[DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

PREPARATION AND PHYSICAL PROPERTIES OF CERTAIN DI-N-ALKYL ZINC COMPOUNDS[1,2]

LEWIS F. HATCH, GORDON SUTHERLAND, AND WILLIAM J. ROSS

Di-n-alkyl zinc compounds were first prepared in 1853 by Frankland (1) by heating zinc and the alkyl iodide in a sealed tube. Since that time the preparation of these compounds has been studied by a number of investigators culminating in the procedure of Noller (2) with modifications by Soroos and Morgana (3). The reaction is that of the alkyl iodide (or a mixture of the iodide and bromide) with an alloy consisting of 90% zinc and 10% copper.

Although there is considerable information in the literature pertaining to the preparation and chemical properties of the lower molecular weight alkyl zinc compounds, there is a paucity of reliable data related to their physical properties. The present study was undertaken to obtain more extensive and more accurate physical data on di-n-propyl zinc, di-n-butyl zinc, di-n-pentyl zinc, di-n-hexyl zinc, and di-n-heptyl zinc. The latter two compounds have not been reported previously.

Of the various methods reported for the preparation of alkyl zinc compounds, the one developed by Noller appeared to be the most efficient and least expensive procedure for the preparation of the relatively large quantities of the compounds required. The halide used was usually the iodide but in some cases a mixture of the iodide and bromide was used. The zinc was in the form of an alloy with copper (Zn 91%, Cu 9%). All preparations were carried out under dry nitrogen or helium. Table I records the yields obtained along with the density and analysis of the alkyl zinc compounds. The compounds were analyzed by determining the amount of zinc oxide formed by slow air oxidation. The yields generally decreased with increase in molecular weight primarily because of increased difficulty of recovery by distillation.

The ease of decomposition of the di-n-alkyl zinc compounds did not permit a determination of their boiling points at atmospheric pressure. Atmospheric boiling points were obtained for each of the five di-n-alkyl zinc compounds by determining the boiling temperatures of each compound at reduced pressures and plotting $\log_{10}P$ vs $1/T$. The "best" representative straight line was drawn through the resulting points and extended to an ordinate corresponding to $\log_{10}760$ (Fig. 1). The value of $1/T$ thus obtained was used to determine the boiling point of the compound at 760 mm. The precision was $\pm2°$. These boiling points are presented graphically in Fig. 2 along with data from the literature (2, 4–10).

TABLE I

ZINC ALKYLS

COMPOUND	YIELD, %	DENSITY $\frac{20°}{4°}$	ANALYSIS zn, %		
			Calc'd	Found	
Di-*n*-propyl zinc.................	67	1.080	43.8	43.9	43.9
Di-*n*-butyl zinc..................	71	1.034	36.5	36.3	36.2
Di-*n*-pentyl zinc.................	58	0.990	31.5	31.2	31.0
Di-*n*-hexyl zinc..................	51	.996	27.8	27.4	27.3
Di-*n*-heptyl zinc.................	41	.997	24.8	24.5	24.4
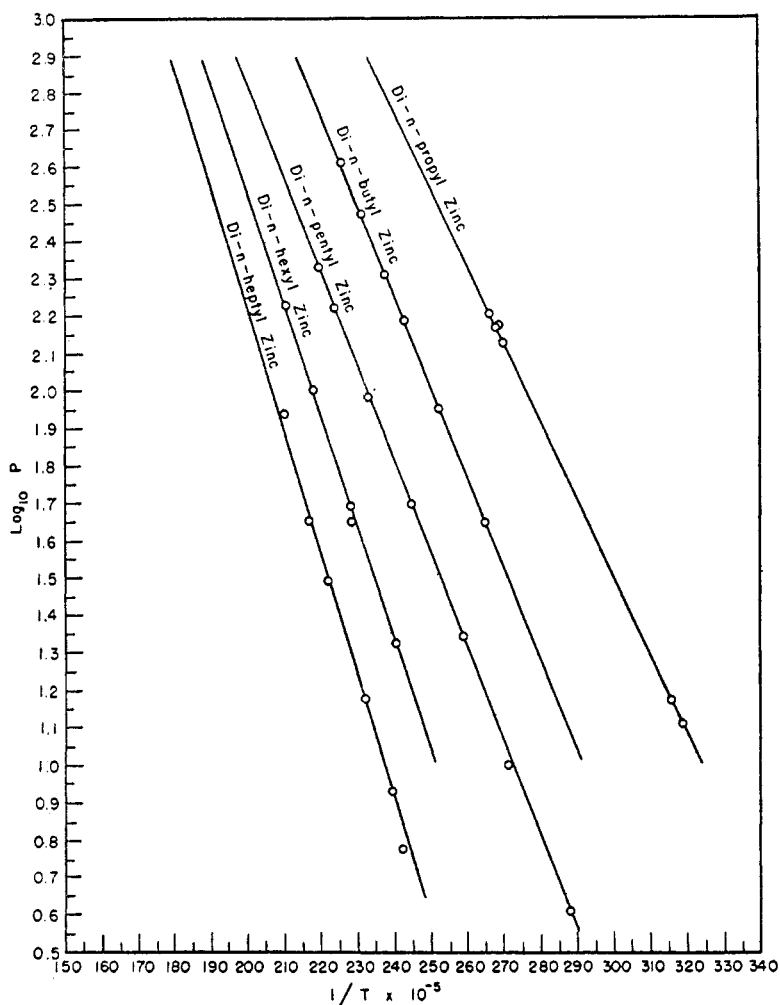
FIG. 1. DI-*n*-ALKYL ZINC COMPOUNDS. RECIPROCAL OF THE BOILING TEMPERATURE *vs.* LOG$_{10}$ OF THE PRESSURE

An average value of the molar heat of vaporization for each of the di-n-alkyl zinc compounds (Fig. 3) was calculated using data obtained in the boiling point determinations. These data were substituted in the Clapeyron equation: $\ln(P_1/P_2) = (\Delta H_v/R) \times (T_2 - T_1/T_1T_2)$. Data from the literature (5, 7) are also
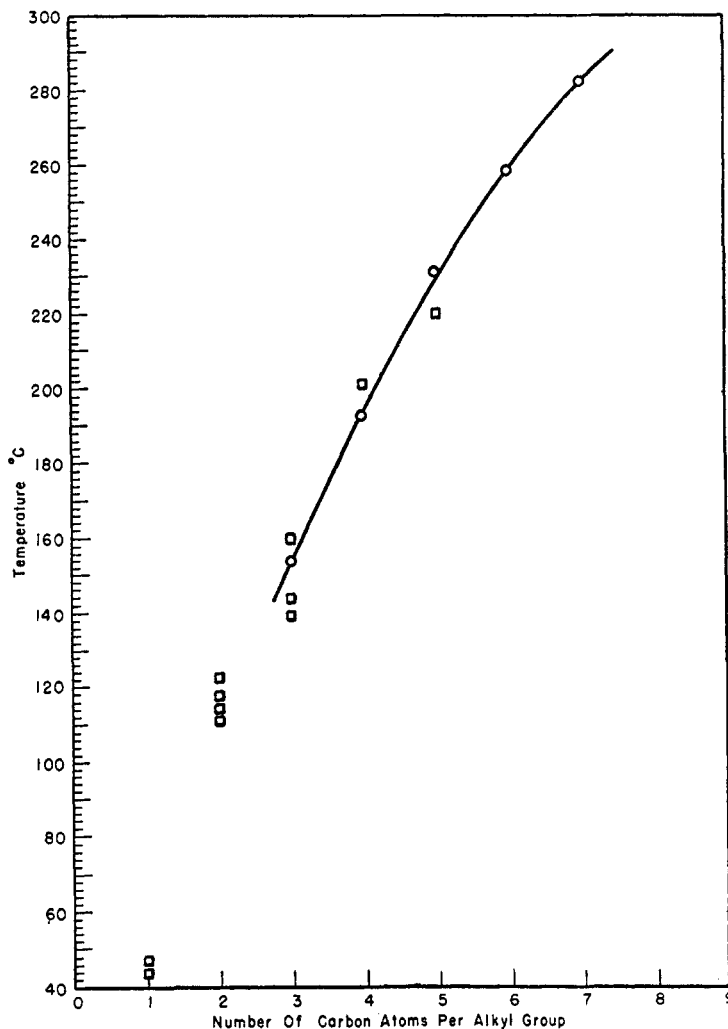

FIG. 2. BOILING POINTS AT 760 MM. PRESSURE OF DI-n-ALKYL ZINC COMPOUNDS. ○, DEFENSE RESEARCH LABORATORY DATA (CALCULATED). □, LITERATURE DATA (MOST POINTS CALCULATED)

given in Fig. 3. The constants were also calculated for the equation, $\log_{10}P = -A/T + B$, which describes the vapor pressure-boiling temperature curves. A value for Trouton's quotient (the normal entropy of vaporization) was calculated using the atmospheric boiling points and the average molar heats of vaporization

for each of the di-*n*-alkyl zinc compounds. All of the quotients are larger than the approximate value, 21, which is given in the literature for various liquids.

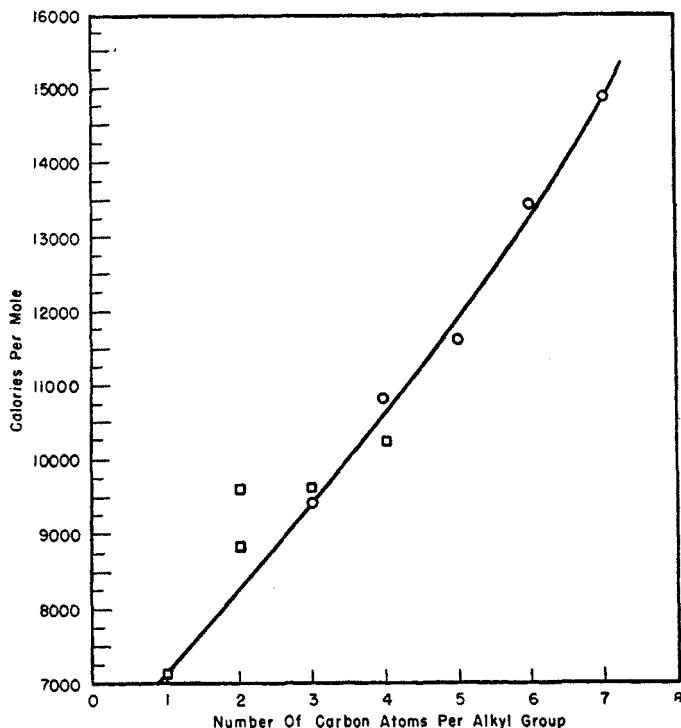The foregoing thermodynamic constants are given in Table II.

FIG. 3. MOLAR HEAT OF VAPORIZATION OF DI-*n*-ALKYL ZINC COMPOUNDS. O, DEFENES RESEARCH LABORATORY DATA (CALCULATED). □, LITERATURE DATA (CALCULATED)

TABLE II

THERMODYNAMIC CONSTANTS OF CERTAIN DI-*n*-ALKYL ZINC COMPOUNDS

COMPOUND	BOILING POINT[a] @ 760 MM, °C.	ΔH_v (cals.)	A	B	$\Delta H_v/T$
Di-*n*-propyl zinc.................	154	9433	2067	7.707	23.086
Di-*n*-butyl zinc.................	193	10828	2366	7.957	23.236
Di-*n*-pentyl zinc.................	231	11627	2543	7.925	23.064
Di-*n*-hexyl zinc.................	258	13434	2920	8.390	25.300
Di-*n*-heptyl zinc.................	282	14896	3296	8.754	26.840

[a] Calculated.

All of the di-*n*-alkyl zinc compounds prepared during this investigation are very sensitive to even traces of oxygen or moisture. On contact with either air or water there is a vigorous exothermal reaction resulting in the formation of various zinc and organic compounds.

Small droplets of di-*n*-propyl zinc were spontaneously flammable in air and in water at 25°. Di-*n*-butyl zinc burned when droplets came in contact with air while receivers were changed during distillation; however, the butyl compound did not inflame when sprayed into air from a hypodermic needle at room temperature. Considerable heat was evolved when the pentyl, hexyl, and heptyl derivatives came in contact with either air or water but they did not ignite.

When the compounds were stored in glass containers which were sealed to prevent access of air, there was no visible evidence of decomposition over a period of eight months. Some type of reaction seems to have taken place, however, because an alkyl compound which has been stored for several weeks or longer will decompose rapidly if the bottle is opened only momentarily. The nature of this decomposition differs from the normal oxidation; very little white zinc oxide is formed but instead a precipitate of black zinc is produced.

EXPERIMENTAL

PREPARATION OF THE DI-*n*-ALKYL ZINC COMPOUNDS

All of the di-*n*-alkyl zinc compounds were prepared in a Grignard type apparatus using a zinc (91%)-copper (9%) alloy and the desired *n*-alkyl iodide under an atmosphere of dry nitrogen (99.99%) or pure helium. The alloy was milled to give pieces approximately 3 × 10 mm. The alkyl iodides were obtained from Columbia Organic Chemical Company and were used without further purification because the small amount of iodine present seemed to be instrumental in initiating reaction.

Both isopropyl ether and *n*-butyl ether were especially dried and used as solvents. Isopropyl ether was used in the preparation of di-*n*-propyl and di-*n*-butyl zinc because its boiling point, while lower than the boiling points of both *n*-propyl iodide and *n*-butyl iodide, was high enough to initiate the reaction. The higher-boiling *n*-butyl ether was used in the preparation of the other three di-*n*-alkyl zinc compounds. The reactions were carried out at the reflux temperature of the ether used.

The tendency towards decomposition during the reaction phase seemed to increase with decreasing size of alkyl groups. A slight amount of fuming was observed during the preparation of the hexyl and heptyl derivatives. The fumes, however, were more dense during the preparation of the pentyl derivative, and a small layer of zinc oxide was deposited above the dark residual powder in the reaction flask. The butyl and propyl reaction mixtures were very sensitive to excessively rapid stirring and excessive heating, and considerable fuming and deposition of zinc oxide were observed. The sensitivities of the *n*-alkyl zinc compounds toward impurities in the nitrogen with resulting decomposition, also increased with decreasing size of the alkyl group.

After a four-hour reaction period (two hours for the addition of the iodide and two hours refluxing) the liquid contents of the reaction flask were then transferred by decantation to the distillation flask. This transfer was accomplished in a nitrogen-filled dry-box. The apparatus used for the distillation of the di-*n*-alkyl zinc compounds consisted of a flask, 180 mm. Vigreux column, 250 mm. condenser, vacuum receiver, and product bottle. The column was insulated with Eagle-Pitcher Company's "Eagle 66". The distillation step in the preparation of these compounds is the most important one and governs the yield obtained. Pressures between 1 and 10 mm. were used in these distillations. The yields obtained are given in Table I.

ANALYSIS

Quantitative determinations of zinc were made on the five di-*n*-alkyl zinc compounds which were prepared in this study. The fact that all the compounds are easily oxidized by

air to form zinc oxide was used as the basis for these analyses. In order to obtain a quantitative conversion of the zinc in the di-*n*-alkyl zinc compound to zinc oxide, the reaction rate was decreased by dissolving a known quantity of the di-*n*-alkyl zinc compound in *n*-pentane, and then permitting the solvent to evaporate slowly.

Small glass capsules were used to handle the di-*n*-alkyl zinc compounds. These capsules were formed by blowing bulbs of 8 mm. diameter from 5-mm. Pyrex glass tubing. The glass tubing was broken two inches above the bulb, and then the two inch neck was drawn into a constriction, yielding a capsule consisting of the bulb with an 1¼ inch neck that had a constricted opening of about 3 mm.

About 0.5 ml. of the compound was transferred quickly from the bottle to the previously weighed capsule by means of a hypodermic syringe. The capsule was then sealed, weighed and placed in a weighed crucible containing *n*-pentane. The capsule was broken at the junction of the bulb and neck. The *n*-pentane was allowed to evaporate in a desiccator which contained calcium chloride. The crucible containing the zinc oxide was heated for one hour in an oven at 100° before determining the amount of oxide formed. The analytical results are in Table I.

<center>DENSITY</center>

A determination of the density of each of the five di-*n*-alkyl zinc compounds was made at $\frac{20°}{4°}$ The determination was made on di-*n*-pentyl, di-*n*-hexyl, and di-*n*-heptyl zinc by using a vacuum-jacketed specific gravity bottle which was equipped with a ground glass stopper containing a capillary tube and a glass stopper cover. An AMINCO refrigerated constant temperature bath was used to obtain a constant temperature of 20°.

In order to reduce decomposition as much as possible, the di-*n*-alkyl zinc compounds and the pycnometer were cooled separately at 20° in the constant-temperature bath before the di-*n*-alkyl zinc was transferred to the pycnometer. When the bottle containing the di-*n*-alkyl zinc had been in the bath for one hour, the pycnometer was removed and dried thoroughly. As quickly as possible, the cover and stopper were removed, the bottle with the di-*n*-alkyl zinc compound was then taken out of the bath and opened. Five and two tenths ml. of the liquid was rapidly removed with a hypodermic syringe and ejected into the pycnometer. When the liquid level had risen a slight distance up the neck of the pycnometer, the glass stopper was replaced. All surplus liquid was forced out through the capillary tube in the stopper and was removed with a towel. All traces of zinc oxide were also wiped away, the glass cover replaced, and the pycnometer quickly weighed. The transference and weighing had to be accomplished as rapidly as possible to prevent the heat of decomposition from changing the temperature of the liquid.

The propyl and butyl derivatives were too reactive to allow their densities to be determined in the manner used for the higher molecular weight compounds. The densities of di-*n*-propyl and di-*n*-butyl zinc were determined by low temperature distillation of the compound into a calibrated dilatometer which was then sealed (11).[3]

At least two determinations of the density of each of the di-*n*-alkyl zinc compounds were made to obtain results which differed by less than one unit in the third decimal place (Table I).

<center>BOILING POINTS AT REDUCED PRESSURES</center>

The ease of decomposition of the di-*n*-alkyl zinc compounds did not permit a determination of their boiling points at atmospheric pressure. The boiling points at 760 mm. pressure were determined by obtaining the boiling points of each compound at a number of different pressures below atmospheric and from these data the desired points were calculated by extrapolation from a line obtained by plotting the reciprocal of the boiling temperature (in degrees Kelvin) at the reduced pressure against the $\log_{10}$ of the pressure. The line thus ob-

---

[3] These data were obtained by Elizabeth A. Mayer.

tained was linear over the limited range used and corresponded to the equation $\log_{10}P = -A/T + B$, where T represents the boiling temperature, P the pressure and A and B are constants.

The apparatus used for the determination of the boiling point-pressure data for these compounds consisted of a flask and a 180-mm. Vigreux column with the appropriate condenser and vacuum receiver. The column was insulated with Eagle-Pitcher Company's "Eagle 66". The vacuum was provided by a Cenco Hyvac vacuum pump operating through a Dry Ice-isobutyl alcohol cold trap and regulated by a needle valve. The pressure was measured by a differential manometer. At each pressure equilibrium was established and the temperature in the still head noted using a standardized thermometer; the appropriate stem corrections were made.

The data obtained are given in Table II and in Fig. 1.

SUMMARY

The following di-n-alkyl zinc compounds have been prepared and certain of their physical properties determined: Di-n-propyl zinc, di-n-butyl zinc, di-n-pentyl zinc, di-n-hexyl zinc, and di-n-heptyl zinc.

AUSTIN, TEXAS

REFERENCES

(1) FRANKLAND, *Ann.*, **85**, 329 (1853).
(2) NOLLER, *J. Am. Chem. Soc.*, **51**, 594 (1929) and *Org. Syntheses*, **12**, 86 (1932).
(3) SOROOS AND MORGANA, *J. Am. Chem. Soc.*, **66**, 893 (1944).
(4) THOMPSON AND LINNETT, *Trans. Faraday Soc.*, **32**, 681 (1936).
(5) BAMFORD LEVI, AND NEWITT, *J. Chem. Soc.*, 468 (1946).
(6) LAUBENGAYER AND FLECKENSTEIN, *Z. anorg. u. allgem. Chem.*, **191**, 283 (1930).
(7) HEIN AND SCHRAMM, *Z. physik. Chem.*, **A149**, 408 (1930).
(8) HERZ, *Z. anorg. u. allgem. Chem.*, **182**, 173 (1929).
(9) ZARTMAN AND ADKINS, *J. Am. Chem. Soc.*, **54**, 3398 (1932).
(10) FRANKLAND AND DUPPA, *J. Chem. Soc.*, **17**, 29 (1864).
(11) KEYES AND FELSING, *J. Am. Chem. Soc.*, **41**, 589 (1919).