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CERTAIN METAL DERIVATIVES OF 2,4-PENTANEDIONE[1]

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In the course of a research program in this Laboratory it became necessary to prepare several metal derivatives of 2,4-pentanedione (acetylacetone) and to determine their solubilities in different types of hydrocarbons. A survey of the literature indicated that the metal derivatives were usually prepared by a reaction between metal hydroxides (1, 2, 3, 4, 5) or carbonates (3, 5, 6, 7) and the enol form of the pentanedione. The metals (8), metal oxides (9), chlorides (5, 10), and acetates (11) have also been used, as well as the double decomposition of an alkali or ammonium salt of pentanedione and a metal salt (12, 13, 14). Although appreciable work has been reported on compounds of this type, only generalizations have been made regarding their solubilities, densities, and melting points.

The sodium, potassium, magnesium, beryllium, and aluminum derivatives of 2,4-pentanedione have now been prepared and their melting points and densities determined. These compounds were prepared from either the corresponding hydroxide or by direct action of the pentanedione on the metal. In each case the previously reported techniques have been modified and very good yields were obtained.

The ultraviolet absorption spectra of the compounds have also been obtained and these data (Figure 1) show that the order of increasing amplitude of absorption is sodium, potassium, magnesium, beryllium, and aluminum. From the general chemical characteristics of these metals it might be expected that the sodium, potassium, and magnesium compounds would have the properties of a salt and the beryllium and aluminum compounds would have the properties of a chelate compound. Because the greatest absorption is caused by the organic portion of the molecule, the molecules with the largest number of pentanedione units might be expected to have the greatest absorption. The chelate bond will also increase the absorption and accounts for the greater amplitude of the beryllium compound over that of the magnesium salt.

n-Hexane, cyclohexane, and benzene have been used as the solvents in the solubility determinations of the various compounds, because they represent the three types of hydrocarbons which would be present in petroleum. Compounds with the same number of carbon atoms were used to prevent any differences in solubility caused by large differences in molecular weight. Only the beryllium and aluminum compounds showed appreciable solubility and they were extensively soluble only in benzene (Figure 2). This solubility behavior might be expected because of the chelate structure of the beryllium and aluminum com-

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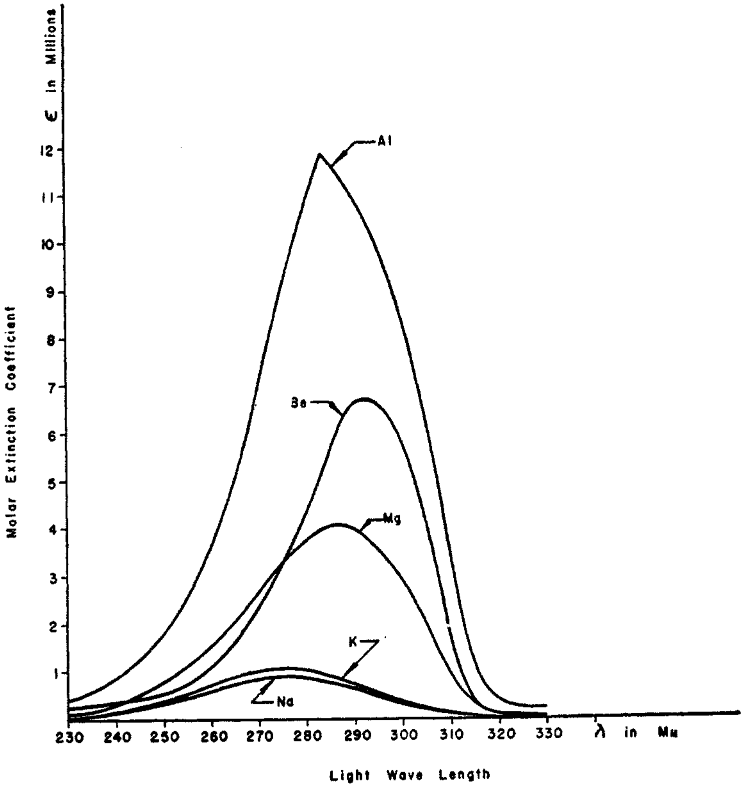

Fig. 1. Ultraviolet Absorption Spectra of Certain Metal Derivatives of 2,4-Pentanedione

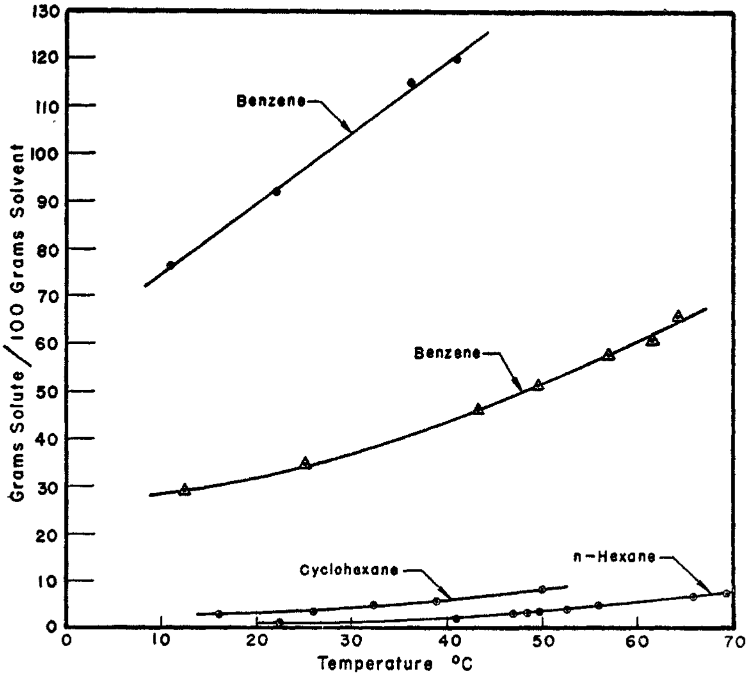

Fig. 2. Solubility of Bis(2,4-pentanediono)beryllium and Tris(2,4-pentanediono)aluminum in Benzene, Cyclohexane and *n*-Hexane. o, Bis(2,4-pentandiono)beryllium; Δ, Tris(2,4-pentanediono)aluminum

pounds. The sodium, potassium and magnesium salts are essentially insoluble in these hydrocarbons.

EXPERIMENTAL

All melting points are corrected.

Materials. The pentanedione was obtained from Carbide and Carbon Chemicals Corp., New York. It was purified by fractional distillation and the material boiling between 140–140.5° was used.

The *n*-hexane and cyclohexane used as solvents were obtained from Phillips Petroleum Company, Bartlesville, Oklahoma. The *n*-hexane contained 95 mole per cent *n*-hexane and 4 mole per cent methylcyclohexane. The cyclohexane was of 99 mole per cent minimum purity. The benzene was of reagent grade.

All the inorganic reagents in this investigation were of C. P. or reagent grade.

Sodium 2,4-pentanedionate. Sodium 2,4-pentanedionate was prepared both by the reaction between sodium hydroxide and the pentanedione in either water or ethanol and by the direct action of sodium metal in toluene on the pentanedione. In the first method 100 g. (1.0 mole) of pentanedione was slowly added to 40 g. (1.0 mole) of sodium hydroxide while maintaining the temperature below 70°. When concentrated solutions of sodium hydroxide were used, the product crystallized when the reaction mixture cooled; yield 98 g. (80%).

Ethanol as the solvent gave the same yield but without the necessity of such close temperature control as with water as the solvent. In previously reported preparations of the salt from sodium hydroxide, solid sodium hydroxide was used and considerable trouble was encountered by the salt coating the sodium hydroxide.

In the second method of preparation 50 g. (0.5 mole) of pentanedione was added to 11.5 g. (0.5 mole) of sodium in 100 ml. of toluene. The temperature was maintained at 100° to keep the sodium molten; yield 101 g. (83%). When lower temperatures and solid sodium were used, salt coated the metal, causing a slower reaction and lower yields.

The sodium 2,4-pentanedionate was recrystallized from ethanol and its melting point determined in soft glass melting point tubes. When the melting point tube was slowly heated to the temperature at which the salt melted, the salt charred considerably. However, if the melting point tube was placed in the bath at about five degrees below the melting point of the salt and then the temperature slowly raised, a fairly sharp and reproducible melting point could be obtained with very little decomposition. This same procedure was also used to determine the melting points of the potassium and magnesium salts.

The density of the sodium salt was calculated from the specific gravity. The specific gravity was determined by the use of a specific gravity balance (gravitometer). The suspending liquid was pure *n*-heptane. This same method was used for the other four compounds with the exception of bis(2,4-pentanediono)beryllium where water was used as the suspending liquid.

It was not possible to obtain a satisfactory carbon analysis for the sodium, potassium, and magnesium salts. For this reason the percentage of metal was determined. Concentrated sulfuric acid was used to decompose the pentanedionate to the metal sulfate. The reaction mixture was heated to dryness over a microburner. The residue was then placed in a furnace and heated to red heat for one-half hour. After cooling, sulfuric acid was again added and the heating process repeated for five minutes in the furnace. The percentage of metal was calculated from the sulfate formed by the foregoing treatment; melting point 217–219°; d_4^{20} 1.213.

Anal. Calc'd for $NaC_5H_7O_2$: H, 5.78; Na, 18.84.
Found: H, 5.58; Na, 18.31.

Potassium 2,4-pentanedionate. The potassium 2,4-pentanedionate was prepared by the same two methods as used for the preparation of the sodium salt. Essentially the same yields were obtained; melting point 261–263°; d_4^{20} 1.216.

Anal. Calc'd for $KC_5H_7O_2$: H, 5.11; K, 28.30.
Found: H, 5.28; K, 27.79.

Magnesium 2,4-pentanedionate. Magnesium 2,4-pentanedionate was prepared by the action of magnesium metal on pentanedione. Two hundred grams (2 moles) of pentanedione in twice its volume of 70% ethanol was added to 48.6 g. of magnesium turnings. A vigorous reaction took place at 60–70° with the evolution of hydrogen. The magnesium 2,4-pentanedionate crystallized from the reaction mixture on cooling; yield 231 g., 93.6%; melting point 265–267°; d_4^{20} 1.162.

Anal. Calc'd for $Mg(C_5H_7O_2)_2$: H, 6.35; Mg, 10.92.
Found: H, 6.59; Mg, 10.62.

Bis(2,4-pentanediono)beryllium. Basic beryllium carbonate was treated with hot concentrated sulfuric acid to convert the carbonate to the sulfate. The beryllium sulfate was then dissolved in boiling water; and, after cooling, an equivalent amount of sodium hydroxide was added to form beryllium hydroxide. Two hundred grams (2 moles) of 2,4-pentanedione in an equal volume of benzene was refluxed for one hour with 43 g. (1 mole) of the beryllium hydroxide. The water which formed was separated from the benzene layer and the bis(2,4-pentanediono)beryllium crystallized from the benzene upon cooling; yield 172 g., 83%; melting point 108–109° [lit. (13) 108.5–109°]; d_4^{20} 1.108 [lit. (6) 1.168].

Anal. Calc'd for $Be(C_5H_7O_2)_2$: C, 57.96; H, 6.82; Be, 4.35.
Found: C, 58.21; H, 6.56; Be, 4.08.

Tris(2,4-pentanediono)aluminum. One hundred fifty grams (1.5 moles) of 2,4-pentanedione in an equal volume of benzene was added to an aqueous solution of 66.6 g. (0.5 mole) of aluminum chloride. The mixture was stirred and heated to reflux temperature. Sixty grams of sodium hydroxide (50% solution) was then added to the mixture. Sodium pentanedionate formed in the benzene layer but disappeared immediately because of the formation of the benzene-soluble tris(2,4-pentanediono)aluminum. The total reaction time was one-half hour. The reaction between 2,4-pentanedione and either aluminum chloride or hydroxide requires from one to three hours to go to completion. The compound was purified by crystallization from benzene; yield 143 g., 89%; melting point 193–194° [lit. (13) 194.6°]; d_4^{20} 1.204.

Anal. Calc'd for $Al(C_5H_7O_2)_3$: C, 55.52; H, 6.54; Al, 8.32.
Found: C, 55.58; H, 6.78; Al, 8.01.

Ultraviolet absorption. A Beckman Quartz Spectrophotometer was used to determine the ultraviolet absorption curves (Figure 1) for the compounds in ethanol.

Solubilities. The solubilities of these compounds were determined in the following manner. Known weights of the solvent and solute were placed in a 1 x 8 inch test tube equipped with a stopper holding a thermometer and a manually operated wire loop stirrer. The tube and its contents were heated until the solid dissolved. These were then cooled until crystals reappeared. On slow, careful reheating, with constant stirring, the temperature was noted at which the last crystals dissolved. This temperature could be reproduced within ± 0.5°. Each value plotted in Figure 2 is the average of several determinations.

The solubility of sodium, potassium, and magnesium pentanedionates is less than 0.01 g. in 100 g. of benzene, cyclohexane, and *n*-hexane at 70°. Tris(2,4-pentanediono)aluminum was soluble in both cyclohexane and *n*-hexane to the extent of less than 0.01 g. in 100 g. of solvent at 70°.

SUMMARY

1. The following metal derivatives of 2,4-pentanedione were prepared and characterized more completely than previously: Sodium 2,4-pentanedionate, potassium 2,4-pentanedionate, magnesium 2,4-pentanedionate, bis(2,4-pentanediono)beryllium, and tris(2,4-pentanediono)aluminum.

2. The ultraviolet absorption spectra of these compounds were obtained, as well as their solubility in benzene, cyclohexane, and *n*-hexane.

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