

Our somewhat higher m. p. need not be interpreted, however, as indicating any greater purity, for at high temperatures a difference of 3° is not serious, and our analytical results do not justify any such claim.

LABORATORIES OF ORGANIC CHEMISTRY  
COLUMBIA UNIVERSITY  
NEW YORK, N. Y.

ALBERT A. PLENTL  
MARSTON T. BOGERT

RECEIVED JULY 18, 1941

#### ADDITION COMPOUNDS OF ZINC, CADMIUM, COBALT AND NICKEL HALIDES WITH 1,4-DIOXANE

Sir:

In a recent paper [THIS JOURNAL, 62, 3522 (1940)] R. Juhasz and L. F. Yntema describe a series of "Addition Compounds of Zinc, Cadmium, Cobalt and Nickel Halides with 1,4-Dioxane." The great majority of these I prepared already some years ago (H. Rheinboldt, A. Luyken and H. Schmittmann, *J. prakt. Chem.*, **149**, 30-54 (1937); *C. A.*, **31**, 6615 (1937)), *i. e.*, the compounds:  $\text{ZnCl}_2 \cdot 2(\text{C}_4\text{H}_8\text{O}_2)$ ,  $\text{ZnBr}_2 \cdot 2(\text{C}_4\text{H}_8\text{O}_2)$ ,  $\text{ZnI}_2 \cdot 2(\text{C}_4\text{H}_8\text{O}_2)$ ,  $\text{CdCl}_2 \cdot (\text{C}_4\text{H}_8\text{O}_2)$ ,  $\text{CdBr}_2 \cdot (\text{C}_4\text{H}_8\text{O}_2)$ ,  $\text{CdI}_2 \cdot (\text{C}_4\text{H}_8\text{O}_2)$ ,  $\text{CoCl}_2 \cdot (\text{C}_4\text{H}_8\text{O}_2)$ ,  $\text{CoBr}_2 \cdot 2(\text{C}_4\text{H}_8\text{O}_2)$ ,  $\text{CoI}_2 \cdot 2(\text{C}_4\text{H}_8\text{O}_2)$  and  $\text{NiI}_2 \cdot 2(\text{C}_4\text{H}_8\text{O}_2)$ .

Besides we described other compounds which belong to the same series:  $\text{CoI}_2 \cdot 4(\text{C}_4\text{H}_8\text{O}_2)$ ,  $\text{NiCl}_2 \cdot 2(\text{C}_4\text{H}_8\text{O}_2)$  and  $\text{NiBr}_2 \cdot 2(\text{C}_4\text{H}_8\text{O}_2)$ .

Further on we described addition compounds of dioxane with certain metal halides:  $\text{CaCl}_2$ ,  $\text{CaBr}_2$ ,  $\text{CaI}_2$ ,  $\text{SrBr}_2$ ,  $\text{SrI}_2$ ,  $\text{BaI}_2$ ,  $\text{MgCl}_2$ ,  $\text{MgBr}_2$ ,  $\text{MgI}_2$ ,  $\text{HgCl}_2$ ,  $\text{HgBr}_2$ ,  $\text{HgI}_2$ ,  $\text{Hg}(\text{CN})_2$ ,  $\text{Hg}(\text{CNS})_2$ ,  $\text{CuCl}_2$ ,  $\text{CuBr}_2$ ,  $\text{SnCl}_2$ ,  $\text{SnBr}_2$ ,  $\text{MnCl}_2$ ,  $\text{MnBr}_2$ ,  $\text{MnI}_2$ ,  $\text{FeCl}_2$ ,  $\text{FeBr}_2$ ,  $\text{FeI}_2$ .

In a previous publication (*J. prakt. Chem.*, **148**, 81-87 (1937); *C. A.*, **31**, 4321 (1937)) we described dioxanates of  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiI}$ ,  $\text{NaI}$ ,  $\text{KI}$  and  $\text{NH}_4\text{I}$ .

INSTITUTO DE QUIMICA

UNIVERSIDADE DE SÃO PAULO (BRAZIL) H. RHEINBOLDT

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#### COMPOUNDS OF 1,4-DIOXANE WITH METAL HALIDES

Sir:

In a list of "New Compounds" of zinc, cadmium, cobalt and nickel halides with 1,4-dioxane (THIS JOURNAL, 62, 3522 (1940)) that had been prepared in this Laboratory (Thesis, St. Louis University, (1934)), there were included a number described by Rheinboldt, Luyken and Schmittmann (*J. prakt. Chem.*, **149**, 30 (1937)). The compounds that should have been reported are

as follows ( $R = 1,4\text{-dioxane}$ ):  $\text{ZnCl}_2 \cdot R$ ,  $\text{CdCl}_2 \cdot \frac{1}{2}R$ ,  $\text{CoI}_2 \cdot 3R$ ,  $\text{CoI}_2 \cdot R \cdot 2\text{H}_2\text{O}$ ,  $\text{CoI}_2 \cdot R \cdot 4\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot R$  and  $\text{NiBr}_2 \cdot R$ .

The writer is glad to make this correction and assumes responsibility for the error.

DEPARTMENT OF CHEMISTRY  
ST. LOUIS UNIVERSITY  
ST. LOUIS, MO.

L. F. YNTEMA

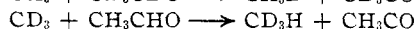
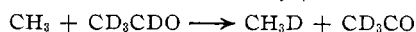
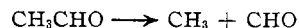
RECEIVED JULY 28, 1941

#### THE THERMAL DECOMPOSITION OF ACETALDEHYDE

Sir:

It is known that reaction chains may be induced in the thermal decomposition of acetaldehyde by the addition of small amounts of oxygen or other materials, but whether pure acetaldehyde decomposes thermally by a chain mechanism is still a matter of controversy. Recently, Burton, Ricci and Davis [THIS JOURNAL, 62, 265 (1940)], employing the Paneth technique with radioactive lead, have obtained some positive evidence for radical chains in the thermal reaction. Their work is open to two objections. (1) Even the slightest trace of impurity, for example 0.001% oxygen [Letort, *J. chim. phys.*, **34**, 428 (1937)] would have initiated reaction chains and thus led to a positive result for their experiments. (2) The experiments could not determine what fraction of the acetaldehyde was decomposing by way of the chains.

A method which seemed to offer better possibilities for deciding this question was to decompose mixtures of acetaldehyde and acetaldehyde- $d_4$ . If a chain reaction occurred, such processes as the following would take place



and the methanes produced in the reaction would be mixed as to deuterium content. On the other hand, if the reaction were intramolecular, only  $\text{CH}_4$  and  $\text{CD}_4$  would be formed. Since Benedict, Morikawa, Barnes and Taylor [*J. Chem. Physics*, **5**, 1 (1937)] have shown that methane and the deuteromethanes may be identified and determined by their infrared spectra, one should be able to evaluate these alternatives through an infrared examination of the products formed in the above experiment.