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The Oxidations of Thiols and Their Lead Salts

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Thiols (thiophenol, thiobenzoic acid and diethyldithiocarbamic acid) react with lead dioxide, chromium trioxide or lead tetraacetate to yield the corresponding metal salts and disulfides together with water or acetic acid. The oxidations of thiophenol by multivalent iodine compounds have been studied. In addition, the redox reaction between a lead salt of a thiol and a disulfide has been investigated and the following order of oxidizing power of the disulfides is indicated: tetraethylthiuram disulfide > bis(thiobenzoyl)disulfide > dibenzoyl disulfide > diphenyl disulfide.

It is generally known that mercaptans and related compounds react easily with many types of oxidants,[1] that is, with molecular oxygen, halogens, metal oxides and salts, to give disulfides. However, there have been few investigations concerning the stoichiometrical conversion of both reactants, oxidants and mercaptans. In the present study, the reactions of various types of thiols, *i. e.*, *N, N*-diethyldithiocarbamic acid, thiobenzoic acid and thiophenol, with some multivalent oxidants were studied in detail and the reactions of lead salts of thiols with disulfides were also examined.

TABLE 1. OXIDATION OF 4 mol OF THIOLS BY 1 mol OF LEAD DIOXIDE

Thiol	Reaction condition		Yield, %	
	Time hr	Temp. °C	$Pb(SR)_2$	RSSR
C_6H_5SH	0.5	20	97	96
$C_6H_5\underset{\overset{\|}{O}}{C}SH$	0.5	20	97	91
$Et_2N\underset{\overset{\|}{S}}{C}SH$	1	70	98	85

Lead dioxide reacted readily with four moles of thiols in chloroform to yield the corresponding lead salts and disulfides in almost quantitative yields (see Table 1).

$$4RSH + PbO_2 \xrightarrow{-2H_2O} Pb(SR)_2 + RSSR$$

When two moles of thiols were treated with lead dioxide, the corresponding lead salts and disulfides were obtained in good yields together with the recovery of one-half mole of lead dioxide (see Table 2). Two moles of thiols also reacted with lead hydroxide at room temperature to give the corresponding lead salts in high yields.

TABLE 2. OXIDATION OF 2 mol OF THIOLS BY 1 mol OF LEAD DIOXIDE

Thiol	Reaction condition		Yield, %		Recovery of PbO_2 %
	Time hr	Temp. °C	$Pb(SR)_2$	RSSR	
C_6H_5SH	0.5	20	81	98	96
$C_6H_5\underset{\overset{\|}{O}}{C}SH$	0.5	20	88	91	91
$Et_2N\underset{\overset{\|}{S}}{C}SH$	1	70	98	92	96

In addition, it was found that two moles of thiophenol or of diethyldithiocarbamic acid reacted with a mixture of equimolar amounts of lead dioxide and lead hydroxide in chloroform at room temperature yielding 56% or 73% of the corresponding lead salt and 38% or 24% of the disulfide, respectively.

$$2RSH \xrightarrow[-H_2O]{PbO_2+Pb(OH)_2} mPb(SR)_2 + nRSSR \qquad (m+n=1)$$

$$R=C_6H_5,\ Et_2N\underset{\overset{\|}{S}}{C}-$$

This result suggests that thiophenol reacts with lead dioxide twice as fast as with lead hydroxide,

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[1] E. Emmet Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., Inc., New York, N. Y. (1958), p. 15.

while diethyldithiocarbamic acid reacts with lead hydroxide twice as fast as with lead dioxide.

An initial intermediate (I), formed by addition of two moles of a thiol to lead dioxide, is a necessary intermediate for the lead dioxide oxidation of thiols. This intermediate I has two possible alternative pathways of reaction, namely(A) redox decomposition to the corresponding disulfide and lead hydroxide, which then further reacts with two moles of the thiol to give the corresponding lead salt, and (B) the formation of an intermediate (II) by an exchange reaction, which also decomposes to yield the disulfide and lead salt as is shown in the following scheme.

Similarly, when four moles[2] of thiols were allowed to react with lead tetraacetate in chloroform at room temperature, the lead salts, disulfides and acetic acid were obtained in good yields (see Table 3).

$$Pb(OAc)_4 + 4RSH \longrightarrow Pb(SR)_2 + RSSR + 4AcOH$$

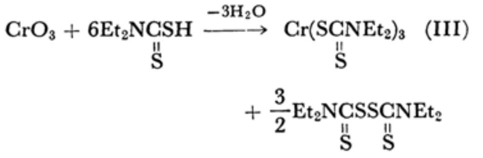
TABLE 3. OXIDATION OF 4 mol OF THIOLS BY 1 mol OF LEAD TETRAACETATE[a]

Thiol	Yield, %		
	$Pb(SR)_2$	RSSR	AcOH
C_6H_5SH	95	89	46
$C_6H_5\underset{\underset{O}{\|}}{C}SH$	96	90	59
$Et_2N\underset{\underset{S}{\|}}{C}SH$	97	10[b]	9[b]

a) The reactions were carried out in chloroform at 20°C for 30 min.

b) The poor yields of tetraethylthiuram disulfide and acetic acid would be caused by the subsequent reaction of the disulfide and the acid.

When chromium trioxide was treated with thiophenol or thiobenzoic acid in boiling chloroform for 2 hr, the thiol and the oxidant were recovered almost quantitatively. On the other hand, six moles of diethyldithiocarbamic acid reacted with this oxidant under the same conditions to give 98% of chromium diethyldithiocarbamate (III) and 62% of tetraethylthiuram disulfide.



$$CrO_3 + 6Et_2N\underset{\underset{S}{\|}}{C}SH \xrightarrow{-3H_2O} Cr(S\underset{\underset{S}{\|}}{C}NEt_2)_3 \quad (III) + \frac{3}{2}Et_2N\underset{\underset{S}{\|}}{C}SS\underset{\underset{S}{\|}}{C}NEt_2$$

The new compound III showed a magnetic moment (μ_{eff}) of 3.91 B. M., corresponding to the theoretical value for Cr^{III} (3.88 B. M.). The isolation of III is significant in that the reduced product, the chromium(III) compound, could be isolated from the chromium(VI) compound in the redox system.

The above reactions, oxidations of thiols with lead dioxide or lead tetraacetate and of diethyldithiocarbamic acid with chromium trioxide, may be written as

$$ML_{\frac{n}{m}} + nRSH \xrightarrow{-\frac{n}{m}LH_m} M(SR)_{\frac{n}{2}} + \frac{n}{4}RSSR$$

$$(m=1 \text{ or } 2,\ n=4 \text{ or } 6)$$

where M is lead or chromium and where L is O or AcO.

Next, oxidations of thiols by the use of multivalent iodine compounds were studied. Treatment of one mole of iodine pentoxide with ten moles of thiophenol at room temperature gave diphenyl disulfide and iodine in 97% and 47% yields, respectively. Similarly, when thiophenol was added to phenyl iodosoacetate at room temperature, acetic acid, iodobenzene and diphenyl disulfide were obtained in good yields.

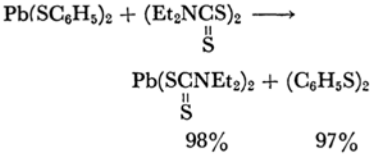
$$I_2O_5 + 10C_6H_5SH \xrightarrow{-5H_2O} 5C_6H_5SSC_6H_5 + I_2$$

$$C_6H_5I(OAc)_2 + 2C_6H_5SH \longrightarrow \underset{50\%}{2AcOH} + \underset{83\%}{C_6H_5I} + \underset{92\%}{C_6H_5SSC_6H_5}$$

The redox reaction containing an organic sulfur compound and an oxidant was extended to the reaction between a "lead thiolate" (a lead salt of a thiol) and a disulfide. Lead thiophenolate

$$Pb(SR)_2 + R'S\text{–}SR' \longrightarrow Pb(SR')_2 + RS\text{–}SR$$

easily reacted with tetraethylthiuram disulfide at room temperature in chloroform to give lead diethyldithiocarbamate and diphenyl disulfide quantitatively.



$$Pb(SC_6H_5)_2 + (Et_2N\underset{\underset{S}{\|}}{C}S)_2 \longrightarrow \underset{98\%}{Pb(S\underset{\underset{S}{\|}}{C}NEt_2)_2} + \underset{97\%}{(C_6H_5S)_2}$$

On the other hand, when lead diethyldithiocarbamate and diphenyl disulfide were treated in

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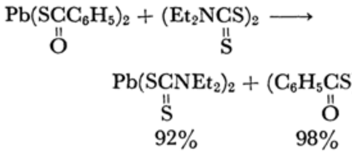
[2] Field and Lawson have reported that when two moles of thiols are treated with lead tetraacetate, lead acetate, disulfides and acetic acid are obtained: L. Field and J. E. Lawson, *J. Am. Chem. Soc.*, **80**, 838 (1958).

boiling chloroform for 2 hr, the starting materials were recovered completely.

These results suggest that this reaction is irreversible, that is, the equilibrium lies completely to the side of the products.

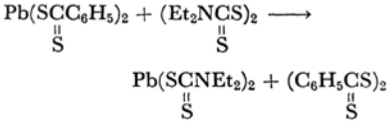
In addition, it was established that when lead thiobenzoate was allowed to react with tetraethylthiuram disulfide in boiling chloroform for 10 min, lead diethyldithiocarbamate and dibenzoyl disulfide were obtained in high yields. In a separate experiment, it was confirmed that this reaction is also irreversible.



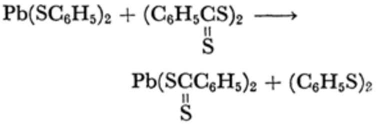
$$\mathrm{Pb(S\underset{\underset{O}{\|}}{C}C_6H_5)_2 + (Et_2N\underset{\underset{S}{\|}}{C}S)_2 \longrightarrow Pb(S\underset{\underset{S}{\|}}{C}NEt_2)_2 + (C_6H_5\underset{\underset{O}{\|}}{C}S)_2}$$

92% 98%

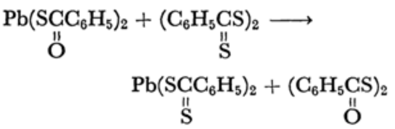
In a similar way, the following reactions were found to occur almost quantitatively at 70°C in chloroform.



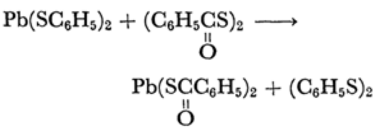
$$\mathrm{Pb(S\underset{\underset{S}{\|}}{C}C_6H_5)_2 + (Et_2N\underset{\underset{S}{\|}}{C}S)_2 \longrightarrow Pb(S\underset{\underset{S}{\|}}{C}NEt_2)_2 + (C_6H_5\underset{\underset{S}{\|}}{C}S)_2}$$



$$\mathrm{Pb(SC_6H_5)_2 + (C_6H_5\underset{\underset{S}{\|}}{C}S)_2 \longrightarrow Pb(S\underset{\underset{S}{\|}}{C}C_6H_5)_2 + (C_6H_5S)_2}$$



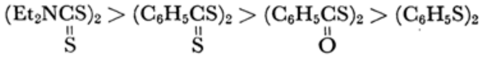
$$\mathrm{Pb(S\underset{\underset{O}{\|}}{C}C_6H_5)_2 + (C_6H_5\underset{\underset{S}{\|}}{C}S)_2 \longrightarrow Pb(S\underset{\underset{S}{\|}}{C}C_6H_5)_2 + (C_6H_5\underset{\underset{O}{\|}}{C}S)_2}$$



$$\mathrm{Pb(SC_6H_5)_2 + (C_6H_5\underset{\underset{O}{\|}}{C}S)_2 \longrightarrow Pb(S\underset{\underset{O}{\|}}{C}C_6H_5)_2 + (C_6H_5S)_2}$$

Concerning the interchange reactions, it has been reported that dialkyldithiocarbamates react with tetraalkylthiuram disulfides to yield the corresponding compounds.[3]

In conclusion, it can be noted that a disulfide is an oxidant, that is, it oxidizes a "thiolate anion" (RS^-) to the corresponding disulfide. The order of oxidizing power of four disulfides can be shown as follows:



$$\mathrm{(Et_2N\underset{\underset{S}{\|}}{C}S)_2 > (C_6H_5\underset{\underset{S}{\|}}{C}S)_2 > (C_6H_5\underset{\underset{O}{\|}}{C}S)_2 > (C_6H_5S)_2}$$

This sequence may depend primarily upon the stabilities of the corresponding thiolate anions of the disulfides.

Experimental

Materials. Lead dioxide, lead tetraacetate, chromium trioxide and iodine pentoxide were all commercial materials and used without further purification. Phenyl iodosoacetate was prepared by the method of Pausacker.[4] Thiophenol was commercial product and purified by distillation before use. Thiobenzoic acid and dithiobenzoic acid were prepared by the method of Tarbell *et al.*[5] and Houben,[6] respectively. Diethyldithiocarbamic acid was prepared by adding diethylamine to carbon disulfide in chloroform and used without isolation.

Lead hydroxide was prepared as follows: An aqueous solution of 2 mol of sodium hydroxide was added dropwise to an aqueous solution of 1 mol of lead nitrate with stirring at room temperature. The white precipitate was filtered, washed twice with water and dried *in vacuo* over P_2O_5.

Reaction of 4 mol of Thiophenol with 1 mol of Lead Dioxide. To a suspension of 2.4 g (0.01 mol) of lead dioxide in 30 m*l* of chloroform, 4.4 g (0.04 mol) of thiophenol was added with continuous stirring at room temperature. A yellow solid precipitated immediately. Stirring was continued for half an hour, then the liberated lead thiophenolate, 4.1 g (97%), mp 191—192°C, was filtered off, and recrystallized from acetic acid to give yellow crystals, mp 194.5—196°C.

Found: C, 34.29; H, 3.13; Pb, 48.29%. Calcd for $C_{12}H_{10}S_2Pb$: C, 33.87; H, 2.37; Pb, 48.69%.

Then the filtrate was concentrated *in vacuo* to give 2.1 g (96%) of colorless diphenyl disulfide, mp 60—61°C.

By a similar procedure, the corresponding lead thiolates and disulfides were obtained from the reactions between 1 mol of lead dioxide and 4 mol of thiols. The results are listed in Table 1.

Reaction of 2 mol of Diethyldithiocarbamic Acid with 1 mol of Lead Dioxide. A solution of diethylamine (3.0 g, 0.04 mol) in 10 m*l* of chloroform was added to a suspension of lead dioxide (4.8 g, 0.02 mol) and carbon disulfide (3.4 g, 0.04 mol) in 20 m*l* of chloroform with stirring at 0°C. After the mixture was refluxed for 1 hr, unreacted lead dioxide (2.30 g, 96%) was filtered off. The filtrate was evaporated to dryness under reduced pressure and the residue was washed with 20 m*l* of ether to dissolve tetraethylthiuram disulfide. The remaining yellow precipitate gave 4.9 g (98%) of lead diethyldithiocarbamate, mp 204—206°C, which was recrystallized from benzene yielding pale yellow crystals, mp 206—207°C.

Found: C, 24.02; H, 3.95; N, 5.72%. Calcd for $C_{10}H_{20}N_2S_4Pb$: C, 23.85; H, 4.00; N, 5.56%.

From the ether solution, 2.5 g (85%) of tetraethylthiuram disulfide, mp 72.5—73.5°C, was obtained. (Found: C, 40.73; H, 7.09; N, 9.66%).

The results from the reactions between 1 mol of lead dioxide and 2 mol of the other two thiols are shown in Table 2.

Reaction of Thiophenol with a Mixture of Equimolar Amounts of Lead Hydroxide and Lead Dioxide. To a suspension of 2.4 g (0.01 mol) of lead hydroxide and 2.4 g (0.01 mol) of lead dioxide in 30 m*l* of chloroform was added dropwise 2.2 g (0.02

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[3] B. Saville, *J. Polymer Sci.*, **40**, 275 (1959).

[4] K. H. Pausacker, *J. Chem. Soc.*, **1953**, 107.

[5] P. Noble, Jr., and D. S. Tarbell, "Organic Syntheses," Coll. Vol. IV, p. 924 (1963).

[6] J. Houben, *Chem. Ber.*, **39**, 3219 (1906).

mol) of thiophenol in 5 m*l* of chloroform with stirring at room temperature. After stirring had been continued for 30 min, a mixture of lead hydroxide, lead dioxide and lead thiophenolate was filtered off. After the removal of chloroform from the filtrate, 0.82 g (38%) of diphenyl disulfide, mp 60—61°C, was obtained. The above mixture was suspended in 20 m*l* of chloroform and 2.1 g (0.007 mol) of tetraethylthiuram disulfide was added to the suspension with stirring at room temperature. After the reaction mixture had been stirred for a few minutes unreacted lead hydroxide and lead dioxide were filtered and the filtrate was concentrated. The yellow precipitate was washed with ether, giving 2.8 g (56%) of lead diethyldithiocarbamate.

Similarly, diethyldithiocarbamic acid was treated with a mixture of equimolar amounts of lead hydroxide and lead dioxide to yield 24% of tetraethylthiuram disulfide and 73% of lead diethyldithiocarbamate.

Reaction of 4 mol of Thiobenzoic Acid with 1 mol of Lead Tetraacetate. A solution of 5.6 g (0.04 mol) of thiobenzoic acid in 10 m*l* of chloroform was added to a pale yellow solution of 4.7 g (0.0105 mol) of lead tetraacetate in 15 m*l* of chloroform with stirring at room temperature. The solution turned colorless and a white crystal precipitated in a short time. The reaction mixture was filtered to remove lead thiobenzoate, 4.6 g (96%), mp 160—163°C (decomp.). Recrystallization from acetic acid gave pale yellow crystals, mp 170—171°C (decomp.). (Found: C, 34.70; H, 2.34; Pb, 43.15%). The filtrate was distilled giving 1.1 g (46%) of acetic acid, bp 50—55°C/50 mmHg. The residue was extracted with ether and treated with charcoal. From the ether extracts, 2.47 g (90%) of dibenzoyl disulfide, mp 125—127°C, was obtained.

By a similar procedure, the other thiols were treated with lead tetraacetate. The results are summarized in Table 3.

Reaction of 6 mol of Diethyldithiocarbamic Acid with 1 mol of Chromium Trioxide. No noticeable reaction was observed, when a solution of 4.5 g (0.06 mol) of diethylamine in 5 m*l* of chloroform was added to a suspension of 1.0 g (0.01 mol) of chromium trioxide and 4.6 g (0.06 mol) of carbon disulfide in 20 m*l* of chloroform with stirring at 0°C. The mixture was further stirred for a few minutes at room temperature and then for 1 hr at 70°C. The solvent was removed and the resulting dark blue precipitate was thoroughly washed with ether to remove the disulfide. The undissolved precipitate was extracted with dichloromethane giving 4.85 g (98%) of chromium diethyldithiocarbamate (III), mp 247—248°C. Recrystallization from benzene gave the pure compound III, mp 250—251°C.

Found: C, 36.10; H, 6.15; N, 8.72%. Calcd for $C_{15}H_{30}N_3S_6Cr$: C, 36.29; H, 6.09; N, 8.46%.

Magnetic moment of this compound III was measured by the Gouy method ($\mu_{eff}=3.91$ BM).

From the ether solution, 2.80 g (62%) of tetraethylthiuram disulfide, mp 70—71°C, was obtained.

Reaction of 10 mol of Thiophenol with 1 mol of Iodine Pentoxide. When a solution of 5.50 g (0.05 mol) of thiophenol in 5 m*l* of chloroform was added to a suspension of 1.67 g (0.005 mol) of iodine pentoxide in 20 m*l* of chloroform with stirring at room temperature, the reaction started at once with liberation of heat. The resulting red solution was concentrated and chromatographed over alumina (80 g). Elution with ether gave 5.3 g (97%) of diphenyl disulfide, mp 59—60°C. Alumina was then extracted with chloroform to yield 0.6 g (47%) of iodine.

Reaction of 2 mol of Thiophenol with 1 mol of Phenyl Iodosoacetate. When a solution of 2.2 g (0.02 mol) of thiophenol in 5 m*l* of dichloromethane was added to a suspension of 3.2 g (0.01 mol) of phenyl iodosoacetate in 20 m*l* of dichloromethane with stirring at room temperature, an exothermic reaction started at once and the resulting yellow solution was stirred for 10 min at 40°C. After removal of the solvent, 0.6 g (50%) of acetic acid, bp 34—35°C/22 mmHg, and 1.7 g (83%) of iodobenzene, bp 72—74°C/22 mmHg, were obtained by distillation. The residue was extracted with ether to give 2.0 g (92%) of diphenyl disulfide, mp 60—61°C.

Reaction of Lead Thiophenolate with Tetraethylthiuram Disulfide. When 1.48 g of tetra ethylthiuram disulfide was added to a suspension of 2.13 g of lead thiophenolate in 20 m*l* of chloroform with stirring at room temperature, the reaction started soon and the reaction mixture turned a clear yellow solution. After stirred for an additional 10 min, the solvent was removed. The precipitate was washed with ether to remove diphenyl disulfide. The undissolved crystals gave 2.45 g (98%) of lead diethyldithiocarbamate, mp 204—205°C.

From the ether solution, 1.05 g (97%) of diphenyl disulfide, mp 59—60°C, was obtained.

When equimolar amounts of diphenyl disulfide and lead diethyldithiocarbamate were treated in boiling chloroform for 2 hr, the starting materials were recovered quantitatively.

Reaction of Lead Thiophenolate with Dibenzoyl Disulfide. A suspension of 1.07 g of lead thiophenolate and 0.69 g of dibenzoyl disulfide was refluxed for 30 min. Then the liberated lead thiobenzoate, 0.85 g (70%), mp 165—166°C, was filtered off and the filtrate was concentrated and pale yellow crystals were obtained. They were washed with a small volume of ethanol yielding diphenyl disulfide, 0.50 g (91%), mp 59—60°C.

Similarly, lead thiolates were treated with disulfides in boiling chloroform to give the corresponding lead thiolates and disulfides almost quantitatively.