Determination of Oxygen in Zinc Compounds[1)]

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Oxygen in zinc compounds was determined by a modification of the method of Schütze. Oxygen in some zinc compounds such as zinc oxide, zinc acetate and zinc oxalate could not be determined by the usual method. The carrier gas method of adding carbon was employed for the determination of total oxygen. Total oxygen could be determined by the addition of 5 mg of carbon to a sample boat and heating at 1000 °C. The determination was also carried out by the carrier gas method by addition of 2 mg naphthalene. As a result, total oxygen could be determined by the addition of 2 mg of naphthalene.

Determination of oxygen in zinc compounds was first reported by Schütze in 1939.[2)] Carbon was placed in a sample boat in an atmosphere of nitrogen, the boat was heated at 1000 °C, and determination of oxygen in zinc oxide was carried out. Oxygen determination in zinc oxide by the method of inert gas fusion was reported by Engelsman *et al.*,[3)] who employed a platinum bath, heating being carried out at 2000 °C. Merz[4)] reported that oxygen in zinc oxide could be determined by the addition of ammonium chloride or an indulin base.

In spite of the publication of several reports, little is known about the determination of oxygen in zinc compounds other than zinc oxide.

We have studied oxygen determination in compounds containing metals such as silver, arsenic, mercury, tin and copper. The present paper deals with the determination of oxygen in zinc compounds.

Experimental

Samples. The following samples were employed for the experiments: zinc oxide, ZnO; zinc acetate, $Zn(CH_3COO)_2 \cdot 2H_2O$; ammonium zinc sulfate, $(NH_4)_2Zn(SO_4)_2$; zinc anthranilate, $Zn(C_7H_6NO_2)_2$; zinc benzoate, $Zn(C_7H_5O_2)_2$; zinc 4-cyclohexylbutyrate, $Zn(C_{10}H_{17}O_2)_2$; zinc formate, $Zn(CHO_2) \cdot 2H_2O$; zinc lactate, $Zn(C_3H_5O_3)_2 \cdot 3H_2O$; zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$; zinc oxalate, $ZnC_2O_4 \cdot 2H_2O$; zinc perchlorate, $Zn(ClO_4)_2 \cdot 6H_2O$; zinc *p*-phenolsulfonate, $Zn(C_6H_5O_4S)_2 \cdot 8H_2O$; zinc stearate, $Zn(C_{18}H_{35}O_2)_2$; zinc salicylate, $Zn(C_7H_5O_3)_2$; zinc sulfate, $ZnSO_4 \cdot 7H_2O$; zinc tartrate, $ZnC_4H_4O_6$; bis[bis(2-hydroxyethyl)dithiocarbamato]zinc, $Zn(C_5H_{10}NO_2S_2)_2$; bis(2,4-pentanedionato)zinc, $Zn(C_5H_7O_2)_2$; bis(2-quinolinecarboxylato)zinc, $Zn(C_{10}H_6NO_2)_2 \cdot H_2O$; bis(8-quinolinolato)zinc, $Zn(C_9H_6NO)_2$; *p*-[N-ethyl(2-hydroxyethyl)amino]benzenediazonium tetrachlorozincate, $C_{20}H_{28}Cl_4N_6O_2Zn$. The results of the determination of carbon and hydrogen are given in Table 1. They are in fair agreement with the corresponding calculated values.

TABLE 1. ANALYTICAL RESULTS OF CARBON AND HYDROGEN IN ZINC COMPOUNDS

Sample	Carbon(%)		Hydrogen(%)	
	Found	Calcd	Found	Calcd
Zinc oxide ZnO	0.05	0.00	0.02	0.00
Zinc acetate $Zn(CH_3COO)_2 \cdot 2H_2O$	21.94	21.89	4.60	4.59
Ammonium zinc sulfate $(NH_4)_2Zn(SO_4)_2$	0.12	0.00	2.89	2.75
Zinc anthranilate $Zn(C_7H_6NO_2)_2$	49.80	49.80	3.48	3.58
Zinc benzoate $Zn(C_7H_5O_2)_2$	54.62	54.66	3.28	3.28
Zinc 4-cyclohexylbutyrate $Zn(C_{10}H_{17}O_2)_2$	59.40	59.48	8.34	8.49
Zinc formate $Zn(CH_2)_2 \cdot 2H_2O$	12.72	12.55	3.28	3.16
Zinc lactate $Zn(C_3H_5O_3)_2 \cdot 3H_2O$	24.32	24.22	5.38	5.42
Zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$	0.18	0.00	4.13	4.07
Zinc oxalate $ZnC_2O_4 \cdot 2H_2O$	12.56	12.68	2.24	2.13
Zinc perchlorate $Zn(ClO_4)_2 \cdot 6H_2O$	0.15	0.00	3.42	3.25
Zinc *p*-phenolsulfonate $Zn(C_6H_5O_4S)_2 \cdot 8H_2O$	26.06	25.93	4.70	4.72
Zinc stearate $Zn(C_{18}H_{35}O_2)_2$	68.39	68.38	11.12	11.16
Zinc salicylate $Zn(C_7H_5O_3)_2$	49.56	49.59	3.09	2.97
Zinc sulfate $ZnSO_4 \cdot 7H_2O$	0.03	0.00	4.94	4.90
Zinc tartrate $ZnC_4H_4O_6$	22.34	22.51	2.00	1.89
Bis[bis(2-hydroxyethyl)dithiocarbamato]zinc $Zn(C_5H_{10}NO_2S_2)_2$	28.03	28.20	4.81	4.73
Bis(2,4-pentanedionato)zinc $Zn(C_5H_7O_2)_2$	45.69	45.56	5.38	5.35
Bis(2-quinolinecarboxylato)zinc $Zn(C_{10}H_6NO_2)_2 \cdot H_2O$	56.01	56.16	3.45	3.30
Bis(8-quinolinolato)zinc $Zn(C_9H_6NO)_2$	61.17	61.13	3.54	3.42
p-[*N*-Ethyl(2-hydroxyethyl)amino]benzenediazonium tetrachlorozincate $C_{20}H_{28}Cl_4N_6O_2Zn$	40.73	40.60	4.51	4.77

Reagents and Apparatus. The reagents and apparatus used were the same as those previously reported.[5)]

Procedure. *(1) Usual Method of Oxygen Determination in Organic Compounds*: Nitrogen was passed throughout the apparatus as a carrier gas at a rate of 10—15 ml/min. Nitrogen was purified by passing through a silica gel drying tube, a deoxidation tube filled with porous copper heated at 550 °C and two tubes one containing sodium hydroxide and the other magnesium perchlorate. The temperatures of the combustion furnace, desulfurization furnace and heating furnace were maintained at 900, 550, and 150 °C, respectively. A boat containing a weighed sample was put into a pyrolysis tube through a sample inlet, nitrogen being flushed at the sample inlet lest air should come into the pyrolysis tube. The boat was moved up to a sample heated by means of an iron ball and a magnet, and the sample was pyrolized over a period of 15 min. Oxygen contained in the sample was completely converted into carbon monoxide by means of platinum-carbon heated at 900 °C. The carbon monoxide was oxidized to carbon dioxide by iodine petaoxide, and the resulting carbon dioxide was allowed to be absorbed into an absorption tube packed with sodium hydroxide. Thirty minutes after the beginning of pyrolysis, the absorption tube of carbon dioxide was disconnected from the apparatus and weighed. The content of oxygen in the sample was calculated as follows:

$$\text{The content of oxygen (\%)} = \frac{0.3636\times(a-b)}{s}\times 100$$

where s=sample weight (mg); a=increase in weight of the absorption tube of carbon dioxide (mg); and b=blank value (mg). The determination took *ca.* 40 min.

(2) Determination by Means of a Solid Reaction Agent: This method was approximately the same as that described in (1) except that carbon powder was sprinkled on the sample boat prior to and after placement of the sample.

(3) Determination by Addition of a Reaction Agent: Purification of the carrier gas and the procedure after oxygen in a sample had been converted into carbon monoxide were the same as those described in (1), except for insertion of the sample boat and pyrolysis of the sample which were carried out as follows. A weighed sample was placed in the sample boat which was then put in the sample inlet after the apparatus was ventilated reversely. An iron ball and then a boat with a weighed reaction agent (2 mg of naphthalene) were inserted into the apparatus, and the apparatus was ventilated reversely for 3—5 min. The direction of the ventilation was then changed and the sample boat was moved up to a sample heater by means of the iron ball and a magnet. During the course of pyrolysis, the iron ball was brought back to the boat with the reaction agent and the boat was moved up to a place about 2—3 cm from the sample heater. The reaction agent was gasified by the heat from the sample heater and the gas was allowed to flow along with the carrier gas toward the sample heater. The sample or oxidation products remaining in the sample boat were allowed to react directly with the gas or the pyrolysis products of the reaction agent. The oxygen compounds resulting from the reaction of the pyrolysis gas produced by the heating of the sample or of the oxygen remaining in the sample boat with the reaction agent were allowed to react with platinum carbon heated at 900 °C in order to convent the oxygen in the sample into carbon monoxide.

Results and Discussion

Determination of Oxygen in Zinc Compounds by the Usual Method. Oxygen in zinc compounds was determined according to the method for determination of oxygen in organic compounds. The results are shown in Table 2. Heating was carried out at 900 °C. The values for oxygen in zinc oxide, zinc acetate, zinc ammonium sulfate, zinc formate, zinc nitrate, zinc oxalate, zinc perchlorate and zinc sulfate was 3—18% lower than the corresponding calculated values. Oxygen in the other 13 compounds, however, could be determined more accurately. Since zinc oxide has a high

Table 2. Analytical results of oxygen in zinc compounds

Sample	Sample taken (mg)	CO_2 (mg)	O-found (%)	O-calcd (%)	Δ%
Zinc oxide ZnO	3.913	0.136	1.26	19.66	−18.40
	3.895	0.119	1.11		−18.55
	4.720	0.186	1.43		−18.23
Zinc acetate $Zn(CH_3COO)_2\cdot 2H_2O$	3.857	4.286	40.40	43.74	−3.34
	3.441	3.851	40.69		−3.05
	3.918	4.303	39.93		−3.81
Ammonium zincsulfate $(NH_4)_2Zn(SO_4)_2$	4.111	4.469	39.53	43.60	−4.07
	4.053	4.422	39.67		−3.93
	3.538	3.877	39.84		−3.76
Zinc anthranilate $Zn(C_7H_6NO_2)_2$	4.212	2.185	18.86	18.96	−0.10
	4.425	2.314	19.01		+0.05
	3.633	1.892	18.94		−0.02
Zinc benzoate $Zn(C_7H_5O_2)_2$	3.501	1.979	20.55	20.81	−0.26
	3.129	1.784	20.73		−0.08
	3.676	2.093	20.70		−0.11
Zinc 4-cyclohexylbutyrate $Zn(C_{10}H_{17}O_2)_2$	3.958	1.728	15.87	15.85	+0.02
	3.846	1.679	15.87		+0.02
	4.128	1.801	15.86		+0.01
Zinc formate $Zn(CHO_2)_2\cdot 2H_2O$	3.417	4.109	43.72	50.15	−6.43
	3.587	4.284	43.43		−6.72
	4.170	4.945	43.12		−7.03
Zinc lactate $Zn(C_3H_5O_3)_2\cdot 3H_2O$	3.907	5.189	48.29	48.39	−0.10
	3.299	4.374	48.21		−0.18
	3.961	5.282	48.49		+0.10
Zinc nitrate $Zn(NO_3)_2\cdot 6H_2O$	4.661	7.628	59.51	64.54	−5.03
	3.279	5.374	59.59		−4.95
	4.668	7.622	59.37		−5.17
Zinc oxalate $ZnC_2O_4\cdot 2H_2O$	4.431	5.275	43.29	50.68	−7.39
	4.592	5.415	42.88		−7.80
	3.898	4.608	42.98		−7.70
Zinc perchlorate $Zn(ClO_4)_2\cdot 6H_2O$	3.905	6.107	56.86	60.15	−3.29
	3.527	5.488	56.58		−3.57
	3.367	5.219	56.36		−3.79
Zinc *p*-phenolsulfonate $Zn(C_6H_5O_4S_2)_2\cdot 8H_2O$	4.490	5.701	46.17	46.06	+0.11
	3.259	4.135	46.13		+0.07
	3.828	4.872	46.28		+0.22
Zinc stearate $Zn(C_{18}H_{35}O_2)_2$	4.419	1.262	10.38	10.12	+0.26
	3.142	0.876	10.14		+0.02
	3.327	0.950	10.38		+0.26
Zinc salicylate $Zn(C_7H_5O_3)_2$	4.202	3.286	28.43	28.27	+0.16
	3.776	2.944	28.35		+0.08
	3.563	2.763	28.20		−0.07
Zinc sulfate $ZnSO_4\cdot 7H_2O$	3.222	4.863	54.88	61.21	−6.33
	3.361	5.064	54.78		−6.43
	3.318	5.063	55.48		−5.73
Zinc tartrate $ZnC_4H_4O_6$	4.140	5.092	44.72	44.98	−0.26
	3.282	4.024	44.58		−0.40
	3.295	4.049	44.68		−0.30
Bis[bis(2-hydroxyethyl)dithiocarbamato]zinc $Zn(C_5H_{10}NO_2S_2)_2$	4.128	1.729	15.23	15.03	+0.20
	3.988	1.680	15.32		+0.29
	3.332	1.397	15.24		+0.21
Bis(2,4-pentanedionato)zinc $Zn(C_5H_7O_2)_2$	3.723	2.459	24.02	24.28	−0.26
	4.101	2.763	24.50		+0.22
	3.912	2.640	24.54		+0.26

Table 2. (Continued)

Sample	Sample taken (mg)	CO_2 (mg)	O-found (%)	O-calcd (%)	Δ%
Bis(2-quinolinecarboxylato)zinc $Zn(C_{10}H_6NO_2)_2\cdot H_2O$	4.437	2.272	18.62	18.70	−0.08
	4.223	2.144	18.46		−0.24
	3.512	1.812	18.76		+0.06
Bis(8-quinolinolato)zinc $Zn(C_9H_6NO)_2$	3.402	0.864	9.23	9.05	+0.18
	3.422	0.881	9.36		+0.31
	3.610	0.906	9.13		+0.08
p-[*N*-Ethyl(2-hydroxyethyl)amino]benzenediazonium tetrachlorozincate $C_{20}H_{28}Cl_4N_6O_2Zn$	3.521	0.535	5.52	5.41	+0.11
	3.631	0.554	5.55		+0.14
	4.103	0.634	5.62		+0.21

TABLE 3. INFLUENCE OF TEMPERATURE ON THE DETERMINATION OF OXYGEN IN ZINC OXIDE BY ADDITION OF SOLID REACTION AGENT (About 5 mg of Carbon)

Sample	Temperature of sample heater (°C)	Sample taken (mg)	CO_2 (mg)	O-found (%)	O-calcd (%)	Δ%
Zinc oxide	850	3.802	0.099	0.95	19.66	−18.71
	900	3.148	0.696	8.04		−11.62
	950	3.105	1.484	17.38		−2.28
	1000	3.042	1.661	19.85		+0.19
	1050	3.639	1.975	19.73		+0.07

TABLE 4. ANALYTICAL RESULTS OF OXYGEN IN ZINC COMPOUNDS BY ADDITION OF SOLID REACTION AGENT (About 5 mg of Carbon)

Heating temperature of sample: 1000 °C

Sample	Sample taken (mg)	CO_2 (mg)	O-found (%)	O-calcd (%)	Δ%
Zinc oxide	3.042	1.661	19.85	19.66	+0.19
	3.509	1.911	19.80		+0.14
	3.256	1.787	19.96		+0.30
Zinc acetate	3.315	3.974	43.59	43.74	−0.15
	3.173	3.828	43.87		+0.13
	3.443	4.116	43.47		−0.30
Ammonium zinc sulfate	4.590	5.527	43.78	43.60	+0.18
	4.383	5.262	43.65		+0.05
	4.295	5.147	43.57		−0.03
Zinc formate	3.884	5.337	49.96	50.15	−0.19
	3.281	4.534	50.25		+0.10
	3.643	5.038	50.28		+0.13
Zinc nitrate	3.882	6.879	64.43	64.54	−0.11
	3.590	6.402	64.84		+0.30
	4.418	7.838	64.51		−0.03
Zinc oxalate	3.799	5.300	50.73	50.68	+0.05
	3.466	4.843	50.81		+0.13
	4.185	5.817	50.54		−0.14
Zinc perchlorate	3.324	5.516	60.34	60.15	+0.19
	4.323	7.180	60.39		+0.24
	4.210	7.005	60.50		+0.35
Zinc sulfate	3.161	5.315	61.14	61.21	−0.07
	3.895	6.563	61.27		+0.06
	4.056	6.810	61.05		−0.16

melting point, we supposed that oxygen in zinc oxide could not be determined at all by the method for determination of oxygen in organic compounds. However, we have found that heating of zinc oxide at 900 °C in an atmosphere of nitrogen is likely to lead to the dissociation of zinc oxide, and we were able to determine about 1% of oxygen in this compound although the calculated content of oxygen was 19.66%. The residue left in the sample boat after determination of oxygen in zinc acetate was white and seemed to be zinc oxide. We see from the analytical results that 5.5 oxygen atoms out of 6 in zinc acetate could be determined. The residue in the sample boat after determination of oxygen in zinc ammonium sulfate, zinc formate, zinc nitrate, zinc oxalate, zinc perchlorate or zinc sulfate was white and seemed to be zinc oxide. The analytical results show that the value found was approximately the same as the calculated value obtained by subtracting one oxygen atom left as zinc oxide from all the oxygen atoms in each sample.

Determination of Total Oxygen in Zinc Compounds by the Carrier Gas Method with a Solid Reaction Agent. Total oxygen in some of the zinc compounds can not be determined by the usual method. We therefore used the carrier gas method with carbon as a solid reaction agent. In order to examine the influence of temperature on oxygen determination, 5 mg of carbon was placed in a sample boat and the temperature was measured according to the carrier gas method with a solid reaction agent. Zinc oxide was used as the

TABLE 5. ANALYTICAL RESULTS OF OXYGEN IN ZINC COMPOUNDS BY ADDITION OF REACTION AGENT (About 2 mg of Naphthalene)

Sample	Sample taken (mg)	CO_2 (mg)	O-found (%)	O-calcd (%)	Δ%
Zinc oxide	3.550	1.923	19.70	19.66	+0.04
	4.177	2.233	19.44		−0.22
	3.736	2.006	19.52		−0.14
Zinc acetate	3.495	4.187	43.56	43.74	−0.18
	4.319	5.171	43.53		−0.21
	3.852	4.623	43.64		−0.10
Ammonium zinc sulfate	4.062	4.857	43.48	43.60	−0.22
	4.221	5.080	43.76		+0.16
	3.613	4.326	43.54		−0.06
Zinc formate	3.441	4.750	50.19	50.15	+0.04
	3.734	5.161	50.26		+0.11
	4.118	5.702	50.35		+0.20
Zinc nitrate	3.968	7.048	64.58	64.54	+0.14
	3.800	6.768	64.76		+0.22
	4.168	7.397	64.53		−0.01
Zinc oxalate	4.134	5.778	50.82	50.68	+0.14
	3.791	5.264	50.49		−0.19
	3.955	5.507	50.63		−0.05
Zinc perchlorate	3.020	5.007	60.28	60.15	+0.13
	3.615	5.951	59.86		−0.19
	4.231	6.997	60.13		−0.02
Zinc sulfate	3.291	5.551	61.33	61.21	+0.12
	4.155	7.006	61.31		+0.10
	4.445	7.491	61.28		+0.07

sample. The analytical results are given in Table 3. It was found that oxygen in zinc oxide can be determined fairly accurately when the sample is heated at 1000 °C or above. With compounds the oxygen of which can not be determined by the usual method, determination of oxygen was also carried out at 1000 °C. The results are given in Table 4. We see that oxygen in zinc compounds can be determined quite accurately by the addition of carbon to a sample boat.

Determination of Total Oxygen in Zinc Compounds by the Carrier Gas Method with a Reaction Agent. The total oxygen in zinc compounds can be determined by the addition of carbon to a sample boat and by heating at 1000 °C. We also attempted the addition of naphthalene (2 mg) instead of carbon. The results are given in Table 5. It was found that total oxygen in the zinc compounds can be determined accurately even in the presence of naphthalene.

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