360°, the nicols being crossed. The crystals were bi-axial, section perpendicular to an optical axis; the isogyra was practically straight at rotation of the section. The angle between the optical axis must be nearly 90°; optically +.

Experimental

The aldehydes and the semicarbazones have been prepared by the usual methods. The latter were recrystallized from water and dried in a vacuum desiccator over calcium chloride. A solution of approximately 100 mg. per liter of benzaldehyde semicarbazone was prepared and solutions at different *p*H values were obtained by adding 2 cc. of the above solution in a 25 cc. volumetric flask and filling up with distilled water and acid (HCl, 1 *N*) or base (NaOH, 1 *N*).[5] A similar procedure was used with the *p*-nitro derivative.

Spectral measurements were carried out in a Beckman D. U. Quartz Spectrophotometer, using 1 cm. silica cells.

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[5] The *p*H's were checked with a potentiometer.

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Melting Point of Magnetite–Silica Mixtures in Air

BY L. S. DARKEN

In commenting on my recent paper, "Melting Points of Iron Oxides in Contact with Silica,"[1] one of the referees questioned the value (1442°) reported there for the melting point of magnetite–silica mixtures in air. Such question arises naturally from several statements in the literature. For example, Bowen and Schairer[2] found "no more than a little liquid" formed by heating mixtures of iron oxide and silica to temperatures approaching 1500°, even in a vacuum furnace. Cook[3] observed fusion of magnetite–silica mixtures only near and above 1600°.

An attempt was made to resolve this apparent discrepancy by determining the approximate melting point by a more common method, namely, to prepare an intimate mixture of magnetite and silica by a preliminary fusion and then to determine the melting point of the mixture. Equal weights of magnetite and quartz were mixed by grinding in a mortar to pass a 400-mesh sieve. The mixture was placed in a small (1 ml.) platinum crucible and heated in an air atmosphere in a tubular "Globar" furnace. Starting at 1540° it was held at each of successively higher temperatures for fifteen minutes, being removed and examined in between. This procedure was continued until 1680° (near the limiting temperature of furnace) was reached, at which temperature the charge had sintered only slightly and was easily broken by gentle tapping or probing with a needle.

The failure to obtain a premelt by the above method was somewhat surprising: In order to avoid a large excess of silica another method was tried. A 2-cm. length of clear vitreous silica rod was placed vertically in the crucible and surrounded with magnetite (the same used by Darken and Gurry[4]). This charge was then heated in air to slightly above the melting point of magnetite (1597°) and held there one hour. The molten oxide was thus undoubtedly saturated, or nearly saturated, with silica. The charge was cooled and removed from the crucible; the silica rod and adjacent portions of the melt were discarded.

Having thus obtained a fused intimate mixture of magnetite and silica the melting point was determined as follows: The finely crystalline massive oxide was broken into small pieces about 3 mm. across. One of these pieces was placed in a platinum wire helix[5] and held about ten minutes at a predetermined temperature in an air atmosphere in the furnace. If extensive melting occurred the molten oxide ran down the helix and adhered to the lowest convolution. If no melting occurred the sharp corners and edges of the broken piece were still visible after cooling. From a series of such tests it was found that melting did occur at 1455 ± 5° but did not occur 20° lower. No attempt was made to establish closer limits.

Thus the difficulty in melting the mechanical mixture confirms the reports of Bowen and Schairer and of Cook, whereas the determination of the melting point by remelting confirms roughly the results of my previous investigation which placed the melting point at 1442°.

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[1] L. S. Darken, THIS JOURNAL, **70**, 2046 (1948).

[2] Bowen and Schairer, *Am. J. Sci.*, **24**, 177 (1932).

[3] W. J. Cook, *J. Am. Ceram. Soc.*, **22**, 322 (1938).

[4] Darken and Gurry, THIS JOURNAL, **68**, 798 (1947).

[5] The platinum helix was previously loaded with the oxide and held near 1500° for several hours so that the surface would absorb sufficient iron to be in substantial equilibrium with the melt. This precaution was taken lest the platinum absorb sufficient iron from the test specimen to seriously lower the iron-oxygen ratio to a value below that corresponding to the gas equilibrium.

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Standard Potential of the Mercury–Mercury(I) Phosphate Electrode

BY THOMAS DE VRIES AND DONALD COHEN

A study was made of the mercury–mercury (I) phosphate electrode in phosphoric acid solutions of various concentrations with cells of the type: H_2, H_3PO_4 (*m*), Hg_2HPO_4 (s), Hg. There is very little information in the literature about mercurous phosphate. Gerhardt[1] in 1849 and Haack[2] in 1891 had prepared mercurous orthophosphate by adding a solution of mercurous nitrate to an excess of sodium phosphate solution. They obtained a white or yellow precipitate. Latimer and Hildebrand[3] give the formula of the orthophosphate as $Hg_6(PO_4)_2$.

Experimental

Mercurous Phosphate.—Mercury(I) nitrate was dissolved in water acidified with nitric acid. This solution was slowly added at room temperature to a solution of primary sodium phosphate, NaH_2PO_4, present in excess. A fine white precipitate first formed and gradually changed to a pale yellow or even a deep yellow color. The temperature at which the precipitation was carried out had no effect on the color. Analysis indicated the yellow compound to be the tertiary phosphate, Hg_3PO_4.

Anal. Calcd. for Hg_3PO_4: Hg, 85.21. Found: Hg, 85.41, 85.50.

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[1] Gerhardt, *Jahresber.*, 288 (1849).

[2] Haack, *Ann.*, **262**, 192 (1891).

[3] Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1940.

When mercury(I) nitrate was added to a dilute solution of orthophosphoric acid, a pure white crystalline precipitate was obtained which did not change color. The precipitate was filtered, washed with water and dried in a desiccator over anhydrous calcium chloride.

Anal. Calcd. for Hg_2HPO_4: Hg, 80.71. Found: Hg, 79.2, 80.8.

The various concentrations of phosphoric acid were made by diluting a stock solution which had been prepared from 85% acid and standardized by titration against standard sodium hydroxide using thymolphthalein as indicator.

The platinized platinum electrodes were prepared with the usual care. Several were used and they checked with each other to within 0.3 millivolt. The hydrogen was bubbled through a solution of chromous chloride acidified with acetic acid[4] to remove oxygen, then through a solution of phosphoric acid of the same concentration as that used in the cell. The cell was H-shaped with a sintered glass diaphragm in the horizontal arm. Potentials were measured with a Rubicon, type B, potentiometer at 25 ± 0.05°.

The cells made with the yellow tertiary mercurous phosphate did not give constant or reproducible potentials. In all cases the potential would decrease with time and approach a minimum value. In some cases the yellow phosphate had changed to a white color in the 0.2 *M* phosphoric acid after several days. Typical potentials were 0.7364, 0.7392 and 0.7492 decreasing to 0.7245, 0.7228 and 0.7313 after seven days.

The cells made with the white secondary mercurous phosphate gave fairly constant and reproducible results and equilibrium values were established within one day. For the cell H_2 ($a = 1$), $H_3PO_4(m)$, $Hg_2HPO_4(s)$, Hg, the cell reaction is $H_2 + Hg_2HPO_4 = H^+ + H_2PO_4^- + Hg$, and if the secondary and tertiary ionizations are assumed to be negligible, the potential at 25° is given by the equation $E = E^0 - 0.02957 \log a_{H^+}a_{H_2PO_4^-}$. For $a_{H^+}a_{H_2PO_4^-} = K_1a_{H_3PO_4}$, the value of $K_1 = 7.516 \times 10^{-3}$ was used as reported by Nims.[5] The activities of the undissociated phosphoric acid were taken from the results of Mason and Blum.[6] The calculated molal standard potential of the cell is given in the last column of Table I. The E^0 for the most dilute solution does not agree with the other values. Excluding that value, the average is 0.639 ± 0.002 volt.

An independent calculation for the E^0 of the cell can be made by using the Debye–Hückel limiting law for the mean ion activity coefficient of phosphoric acid and by using the degree of dissociation, α, tabulated by Mason and Blum,[6] to calculate the concentration, m_1, of the hydrogen and the dihydrogen phosphate ion. The previous equation becomes $E^{0\prime} = E + 0.05914 \log \alpha m = E^0 + 0.0301\sqrt{\alpha m}$, using $\log \gamma_{\pm} = -0.5085\sqrt{\mu}$ and $\mu = m_1 = \alpha m$. The results of such a calculation are given in Table II. The average value of 0.638 ± 0.002 for the E^0 of the cell agrees better than one should expect. The molal potential for the electrode Hg, Hg_2HPO_4, $H_2PO_4^-$ is -0.639 ± 0.002 volt at 25°.

TABLE I

POTENTIAL OF CELLS AND CALCULATION OF STANDARD POTENTIAL, E^0, OF THE CELL

m	E		$a_{H_3PO_4}$	$E^0_{298.1}$
0.001026	0.7998	0.7995	0.0001050	0.6191
.01026	.7730	.7750	.004204	.6409
.02052	.7601	.7600	.01223	.6406
.05130	.7433	.7453	.03440	.6382
.1032	.7341	.7336	.08057	.6388
.2071	.7215	.7221	.1776	.6368

TABLE II

STANDARD POTENTIAL CALCULATED FROM DEGREE OF IONIZATION DATA

m	α	E	$E^{0\prime}$	E^0
0.01026	0.599	0.7740	0.6432	0.6400
.02052	.492	.7600	.6421	.6378
.05130	.366	.7443	.6423	.6365
.1032	.290	.7339	.6438	.6365

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(4) Stone and Skavinski, *Ind. Eng. Chem., Anal. Ed.*, **17**, 495 (1945).

(5) Nims, THIS JOURNAL, **56**, 1110 (1934).

(6) Mason and Blum, *ibid.*, **69**, 1246 (1947).

The Ziegler Bromination of Ethyl Tetrolate

BY J. ENGLISH, JR., AND J. DELAFIELD GREGORY[1]

In a recent review article Djerassi[2] commented on the lack of data on the reactions of N-bromosuccinimide with acetylenic compounds. This prompts us to record our observations on the bromination of ethyl tetrolate by this method.

Tetrolic acid was synthesized by the action of carbon dioxide on propynylmagnesium bromide and converted to its ethyl ester in the usual manner.[3] Pure samples of the ester were then dissolved in carbon tetrachloride and treated with N-bromosuccinimide at reflux temperatures, with addition of benzoyl peroxide, under ultraviolet light, without either, and finally in a sealed vessel at 150°. In all cases most of the ester was recovered unchanged. The only product that could be isolated in pure form was ethyl α,β-dibromocrotonate, resulting apparently from the addition of two atoms of bromine at the triple bond.

A somewhat analogous addition reaction accompanying the Ziegler bromination of cyclobutene and methylene cyclobutane has been reported by Buchman and Howton.[4] In the present instance, although no hydrogen bromide was noted, the rather extensive decomposition observed might well have produced some of this substance and hence made bromine available to the reaction mixture as pointed out by these authors.

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(2) C. Djerassi, *Chem. Rev.*, **43**, 296 (1948); see also A. Wohl and K. Jachinowski, *Ber.*, **54**, 476 (1921).

(3) Stolz, communication cited in Beilstein, II, p. 480.

(4) E. R. Buchman and D. R. Howton, THIS JOURNAL, **70**, 2517, 3510 (1948).