

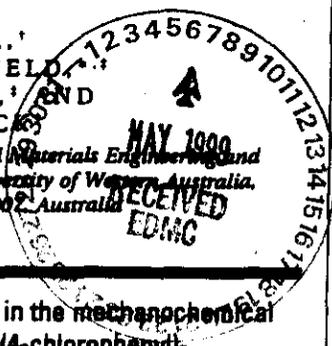
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Research

# Mechanochemical Reaction of DDT with Calcium Oxide

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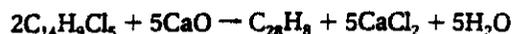
Evidence is presented that, in the mechanochemical destruction of DDT [2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane] by ball milling in the presence of calcium oxide, a complex series of reactions occurs along the pathway to a product that appears to be essentially graphitic, though aromatic chloro 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-dichloroethane], 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 (2)], 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-dichloroethane] and CaCl<sub>2</sub>. 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:



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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