A Preparation of Lead Thiocyanate

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SINCE Kaufmann's (7) development of the thiocyanogen method for determining the degree of unsaturation of fatty acids and glycerides, the technique has found wide use in the analysis of fats and oils. The accuracy of the original method has been improved by the establishment of empirical values for the addition of thiocyanogen to the various unsaturated acids and esters (10). Despite repeated demonstration that the modified method can be made to yield accurate results in the analysis of pure fatty acid esters, close agreement has been lacking between various laboratories in collaborative studies (11) of the method as applied to commercial fats. Because of this, an extensive investigation (9) of methods for determining thiocyanogen values was undertaken, in the course of which it became necessary to examine the various procedures described and recommended for the preparation of lead thiocyanate.

A survey of the literature (1, 2, 3, 6, 7, 8) revealed that lead thiocyanate, $Pb(SCN)_2$, has been prepared by the double decomposition of a number of different lead and thiocyanate salts. However, preparation of this salt by what is probably the most efficient combination of reagents, namely, lead nitrate and ammonium thiocyanate, has been entirely neglected. Preliminary work indicated that the reaction of lead nitrate and ammonium thiocyanate produces a pure and relatively stable lead thiocyanate in practically theoretical yield.

In the course of the investigation reported here a number of commercial products, laboratory preparations, and the lead thiocyanate prepared according to the above proposed method were compared with respect to purity, stability, and capacity to saturate double bonds. The comparative data to be presented show that the source of lead thiocyanate or its method of preparation is of utmost importance in the production of a dependable thiocyanogen reagent.

The Preparation of a Pure Lead Thiocyanate

Method. The preparation of lead thiocyanate was readily carried out by adding 500 ml. of 1 M lead nitrate to 136 ml. of 10 M ammonium thiocyanate. Solutions of both reactants (ACS Reagent Grade) were filtered and cooled to 5°C. before mixing. The reaction is exothermic, producing a rise of 5° C. in the temperature of the reaction mixture. The solution of lead nitrate was added in 50-ml. portions with moderate stirring which was continued for 30 minutes after addition of the last aliquot of the precipitant. A copious, heavy, white precipitate settled out. In order to free it of nitrates it was washed by decantation with distilled water cooled to 5° C.

The lead thiocyanate precipitate was transferred to a Buchner funnel and a rubber dam employed to dry it as much as possible on the funnel, after which the product was placed in a vacuum desiccator containing P_2O to remove the last traces of moisture. Six to eight days in the desiccator with the required changes of P_2O_5 produced a sufficiently dry product for use in making the thiocyanogen reagent. The product must be protected from sunlight and glare not only during its preparation but during storage as well. When these precautions are observed, the reagent is sufficiently stable to be stored over P_2O_5 for at least 18 months.

From the above-mentioned quantities of reagents 156.8 grams of a pure white lead thiocyanate were obtained. This corresponds to a yield of 97%, based on the weight of lead nitrate. When larger quantities of $Pb(SCN)_2$ were prepared, the product was conveniently filtered and washed in a stainless steel centrifuge basket lined with a well-fitted strip of No. 6 cotton duck filter-press cloth.

The pH of the Reaction. The pH of the reaction mixture was found to be practically constant at all stages of the reaction, varying between 4.17 near the beginning and 4.13 at the end. It may be assumed, therefore, that the preparation is unaffected by side reactions. It is well known that if solutions of reagents with low pH values are used, surface absorption of CO_2 is obviated. For that reason, use of ammonium thiocyanate is preferable to either sodium or potassium thiocyanates. For example, in the case of the lead thiocyanate prepared according to the A.O.A.C. method (2), the initial pH of the potassium thiocyanate solution was 7.68 while the pH of the reaction mixture on completion of the precipitation was 4.46. As previously indicated, if ammonium thiocyanate is employed, the entire reaction takes place at a pH lower than that obtained at the end of the A.O.A.C. preparation.

Recrystallization of Lead Thiocyanate. As shown in Table 1, the analyses indicate that Preparation CX_3 is of the highest purity among the products investigated. However, it can be purified even further by recrystallization from water. As reported by Hall (5), 3.3 parts of lead thiocyanate dissolve in 100 parts of boiling water. Accordingly, 100 grams of lead thiocyanate were boiled in 3,000 ml. of distilled water. The solution was filtered while hot and allowed to cool to room temperature slowly. The crystals were collected by filtering and washing with cold distilled water, after which the product was dried at room temperature and atmospheric pressure. A material reduction in the volume of the combined filtrate and washings produced another batch of crystals on cooling. A total of 92 grams of the pure crystalline product were obtained by this treatment.

Composition and Characteristics of the Various Preparations

Physical Properties. Lead thiocyanate is a white crystalline salt composed of large irregular rhombohedral prisms resembling arrow heads and spear points, which exhibit comparatively low birefringence and extinguish parallel to the direction of elongation of the crystals. The index of refraction of the lead thiocyanate crystals is higher than that of methylene

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FIG. 1. Effect of ultraviolet irradiation.

Lower half shows respective changes after three hours' exposure to ultraviolet light on: 1, K & S_1; 2, K & S_2; 3, CX_3; 4, K_2; 5, K_1; 6, B; 7, D; 8, A.O.A.C.; and 9, A.O.C.S. (Originals in upper half).

iodide. As stated above, 3.3 grams of this salt are soluble in 100 ml. of boiling water.

Chemical Composition. The chemical composition of the various preparations of lead thiocyanate was determined by precipitating lead as the chromate (14) and titrating the thiocyanate ions with silver nitrate solution according to the method described by Volhard (12). The A.S.T.M. gravimetric factor for the conversion of lead chromate to lead was employed after the method had been applied to several samples of pure lead nitrate and found to give the theoretical value for lead (4).

The sulfur determinations were made by oxidizing the sulfur to $SO_4^=$ with bromine, removing the lead ions as lead carbonate, and precipitating the $SO_4^=$ ions as barium sulfate (13). The analytical data and the composition of the samples of lead thiocyanate, calculated on the basis of the percentage of lead found, are given in Table 1. The calculated compositions and capacities of the reagents to saturate double bonds indicate that only four products are impure, *i.e.,* comprise mixtures of normal and basic lead thiocyanates or contain excessive quantities of mineral impurities.

The equation:

$$PB(R^-)_2 + 2M^+SCN \longrightarrow Pb(SCN)_2 + 2M^+R^-$$

representing the double decomposition involved in the preparation of lead thiocyanate, indicates that one gram-molecular weight of the lead salt should be reacted with two gram-molecular weights of thiocyanate. This is erroneous; better yields and purer products are obtained with an excess of thiocyanate, as may be observed from the experimental data in columns 6 and 7 of Table 1. Reference to this table shows the relatively poor yields that are obtained if the products are prepared according to the method of Kaufmann or the A.O.C.S. However, a more important consideration is that these preparations are unstable and cannot be kept for long periods of time. In both of the above-mentioned methods, lead acetate is used as the source of Pb ions. The anomalous behavior of lead acetate in aqueous solutions casts serious doubt on the purity of any product prepared with this reagent.

Karaoglanov and Sagortschev (6) investigated the mechanism of the precipitation of lead thiocyanate and discovered various factors influencing the purity of the product. They found that combining an aqueous solution of a lead salt with that of a thiocyanate salt produced either normal lead thiocyanate, $Pb(SCN)_2$, or basic lead thiocyanate, $Pb(OH)SCN$, or a mixture of the two, depending upon the conditions of the precipitation. They were unable to obtain a normal lead thiocyanate from $Pb(CH_3COO)_2$ and KSCN except in the presence of excess hydrogen ions. The hydrogen ions were furnished by the addition of acetic acid. They experienced no difficulty, however, in obtaining the normal salt when lead nitrate was substituted for lead acetate. However, in the presence of either small or large quantities of ammonium acetate, varying percentages of the basic salt were precipitated in conjunction with the normal salt even when lead nitrate was used as the source of lead ions. In addition, they reported that normal lead thiocyanate could be converted in aqueous solution to the basic salt in the presence of either ammonium, sodium, or potassium acetate and that the conversion was favored by increasing the temperature.

The conclusions of Karaoglanov and Sagortschev were partly substantiated by repeating one of their experiments (Preparation 4, Table 1). The analysis of the compound obtained by their method showed it to be basic lead thiocyanate. Another preparation by this method, but modified to increase the concentration of hydrogen ions, produced a pure lead thiocyanate (Preparation 3, Table 1). The suspicion that the Kaufmann and A.O.C.S. products are not pure is substantiated by the compositions of these preparations calculated on the basis of their lead content as shown in Column 11 of Table 1.

Products 8, 9, 10, and 11 furnish examples of the results obtained with various combinations of lead nitrate and ammonium thiocyanate which produce a nearly theoretical yield of lead thiocyanate when the ratio of Pb^{++}/SCN^- is maintained at 1/2.72, and the order of addition is Pb ions added to SCN ions. Equally good yields are obtained when lead nitrate is added to sodium and potassium thiocyanates, respectively, providing the same ratio of Pb^{++}/SCN^- and order of addition are observed.

Effect of Ultra-Violet Irradiation. It is well known that lead thiocyanate is sensitive to ultra-violet light, consequently each preparation was subjected to irradiation of this type and the effect noted. The products were arranged on a white porcelain spot-test plate and exposed for three hours to radiation from an ultra-violet lamp (Hanovia Utility Model Quartz Lamp) placed at a distance of 18 inches from the samples. The effect of exposure to ultra-violet light is shown in Figure 1.

It is evident from even a casual inspection of Figure 1 that the individual preparations of lead thiocyanate are affected in varying degrees by ultra-violet irradiation. Some preparations are very markedly affected, others moderately so, and still others hardly at all. The amount and intensity of the discoloration brought about by ultra-violet irradiation is a qualitative indication of the amount of impurities present and the general instability of any given sample of lead thiocyanate. It is apparent that preparations 3 and 6, which are, respectively, the CX_3 (laboratory preparation) and B (commercial product), are only slightly affected visually by irradiation and that preparations 4, 5, and 9, namely K_2, K_1, and A.O.C.S., are markedly affected. A considerable increase in color is shown by product 2, or K & S_2, which is the pure basic lead thiocyanate, $Pb(OH)SCN$. Preparations 5 and 9 exhibit more color change than the remaining products, and it is concluded that this change is due to a combination of the effect of other metallic impurities and the presence of the basic compound.

It was subsequently observed that if the lead thiocyanate preparations were recrystallized from water, they did not exhibit any visible instability to ultra-violet light under the conditions mentioned above. This is further evidence that most of the effect of ultra-violet irradiation is associated with the impurities present in the products.

Microscopic Examination. All of the products were examined microscopically and photomicrographs were made and compared. Two of these photomicrographs are reproduced in Figures 2 and 3. Figure 2 represents crystals of the pure basic compound, Pb(OH)-

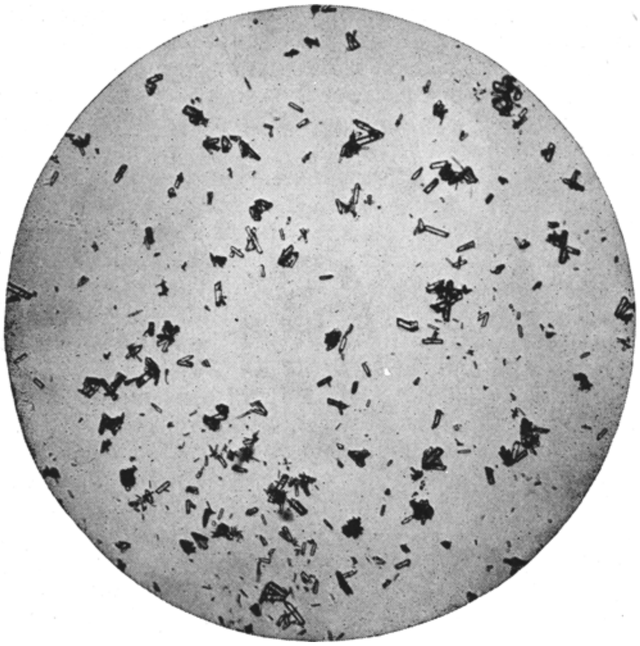

FIG. 2. Pure Pb(OH)SCN, (K&S$_2$). 91×.

SCN. They are small rectangular prisms that show a high birefringence and, predominantly, parallel extinction. The twinning habit characteristic of these crystals is clearly exhibited. Figure 3, which is representative of the A.O.C.S. product, furnishes conclusive visual evidence of the presence of the basic compound. Even the twinning habit observed in Figure 2 is clearly in evidence in the photomicrograph. The larger crystals are the irregular rhombohedral prisms resembling arrow heads and spear points characteristic of the lead thiocyanate itself.

The Effect of Recrystallization on Purity. Since the solubility of lead thiocyanate in water provides a means for its purification, some of the products listed in Table 1 were recrystallized from this medium, and the insoluble impurities, recrystallized product, and soluble residue were spectroscopically examined for traces of other elements. Table 2 shows the results obtained for four commercial products and two laboratory preparations. The solubility of lead thiocyanate in water is important because it provides a means of removing the impurities which substantially contribute to the darkening of the product on exposure to sunlight and impart hygroscopic properties to the compound. Following recrystallization from water, the products can be dried at atmospheric pressure and room temperature. This procedure eliminates drying over P_2O_5 in a vacuum desiccator. Moreover, the crystals do not contain any water of crystallization.

It is recommended, therefore, that lead thiocyanate be recrystallized from hot water if the salt is to be used in the preparation of the thiocyanogen reagent unless the investigator is thoroughly acquainted with the source and purity of the reagent.

Behavior of the Different Reagents in the Determination of Thiocyanogen Values

Each of the preparations of lead thiocyanate was used to prepare a thiocyanogen reagent which was applied to the determination of the thiocyanogen values of soybean, peanut, and cottonseed oils. The

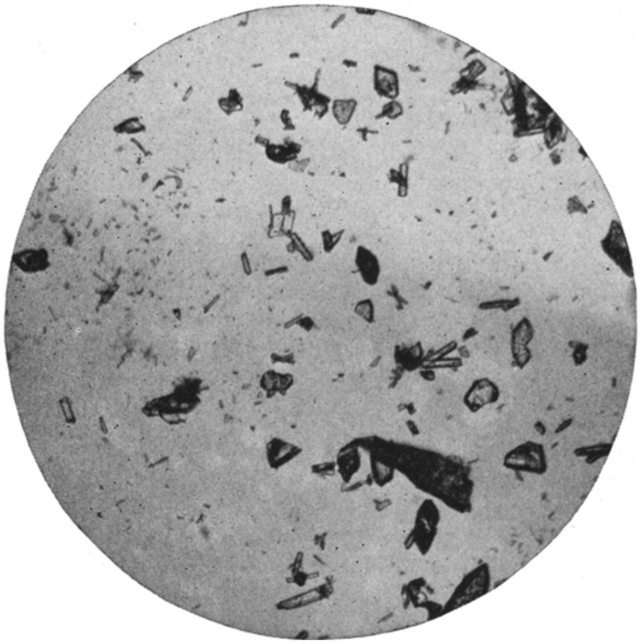

FIG. 3. Product prepared according to the A.O.C.S. directions. 91×.

TABLE 2

Spectroscopic Analyses of Several Products

Product	Fraction	Elements Present												
		B	Si	Ca	Mg	Na	Zn	Cu	Fe	Ba	Al	Mn	Ag	Mo
CX_3	Original	m	m	t	t	t	t	t	t					
	Once recryst.			t	t	t	t	t						
	Twice recryst.				t	t		t						
	Insol. residue	m	m	t	t	t	t	t	t					
	Soluble residue	m	m	m	m	M	t	m	m	m	m	t		
B	Original	m	m	t	t	t	t	t	t	t				
	Once recryst.			t	t	t	t	t						
	Twice recryst.				t	t		t						
	Insol. residue	m	m	t	t	t	t	t	t	t				
	Soluble residue	m	m	m	m	m	t	m	m	M	t			
D	Original	m	m	t	t	t	t	t	t					
	Once recryst.			t	t	t	t	t						
	Twice recryst.				t	t		t						
	Insol. residue	m	m	t	t	t	t	m	m					
	Soluble residue	m	m	m	m	M	t	m	M	m	t	t		
K_1	Original			t	t	t	t	t						
M_1	Original				t	t	t	t	t				t	
M_2	Original				t	t	t	t	t				t	t

Spectroscopic trace = t.
Minor constituent = m.
Major constituent = M.

TABLE 1

Survey of Products Showing Origin, Analyses, Purity, and Activity as a Reagent

Product		Origin of product and reference	Reactants		Ratio of Pb/SCN	Yield[7]	Analyses			Purity calculated on basis of lead content		Activity of reagents based on T. C. determinations with various oils[4]			
No.	Symbol		A[8]	B			Pb[1]	SCN[2]	S[3]	$Pb(SCN)_2$	Pb(OH) SCN	Soybean	Peanut	Cottonseed	Deviation from average
						per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*				
1	K_1	Prepared according to Kaufmann (1935), (7)	1800 ml. of 1.11M $Pb(C_2H_3O_2)_2$	300 ml. of 13.32M NH_4SCN	1:2.0	66.0	64.07	35.73		pure					
2	K_2	Prepared according to Kaufmann (1938), (8)	500 ml. of 4M NH_4SCN	1000 ml. of 1M $Pb(C_2H_3O_2)_2$	1:2.0	64.2	64.53	35.42	19.56	95.2	4.8	83.8[6]	69.9[6]	65.7[6]	—0.9 —0.9 —0.7
3	K & S_1	Prepared according to Karaoglanov and Sagortschev (6)	2200 ml. of 0.26M $Pb(C_2H_3O_2)_2$	600 ml. of 1M KSCN[10]	1:1.05	26.3	64.09	35.12		pure		85.0	71.0	66.5	
4	K & S_2	Prepared according to Karaoglanov and Sagortschev	1100 ml. of 0.26M $Pb(C_2H_3O_2)_2$	300 ml. of 1M KSCN	1:1.05	31.7	73.38	20.58	11.60		99.8				
5	$AOAC_1$	Assoc. Official Agr. Chem. (2)	700 ml. of 1.42M $Pb(NO_3)_2$	500 ml. of 4M KSCN	1:2.0	86.7	64.16	35.66	19.73	99.1		84.4	70.9	66.3	
6	AOCS	Amer. Oil Chemists' Soc. (1)	500 ml. of 1.31M $Pb(C_2H_3O_2)_2$	500 ml. of 5.15M KSCN	1:3.9	72.6	65.17	32.93	15.18	88.3	11.7	81.2[6]	67.8[6]	63.3[6]	—3.5 —3.0 —3.1
7	BOO_1	Prepared according to Booth (3)	100 ml. of 3M NaSCN	100 ml. of 1.36M $Pb(NO_3)_2$	1:2.26										
8	CX_1	From Pb $(NO_3)_2$ and NH_4SCN	100 ml. of 10M NH_4SCN	500 ml. of 1M $Pb(NO_3)_2$	1:2.0	91.2									
9	CX_2	From Pb $(NO_3)_2$ and NH_4SCN	140 ml. of 10M NH_4SCN	500 ml. of 1M $Pb(NO_3)_2$	1:2.8	72.0									
10	CX_2	From Pb $(NO_3)_2$ and NH_4SCN	500 ml. of 1M $Pb(NO_3)_2$	100 ml. of 10M NH_4SCN	1:2	85.0									
11	CX_3	From Pb $(NO_3)_2$ and NH_4SCN	500 ml. of 1M $Pb(NO_3)_2$	136 ml. of 10M NH_4SCN	1:2.72	97.0	64.07	35.90	19.84	pure		85.0	71.1	66.5	
12	$AOAC_2$	Proportion of SCN increased	500 ml. of 1M $Pb(NO_3)_2$	100 ml. of 13.6M KSCN	1:2.72	97.0									
13	BOO_2	Proportion of SCN increased	300 ml. of 2.72M $Pb(NO_3)_2$	50 ml. of 7.4M NaSCN	1:2.72	97.6									
14	B	J. T. Baker Chemical Co.					64.05	35.79	19.78	pure		84.9	71.0	66.5	
15	D	E. I. duPont de Nemours & Co.					64.05	35.54	19.48			80.8[6]	68.1[6]	63.0[6]	—3.9 —2.7 —3.4
16	M_1	Merck & Co. Lot No. 31609[9]					64.52		19.51	95.2	4.8	81.0[6]	67.6[6]	63.6[6]	—3.7 —3.2 —2.8
17	M_2	Merck & Co.					64.07					84.8	70.7	66.4	
		Average values........										84.7±0.4	70.8±0.3	66.4±0.1[5]	

[1] Theoretical values for Pb in Pb $(SCN)_2$ and Pb(OH)SCN are 64.08% and 73.40%, respectively.
[2] Theoretical values for SCN in $Pb(SCN)_2$ and Pb(OH)SCN are 35.92% and 20.5%, respectively.
[3] Theoretical values for S in $Pb(SCN)_2$ and Pb(OH)SCN are 19.83% and 11.36%, respectively.
[4] Reagents prepared according to method outlined in reference (9).
[5] Includes values obtained with reagents made from twice recrystallized CX_3, B and D.
[6] Not included in average values.
[7] Based on weight of lead salt used.
[8] Reactant A was added to reactant B.
[9] It is believed that this product is considerably older than M_2
[10] Containing large concentration of H^+.