

The purple-colored filtrate decomposed and deposited a dark solid which was insoluble in the carbon tetrachloride. The residue could be extracted with chloroform to yield more purple solution, which also decomposed in a few minutes.

It was found possible to add sufficient chlorine to a sample of nickel  $\alpha$ -benzildioxime to dissolve it completely, but this solution was also unstable.

**Hydrolysis of  $\alpha$ -Benzildioximonickelic(III) Bromide.**—Approximately 1 g. of  $\alpha$ -benzildioximonickelic(III) bromide was stirred in 50 ml. of cold concentrated ammonium hydroxide. A maroon-colored compound formed which was somewhat soluble in the ammonia solution. The product was filtered, washed with distilled water, and dried in a desiccator.

The product decomposes slowly to give nickel  $\alpha$ -benzildioxime. It is slightly soluble in dioxane but insoluble in water and in organic liquids such as benzene, carbon tetrachloride, diethyl ether, ethanol and acetone.

**Action of Bromine on Other Nickel-oximes.**—Besides  $\alpha$ -benzildioxime and dimethylglyoxime, other nickel-oxime derivatives were treated with bromine in carbon tetrachloride solution. These include  $\alpha$ -furdioxime, cyclohexanedionedioxime, glyoxalglyoxime, diacetylmono $\alpha$ xime monophenylhydrazide and ethylenediaminebis-diacetyldioxime. The last of these gave a stable bromide and the glyoxalglyoxime gave an unstable derivative. The other compounds were decomposed by the bromine.

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## The *p*-Phenylphenacyl Ester of Phenylacetic Acid

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Drake and Sweeney<sup>1</sup> reported 63° (dec.) as the melting point of the *p*-phenylphenacyl ester of phenylacetic acid. In the course of undergraduate instruction we recently had occasion to prepare this ester and found it to melt at 88.2–88.8° (cor.). Five preparations<sup>2</sup> showed the same melting point.

### Experimental

***p*-Phenylphenacyl Phenylacetate.**—This compound was prepared by the standard method.<sup>3</sup> The light tan crude product was recrystallized three times from ethanol (once with charcoal). The pure white analytical sample melted 88.2–88.8° (cor.) to a completely colorless melt.

*Anal.* Calcd. for C<sub>22</sub>H<sub>18</sub>O<sub>2</sub>: C, 79.98; H, 5.49. Found: C, 79.43; H, 5.60.

(1) N. L. Drake and J. P. Sweeney, *THIS JOURNAL*, **54**, 2059 (1932).

(2) Two of these were performed by Mitó Wheeler and Donald Cranger.

(3) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1947, p. 185.

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## The Dissociation Constant of Hypobromous Acid

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In studying the decomposition of hypochlorite solutions, it is necessary to know the composition of these solutions which depend on the dissociation constants of the acids. Since there is some controversy over this constant in the literature, we have redetermined this constant for hypobromous acid. Shilow and Gladchikova<sup>2</sup> found by electrometric titration that  $K_{\text{HOBr}}$  at 20° =  $2.06 \times 10^{-9}$  and according to the same method,  $K_{\text{HOCl}}$  at 20° =  $3.16 \times 10^{-8}$ . While the latter value is in good agreement with the results of other investigators<sup>3,4</sup> and is also close to the figure obtained by Skrabal and Berger<sup>5</sup> from the kinetics of the hypochlorite decomposition (*viz.*,  $5.6 \times 10^{-8}$  at 25°), the correctness of the above value of  $K_{\text{HOBr}}$  was questioned by Skrabal.<sup>6</sup> He calculated from data on the rate of decomposition of hypobromite depending upon the *pH*, the much lower value of  $2 \times 10^{-11}$  at 25°.

The following method was used for the determination of the dissociation constant of the hypobromous acid: To a hypochlorite solution, kept at a *pH* approximately equal to its *pK*, the equivalent amount of bromide was quickly added and the change of the *pH* was accurately measured by means of a glass electrode. Since, upon the addition of the bromide, all the hypochlorite was converted to hypobromite,<sup>7</sup> the observed  $\Delta pH$  according to the Henderson-Hasselbach formula was in good approximation, equal to the  $\Delta pK$  of hypochlorous and hypobromous acid.

In Table I, the results of a series of experiments are given. In these experiments, the solutions used were prepared by a method previously described.<sup>8</sup> The bromide was added to the hypochlorite solution while the electrodes were immersed in that solution. The final *pH* was established within a few seconds after the addition of the bromide<sup>7,9</sup> and remained constant for more than 15 minutes. The solutions were analyzed for hypochlorite before, and for hypobromite immediately after, the addition of the bromide according to the method already described<sup>8</sup>; no change in the oxidation capacity was found, the hypochlorite being quantitatively converted to hypobromite.

TABLE I

Expt. no.	Total hypochlorite moles/liter	Init. pH	Final pH	$\Delta pH$
9	0.00344	7.21	8.46	1.25
12	.00344	7.46	8.72	1.26
1	.0172	7.54	8.80	1.26
5	.00344	7.57	8.83	1.26
6	.00344	7.73	9.00	1.27
2	.0172	8.09	9.32	1.23

(2) Shilow and Gladchikova, *THIS JOURNAL*, **60**, 490 (1938).

(3) J. W. Ingham and J. Morrison, *J. Chem. Soc.*, 1200 (1933).

(4) Hagiwara, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **19**, 1220 (1940).

(5) A. Skrabal and A. Berger, *Monatsh.*, **70**, 163 (1937).

(6) A. Skrabal, *Z. Elektrochem.*, **48**, 314 (1942).

(7) L. Farkas, M. Lewin and R. Bloch, *THIS JOURNAL*, **71**, 1988 (1949).

(8) L. Farkas and M. Lewin, *Anal. Chem.*, **19**, 662 (1947).

(9) In case the initial *pH* of the hypochlorite solution is below 7 or above 8.2, the observed  $\Delta pH$  is smaller than the above figure.

(1) Research Council of Israel, Hakirya, Israel.