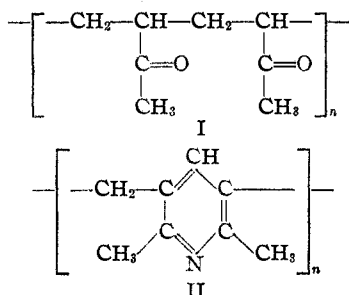


## NOTES

### Structure of Vinyl Polymers. V.<sup>1</sup> Some Reactions of the Polymer of Methyl Vinyl Ketone

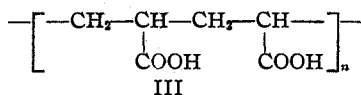
BY C. S. MARVEL AND CHARLES L. LEVESQUE<sup>2</sup>

Work from this Laboratory has shown<sup>3</sup> that the polymer of methyl vinyl ketone has a "head to tail" structure (I), and hence contains 1,5-dike-



tone units. However, when this polyketone was treated with hydroxylamine, the corresponding polyketoxime rather than the expected polypyridine (II)<sup>4</sup> was obtained. It has now been found possible to prepare the polypyridine (II) by heating the polyketoxime with alcoholic hydrogen chloride.<sup>5</sup> Flory has shown<sup>6</sup> that no more than 86.47% of the ketoxime groups can participate in this reaction. Analytical results support the conclusion that under the conditions employed in our experiment, the remaining 13.53% of the ketoxime groups were hydrolyzed.

By treating a dioxane solution of the polymer of methyl vinyl ketone with aqueous sodium hypochlorite,<sup>7</sup> a polyacrylic acid (III) has been obtained. Attempts to compare this polyacid with that obtained by the polymerization of acrylic acid are now in progress.



#### Experimental

**Preparation of the Polypyridine.**<sup>5</sup>—A solution of 3.2 g. of the oxime of the polymer of methyl vinyl ketone<sup>3</sup> in

(1) For the fourth communication in this series see *THIS JOURNAL*, **61**, 3156 (1939).

(2) Du Pont Fellow in Chemistry.

(3) Marvel and Levesque, *THIS JOURNAL*, **60**, 280 (1938).

(4) Knoevenagel, *Ann.*, **281**, 56 (1894).

(5) Blaise and Montagne, *Compt. rend.*, **180**, 1760 (1925).

(6) Flory, *THIS JOURNAL*, **61**, 1518 (1939).

(7) Fuson and Tullock, *ibid.*, **56**, 1638 (1934).

50 cc. of concentrated hydrochloric acid was placed in a 1-liter flask and a solution of 135 g. of hydrogen chloride in 500 cc. of alcohol was added. A reflux condenser was attached, and the milky solution was heated to boiling. Enough water to effect complete solution (40 cc.) was added and the mixture was refluxed for nineteen hours. The clear red reaction mixture was concentrated to 15 cc. and neutralized with ammonium hydroxide. The solid which precipitated was collected on a filter and dried under reduced pressure over solid potassium hydroxide. The product was 2.0 g. of light brown powder, readily soluble in acids, but insoluble in aqueous sodium hydroxide.

*Anal.* Calcd. for 0.4323 mole of  $C_8H_8N$  + 0.1353 mole of  $C_4H_4O$ : N, 9.94. Found: N, 9.53.

This product may be identical with the basic polymer which Balthis has obtained by the action of ammonia on the polymer of methyl vinyl ketone.<sup>8</sup>

**Preparation of the Polyacid.**<sup>7</sup>—A solution of sodium hypochlorite was prepared by bubbling chlorine into 160 g. of cold 10% sodium hydroxide until the gain in weight was 12 g. This solution was cooled by an ice-bath and stirred while a solution of 2.8 g. of the polymer of methyl vinyl ketone in 450 cc. of dioxane was added slowly. After the addition was complete, the mixture was stirred at room temperature for six hours. The lower aqueous layer was separated and concentrated under reduced pressure to 35 cc. The concentrate was filtered and the filtrate was acidified with concentrated hydrochloric acid. A white precipitate formed. The mixture of solution and precipitate was placed in a parchment paper sack and dialyzed until freed from chloride ion. The yellow solution remaining in the sack was filtered and the filtrate was evaporated to dryness. The residue was 1.15 g. of brittle, brown solid.

*Anal.* Calcd. for  $(C_7H_6O_2)_n$ : C, 50.0; H, 5.55. Found: C, 53.19; H, 5.92. The analysis indicates that about 90% of the methyl ketone groups have been oxidized.

(8) Balthis, U. S. Patent 2,122,707 (1938).

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### The Rotatory Power of Zinc Lactate<sup>1</sup>

BY W. DAYTON MACLAY, RAYMOND M. HANN AND C. S. HUDSON

In a recent article<sup>2</sup> we published measurements of the specific rotation of pure zinc D-lactate dihydrate in water for the concentrations 3.2 and 5.2%, which indicated that the change in rotation with concentration is a small one. Professor

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) MacLay, Hann and Hudson, *THIS JOURNAL*, **61**, 1666 (1939).

Karl P. Link has kindly informed us that he and Mr. R. J. Dimler have measured the rotation of zinc L-lactate in the course of a research on some derivatives of lactic acid, soon to be published, and have found considerable variation in rotation with concentration. We have repeated and confirmed their measurements and, at their suggestion, now record the two sets of values over the wider range of concentrations from 1.5 to 7.0%. In this range the  $[\alpha]_D$  values may be expressed approximately as  $[\alpha]_D^{20} = -9.2^\circ + 0.4(c)$ , in aqueous solution, for zinc L-lactate dihydrate. (The configuration of L-lactic acid is  $\text{CH}_3-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{COOH}$ .)

TABLE I  
VARIATION OF ROTATION WITH CONCENTRATION, AQUEOUS SOLUTIONS OF ZINC L-LACTATE DIHYDRATE (ACCURACY  $\pm 0.1^\circ$ )

Concn. (as dihydrate)	$[\alpha]_D^{20}$ (Dimler and Link)	$[\alpha]_D^{20}$ (Maclay, Hann and Hudson)
1.5	-8.7°	-8.7°
3.0	-7.9	-7.9
4.0	-7.6	-7.5
5.0	-7.2	-7.1
7.0	-6.7	-6.6

In our article we expressed the opinion that the rotations  $[\alpha]_D^{15} + 6.84^\circ$  (*c*, 5.6) for zinc D-lactate dihydrate and  $[\alpha]_D^{20} - 6.83^\circ$  (*c*, 7.1) for zinc L-lactate dihydrate, found by Irvine,<sup>3</sup> indicated some racemization of the lactic acids. It is now seen, however, that these values fit the new measurements very well, from which it may be concluded that the procedure which Irvine used in preparing the zinc lactates does not cause racemization and is therefore preferable to the more laborious procedure which we employed in order to exclude the possibility of racemization.

(3) Irvine, *J. Chem. Soc.*, **89**, 935 (1906).

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## Molecular Structure of Aliphatic Compounds and their Boiling Points

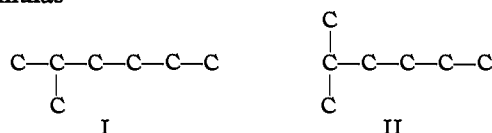
BY E. NEYMAN-PILAT

On the basis of Walker's formula C. R. Kinney recently<sup>1</sup> has developed a new system correlating molecular structure of organic compounds with their boiling points. In a paper dealing specially with aliphatic compounds, the boiling point numbers (b. p. n.) for carbon and hydrogen as well as

(1) C. R. Kinney, *THIS JOURNAL*, **60**, 3032 (1938).

for some radicals and characteristic groups have been presented. From these data and the given formula the boiling points at atmospheric pressure of aliphatic compounds may be calculated easily and with fair accuracy.

C. R. Kinney has stated that due to the lack of adequate boiling point determinations recorded in the literature for the branched hydrocarbons, the b. p. n.'s for only the methyl, ethyl, propyl and butyl radicals were calculated and that even those may undergo some alteration when more boiling points will be recorded. This point of view would seem to be open to question, as some of the paraffin hydrocarbons listed in Table I of the quoted paper may be considered as being derivatives of different radicals. For example the 2-methylhexane may be treated as a methyl (I) as well as a butyl derivative (II) according to the structural formulas



In the same way the 3-methyloctane may be regarded as 2-pentylbutane and the 3-methylnonane as 2-hexylbutane, etc.

The calculated B. P. N. obviously must be independent of the way in which the structural formulas are expressed.

Taking as a basis the values of 0.8, 1.0 and 3.05 for C, H and  $\text{CH}_3$  as given by Kinney, and calculating the B. P. N. for both formulas of each hydrocarbon, the characteristic values for the alkyl radicals have been established. The values as presented in Table I differ by 2.8 for all the neighboring members of the series, this being in accordance with the value calculated from Kinney's data for the  $\text{CH}_2$  group. The calculated b. p. n.'s as seen from Table I are somewhat higher

TABLE I

Alkyl radical	B. p. n. calcd. by Kinney	B. p. n. calcd. by the author
$\text{CH}_3$	3.05	3.05
$\text{C}_2\text{H}_5$	5.5	5.85
$\text{C}_3\text{H}_7$	7.0	8.65
$\text{C}_4\text{H}_9$	9.7	11.45
$\text{C}_5\text{H}_{11}$		14.25
$\text{C}_6\text{H}_{13}$		17.05
$\text{C}_7\text{H}_{15}$		19.85
$\text{C}_{10}\text{H}_{21}$		28.25
$\text{C}_{15}\text{H}_{31}$		42.25

than those of Kinney but seem to be more accurate as may be seen from the following examples.