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THERMAL DEGRADATION OF ZINC-O, O-DIETHYL DITHIOPHOSPHATE

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ABSTRACT

The thermal degradation of Zinc-O, O-diethyl dithiophosphate has been investigated at 190°C in n-hexadecane. The major products have been identified as O, S, S-triethyl trithiophosphate, $(EtS)_2P(S)OEt$, O.O.S-triethyl dithiophosphate, EtS P(S) (OEt).,, S,S,S-triethyl tetrathiophosphate, (EtS), PS, O.S,S-triethyl dithiophosphate, (EtS), PS, 0,S,S-triethyl dithiophosphate, (EtS)., P(O) OEt, and O.O.S-triethyl thiophosphate, EtS P (O) $(OEt)_2$. The degradation is suggested to involve thiono-thiolo isomerisation coupled with disproportionation of sulfur and oxygen linked to phosphorus.

Key words: Zinc-O, O-diethyl dithiophosphate, thermal degradation, thionothiolo isomerization disproportionation.

INTRODUCTION

As part of our interest in the chemistry of organophosphorous compounds,[1-3] we report herein our results of the thermal degradation behaviour of Zinc-O,O-diethyldithiophosph ate at 190°C. Zinc dialkyl dithiophosphate (ZDTPs) have been widely used as commercial lubricant additives in the engine oils for theri anti-wear action over half-a-century now. Despite a great deal of reasearch,[4-9] precisely how do the 2DTPs perform their anti-wear function is not clear as yet, although it is widely beleived that they act by undergoing thermal degradation at higher temperatures of the order of 170-190°C. So, we became interested in investigating their thermal degradation under such conditions.

EXPERIMENTAL

All ^{31}P NMR spectra were recorded on a JEOL FX90Q spectometer operating at 28°C with an internal C_6D_6 capillary lock. ^{31}P chemical shifts are quoted with reference to 85% phosphoric acid with shifts to high frequency being positive in sign. The spectal window for kinetic measurements was 5200 Hz with 8K data, giving a digital resolution of 0.635 Hz per point. A pulse width of 4 (20°) was used with acquisitions over$^{\mu s}$ 100 scans per spectrum gave a typical signal: noise ratio of > 10:1 with solution strengths of ca 0.33

mol dm^{-3}. The ZDTP was prepared as described previously.[1-3]

The degradation studies were carried out which in an oil bath maintained at 190°± 2°C and samples regularly taken out for analysis.

RESULTS AND DISCUSSION

Zinc-O,O-diethyl dithiophosphate $[(EtO)_2\ PSS]_2Zn$ was readily obtained in pure form by reacting $(EtO)_2PS_2K$ with $ZnS0_4$ (in 2:1 ratio), rather than with $ZnCI_2$ which also leads to the concomitant formation of the basic salt along with the desired title ZDTP. Its purity was checked by its PMR spectrum and other analyses and also confirmed by the observation of a discrete signal at 96.5ppm (n-hexadecane) in its proton-decoupled ^{31}P NMR spectrum. We initiated our studies at 85°C in dry n-hexadecane. No reaction took place for ca 3h as revealed by spectroscopic analysis of the reaction mixture after regular time intervals.

However, when heated at 190°C in dry n-hexadecane under nitrogen, the ZDTP readily underwent total decomposition in ca 45 min giving a complicated mixture of products as indicated by the appearance of 7 new peaks in its ^{31}p NMR spectrum at 109.5, 95.8, 90.7, 69.5, 66.1, 53.7 and 27.6 ppm. Since the peak at 96.5 ppm due to the diethyl ZDTP itself was absent, it was clear that the zinc dithiophosphate had undergone complete thermal decomposition to give rise to a number of phosphorous containing products.

Attempts to isolate the products by chromatography proved unsuccessful. Similarly, the spectrum of the product mixture was very complicated, although it did show the presence of both P-O-CH as well as P-S-CH signals, therefore, the suspected compounds (on the basis of thiono-thiolo isomerization coupled with and disproportionation) were synthesized according to the standard reported methods[10] for direct comparison of their ^{31}P chemical shifts with those of the reaction products. Thus, the major products with ^{31}P chemical shifts at 109.5, 95.8, 90.7, 53.7 and 27.6 ppm were identified as O.S, S-triethyl trithiophosphate $(EtS)_2$ P(S) OEt, 0,0,S-triethyl thiophosphate, (EtS) P(S) $(0Et)_2$, S,S,S-triethyl tetrathiophosphate $(EtS)_3$ P(S), 0,S,S-triethyl dithiophosphate $(EtS)_2$ P(O) (OEt) and O.O.S-triethyl thiophosphate, EtS P(O) $(OEt)_2$ respectively. Such types of products have been identified in the thermal depredation of zinc n-butyl dithiophosphate complexes.[11] Based upon ^{31}p NMR analysis, these products were obtained in 19.8, 44.9, 10.8, 4.5 and 9.3% yield respectively. The identity of the retaining two (minor) peaks with shifts 69.5 (7.2%) and 66.1 ppm (3.6%) is unknown at this stage. However, neither was shown to correspond to 0,0,0-triethy! thiophosphate, $(EtO)_3$ PS, an authentic sample of which resonated at 68.3 ppm. Identification of products was based on the "peak enhancement" of the ^{1}H-decoupled ^{31}P NMR signal on addition of an authentic samples to the reaction mixtures as used previously.[13] The products identity was further confirmed by infra-red analysis which showed the presence of P-O-C (900-1300 cm^{1}), P.S.C. (500 cm^{1}) and P=S (800-850 cm^{1}) groups.[1312] Hydrogen sulfide and ethyl mercaptan were also identified as the volatile products. A colorless solid was also formed which gave off hydrogen sulfide upon treatment with dilute HCI, indicating to be mainly zinc sulfide.

Judging from the nature of the products formed, it seems highly likely that the mechanism of this fascinating degradation involves thiono-thiolo isomerization coupled with disproportionation as reported for some thiophosphoryl compounds.[13]

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