

Mechanisms of Antioxidant Action: Transformations Involved in the Antioxidant Function of Zinc Dialkyl Dithiocarbamates. I

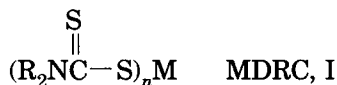
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Synopsis

The antioxidant mechanism of zinc dialkyl dithiocarbamate is examined in detail in model compounds. The kinetics of the reaction of zinc dialkyl dithiocarbamate with hydroperoxides were studied in inert and oxidizable substrates. A typical electron donor antioxidant and a base (CaCO_3) were found to inhibit the peroxide decomposition. The oxidation products of the Zinc II complex appear to be quite different from those of the nickel II and iron III complexes. Two processes are involved in the antioxidant function of the zinc complex: The first is a free radical decomposition of the peroxides, which predominates at molar cumene hydroperoxide (CHP)/zinc diethyl dithiocarbamate (ZnDEC) ratios of 10 or less. At higher molar ratios an ionic reaction predominates, although there is a radical contribution at all ratios. Thiocarbamoyl disulfide does not seem to be formed as an intermediate from ZnDEC during the ionic process.

INTRODUCTION

It has been known for many years that the antioxidant activity of the metal dithiocarbamates (MDRC) is due to their oxidation by hydroperoxides to give sulphur acids which are ionic catalysts for the decomposition of hydroperoxides.^{1,2} This fact has been exploited in the development of highly effective thermal and UV stabilizers for polyolefins,³ and the principle has also been applied in the time-controlled photooxidation of polyolefins by some transition metal dithiocarbamates, notably FeDRC (I, $M = \overline{Fe}$, $n = 2$ or 3)⁴⁻⁷



The steps by which the sulfur acids are generated from the dithiocarbamates have not been fully resolved. The purpose of this investigation and other studies in this series is to investigate the nature of the intermediates involved in the antioxidant behavior of different metal dithiocarbamates under similar experimental conditions and to relate their behavior in polymers. The present work deals with the behavior of zinc dialkyl dithiocarbamates in model compounds.

EXPERIMENTAL

Materials and Product Analysis

Zinc diethyl dithiocarbamate was supplied by Robinson Brothers Ltd. Cumene hydroperoxide (BDH) and tertiary butyl hydroperoxide (Koch-Light) were purified via their sodium salts by the method of Kharash.⁸ Puriss grade chlorobenzene and α,α -bisisobutyronitrile (Koch-Light) were used without further purification. Cumene (technical grade, BDH) was washed four times with concentrated sulfuric acid, followed by water, 10% sodium carbonate solution, and finally with water. After thorough drying with magnesium sulfate, the product was distilled from phosphorous pentoxide under nitrogen and used.

Thermal decomposition of hydroperoxides, GLC analysis (using Perkin-Elmer F30 Chromatograph) of products obtained from the above studies and oxygen absorption studies were carried out as described previously.^{9,10}

RESULTS

Reactions of ZnDEC with CHP and Their Product Analysis

Nickel complexes of dithioic acids (e.g., nickel dithiophosphates, xanthates, and dithiocarbamates) have been shown^{9,11} to have the same general behavior in decomposing CHP at 110°C. Their decomposition curves are composed of three distinct steps: a first rapid initial catalytic stage involving homolytic peroxide breakdown, followed by a secondary induction period, which leads into a slower first-order catalytic reaction essentially ionic in nature.

Figure 1 shows the kinetics of CHP decomposition at 110°C in the presence of ZnDEC at different (CHP)/(ZnDEC) molar ratios. The kinetics of product formation (by GLC) in some of these reactions is shown in Figure 2. The pattern of decomposition of CHP by the zinc complex under all ratios examined is quite different from that of the nickel dithiolates discussed earlier.⁹ The initial rapid catalytic stage is completely missing, but the induction period during which there is no apparent peroxide decomposition appears to be similar and is followed by a first-order catalytic reaction. The length of the induction period increases with increasing zinc complex con-

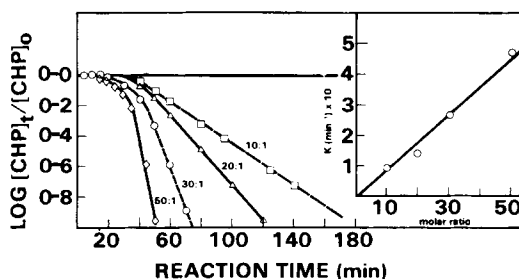


Fig. 1. Decomposition of CHP (1×10^{-2} mol) in chlorobenzene at 110°C by ZnDEC, at different molar ratios of (CHP)/(ZnDEC). Inset shows changes of the first order reaction-rate (k) of the second stage with molar ratio. Medium: Φ_{cl} .

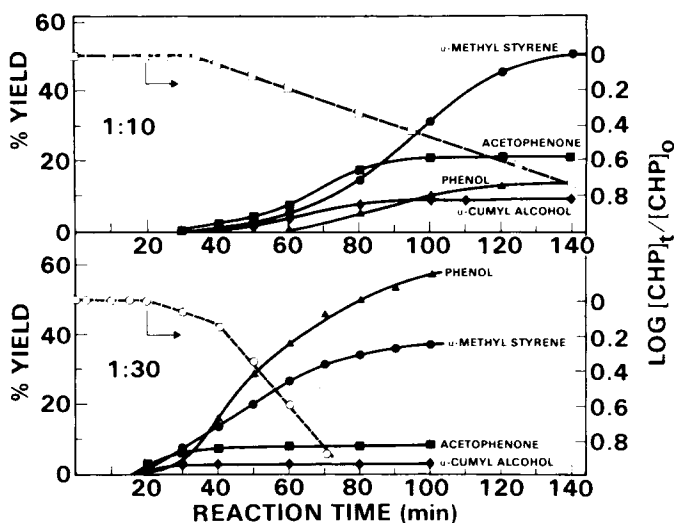


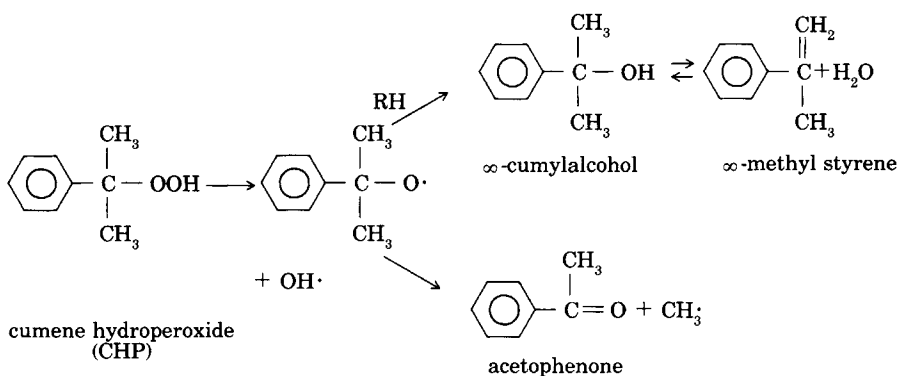
Fig. 2. Product distribution (by GLC) of reactions of CHP (1×10^{-2}) and ZnDEC in chlorobenzene at 110°C at different molar ratios.

centration. This is the opposite of what happens in the case of the nickel dithiolates.⁹ Moreover, the catalytic stage becomes faster as the molar ratio (CHP)/(ZnDEC) increases (see Fig. 1), which is again the reverse of the behavior of the nickel analogs.^{9,11} The inset in Figure 1 shows that there is a good straight line relationship, between the rate of the first-order catalytic stage and the (CHP)/(ZnDEC) molar ratio.

Product distribution curves at molar (CHP)/(ZnDEC) ratios of 10 and 30 are superimposed on their corresponding peroxide decomposition curves in Figure 2. The reaction of CHP with ZnDEC at a molar ratio of 10 [Fig. 2(a)] shows that at the beginning of the catalytic stage (i.e., after 30 min) mainly free radical products (acetophenone, α -cumyl alcohol, and a small amount of α -methyl styrene) are formed. After 60 min ionic products (e.g., phenol) start to form, but the maximum concentration of phenol at the end of the reaction was only a fraction of the final concentration of radical derived products. However, Figure 2(a) shows clearly that the amount of α -cumylalcohol is limited and α -methyl styrene becomes the major product in the later stages of the reaction. This suggests that the acidic species which are responsible for the formation of phenol also cause dehydration of α -cumyl alcohol to the corresponding olefins. Both free radical and ionic reactions are therefore involved in this case but with a higher overall contribution from the former. On the other hand, when hydroperoxide is present in molar excess (CHP)/(ZnDEC) = 30, reactions during the second stage appear to be more complex. The kinetics of the peroxide decomposition clearly consists of two separate reactions [Fig. 2(b)]. The first appears to start after approximately 15 min and leads to the formation of mainly free radical products. At the end of this stage, however (i.e., from 40 min to the end of the reaction), the concentration of phenol, the ionic decomposition product, increases rapidly while the concentrations of α -cumyl alcohol and acetophenone remain at a low constant level. It is interesting to note here that

there is an increase of α -methyl styrene concentration which more or less parallels that of the phenol, as the reaction continues.

Figure 3 records the formation of CHP decomposition products for high temperature reactions with ZnDEC at various molar ratios. It is clear that at the stoichiometric ratio (1:1) no phenol is formed, indicating the absence of an ionic process while the formation of α -cumyl alcohol suggests that the mechanism of peroxide decomposition is mainly a homolytic process. However, as the ratio increases above stoichiometric, the concentration of phenol increases rapidly, and the contribution of the heterolytic process becomes dominant. However, it is also clear from Figure 3 that the concentration of α -methyl styrene remains high at all catalytic ratios. α -Methyl styrene is formed from α -cumylalcohol by Lewis acid dehydration and is therefore a radical product. Figure 3 shows that the changes in concentration of the α -methyl styrene closely follows that of acetophenone, the other radical product, and that both reach a maximum at (CHP)/(ZnDEC) = 10 confirming that they result from the same radical intermediate:



In a closed system α -cumyl alcohol will be in equilibrium with α -methyl styrene. It follows then that there is an appreciable contribution of the homolytic process even in the catalytic decomposition of CHP.

Oxidation of Cumene in the Presence of ZnDEC Initiated by AIBN and the Effect of a Free Radical Inhibitor (BHT)

Figure 4 shows that in cumene oxidation initiated by azobisisobutyronitrile (AIBN) the zinc dithiocarbamate caused a short initial induction period. This suggests that the zinc complex is a weak radical scavenger. These results differ from those reported earlier¹ for tetraline, where retardation but no induction period was observed. At lower concentrations where electron donor (CB-D) antioxidants are normally effective, ZnDEC was found¹ to have little effect. ZnDEC behaved in a completely different way in cumene autoxidation initiated by CHP. Figure 5 shows that there is an initial prooxidant effect, which is followed by complete inhibition of oxidation; consistent with the earlier results in tetralin.¹ The prooxidant effect observed during the early stages of the hydroperoxide-initiated oxidation confirms that the main species responsible for the nonradical decomposition of CHP is not

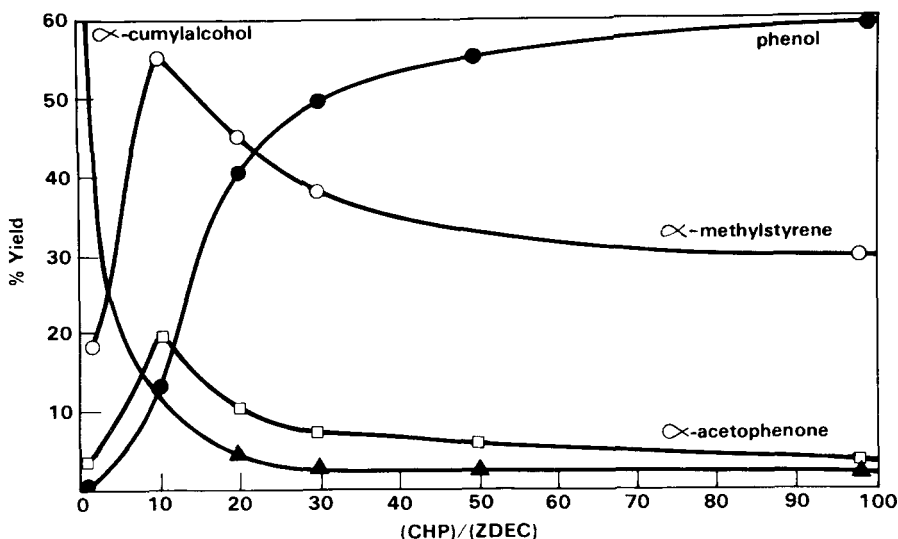


Fig. 3. Product yields after complete reaction of ZnDEC with CHP at 110°C in chlorobenzene at various molar ratios of (CHP)/(ZnDEC).

the zinc complex itself but products of its oxidation by the hydroperoxide. The nature of these transformation products will be discussed elsewhere.¹² Zinc diethyl dithiocarbamate therefore appears to operate by both free radical trapping and nonradical peroxidolytic mechanisms. The contributions of these reactions depend on the molar ratio of the peroxide to metal complex (see Fig. 3).

Figure 6 shows the effect of adding a typical CB-D inhibitor (2,6-ditertiary butyl-4-methylphenol, BHT) at different stages of the decomposition of CHP in the presence of ZnDEC (at 110°C). It is clear that addition of BHT after the end of the initial induction period (i.e., after the catalytic stage has started) has no effect on the hydroperoxide decomposition. However, addition of the same concentration of BHT at the beginning of the reaction

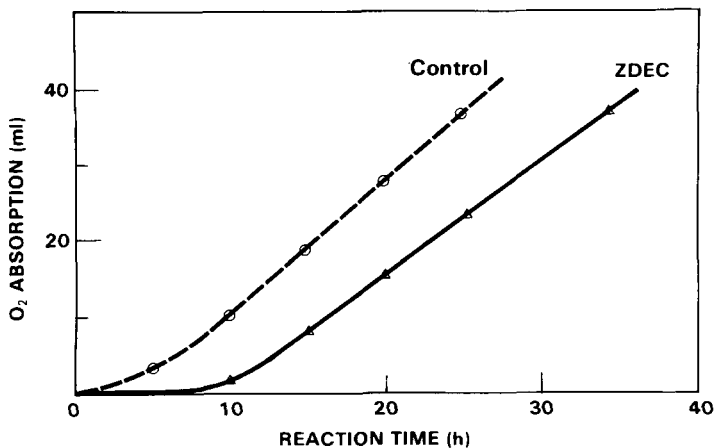


Fig. 4. Effect of ZnDEC (5×10^{-5} mol) on the oxidation of cumene in the presence of AIBN (1×10^{-2}) at 50°C.

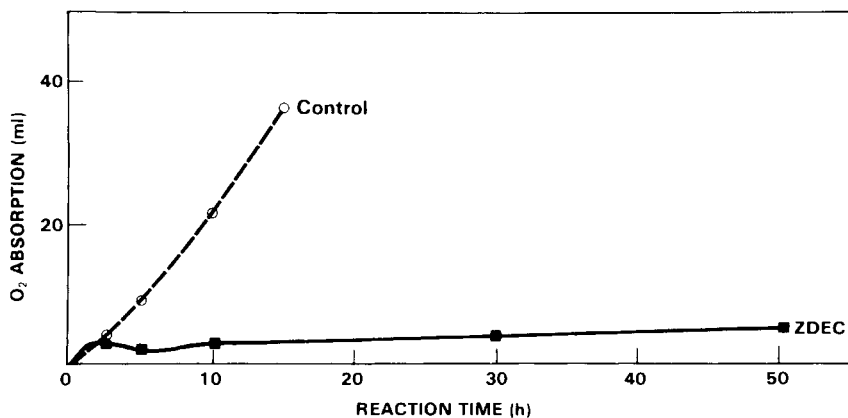


Fig. 5. Effect of ZnDEC (5×10^{-5} mol) on the oxidation of cumene in the presence of CHP (1×10^{-1} mol) at 110°C .

inhibits the peroxide decomposition completely. This shows clearly that alkyl peroxy or alkoxy radicals are involved in the conversion of ZnDEC to the acid species, but once the second catalytic stage has started, during which the concentration of ionic products build up rapidly [see Fig. 2(b)], the mechanism is mainly ionic, and addition of an electron donor antioxidant does not effect the decomposition to any extent.

Effect of a Base on the Thermal Decomposition of CHP in the Presence of ZnDEC

Figure 7 shows the effect of different concentrations of CaCO_3 on the peroxide decomposition curve in the presence of ZnDEC at a molar ratio

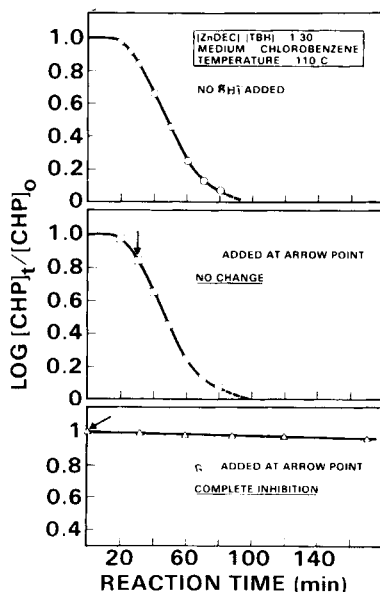


Fig. 6. Effect of free-radical inhibitor (2,6-ditertiary butyl-4-methyl phenol) (BHT) at different stages during the reaction of tertiary butyl hydroperoxide (TBH) with zinc diethyl dithiocarbamate at a molar ratio of 30.

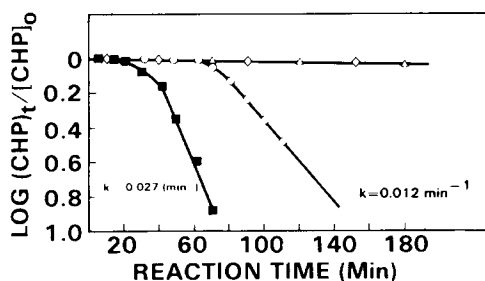


Fig. 7. Effect of a base (CaCO_3) on thermal decomposition of CHP (1×10^{-2} mol) at 110°C in chlorobenzene in the presence and absence of ZnDEC. Molar ratios of CHP: ZnDEC: CaCO_3 : (Δ) 30:0:0.25; (\diamond) 30:1:2; (\circ) 30:1:0.25; (\blacksquare) 30:1:0.

$(\text{CHP})/(\text{ZnDEC}) = 30$. Addition of a small amount of the base causes an increase in the length of the induction period which then leads to a slower second stage decomposition (see k values on curves). However, addition of a molar excess of the base inhibits the peroxide decomposition completely.

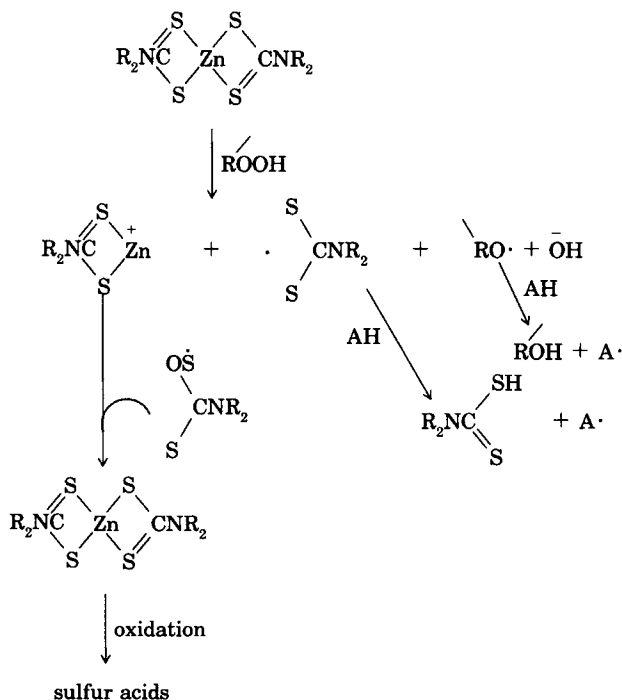
DISCUSSION

It is clear from all the above results that the initial step in the reaction of a hydroperoxide with a zinc dithiocarbamate is different from those of the nickel dithiocarbamates and other nickel dithiolates.⁹ The CHP decomposition consists of an induction period during which there is no measurable peroxide decomposition leading to a catalytic stage which causes then the complete decomposition of hydroperoxide. The radical catalysed decomposition of hydroperoxide observed with the nickel complexes is completely missing. It has been shown^{11,13,14} that in the case of hydroperoxide oxidation of the nickel dithiolates, the first transformation product formed is the corresponding disulphide, which then oxidizes further to give acidic products. The fact that addition of either a free radical inhibitor (CB-D) or an excess of a base at the beginning of the reaction completely inhibits the peroxide decomposition suggests that, although no peroxide decomposition was detected, homolytic decomposition of hydroperoxide must be occurring and that the process occurs by a radical mechanism. The higher the $(\text{CHP})/(\text{ZnDEC})$ ratio, the faster the rate of formation of the acidic species and hence the shorter the induction period and the faster the second catalytic process (see Fig. 1).

Figure 7 confirms that oxidation of the zinc complex to form acidic species must occur during the first stage (i.e., during the "induction period"). These products are mainly responsible for the ionic process in the second stage. Addition of a less than stoichiometric amount of a base cannot effect complete inhibition of the peroxide decomposition since it neutralizes only part of the acids formed. It does, as expected, reduce the rate of the catalytic stage. Addition of excess base, however, leads to the neutralization of all the acids, and hence no rapid second stage reaction occurs.

Figure 3 shows that the antioxidant mechanism of zinc dithiocarbamate is similar to that of the ionic catalytic mechanism of the nickel dithiolates⁹ in that both homolytic and ionic processes are involved, and the contribution of each is a function of the molar ratio of the peroxide to the complex. This

is also analogous to the behavior of zinc mercaptobenzthiozolate¹⁵ and of the dialkyl thiodipropionate esters.¹⁶ However, in the case of ZnDEC the concentration of α -methyl styrene remains high even at high (CHP)/(ZnDEC) molar ratios, suggesting that the latter is formed in a redox reaction between the hydroperoxide and one or more of the oxidation products:



Scheme 2.

It has been shown^{9,13,14} in the case of nickel dithiolates that the first transformation product formed from the oxidation of these complexes by hydroperoxides are the corresponding disulfides which then oxidize further to other acidic products. In the case of zinc dithiocarbamate, however, no evidence could be found for disulfide formation using the diagnostic tellurium powder test for thiuram disulphides.* Oxidation of the zinc complex to sulfur acids takes place therefore through different intermediates. The chemical nature of these species and their participation in the radical sequence during the formation of the acidic species will be discussed in a subsequent publication.

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* This test involves addition of tellurium powder to the unknown solution. If thiuram disulfide is present, then the tellurium powder reacts with it to form the divalent tellurium dithiocarbamate, which is brick-red in color.¹⁸

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