# Study on Zinc *O,O*-Diisobutyl Dithiophosphate as Antioxidant

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Cumyl hydroperoxide has been decomposed using zinc *O,O*-diisobutyl dithiophosphate. The decomposition reaction consisted of three stages including the first homolytic decomposition and the last heterolytic decomposition. These decomposition modes depended considerably on the relative concentration of the complex to the hydroperoxide and the total concentration. From these results and on the basis of decomposition reaction in the presence of both zinc *O,O*-diisobutyl dithiophosphate and bis(*O,O*-diisobutoxyphosphonothioyl) disulfide, it has been shown that the formation of sulfuric acid was most important for heterolytic decomposition.

The zinc *O,O*-diisoalkyl dithiophosphates are widely used as antioxidants, especially as hydroperoxide-decomposers. However it is not easy in practice to determine the kind and effective amount of such antioxidants, because the activities of decomposition of the hydroperoxides are very complicated, and considerably affected by the circumstances. Elucidation of the complicated action mechanism of such decomposes would clarify the mechanisms.

Burn *et al.*[1] found that the decomposition reaction of cumyl hydroperoxide with zinc *O,O*-diisopropyl dithiophosphate consisted of three stages: 1) a first homolytic decomposition, 2) an induction period, and 3) a fast heterolytic decomposition. However, they did not satisfactorily explain what kind of species induced the third stage which was the most important action expected of the complex. Other investigators[2-4] have proposed such species.

The decomposition reaction of cumyl hydroperoxide with bis(*O,O*-diisobutoxyphosphonothioyl) disulfide[5] (referred to as "the disulfide"), which is reported[1,6] to be formed during the decomposition reaction of a hydroperoxide with zinc *O,O*-diisoalkyl dithiophosphate. It was also found[5] that sulfuric acid from the disulfide was most effective for heterolytic decomposition. In this paper, the action mechanism of zinc *O,O*-diisobutyl dithiophosphate and the role of the disulfide in the decomposition of cumyl hydroperoxide are discussed.

## Experimental

*Materials.* Zinc *O,O*-diisobutyl dithiophosphate (Zn–$Bu^i_2$–DTP),[6] and copper and nickel *O,O*-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propyl] phosphorodithioate (Cu and Ni–P–$C_3$–DTP)[7] were synthesized according to known procedures. Bis(*O,O*-diisobutoxyphosphonothioyl) disulfide was also prepared by a known method.[5]

Cumyl hydroperoxide and chlorobenzene were purified by convertional methods.

*Procedure.* Decomposition of cumyl hydroperoxide (CHP) was carried out using a reaction flask fitted with stirrer and sampling neck. For hydroperoxide analyses, an iodometric method was used.[1]

Decomposition products of cumyl hydroperoxide were analyzed by a GLC method (10% Silicone rubber on Diasolid S). ESR measurements were conducted on a JEOL Model JES-PE-lX spectrometer.

## Results and Discussion

*Decomposition of Cumyl Hydroperoxide.* Cumyl hydroperoxide (0.1 M) was decomposed by Zn–$Bu^i_2$–DTP in chlorobenzene under a nitrogen or oxygen atmosphere at 70 °C. The results are shown in Figs. 1 and 2. The decomposition reactions, regardless of the kind of atmosphere, proceeded as reported by Burn *et al.*,[1] and consisted of three stages,** an initial fast homolytic decomposition, a slow reaction (induction period), and a last fast heterolytic decomposition. With decresing concentration of Zn–$Bu^i_2$–DTP, the induction period decreased. The presence of oxygen in the reaction system shortened the induction period and accelerated the final decomposition.

The formation of the cumylperoxyl radical during the initial stage of the decomposition of cumyl hydroperoxide with *O,O*-dialkyl dithiophosphates, such as Zn, Cu, and Ni *O,O*-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propyl]-phosphorodithioates (Me–P–$C_3$–DTP) was indirectly observed; the signal of the phenoxy radical derived from the secondary reaction of the phenolic moiety of

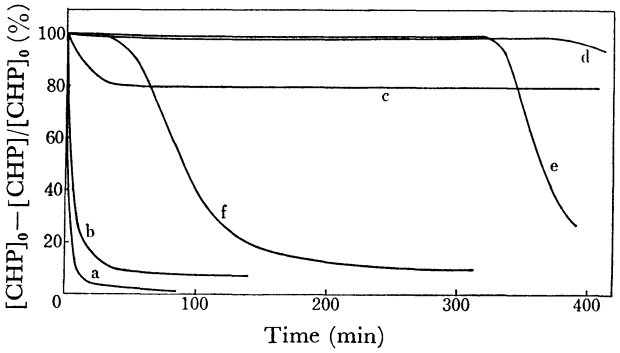



Fig. 1. Decomposition of cumyl hydroperoxide (0.1 M) with Zn–$Bu^i_2$–DTP in chlorobenzene under nitrogen atmosphere at 70 °C.
[Zn–$Bu^i_2$–DTP]: a, $10^{-1}$ M; b, $5\times10^{-2}$ M; c, $10^{-2}$ M; d, $10^{-3}$ M; e, $5\times10^{-4}$ M; f, $10^{-4}$ M.

** In Fig. 1, for example, curves a and b show only the initial decomposition, curve c shows the initial decomposition and induction period, and curve f shows the initial decomposition (not observed clearly due to a little amount of cumyl hydroperoxide decomposed at this stage, corresponding to a lower concentration of Zn–$Bu^i_2$–DTP), induction period and last decomposition.

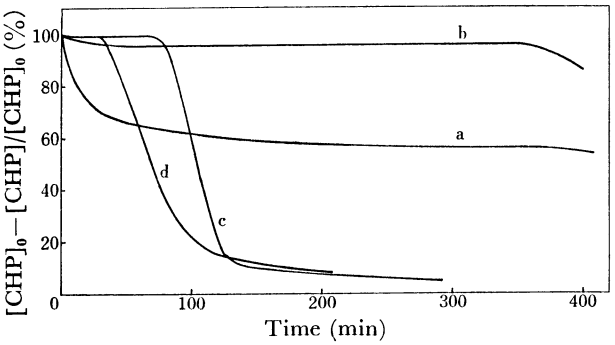



Fig. 2. Decomposition of cumyl hydroperoxide (0.1 M) with Zn-Bu$^i_2$-DTP in chlorobenzene under oxygen atmosphere at 70 °C.
[Zn-Bu$^i_2$-DTP]: a, $10^{-2}$ M; b, $10^{-3}$ M; c, $5\times10^{-4}$ M; d, $10^{-4}$ M.

Me-P-$C_3$-DTP with cumylperoxyl radical, which is formed by the decomposition reaction of cumyl hydroperoxide with Me-P-$C_3$-DTP, being observed.[7] Figures 3 and 4 show the peak heights of the ESR signal of the phenoxy radical observed in the decomposition reactions of cumyl hydroperoxide with Ni-P-$C_3$-DTP and Cu(II)-P-$C_3$-DTP, respectively. The figures also include the

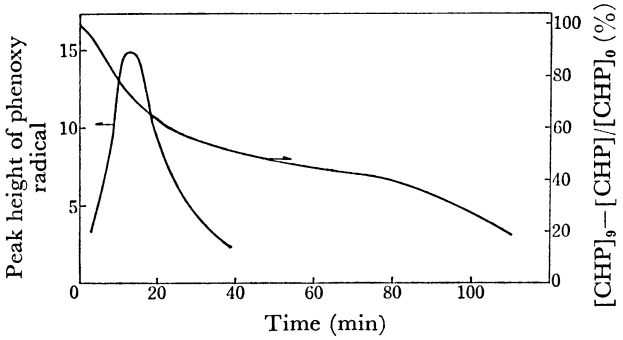



Fig. 3. Decomposition of cumyl hydroperoxide with Ni(II)-P-$C_3$-DTP in chlorobenzene at 70 °C.
Conditions: $[CHP]_0=1.25\times10^{-2}$ M, [Ni(II)-P-$C_3$-DTP]$=2.5\times10^{-3}$ M.

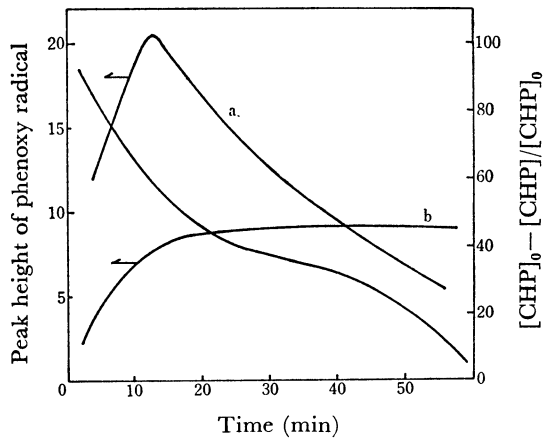



Fig. 4. Decomposition of cumyl hydroperoxide with Cu(II)-P-$C_3$-DTP in chlorobenzene at 70 °C.
Conditions: $[CHP]_0=1.25\times10^{-2}$ M, [Cu(II)-P-$C_3$-DTP]$=6.25\times10^{-3}$ M.

titration curves of cumyl hydroperoxide against time in decomposition reactions. When the titration curves are compared with the corresponding curves for the phenoxy radical, it is clearly seen that homolytic decomposition occurs in the initial stage as proposed by Burn *et al.*[1] Furthermore, cupric sulfate begins to form at the same time as the homolytic decomposition (Fig. 4). These results indicate that an acid, probably sulfuric acid, forms cupric sulfate by reacting with Cu-P-$C_3$-DTP during homolytic decomposition. The results with respect to Me-P-$C_3$-DTP may be employed to determine the decomposition activity of Zn-Bu$^i_2$-DTP, since the effect of the phenolic moieties of Me-P-$C_3$-DTP on the decomposition activity of cumyl hydroperoxide is negligible.[7]

The initial rates were found to be first order dependent on both Zn-Bu$^i_2$-DTP and cumyl hydroperoxide (CHP) (Table 1):

$$-d[CHP]/dt = k_D[Zn\text{-}Bu^i_2\text{-}DPT][CHP].$$

The rate constant, $k_D$, has been calculated to be $2.07\times10^{-2}$ $M^{-1}$ $s^{-1}$ at 70 °C. This value seems somewhat

Table 1. Initial reactions betweenzinc *O,O*-diisobutyl dithiophosphate and cumyl hydroperoxide in chlorobenzene at 70 °C

| Zinc *O,O*-diisobutyl dithiophopahte ($\times10^2$ M) | Cumyl hydroperoxide ($\times10$ M) | $k_D$ [cumyl hydroperoxide] ($\times10^3$ $s^{-1}$) | $k_D$ ($\times10^2$ $M^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 1.0 | 1.0 | 1.87 | 1.87 |
| 1.0 | 5.0 | 10.7 | 2.14 |
| 1.0 | 10 | 20.6 | 2.06 |
| 2.5 | 1.0 | 1.73 | 1.73 |
| 2.5 | 5.0 | 10.8 | 2.15 |
| 5.0 | 5.0 | 10.6 | 2.13 |
| 5.0 | 10 | 24.2 | 2.42 |
| | | | Av. 2.07 |
| 5.0 | 1.0 | 0.644 | 0.644[a] |
| 5.0 | 1.0 | 0.119 | 0.199[b] |

a) Zn-Pr$^i$-X. b) Zn-$Bu_2$-DTC. *Cf.* $k_{D,\ 70°C}$ for zinc *O,O*-diisopropyl dithiophosphate$=1.55\times10^{-2}$ $M^{-1}$ $s^{-1}$ from Ref. 1.

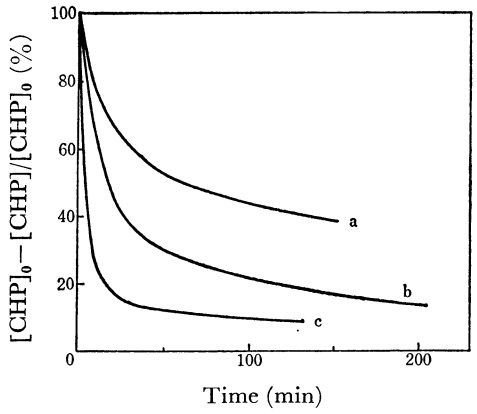



Fig. 5. Decomposition of cumyl hydroxide (0.1 M) with a complex ($5\times10^{-2}$ M) in chlorobenzene at 70 °C.
a: zinc *N,N*-dibutyl dithiocarbamate, b: zinc isopropyldithiocarbonate, c: zinc *O,O*-diisobutyl dithiophosphorate.

Table 2. Products of complete decomposition of cumyl hydroperoxide (1M) with zinc *O,O*-diisobutyl dithiophosphate in chlorobenzene at 70 °C

| Zn–$Bu^i_2$–DTP (M) | Products (mol %) | | | | |
|---|---|---|---|---|---|
| | Acetone | Phenol | α-Methyl styrene | α,α-Dimethyl benzylalcohol | Aceto-phenone |
| 1.0 | 1 | 1 | 24 | 71 | 4 |
| $1.0\times10^{-1}$ | 1 | 1 | 25 | 72 | 3 |
| $1.0\times10^{-2}$ | 62 | 75 | 19 | 8 | 1 |
| $1.0\times10^{-3}$ | 62 | 78 | 16 | 5 | 1 |
| $1.0\times10^{-4}$ | 79 | 79 | 13 | 6 | 2 |
| $1.0\times10^{-4}$ [a] | — | — | 9 | 87 | 5 |
| 2 vol %[b] | 94 | 100 | — | — | — |

a) Co(II) octanoate. b) $H_2SO_4$.

Table 3. Products of complete decomposition of cumyl hydroperoxide with zinc *O,O*-diisobutyl dithiophosphate in chlorobenzene at 70 °C

| Zn–$Bu^i_2$–DTP (M) | Cumyl hydroperoxide (M) | Products (mol %) | | | | |
|---|---|---|---|---|---|---|
| | | Acetone | Phenol | α-Methyl styrene | α,α-Dimethyl benzylalcohol | Aceto-phenone |
| 1.0 | 1.0 | 1 | 1 | 24 | 71 | 4 |
| $1.0\times10^{-1}$ | $1.0\times10^{-1}$ | 12 | 13 | 32 | 53 | 2 |
| $1.0\times10^{-1}$ [a] | $1.0\times10^{-1}$ | 8 | 8 | 29 | 61 | 2 |
| $1.0\times10^{-1}$ [b] | $1.0\times10^{-1}$ | 5 | 5 | 26 | 68 | 1 |
| $1.0\times10^{-2}$ | $1.0\times10^{-2}$ | 66 | 65 | 19 | 14 | 2 |
| $1.0\times10^{-3}$ | $1.0\times10^{-3}$ | 86 | 87 | 12 | 1 | 1 |

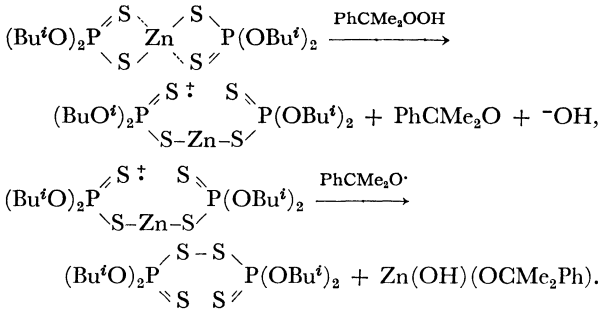
a) In the presence of 2,6-di-*t*-butyl-4-methoxyphenol: $2\times10^{-3}$M. b) In the presence of 2,6-di-*t*-butyl-4-methoxyphenol: $2\times10^{-2}$M.

higher than that for zinc *O,O*-diisopropyl dithiophosphate[1] and considerably higher than that for zinc *N,N*-diisobutyl dithiocarbamate (Zn–$Bu^i_2$–DTC) and isopropyl dithiocabonate (Zn–$Pr^i$–X) studied for comparison (Table 1 and Fig. 5).

*Products Derived from Decomposition of Cumyl Hydroperoxide with Zinc* O,O-*Diisobutyl Dithiophosphate.* When cumyl hydroperoxide (1 M) was completely decomposed with Zn–$Bu^i_2$–DTP ($1—1\times10^{-4}$ M) in chlorobenzene at 70 °C, several decomposition products were obtained (Table 2). The results shown in Table 2 suggest† the heterolytic decomposition of cumyl hydroperoxide in the presence of Zn–$Bu^i_2$–DTP above $1.0\times10^{-1}$ M. When the ratio of cumyl hydroperoxide to Zn–$Bu^i_2$–DTP exceeded 100, cumyl hydroperoxide decomposed heterolytically. This suggests that one mole of Zn–$Bu^i_2$–DTP is able to decompose at least 10 mol of cumyl hydroperoxide homolytically.†† Cosequently, it appears that the decomposition modes (homolytic or heterolytic) are drastically dependent on the relative ratio of cumyl hydroperoxide to Zn–$Bu^i_2$–DTP.

It was found, however, that the decomposition modes were also affected by the total concentration of Zn–$Bu^i_2$–DTP and cumyl hydroperoxide, even though they coexist in the relative ratio of unity (Table 3). A total concentration above $2\times10^{-1}$ M was preferable for homolytic decomposition; this was also supported by the increase in amount of α,α-dimethylbenzyl alcohol formed in the presence of 2,6-di-*t*-butyl-4-methoxyphenol. The total concentration below $2\times10^{-2}$ M, on the other hand, was preferable for heterolytic decomposition.

In the decomposition reactions mentioned above, Zn–$Bu^i_2$–DTP itself was also decomposed into compounds, such as zinc sulfate, bis(*O,O*-diisobutoxyphosphonothioyl) disulfide and sulfuric acid, depending on the concentrations of Zn–$Bu^i_2$–DTP and the hydroperoxide. Zinc sulfate and bis(*O,O*-diisobutoxyphosphonothioyl) disulfide were separated from the reaction solution after the homolytic decomposition (for example, cumyl hydroperoxide, 1.0 M and Zn–$Bu^i_2$–DTP, $1\times10^{-1}$ M), while sulfuric acid was obtained from the decomposition reaction (for example, cumyl hydroperoxide, $1\times10^{-2}$ M and Zn–$Bu^i_2$–DTP, $1\times10^{-2}$ M). These results support the formation of the disulfide, as reported by Burn *et al.*,[1] as follows:




† It is well documented that the homolytic decomposition of cumyl hydroperoxide gives α,α-dimethylbenzyl alcohol, acetophenone and α-methylstyrene, while the heterolytic decomposition gives phenol and acetone.

†† J. A. Howard reported[8] that nickel diisopropyl dithiophosphate decomposed about 25 times of cumyl hydroperoxide homolytically.

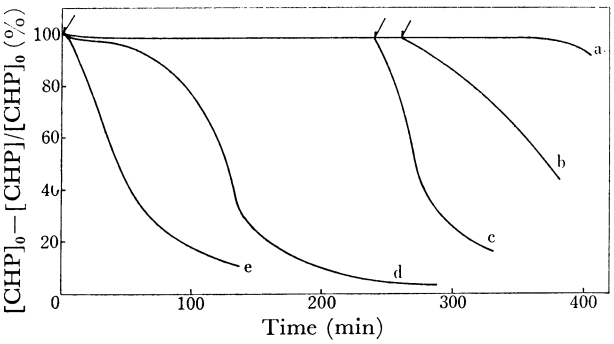



Fig. 6. Decomposition of cumyl hydroperoxide (0.1 M) with Zn–$Bu^i_2$–DTP and/or bis(*O,O*-diisobutylphosphonothioyl)disulfide in chlorobenzene at 70 °C.

| | a | b | c |
|---|---|---|---|
| Zn–DTP | $1\times10^{-3}$ M | $1\times10^{-3}$ M | $1\times10^{-3}$ M |
| Disulfide | 0 | $1\times10^{-2}$ M | $3\times10^{-2}$ M |
| | d | e | |
| Zn–DTP | $1\times10^{-3}$ M | 0 | |
| Disulfide | $1\times10^{-2}$ M | $1\times10^{-2}$ M | |

The resulting disulfide will react rapidly with the hydroperoxide and/or a free radical to form the sulfate ion,[5] which may be converted into zinc sulfate and free sulfuric acid.

*Decomposition of Cumyl Hydroperoxide Using Zinc* O,O-*Diisobutyl Dithiophosphate with Bis(*O,O-*diisobutoxyphosphonothioyl) Disulfide.* Cumyl hydroperoxide was decomposed in the presence of Zn–$Bu^i_2$–DTP and the disulfide. The result is shown in Fig. 6, in which the decompositions by either Zn–$Bu^i_2$–DTP or the disulfide are also shown for comparison. Only the Zn–$Bu^i_2$–DTP decomposed a little of the hydroperoxide after the start of decomposition (Curve a), while only the disulfide did considerably without any induction period (Curve e). When both decomposers co-existed in the same concentration ($1\times10^{-3}$ M) of Zn–$Bu^i_2$–DTP (Curve a) and in the same concentration ($1\times10^{-2}$ M) of the disulfide (Curve e), however, the curve of decomposition (Curve d) was not unexpectedly comparable to Curve e. This may be interpreted assuming that sulfuric acid, which is most effective for ionic decomposition and is derived from the decomposition of cumyl hydroperoxide with the disulfide,[5] is rapidly trapped by Zn–$Bu^i_2$–DTP present to form zinc sulfate as seen in Fig. 4 for Cu(II)–P–$C_3$–DTP. Sulfuric acid formed, therefore, is not an effective catalyst till all of the Zn–$Bu^i_2$–DTP is consumed as zinc sulfate, resulting in the induction period as shown by Curve d.

The assumption made may be supported by the result of Curves b and c. When the disulfide was added during decomposition started with the same concentration of Zn–$Bu^i_2$–DTP as in Curve a, no induction periods were observed (Curves b and c). This indicates that the addition of the disulfide, at the time of which almost all of the Zn–$Bu^i_2$–DTP is presumably converted into zinc sulfate, decomposes cumyl hydroperoxide immediately, as if only the disulfide were added at the beginning of decomposition reaction, for example, as shown in Curve e.

## Conclusion

The present study has clarified the effects of the relative concentration of the complex to cumyl hydroperoxide (Table 2) and the total concentration of the complex and cumyl hydroperoxide (Table 3) on the decomposition activity of the complex.

It was also found that zinc *O,O*-dialkyl dithiophosphate was not an effective decomposer for the heterolytic decomposition till free sulfuric acid was formed. These results must contribute to select an useful amount of the zinc complex.

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