prominence of this constituent in the gaseous product.

Details of the temperature effect, which so far indicates a very small temperature coefficient for the photo-decomposition of ketene in hydrogen,[8] as well as the influence of varying concentrations of reactants and the addition of hydrocarbons, are being investigated.

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(8) See also Ross and Kistiakowsky[3] in the absence of hydrogen.

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Potassium Acid Phthalate as a Buffer for Use with the Hydrogen Electrode

BY JOHN RUSSELL AND R. ELIOT STAUFFER

Several investigators[1] have reported in the literature that accurate measurements on 0.05 molar potassium acid phthalate cannot be made with the hydrogen electrode. On the other hand, Clark[2] states that repeated experiments have shown measurements on phthalate buffers to be reliable. Recently, MacInnes and co-workers[3] again have intimated that phthalate solution is unstable and cannot be measured satisfactorily with the hydrogen electrode, especially at 38°.

Our experience in this connection definitely supports Clark's statement, and, since the 0.05 *M* phthalate is so convenient a buffer for use in *p*H standardization, we are submitting the following data as evidence for the stability and reproducibility of hydrogen electrode potentials observed in it. We have used the following type of cell for *p*H measurements in these Laboratories (Pt) H_2; Solution X: 3.5 *N* KCl: 3.5 *N* KCl, satd. Hg_2Cl_2; Hg_2Cl_2; Hg, with 0.05 *M* phthalate as solution X in this cell both at 25 and 40°.

An essential feature in the design of the cell, which we hope to describe in detail later in connection with other studies, is the possibility of creating a very reproducible and constant junction between the potassium chloride bridge solution and solution X. Equally important in the obtaining of consistent and accurate measurements is the elimination of rubber connections in contact with the hydrogen supply or solution X, and the use of hydrogen prepared electrolytically in glass and passed over a hot platinum gauze catalyst in a fused silica tube. As a result, the cell in question has yielded highly reproducible and constant e. m. f. values with phthalate and other buffers. A few of these for phthalate at 40° are given in Table I.

TABLE I

ELECTROMOTIVE FORCE MEASUREMENTS OF POTASSIUM ACID PHTHALATE (0.05 *M*) WITH THE HYDROGEN ELECTRODE AT 40°

Reference half-cell	Phthalate soln.	E. m. f., v.	Date
A	1 X	0.49500	8-28-36
B	2 Y	.49504	9-21-36
B	2 Y	.49503	9-24-36
B	2 Y	.49496	9-28-36
B	3 X	.49503	9-25-36
B	3 X	.49501	9-28-36
C	4 Z	.49494	1-20-37
D	5 X	.49502	5- 5-37
	Average	.49500	

These measurements cover a period of about nine months during which four different calomel half-elements and bridging solutions were prepared, and five different phthalate solutions from three commercial sources of potassium acid phthalate were used. Each value in the table represents an average of values obtained by two or more platinum electrodes whose differences were rarely more than a few hundredths of a millivolt. Table II taken from a typical page of data shows that the e. m f. of the cell using phthalate as solution X remains substantially constant for periods as long as four hours after creating the liquid junction. The junction was formed as soon as the solution reached the temperature of the thermostat (*ca.* fifteen minutes).

TABLE II

CONSTANCY OF HYDROGEN ELECTRODE AND JUNCTION POTENTIALS WITH 0.05 *M* PHTHALATE BUFFER AT 40°

Hours after formation of junction	E. m. f., v.
0	0.49495
0.5	.49501
1	.49504
2	.49505
4	.49506

These data indicate that in our experience 0.05 *M* potassium acid phthalate can be used very satisfactorily as a buffer with the hydrogen elec-

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(1) I. M. Kolthoff and F. Tekelenburg, *Rec. trav. chim. Pays-Bas.*, **46**, 39 (1927); E. T. Oakes and H. M. Salisbury, THIS JOURNAL, **44**, 948 (1922); C. Z. Draves and H. V. Tartar, *ibid.*, **47**, 1226 (1925).

(2) W. Mansfield Clark, "The Determination of Hydrogen Ions," 3rd ed., The Williams and Wilkins Company, Baltimore, Md., 1928, p. 437.

(3) D. A. MacInnes, D. Belcher and T. Shedlovsky, THIS JOURNAL, **60**, 1099 (1938).

trode at temperatures as high as 40° for even the most precise work.

EASTMAN KODAK COMPANY
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The Preparation of *m*-Bromobenzaldehyde

BY FLOYD T. TYSON

For work in progress in this Laboratory it was necessary to prepare *m*-bromobenzalaminoacetal by the interaction of *m*-bromobenzaldehyde with aminoacetal. The *m*-bromobenzaldehyde was prepared by the reduction of *m*-nitrobenzaldehyde by stannous chloride and hydrochloric acid, followed by diazotization and conversion to bromobenzaldehyde by the Sandmeyer method as originally described by Einhorn and Gernsheim[1] and modified by Buck and Ide.[2] In these procedures, no attempt is made to isolate the intermediate *m*-aminobenzaldehyde from admixture with stannic chloride and hydrochloric acid.

Analysis of the *m*-bromobenzalaminoacetal yielded uniformly low results for halogen calculated as bromine and very high results for carbon and hydrogen. These analytical values were in accord with the assumption that much of the chloro compound was present with the bromo compound.

The *m*-bromobenzaldehyde used for the preparation of the impure *m*-bromobenzalaminoacetal was analyzed for halogen and the halogen calculated as bromine. The analytical values obtained were in agreement with the theoretical values for bromobenzaldehyde. However, analyses of the *m*-bromobenzaldehyde preparations for both chlorine and bromine proved the presence of both chlorine and bromine. The amounts of chlorine indicated a percentage of chlorobenzaldehyde ranging from 20 to 72 depending upon details of procedure.

Since *m*-nitrobenzaldehyde should be a convenient source for the preparation of pure *m*-bromobenzaldehyde, a procedure has been devised which will be published elsewhere, in which the presence of chlorides in the reaction mixture was avoided.

Experimental

The following table summarizes data obtained in the analysis of products resulting from the attempted preparation of pure *m*-bromobenzaldehyde from *m*-nitrobenzaldehyde as described in the literature. The preparations analyzed were fractionated; b. p. 92–97° (6 mm.).

TABLE I

Prepn.	Analyses, % Cl	Analyses, % Br	Calcd. % chlorobenzaldehyde present
1	18.17	11.86[3]	72.0
	18.31	11.57[4]	
2	5.11	34.50[3]	20.3
3	6.78	31.58[3]	26.9

Preparation No. 1 was made as described by Buck and Ide.[2] Preparation No. 2 was made as No. 1 except that the hydrobromic acid was added to the cuprous bromide mixture before mixing with the diazotized solution. Preparation No. 3 was made as described by Einhorn and Gernsheim.[1]

The analytical results reported in the following table were calculated on the erroneous assumption that the mixtures of silver chloride and bromide actually obtained in the analyses of preparations No. 1, 2 and 3 (Table I) were pure silver bromide. The satisfactory agreement with the values for *m*-bromobenzaldehyde may explain the fact that the preparations as recorded in the literature[1,2] were reported as essentially pure.

TABLE II

Prepn.	% Br found as assumed	% Br calcd. for *m*-bromobenzaldehyde
1	43.12	43.19
2	43.18	
3	43.25	

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[1] Einhorn and Gernsheim, *Ann.*, **284**, 141 (1894).

[2] Buck and Ide, *Org. Syntheses*, **13**, 30 (1933).

[3] Analyses made by the method of displacement of bromine from weighed silver chloride and bromide by chlorine as described in "Quantitative Analysis of Inorganic Materials," by N. Hackney, J. B. Lippincott, Philadelphia.

[4] Analysis made by the method of Baubigny [*Compt. rend.*, **136**, 1197 (1903)] as described by Hackney.[4]

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The Optical Rotation of a Grignard Reagent

BY FRANK C. WHITMORE AND BENJAMIN R. HARRIMAN

Frequent use is made of the Grignard reaction in preparing optically active compounds from optically active halogen compounds, but not to our knowledge has the rotation of an optically active Grignard reagent been measured previously. Porter[1] observed a very small rotation in an ethereal solution of methyl-*n*-hexylmagnesium

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[1] Porter, THIS JOURNAL, **57**, 1436 (1935).