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Note

Liquid chromatography of dibutyldithiocarbamate degradation products

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The separations of some dimethyldithiocarbamate derivatives and their degradation products by high-performance liquid chromatography (HPLC) were described in our previous papers[1–3]. A method has been developed for the determination of iron(III) dimethyldithiocarbamate (ferbam) and its degradation products in natural samples. Ethylenethiourea in some fungicides has also been determined by HPLC[4].

All our results confirmed that many derivatives of dithiocarbamates (DTCs) are not stable and decompose very quickly.

In previous papers[5,6] we described the formation and the identification of some mixed ligand DTC complexes with different N-alkyl substituents. The values of the equilibrium and the rate constants for ligand exchange in the DTC metal complexes estimated by means of HPLC confirmed some previously published assumptions[7].

The influence of UV radiation, temperature and oxidizing agents on the decomposition of dimethyldithiocarbamates and the evaluation of the decomposition in real samples was studied using thin-layer chromatography and HPLC[8]. The degradation products of DTC complexes were found to be more biologically effective than the original chelates[9–11] and their biological activity has been studied in detail[12–14].

The detemination of dithiocarbamates by liquid chromatography using transition-metal salts as "ion-pair" reagents has been studied, and the examination of different metal ions as potential complexation reagents has been discussed[15,16].

In this paper, results are presented on the effects of UV radiation, temperature and time on the degradation of iron(III) dibutyldithiocarbamate. The use of HPLC and mass spectrometry (MS) has improved the identification and determination of this complex and of the products of its transformation.

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EXPERIMENTAL

Apparatus

A Packard Model 8200 HPLC system with an UV detector operated at 254 and 280 nm) was used for all the separations. The stainless-steel columns (250 mm × 2.2 mm I.D.) were packed with LiChrosorb RP-18 and RP-8. The mobile phases used were 25% water in isopropanol, 35% water in isopropanol and 20% water in methanol.

All gas chromatographic and mass spectrometric measurements (GC–MS) were performed using a GC–MS Finnigan 4000 instrument in cooperation with Dr. P. Leclerq, Laboratory of Instrumental analysis, University of Technology, Eindhoven. A glass capillary column (30 m × 0.4 mm I.D.) packed with 3% SE was coupled to a Finnigan 4000 quadrupole mass spectrometer via a 40 cm × 0.4 mm I.D. Helium was used as he carrier gas. A glass "falling needle" device was used as injector. All experiments were carried out under the following conditions: inlet pressure, P_i = 2.0 bar (absolute); injection temperature = 250°C; column temperature = 230°C; GC–MS interface (GLT) temperature = 240°C; ion source temperature = 250°C. The MS was operated in the electron impact (EI) mode under the following conditions: electron energy = 70 eV; electron current = 0.25 mA; multiplier voltage = 1.70 kV; mass range = 40–550; scan speed = 1 spectrum per s.

A Mettler-Thermoanalyzer, Model 2 was used for the thermal analysis (differential thermal analysis, DTA; thermal gravimetry, TG; differential thermal gravimetry, DTG). All measurements were made with masses of 7 mg in a dynamic atmosphere of oxygen-free nitrogen (7 l h^{-1}) at a constant heating rate of 10°C min^{-1}. Platinum/platinum + rhodium thermocouples were used and alumina was the standard for DTA.

An UV-RI lamp (UVR, Chirana, Stará Turá, Czechoslovakia) was used for the UV irradiation.

Chemicals

Iron(III) dibutyldithiocarbamate[14], tetrabutylthiuramdisulphide (TBTD)[17] and tetrabutylthiuram monosulphide (TBTM)[18] were synthesized by literature procedures. Tetrabutylthiourea (TBTU) was prepared by the reaction of dibutylamine and thiophosgene in benzene[17]. The identities and purities of the products were confirmed by elemental analysis and mass spectrometry.

All organic solvents were of analytical reagent grade (Lachema, Brno, Czechoslovakia) and were dried over magnesium perchlorate and redistilled.

Procedures

All components were decomposed upon UV irradiation in the dry state and also in solutions (chloroform, methanol and water) as thin films on glass plates. The times for UV irradiations were 10, 20, 30 and 60 min.

RESULTS AND DISCUSSION

The choice of separation conditions for the simultaneous separation of iron(III) dimethyldithiocarbamate and its possible degradation products has been discussed in detail previously[1–3].

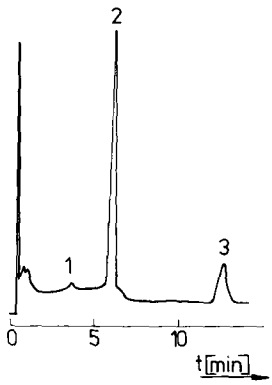
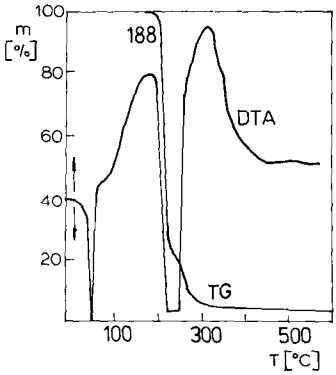


Fig. 1. GC separation of TBTD and TBTM. Column: SE-30 (30 m × 0.4 mm I.D.), Temperature: 230°C. Carrier gas: helium; pressure 200 kPa. Peaks: 1 = inert (solvent); 2 = TBTM; 3 = TBTD. UV detection at 254 nm; injected amount, 10 μl.

The present work confirmed that dibutyldithiocarbamates are also not stable and decompose very quickly. We were interested especially in an HPLC analysis of iron(III) dibutyldithiocarbamate used as an antioxidant in plastic foils applied in agriculture for growing cucumbers.

The rate of the degradation was studied in a series of experiments. Solutions of iron(III) dibutyldithiocarbamate in chloroform and methanol were injected into the liquid chromatograhic reversed-phase system after certain time intervals. After only 10 min some degradation product was present. After 3 months the peak area of the degradation product was larger than the peak area of the original antioxidant. The degradation product was identified as TBTD by HPLC, GC and mass spectrometry. All three possible degradation products were synthesized and their purities were monitored by elemental analysis and mass spectrometry. The GC separation of



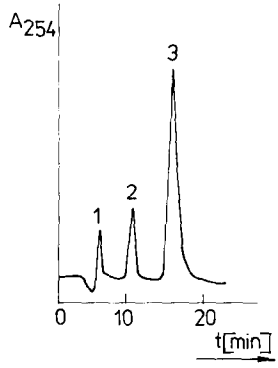


Fig. 2. DTA and TG diagrams for TBTD. Oxygen flow-rate: 7 l h^{-1}. Heating rate: 10°C min^{-1}. Platinum/platinum + rhodium thermocouples; alumina as the standard.

Fig. 3. HPLC separation of TBTD and TBTM. Column: RP-8 (250 mm × 2.2 mm I.D.). Mobile phase: 25% water in isopropanol; flow-rate 0.21 cm^3 min^{-1}. UV detection: 254 nm. Amount injected: 10 μl of a mixture of TBTD and TBTM in chloroform (1 mg cm^{-3}). Peaks: 1 = inert; 2 = TBTM; 3 = TBTD.

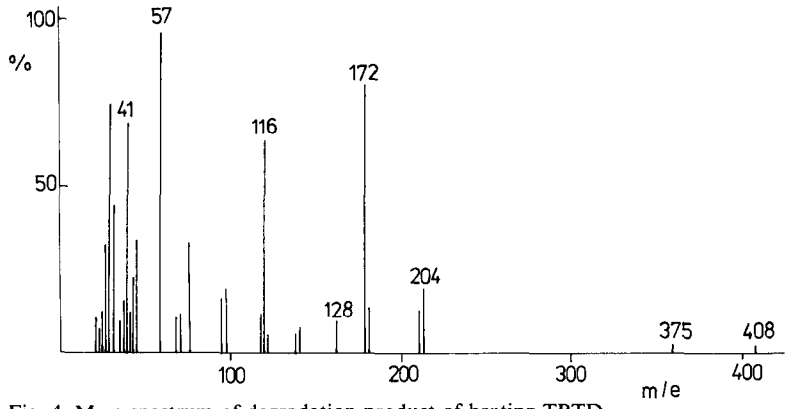


Fig. 4. Mass spectrum of degradation product of heating TBTD.

TBTD was complicated by the fact that, at a temperature of 230°C, TBTD was converted into TBTD (Fig. 1), as was verified by GC–MS and DTA. This method has also been used for the identification of the degradation products.

The DTA and TG diagrams (Fig. 2) confirmed that TBTD decomposes at about 190°C. The conversion of TBTD was performed at about 230°C in a silicon oilbath and the product was them injected into the chromatographic column. Fig. 3 shows the HPLC separation of a model mixture of TBTD and TBTM. The main conversion product of TBTD was identified as TBTM. This was confirmed by mass spectrometry at low voltage (Fig. 4).

Table I shows the capacity factors of all three degradation products of iron(III) dibutyldithiocarbarate in the recommended mobile phases.

The influence of UV radiation was studied in a series of model experiments in solvents with different polarities (chloroform and methanol). After the degradation the samples were injected into the HPLC column. It was evident that decomposition occurred after only 10 min of UV irradiation. The degradation product was identified as TBTD. After 30 min, TBTM was also present as a degradation product. After 120 min the percentage of the complex had decreased to about 6% of the original content. The identification of TBTD and TBTM was also confirmed by mass spectrometry at 12–16 eV.

TABLE I

CAPACITY FACTORS, k', OF TBTD, TBTM AND TBTU

Degradation product	*Separation conditions*			
	RP-18, 25% water in isopropanol, 12.4 MPa	*RP-18, 25% water in isopropanol, 10.3 MPa*	*RP-8, 35% water in isopropanol, 13.1 MPa*	*RP-8, 20% water in methanol, 8.3 MPa*
TBTU	1.06	1.12	1.47	1.45
TBTM	1.21	1.68	1.82	2.05
TBTD	1.92	2.42	2.63	3.04

TABLE II

UV DEGRADATION OF IRON(III) DIBUTYLDITHIOCARBAMATE IN CHLOROFORM SOLUTIONS

Time (min)	*TBTM (%)*	*TBTD (%)*	*Starting complex (%)*
10	–	37.64	62.36
20	–	32.88	57.12
30	2.88	46.10	51.02
60	8.15	54.63	37.22
120	12.29	82.67	5.03
180	14.05	83.90	2.05

TABLE III

DEGRADATION OF IRON(III) DIBUTYLDITHIOCARBAMATE WITH TIME

Time	*Complex (%)*
6 h	91.1
24 h	66.9
48 h	59.8
1 month	42.7
3 month	35.2
6 months	12.3
8 months	5.4

The UV degradation of iron(III) dibutylidithiocarbamate in methanol occurred much more quickly, the original complex none of remaining after 120 min of UV irradiation. Only TBTD and TBTM were present in irradiated samples.

Table II shows the results of UV irradiation of iron(III) dibutyldithiocarbamate in chloroform solutions, and Table III gives the rate of degradation. Only about 5% of the original complex was present after 8 months. However, this degradation is considerably slower than the degradation is considerably slower than the degradation of iron(III) dimethyldithiocarbamate (ferbam)[1].

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