	0	15.22
$C_{42}H_{24}Cl_6$[b]	68.04	3.21	28.69	0
$C_{35}H_{15}ClO_6$[c]	74.15	2.67	6.25	16.93

[a] Estimated by difference. [b] Theoretical figures for some possible reaction products (see Figure 6). [c] Best fit formulation (see text).

prolonged milling resulted in a slow approach of the released chloride value to 100%, for practical purposes the carbon-containing product of milling of DDT with CaO is best described as a high molecular weight aromatic compound (possibly a mixture of compounds) with some chlorine and oxygen substituents. Microanalyses on these black materials (Table 1) were somewhat variable, perhaps because of the adsorption of water and iron oxychlorides, but were indicative of the presence of at least one chlorine and possibly up to six oxygen atoms for every 35 carbons. The solid-state ^{13}C NMR spectrum of the black solid showed only a broad peak at δ 130, the breadth of the peak being consistent with a range of carbon environments and thus not excluding the presence of chloro and/or hydroxy substituents on some aromatic carbons. An attempt was made to directly detect residual hydrogen in the black product that could not have arisen from adsorbed solvent by measuring the (solid-state) ^2H NMR spectrum of the 24-h milling product from deuterated DDT, but no signal could be detected. It is presently uncertain whether this was due to a true lack of bound deuterium or an extreme signal breadth. As is shown below, there appear to be many pathways involved in the reaction between DDT and CaO in a ball mill; there are, therefore, reasons for expecting the ultimate product to be a complex mixture, but it is possible to speculate (see ahead) that one significant pathway might give rise to a product with the limiting empirical formula C_7H_3 and the available microanalytical data at least are not incompatible with an approach to this C:H ratio. Note that X-ray powder diffraction served only to confirm that the black product was truly amorphous, and infrared spectra showed only broad, featureless absorptions similar to those of graphite. Thermogravimetric measurements under the normal atmosphere provided evidence for the occurrence of at least two oxidative processes, with one occurring under conditions closely similar to those for the single event observed with pure graphite.

Organic Intermediates in DDT Destruction. By extraction of the milling product at various reaction times (typically, every 1–2 h), it was possible to detect and quantify (at least approximately) both residual DDT and a large number of intermediates through GC/MS measurements. In many instances, these intermediates were compounds well characterized from studies of other aspects of DDT chemistry (*13–15*) and expected to be present as a result

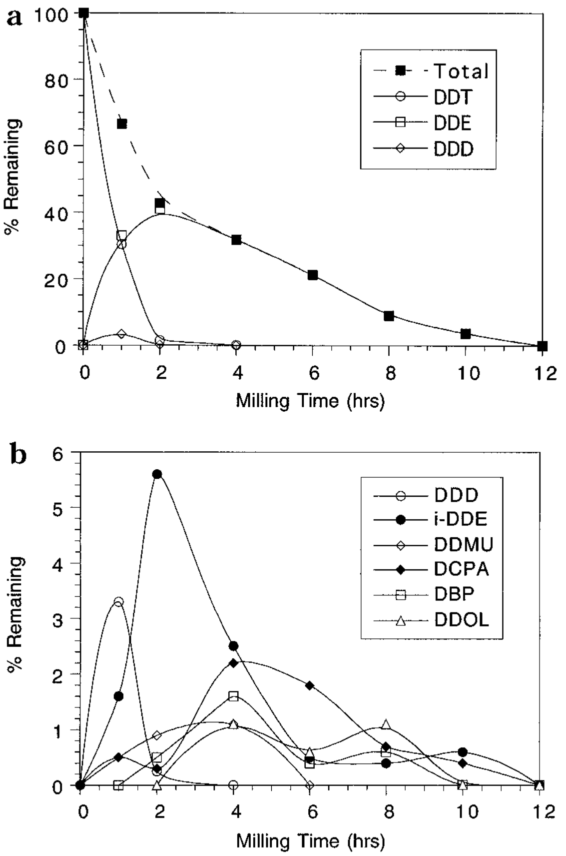

FIGURE 3. (a) Time dependence of the concentrations of DDT, DDE, and DDD during mechanochemical destruction of DDT in the presence of CaO. (b) Time dependence of the concentrations of several trace intermediates observed during the mechanochemical destruction of DDT in the presence of CaO. [i-DDE, an isomer of 4,4-DDE; DDMU, 1,1-bis(4-chlorophenyl)chloroethene; DCPA, bis(4-chlorophenyl)-acetylene; DBP, 4,4-dichlorobenzophenone; DDOL, 1-(4-hydroxyphenyl)-2-(4-chlorophenyl)dichloroethene].

of the use of a basic destruction agent. In others, however, the compounds appeared to be previously unknown or nearly so, and where their characterization remains based exclusively on a mass spectrum, we cannot claim firm establishment of their structures. Under this proviso, basic structures for the nearly 50 compounds we have detected as intermediates in DDT destruction by ball milling with CaO are shown in Figure 2. In general, with the exception of the six compounds for which standards were available, it must be said that considerable uncertainty remains with respect to an attribute such as the position of chloro substituents on aromatic rings but that otherwise fragmentation patterns (see Supplementary Information) are fully consistent with the suggested structures. An interesting case, however, is that of the acetylene bis(4-chlorophenyl)ethyne [= 4,4′-dichlorotolane or simply tolane, also referred to as dichlorophenylacetylene (DCPA in Figure 2)], which was first identified on the basis of a computer-assisted mass spectral data base search as (dichloromethylene)-fluorene. Fortunately, this compound is present in sufficient quantities after several (4−6) h milling for it to be easily isolated from the reaction mixture extract by column chromatography (SiO_2/hexane). Both ^1H (AA′BB′ aromatic proton resonances at δ [7.465, 7.460, 7.456, 7.447, 7.443, 7.438, 7.347, 7.343, 7.339, 7.329, 7.326, and 7.321] and ^{13}C [δ 89.1 (C alkyne), 121.4 (C(Ar) bound to C alkyne), 128.7, 132.7 (CH(Ar)), 134.4 (C(Ar) bound to Cl)] NMR spectra clearly establish its nature as the symmetrically substituted acetylene, and in fact dichlorotolane has been previously identified, during studies of thermal decomposition of DDT and related compounds, as a decomposition product of DDD [1,1-dichloro-2,2-bis(4-chlorophenyl)ethane] (*18*). Much more recently (*19*), the difficulties in identifying such compounds on the basis of mass spectral measurements have been discussed.

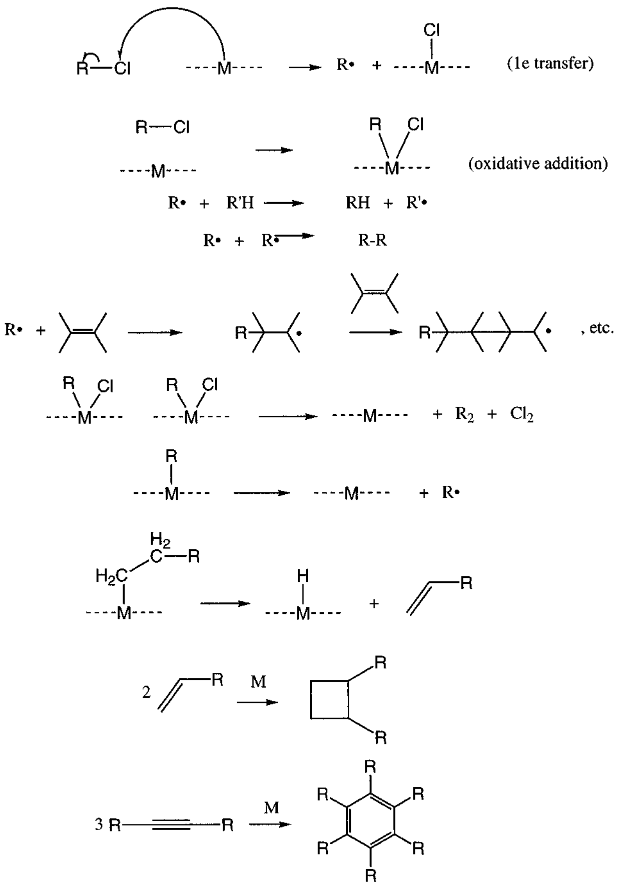

FIGURE 4. Processes possibly initiated at a metal surface in contact with an organochlorine (*16*).

The only organic materials detectable by extraction/GC/MS in quantities exceeding 10 mol % of the initial DDT were residual DDT and its elimination product, DDE [2,2-bis(4-chlorophenyl)-1,1-dichloroethene]. After ~2 h milling, DDE is the only extractable/volatile organic present in significant amounts (Figure 3a), although trace levels of a variety of the other compounds listed in Figure 2 remain detectable for at least 10 h (Figure 3b). Given the well-known ease of base-catalyzed elimination of HCl from DDT to give DDE (*13*), it is hardly surprising that major amounts are formed in the presence of CaO. It is therefore tempting to describe the destruction of DDT under the present circumstances as involving simply the formation of DDE as the initial step. There are, however, several lines of evidence that contradict this conclusion. One, possibly weak because experimental error is large, is that the form of the %DDE vs time plot does not fit that expected for a simple A → B → C process. More significant are the observations of the various minor reaction intermediates. Thus, when DDE is used as a starting material for milling, *no* intermediates detectable by extraction/GC/MS are observed to intervene between it and the final black powder. Thus, the relatively abundant intermediates such as dichlorotolane and DDD observed in DDT milling must surely arise directly from DDT itself. Though the presence of DDD

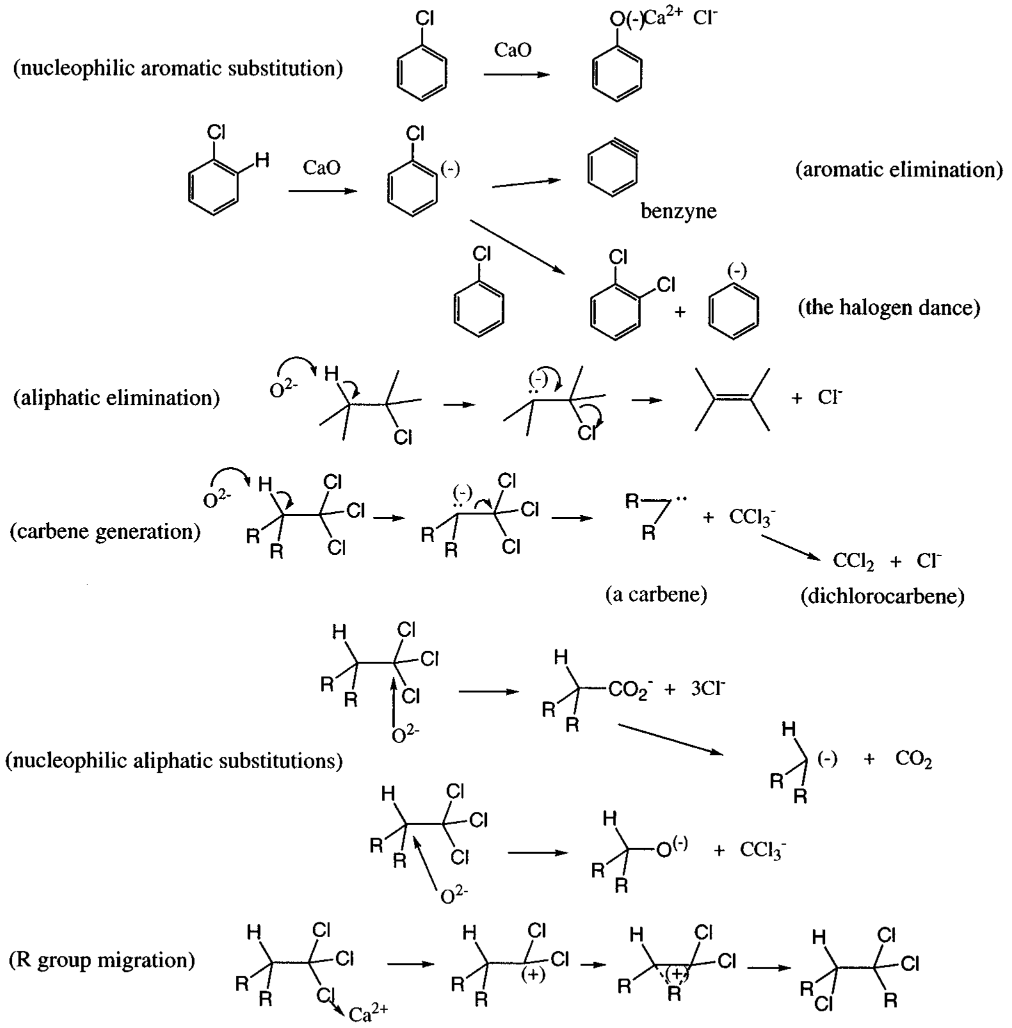

FIGURE 5. Processes possibly initiated at a CaO surface in contact with an organochlorine (*20, 22*).

is perhaps surprising given that CaO is not a reducing medium, DDD could however well be a product of hydrogen abstraction by a radical formed subsequent to the oxidative addition of DDT to a metal surface (Figure 4), and in this regard it may be significant that, despite the lack of any marked etching of metal surfaces within the mills, it was always possible to detect trace amounts of Fe(III) in the final powder. We are therefore led to conclude that both the steel and CaO surfaces (Figure 5) must be involved in the overall DDT destruction. It is quite probable that initial products of reaction at one surface may undergo further reaction at the other, and it is also possible that more than one process may be initiated at a given surface. Thus, the fact that isomers of DDE could be detected despite the fact that the original DDT was essentially isomerically pure suggests that the "base-catalyzed halogen dance" (*20*) may well have accompanied reactions such as elimination on the CaO surface.

An obvious means of establishing the roles of different surfaces within a mill is to vary the surfaces and although, for practical reasons, our primary interest lies in the use of standard stainless steel mills, an experiment in which ceramic (zirconia) balls were used in place of those of stainless steel, although still within a steel vial, provided revealing data. Reaction was greatly slowed, and after 12 h, DDE in particular remained present at a level equivalent to ~46% of the initial DDT, suggesting that, although DDE might be formed from DDT on the basic CaO surface, its further reactions must proceed more rapidly on a metal surface. Another significant observation was that the ceramic balls appeared to give rise to some minor reaction products not seen in the all-steel system. An oxygen-containing species, $C_{14}H_8Cl_4O$, is one of the most readily detected, and its formula is consistent with the possibility of oxidation of an elimination product from DDT, a reaction that might occur if hypochlorite (OCl^-) were present (to form, say, the epoxide of DDE). Hypochlorite is, of course, the product of the reaction of chlorine (Cl_2) with oxide, and another minor product that occurs in similar amounts to the $C_{14}H_8Cl_4O$ species is a compound, $C_{14}H_7Cl_5$, that could be formulated as a chloro-substituted DDE (i.e., as a product of electrophilic substitution by chlorine on one of the aromatic rings of DDE). Chlorine is a possible product of a pathway (Figure 6) that would generate dichlorotolane, and so the generation of these various compounds could be interconnected, although since it is known to be possible to produce dichlorotolane from DDD (*18*), there may be more than one pathway involved. If chlorine is produced during milling, then certainly it must react further since there is no evidence of significant oxidizing power in the final product, so that the above results indicate that under "normal" milling conditions it must be reduced by the metal surfaces.

The possibility that calcium alkyls were formed as important reaction intermediates was excluded by the lack of marked oxygen sensitivity of the reaction mixture and

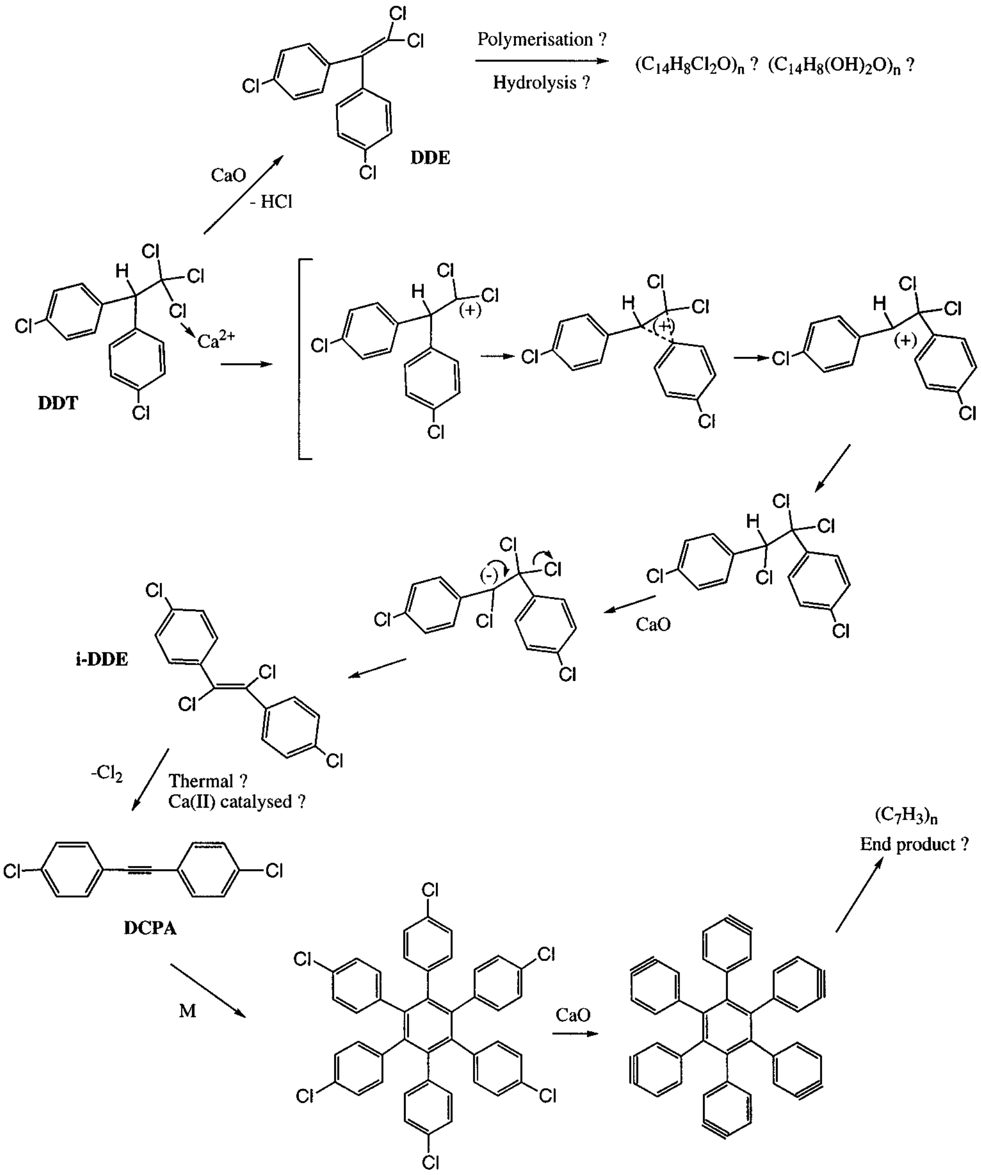

FIGURE 6. Some plausible pathways in DDT destruction.

by the fact that quenching/extraction with hexane/acetone/ DCl/D_2O did not result in appreciable incorporation of deuterium into any of the relatively abundant intermediates detected by GC/MS. Nonetheless, the presence of acid in the quenching/extraction mixture did seem to be necessary to achieve full release of the intermediates, possibly because it prevented adsorption or occlusion of these materials by solid $CaO/CaCl_2$, and some of the very minor but rather persistent intermediates did not appear to be released at all in the absence of acid. Since these were oxygenated species, we interpret this behavior as evidence that they were phenolic compounds, present in the reaction mixture as calcium phenoxides. A further indication of this was that they were more efficiently extracted by ether than by the rather apolar hexane−acetone mixture. Significantly, phenol and catechol (1,2-dihydroxybenzene), for example, both undergo only very slow destruction when milled with CaO under an inert atmosphere.

Overall conclusions that may be drawn on the basis of the proposed chemical structures of the intermediates observed in DDT destruction by the present method are (refer also to Figures 4−6):

(i) Reactions at least formally involving the elimination of HCl and Cl_2 may occur readily. As noted previously, elimination of HCl from DDT is to be expected in the presence of a base as strong as CaO (and is the cause of DDE formation). Cl_2 elimination might well be catalyzed by the action of Ca(II) as a Lewis acid, although it has already been noted that the milled powders display no significant oxidizing capacity, and therefore any Cl_2 (or OCl^-) formed initially must be subsequently reduced.

(ii) The chloro substituents of DDT may be replaced by hydrogen in the intermediates. This could occur via formal loss of Cl^+ and ultimate protonation of the product carbanion during quenching, but deuteriation quenching experiments indicate that such carbanions cannot be persistent. Thus the reaction is perhaps better explained as being due to hydrogen abstraction by a radical produced at the metal surfaces of the mill system.

(iii) Phenyl group migration may occur from C1 to C2 of the original DDT molecule. Such Wagner−Meerwein rearrangements (*21*) indicate the involvement of an electron-deficient carbon species at some point.

(iv) Loss of one carbon atom from the DDT skeleton occurs quite commonly. The trichloromethyl (CCl_3) group is the most obvious cleavage unit.

(v) Migration of chloro substituents around the phenyl rings appears to be possible. This may indicate that other reactions known to be undergone by molecules in which the base-catalyzed halogen dance (*20*) is observable are also taking place. Of possibly considerable significance would be the formation of benzyne derivatives. We have in fact attempted to detect putative benzyne intermediates during milling of 1,4-dichlorobenzene by the use of furfuryl alcohol as a trap but have observed no addition products, a result which may simply mean that these products themselves are rapidly destroyed by the milling. The experiment was also complicated by the rapid oligomerization of furfuryl alcohol in the mill.

(vi) Aromatic nucleophilic substitution of Cl by O^{2-} to give calcium phenoxides is not an important reaction pathway (although it seems it can be detected).

(vii) The reactivity of the observable intermediates must be such as to produce high molecular weight materials involving (as shown by their spectroscopic properties) graphitic aromatic units.

The complexity of the observations we have made on the ball milling-induced reactions between DDT and CaO allows considerable speculation with regard to their rationalization (Figures 4 and 5). Some plausible pathways to various observed intermediates and to possible end products are shown in Figure 6. Regardless of the validity of these speculations, it is most important to note that the process (*23*) does result in efficient destruction of DDT and the generation of innocuous products, specifically calcium chloride and a highly insoluble and involatile graphitic carbon that may remain partly chlorinated.

Acknowledgments

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Supporting Information Available

Quantitative analytical data for the time dependence of the concentrations of various intermediates observed during ball milling of CaO/DDT (mass ratio 7:1), data plotted in Figure 3 (1 page), and total ion chromatograms and mass spectra for reaction mixtures of CaO/DDT (7:1) under ball milling (28 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supporting information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$51.00 for photocopy (\$53.00 foreign) or \$12.00 for microfiche (\$13.00 foreign), are required. Canadian residents should add 7% GST. Supporting information is available to subscribers electronically via the Internet at http://pubs.acs.org (WWW) and pubs.acs.org (Gopher).

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