quite definitely that in all cases studied the reaction is faster for the heavy compound.

TIMES OF ONE-HALF REACTION (IN M1N.)			
Catalyst	Temp., °C.	$C_2H_2D_2$	$C_2H_4$
Nickel	+64	13	28
Platinum	-21	12	18
Cobalt	0	2.8	3.5

The columns give the nature of the catalyst, the temperature of the experiment, the time of half reaction for the heavy and light compound.

DEPARTMENT OF CHEMISTRY UNIVERSITY OF LOUVAIN LOUVAIN, BELGIUM

# Some Phenacyl and *p*-Substituted Phenacyl Esters

#### By R. V. LUNDQUIST

Some phenacyl and p-substituted phenacyl esters of organic acids have been prepared for the identification of those acids. They were prepared by the method of Judefind and Reid.<sup>1</sup>

**Heptylic Acid.**—The phenacyl ester was a liquid.

**Dichloroacetic Acid.**—The phenacyl ester was a liquid; the *p*-bromophenacyl ester, observed m. p. 98.2 to 99.3°; the *p*-chlorophenacyl ester, observed m. p. 93.0 to  $93.8^{\circ}$ .

*a***-Bromo-***n***-butyric Acid.**—The phenacyl ester was a liquid; the *p*-phenylphenacyl ester, observed m. p. 103.5 to  $104.0^{\circ}$ .

Acetylsalicylic Acid.—The phenacyl ester, observed m. p. 105.0 to  $105.5^{\circ}$ .

The esters were obtained in excellent yield and the solid esters were purified easily to a constant melting point.

(1) Judefind and Reid, THIS JOURNAL, 42, 1043 (1920).

CONTRIBUTION FROM THE RECEIVED MAY 25, 1938 CHEMISTRY LABORATORY UNIVERSITY OF IDAHO MOSCOW, IDAHO

## Acid Dissociation Constants in Dioxane-Water Mixtures. A Correction of the Dissociation Constant of Benzoic Acid

BY CECIL C. LYNCH AND VICTOR K. LA MER

Professor Martin Kilpatrick and Dr. L. John Minnick of the University of Pennsylvania kindly called our attention to the fact that the dissociation constants of benzoic acid as given in the "International Critical Tables," Vol. VI, p. 279, are in error by a factor of ten and that this had led to an unnecessary restriction of statement in our paper of the above title.<sup>1</sup> When the most recent value for  $25^{\circ}{}^2$  is plotted in our Fig. 8 instead of the erroneous "I. C. T." value ( $6.15 \times 10^{-4}$ ), the anomalous behavior of benzoic acid as compared with acetic, propionic and butyric acids disappears. Log  $K_{\text{benzoic}}$  becomes a linear function of the reciprocal of the dielectric constant between D = 78 and 21, and now conforms closely to the behavior of the three aliphatic acids. In Table III, p. 1257,  $K_{\text{acetic}}$  (D = 34.3) should read 5.62  $\times 10^{-7}$  instead of 5.01  $\times 10^{-7}$  and the second datum for propionic acid (D = 21.0) should read  $5.33 \times 10^{-9}$  instead of 5.30  $\times 10^{-9}$ .

(1) Lynch and La Mer, THIS JOURNAL, 60, 1252 (1938).

(2)  $6.31 \times 10^{-3}$ , Brockman and Kilpatrick, *ibid.*, **56**, 1483 (1934). DEPARTMENT OF CHEMISTRY

COLUMBIA UNIVERSITY

NEW YORK, N. Y.

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### The Hydrolysis of Methyl Iodide

## By Richard A. Ogg, Jr.

The hydrolysis of methyl iodide in pure water<sup>1</sup> has been shown to be kinetically first order with respect to methyl iodide, and unretarded in rate by the resulting hydriodic acid. Essentially similar results have been found by the author in a brief study of methyl iodide hydrolysis in a mixture of equal volumes of anhydrous methanol and water. The solutions (some 0.02-0.08 molar in methyl iodide) were heated in sealed nitrogenfilled tubes. Reaction was followed by titration of the resulting hydriodic acid. The last stages of the reaction were complicated by formation of considerable iodine (Moelwyn-Hughes found only traces)-undoubtedly as a result of the side reaction  $CH_3I + H_3O^+ + I^- \longrightarrow CH_4 + I_2 +$  $H_2O$ . (The solutions containing most iodine gave off inflammable gas on opening the tubes.) Displacement of the equilibrium

$$CH_{3}OH + H_{3}O^{+} + I^{-} \swarrow CH_{8}I + 2H_{2}O$$

to the right by the large concentration of methanol in the solvent explains the importance of the side reaction—as contrasted to the results in pure aqueous solution.

Very good first order rate constants were obtained up to some 60% completion of the reaction (iodine formation then became troublesome). At 100 and 55° the rate constants were found to be, respectively, some  $3 \times 10^{-4}$  (average from (1) E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **A164**, 295 (1938).