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SHORT COMMUNICATION

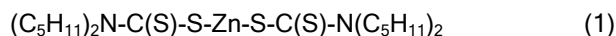
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THE OPTIMIZATION OF ZINC DIALKYLDI- THIOCARBAMATES SYNTHESIS AND DETERMINATION OF THEIR ANTIOXIDANT ACTIVITY

A two-step optimized laboratory synthetic method of zinc dialkyldithiocarbamates is presented. In the course of the first phase, a sodium salt of dialkyldithiocarbamic acid has been synthesized from the dialkylamines, carbon disulfide and sodium hydroxide. The synthesis of zinc dialkyldithiocarbamates was achieved by the precipitation from sodium dialkyldithiocarbamic acid by zinc sulfate under the optimized conditions. The synthesized products have been characterized by FTIR, ¹H and ¹³C NMR, AAS spectroscopic methods, as well as by elemental analysis and melting points. Kinetic studies of the motor oil oxidation inhibited by synthesized compounds have been tested using a standard method.

Key words: zinc dialkyldithiocarbamates; optimization; inhibition rate constant.

Zinc dialkyldithiocarbamates are an additive for liquid lubricants, an antioxidant (oxidation inhibitor), and an oil additive for the transmission car mechanism [1]. Zinc dialkyldithiocarbamates combine antioxidant properties with an ability to inhibit corrosion and to function as antiwear and as extreme pressure agents for motor oils and automatic transmission fluids [2]. Dithiocarbamates are a salt of dithiocarbamic acid with different amines and a divalent cation which determine the area of their application. Zinc diamyldithiocarbamates are zinc salts of dithiocarbamic acid presented by following formula:

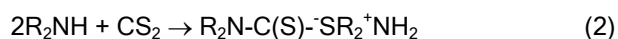


Zinc diamyldithiocarbamates have been widely used as lubricating oil additives, and it is a preferable commercial product because of the cheap starting mixture of di-amyamines (by-product). These compounds, or their decomposition products, have long been known to catalyze the decomposition of hydroperoxides or to trap free radicals. The aim of this work

was to define the optimal laboratory synthetic method for synthesis of zinc dialkyldithiocarbamates. The synthesis of zinc dialkyldithiocarbamates has been performed in two steps. In the first step, a synthesis of sodium salt of dialkyldithiocarbamic acid was achieved by the known literature method [3], in the reaction of dialkylamine, carbon disulfide and sodium hydroxide. Also, the synthesis of the ammonium salt of dialkyldithiocarbamic acid has been described [4]. In the second step, the precipitation of sodium salt of dialkyldithiocarbamic acid using zinc sulfate was achieved under the optimized reaction conditions producing a pure compound.

THEORETICAL PART

The synthesis of dialkylamine salt dithiocarbamic acid takes place according to the presented reaction [3]:



In the presence of an oxidative agent, the salt of dialkyldithiocarbamic acid has been transformed to the oxidative product thiuram [5]:



On the other side, sodium hydroxide produces the sodium salt of dialkyldithiocarbamic acid [6]:

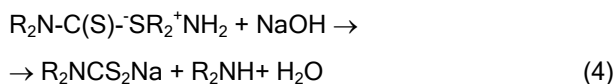
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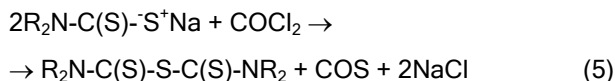
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The produced sodium salt could be transformed to tetraalkyl thiuram monosulfide introducing phosgene to the reaction mixture [7,8]:



The reaction has been performed by reacting 42 % water solution of sodium dialkyl dithiocarbamates with the mixture of phosgene and air (ratio 10/1) at the reaction temperature of 50 °C.

THE EXPERIMENTAL PART

The synthesis of zinc dialkyldithiocarbamates has been optimized with the respect to the reaction parameters: time, temperature and the reactant concentration.

Synthesis of sodium diamyldithiocarbamate

In a three-necked 500 cm³ flask, equipped with a magnetic stirrer, an electric heater, a reflux condenser, a thermometer and a dropping funnel, 50 cm³ water and 87.8 cm³ (0.41 mol) diamylamine (mixture of 20 % di-*n*-pentylamine, 18 % di-(2-methylbutyl)amine and 62 % di-(3-methylbutyl)amine) was added. After homogenization, a 25.3 cm³ (0.41 mol) carbon disulfide was gradually added during 30 min at 30 °C. Neutralization of the reaction mixture was achieved by using a 38.0 cm³ (0.41 mol) sodium hydroxide solution (added at 35 °C) during 30 min. The upper organic layer disappeared and the reaction mixture became light yellow colored, containing sodium diamyldithiocarbamate. The solvent was removed until light yellow crystals appeared. Two successive crystallizations from benzene gave a pure product.

Synthesis of zinc diamyldithiocarbamate

In a beaker of 500 cm³, 100 cm³ water was added and heated to 50 °C, followed by the addition of 29.5 cm³ (0.07 mol) 50 % water solution of zinc sulfate. A sodium diamyldithiocarbamate water solution 96.8 cm³ (0.14 mol) 36.5 % was added into the reaction mixture, (at 50 °C) during 30 min. After the addition was completed, the reaction mixture was heated to 65 °C, following with the addition of 100 cm³ toluene, and continuing mixing for 15 min. The upper toluene layer was separated, washed twice with distilled water and dried with sodium sulfate. After the toluene removal at rotavapor, a 98 % of pure product (99.2 %) of zinc diamyldithiocarbamate was obtained.

The yield and purity of all synthesized compounds is given in Table 5.

Inhibition of oxidation of motor oil

The autoxidation apparatus and general experimental techniques have been adequately described in the previous papers on inhibition by phenols [9] and amines [10] and on the determination of the rate constants for hydrocarbon autoxidation [11]. The autoxidation process was initiated by the thermal decomposition of α,α' -azo-*bis*-isobutyronitrile (AIBN) at 50 °C. The rates of the chain initiation were determined by the usual induction period method [11] using 2,6-di-*tert*-butyl-4-methoxyphenol as the inhibitor. The hydrocarbon substrates and the solvents were carefully purified by the standard techniques. Adventitious hydroperoxides were the most troublesome impurity and were removed by distillation and/or percolation through basic alumina.

Kinetics of electronic paramagnetic resonance experiments

tert-Butylperoxy radicals were generated directly in the cavity of a Varian E-3 e.p.r. spectrometer at temperatures in the range of 0 to -70 °C. The radicals were formed by the photolysis of di-*tert*-butyl peroxide in the air saturated isobutane. Decays of the radicals upon the interruption of the irradiation were followed in a usual way [12]. In the absence of a peroxy radical trap, 1-butylperoxy decayed bimolecularly, but in the presence of a sufficient concentration of a trap the decay was first order. Rate constants for the reaction of this peroxy radical with the inhibitor were calculated from the measured rates of the radical decay and the concentration of the inhibitor.

Characterization of the synthesized compounds

All synthesized compounds have expected a composition, based on the satisfactory elemental (C, H, N, S) analysis, determined on Vario EL III elemental analyzer. Their structures were confirmed by the melting point, infrared spectroscopy, ¹H and ¹³C NMR data. IR spectra were taken on Bomem MB 100 FTIR spectrophotometer. The ¹H and ¹³C NMR spectral measurements were performed on a Bruker AC 250 spectrometer at 250 MHz. The spectra were recorded at room temperature in deuterated dimethyl sulfoxide (DMSO-*d*₆). The chemical shifts are expressed in ppm values referenced to the residual solvent signal at 39.5 ppm. The chemical shifts were assigned by the complementary use of Dept-, two dimensional ¹H-¹³C correlation Hector- and by selective Inept long-range experiments. The amount active metal was determined by the standard EDTA titration of zinc after the

careful destruction of the starting material or by an atomic absorption spectroscopy using a Perkin-Elmer 1100B spectrometer. The absorption of carbon disulfide, released from the synthesized compounds in Wiles' reagent [14], was used for purity determination.

RESULTS AND DISCUSSION

The first series of experiments presents the definition of the optimized laboratory procedure for the synthesis of sodium dialkyldithiocarbamates, and the second one the optimized procedure for the synthesis of zinc dialkyldithiocarbamates.

Optimization of synthesis of sodium dialkyldithiocarbamate

The optimized method for the synthesis of sodium dialkyldithiocarbamate from dialkylamine salt of diamyldithiocarbamic acid in the reaction with sodium hydroxide was presented by the reaction (4). Released amine reacts with carbon disulfide produce amine salt which further reacts with sodium hydroxide producing sodium diamyldithiocarbamate. According to the reaction mechanism a double quantity of amine reacts with carbon disulfide producing the salt of dialkyldithiocarbamic acid, which after the reaction with sodium hydroxide liberates amine, which again reacts with the excess of carbon disulfide. In this part of experimental work, the influences of the temperature, the reaction time and the reactant concentrations on the yield of sodium salt of diamyldithiocarbamic acid were studied. The results of experimental work have been presented in Table 1.

Table 1. The yield of sodium diamyldithiocarbamic acid vs. reaction time (reaction temperature 30 °C, equimolar ratio of reactants)

No.	Time, min	Yield			Purity, %
		g	mol	%	
1	15	75.00	0.294	71.40	98.70
2	20	89.20	0.349	84.95	99.80
3	30	103.50	0.405	98.57	99.81
4	45	103.0	0.406	98.66	99.80

On the basis of the results from Table 1 it could be observed that the highest yield was achieved for 45 min (experiment No. 4, 98.66 %), giving almost a quantitative yield of product, but the choice of the optimal reaction time would be 30 minute (98.75 %), providing a significant benefit to achieve a successful technology transfer from a laboratory to the industrial level.

The dependence of the product yield with respect to the reaction temperature is presented in Table 2.

The optimal yield has been achieved by conducting the experiment 3 (99.82 %), while by lowering the temperature the yield was significantly decreased. This could be due to the side reaction (trithiocarbonate product), which caused difficulties with purification of the crude product. The reaction of carbon disulfide with sodium hydroxide is strongly favored at the temperature lower than 30 °C, while its increase is closely related to the problem of the easy evaporation and flammability of reactants. All these points are very important for the large-scale industrial production of the final product. The optimization of the product yield with respect to reactant concentrations is presented in Table 3.

Table 2. The yield of sodium diamyldithiocarbamate vs. the reaction temperature (the reaction time 30 min; equimolar ratio of reactants)

No.	t, °C	Yield			Purity, %
		g	mol	%	
1	20	64.03	0.215	52.40	86.02
2	25	100.20	0.368	89.51	93.80
3	30	103.82	0.406	98.69	99.82
4	35	103.80	0.406	98.69	99.81
5	40	102.60	0.401	97.53	99.82

Table 3. The yield of sodium diamyldithiocarbamate vs. reactant concentration (reaction time 30 min; reaction temperature 30 °C)

No.	Amine		Carbon disulfide		Sodium hydroxide		Yield %	Purity %
	g	mol	g	mol	g	mol		
	1	68.00	0.41	31.93	0.41	51.47		
2	72.97	0.44	34.26	0.44	51.47	0.41	90.02	93.20
3	72.97	0.44	31.93	0.41	51.47	0.41	98.52	99.80

On the basis of the results from Table 3 it could be observed that a good yield was achieved at equimolar ratio of reactants (98.50 %), which is in concordance with the reaction mechanism. The molar increase of any reactant causes the increase of the reaction by-product, causing a yield decrease connected with a time-consuming purification process.

Experimental results of zinc dialkyldithiocarbamates synthesis

Zinc dialkyldithiocarbamates has been synthesized by the reaction of zinc sulfate water solution with sodium dialkyldithiocarbamate. The optimal synthetic procedure has been described as the synthesis of zinc diamyldithiocarbamate. For example, different water suspension of zinc diamyldithiocarbamate (5, 8, 15 and 25 % of active substance), varying temperature in the range from 20 to 70 °C, have been reacted with the water solution of zinc sulfate. The product yield depen-

dence with respect to the reactant concentration and the reaction temperature is presented in Table 4.

Table 4. The yield of zinc diamyldithiocarbamate vs. reactant concentrations and temperature (reaction time 30 min)

No.	Suspension, %	Yield, %			
		$t, ^\circ\text{C}$			
		20	40	50	70
1	5	40.20	46.00	83.00	83.30
2	8	42.00	79.32	89.50	80.20
3	15	89.00	90.50	98.00	98.08
4	25	63.00	70.21	86.00	79.06

The highest yield of zinc diamyldithiocarbamate was achieved (Table 4, 98 %) using 15 % the water suspension of zinc diamyldithiocarbamate, at 50 °C. According to the optimized synthetic procedure other zinc dialkyldithiocarbamates have been synthesized, and the reaction yields, zinc and sulfur content in pure products are given in Table 5.

Table 5. The yield of zinc dialkyldithiocarbamate, zinc and sulfur content

Compound	Yield/purity	Melting point °C	Zinc %	Sulfur %
Zinc dimethyl dithiocarbamate	95.4/99.6	242-255	20.2	10.44
Zinc diethyl dithiocarbamate	96.6/99.7	175-182	17.6	8.82
Zinc dipropyl dithiocarbamate	98.4/99.5	138 (dec.)	19.2	7.62
Zinc dibutyl dithiocarbamate	98.8/99.1	102-108	14.2	6.72
Zinc diamyl dithiocarbamate	98.0/99.2	80-85	12.4	5.99

Determination of the inhibition activity

The inhibition rate of AIBN initiated autoxidation of cyclohexene and styrene by zinc dialkyldithiocarbamates have been followed by the standard method [9-12]. The initial oxidation rate is given by

$$-\left(\frac{dc(\text{O}_2)}{dt}\right)_0 = \frac{k_p c_0(\text{RH})R_i}{nk_{\text{inh}}c_0(\text{A})}$$

where: $c_0(\text{RH})$ is the monomer concentration, $c_0(\text{A})$ the inhibitor concentration, R_i the AIBN concentration, k_p the literature values (98 for styrene [15] and 12 for cyclohexene [16]), and n is a number of peroxy radicals trapped by each molecule of A, while 0 refers to the initial concentrations. Using the usual induction period method [11], $n \approx 1$ was obtained for AIBN initiated oxidation. The expression for the initial rate oxidation could be transformed to:

$$\frac{c_0(\text{RH})R_i}{c_0(\text{A})(dc(\text{O}_2)/dt)_0} = \frac{nk_{\text{inh}}}{k_p}$$

which was used for graphical calculation of the inhibition rate constants presented in Table 6.

Table 6. The inhibition rate constants ($10^3 \text{ mol}^{-1} \text{ s}^{-1}$) for zinc dialkyldithiocarbamates

Compound/substrate	Methyl	Ethyl	Propyl	Bbutyl	Amyl
styrene	9.1	9.6	8.4	4.5	5.5
cyclohexene	8.2	7.8	6.6	5.6	6.2

There is no experimental evidence to indicate that peroxy radicals react with organosulfur compounds at the sulfur atom [17]. Furthermore, the disulfide, ((i-PrO), PS), [18] or esters of the structure (RO)P(S)SR, *e.g.*, *O,O*-diisopropyl-*S*-methylthionophosphate do not inhibit autoxidation or react with *t*-butylperoxy radicals at low temperatures [18]. It therefore seems most probable that the reaction of zinc dialkyldithiocarbamates with peroxy radicals occurs at the metal center rather than at the sulfur one. Moreover, the decrease of the rate constants for more sterically protected central atom provides the information that not only the electron transfer process is a limited step, but some other factor determine a degree of the electron transfer. More details could be obtained from mechanistic and kinetic (kinetic parameters) investigation of the reaction.

On the other hand, in the inhibition of the AIBN initiated oxidation of squalene at 60 °C, the order inhibition activity is dithiophosphate > xanthate > dithiocarbamate [4], and in the inhibition of the tetralin at 50 °C it is dithiocarbamate > dithiophosphate [19]. The difficulties encountered in obtaining the reproducible data by the applied experimental methods are one of the reasons for these conflicting orders in reactivity. Although, it could be reasonably accepted that peroxy radicals react with zinc complexes at the metal center, the experimental results presented in this paper do not enable us to distinguish between different rate controlling reactions. A more efficient scavenger of peroxy radicals are the compounds which could donate an electron more readily to an electrophilic species (radical), which could form stable species and prevent a transfer of the electron (radical propagation reaction). Kinetic studies on the inhibition of autoxidation of the motor oil inhibited by investigated compounds show that not only the electron-donating effect of the alkyl chain could increase the electron donation, but also steric hindrance determines their activity, more active compounds with a shorter alkyl chain.

CONCLUSIONS

The optimization of the sodium dialkyl dithiocarbamates synthesis from dialkylamines, carbon-disulfide and sodium hydroxide is described. These compounds were obtained in the yields from 96 to 98.5 %. In addition, the optimization of the zinc dialkyldithiocarbamates synthesis by the reaction of zinc sulfate and sodium dialkyldithiocarbamates was also described, the yields in the range from 95.4 to 98.8 % were obtained. The structure and the purity of the synthesized compounds have been confirmed by the melting point, infrared spectroscopy, ^1H and ^{13}C NMR data. The optimized laboratory procedure could be used as a template for a technology transfer to the industrial level. The inhibition rate constants of the synthesized compounds by thermally initiated autoxidation shows the significance of steric hinderance of the alkyl chain, and it proves the necessity of the further mechanistic and kinetic investigation of the inhibition process.

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