Our work, together with that of Newman and Smith, suggests the following order of reactivity of groups toward phenylmagnesium bromide at $-70°$: $\text{-CH=O} > \text{-NO}_2 > \text{-COOCH}_3$

Experimental[3]

Phenylmagnesium bromide prepared from 35.3 g. (0.195 mole) of redistilled bromobenzene and 6.5 g. of magnesium turnings in 100 ml. of dry ether was added dropwise over a period of 5 hours to 12.5 g. (0.069 mole) of methyl *p*-nitrobenzoate, m.p. 95–96°, in 175 ml. of dry toluene and 40 ml. of dry ether. The reaction mixture was continuously agitated and maintained at −70° under a nitrogen atmosphere. The product was hydrolyzed at −70° by addition of 30 ml. of saturated aqueous ammonium chloride. After removal of the solvent the product was dissolved in 200 ml. of ether, washed with 10% sulfuric acid, 10% sodium carbonate and water. It was then dried over calcium chloride and passed through a separatory funnel containing 300 g. of activated alumina (Harshaw A1-0109P) with 500 ml. of ether. Evaporation of the solvent followed by recrystallization from hexane produced 5 g. (45%) of brown crystals, m.p. 106–112°. Recrystallization from 95% methanol raised the m.p. to 114–116°. Purification by chromatography on an alumina column (with benzene as the eluant) gave white crystals of *p*-carbomethoxydiphenylamine, m.p. 115.8–116.5° (lit.[4] 115°). The structure was confirmed by infrared analysis (ester carbonyl at 1720 cm.$^{-1}$) and by hydrolysis with 2% sodium hydroxide in quantitative yield to *p*-carboxydiphenylamine which had m.p. 159.3–159.8° (lit.[4] 156°) after recrystallization from a benzene–hexane mixture.

---

(3) Melting points are corrected. We are indebted to Miss Helen Miklas for the infrared spectrum.

(4) H. Gilman and G. E. Brown, THIS JOURNAL, **62**, 3208 (1940).

NOYES CHEMICAL LABORATORY
THE UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

The Half-Wave Potential of Lithium

BY WALTER E. CLARK

RECEIVED JULY 27, 1953

An accurate determination of the half-wave potential of aqueous lithium ion recently has been made in this Laboratory. When the dropping electrode assembly is carefully damped to eliminate all vibration, it is possible to obtain a regular, well-defined lithium wave having the theoretical slope for a one-electron reversible reduction. The point of inflection corresponding to $E_{1/2}$ is not sharply defined, however, since $E_{1/2}$ could not be accurately determined by means of Muller's oscillographic technique.[1] As expected, the half-wave potential was found to be independent of concentration, of mercury height, and of the capillary employed. The average experimental value of the half-wave potential, corrected for cell resistance, was found to be -2.331 ± 0.003 v. *vs.* the S.C.E.

$E_{1/2}$ for the anodic wave obtained by using dilute (approx. 1×10^{-3} *M*) lithium amalgam as the dropping electrode agreed approximately with the value obtained by conventional electrolysis. Very accurate data could not be obtained from the dropping amalgam electrode due to frequent plugging of the capillary.

Even with the utmost precautions it was not possible to obtain a constant value for $i_d/Cm^{2/3}t^{1/6}$ at any concentration. The polarographic waves were well-defined except that when the concentration of lithium was greater than about 2×10^{-3} *M* the diffusion current became increasingly ill-defined; below about 1×10^{-4} *M* the residual current of the supporting electrolyte became inconveniently large compared to the height of the lithium wave.

Experimental

The polarograph employed was the high sensitivity visual recording instrument described by Kelley and Miller.[2] The supporting electrolyte was 0.1 *M* tetra-*n*-butylammonium hydroxide obtained by diluting the 1 *M* product supplied commercially by Southwestern Analytical Chemicals, Austin, Texas. The discharge potential of this electrolyte is about −2.8 v. *vs.* the S.C.E. which makes it preferable to the corresponding tetraethyl or tetramethyl compound. Occasionally a wave was observed in the supporting electrolyte which appeared to be due to some impurity as reported by Zlotowski and Kolthoff.[3] In 0.1 *M* solution this wave was usually negligible and in any event its effect was eliminated by determining the residual current before adding the lithium compound. The latter was hydroxide from a specially purified stock solution.

Half-wave values were determined from the plot of *E vs.* log $i/i_d - i$, which allows the $E_{1/2}$ value to be read to a precision greater than the accuracy of the experimental data. The limiting factor in the accuracy of the method appears to be the determination of the diffusion current. It was found advantageous to employ an undamped circuit in this determination.

The values of *E* used in the log plots were determined in the conventional way by interpolation on the polarogram between points the potentials of which were accurately determined with a potentiometer. In the course of the investigation several different calomel electrodes were employed. These were checked against each other prior to making a run and the maximum variation observed was 0.2 millivolt.

The polarographic cell employed was of the "H" type described by Lingane and Laitinen.[4] Instead of housing the reference anode in the second arm of the cell, this arm was filled with a solution of the supporting electrolyte and used as a salt bridge to make connection with a separate calomel electrode. As further insurance against diffusion of potassium ion into the polarographic cell, an agar plug containing 0.1 *M* tetra-*n*-butylammonium chloride was inserted next to the fritted disc in the salt bridge arm of the cell. The cell was immersed in a water-bath thermostatically controlled to a temperature of 25 ± 0.1°.

The author wishes to acknowledge his indebtedness to Dr. W. B. Schaap and to Dr. D. J. Fisher for helpful suggestions on experimental technique and on instrumentation, respectively.

---

(1) R. H. Muller, R. L. Garman, M. E. Droz and J. Petras, *Ind. Eng. Chem., Anal. Ed.*, **10**, 339 (1938).

(2) M. T. Kelley and H. H. Miller, *Anal. Chem.*, **24**, 1895 (1952).

(3) I. Zlotowski and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 473 (1942).

(4) J. J. Lingane and H. A. Laitinen, *ibid.*, **11**, 504 (1939).

MATERIALS CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

The Leuckart Reaction of Some 1,5-Diketones

BY FRANCIS CHUBB, ALLAN S. HAY AND REUBEN B. SANDIN

RECEIVED JULY 20, 1953

In an attempt to prepare some 1,5-diamines it was decided to examine the behavior of some 1,5-diketones toward the ammonium formate–formamide reagent, described by Ingersoll and co-workers in their investigation of the Leuckart reaction.[1]

---

(1) A. W. Ingersoll, J. H. Brown, C. K. Kim, W. D. Beauchamp and G. Jennings, THIS JOURNAL, **58**, 1808 (1936).