vapor we made two different types of measurements. In the first we measured the sorption of HCl gas on a $Na_2SO_4 \cdot 10H_2O$–Na_2SO_4 mixture in the absence of protein.[11] We found in these experiments that the decahydrate reacted stoichiometrically and irreversibly at 25° with HCl and the sorption curves could be interpreted as corresponding to the consecutive reactions[12]

$$HCl(g) + Na_2SO_4 \cdot 10H_2O(s) \longrightarrow NaCl(s) + NaHSO_4(s) + 10H_2O(g) \quad (1)$$

$$HCl(g) + NaHSO_4(s) \longrightarrow NaCl \cdot H_2SO_4 \text{ (solid solution)} \quad (2)$$

The first reaction occurs at constant pressure indicating the formation of a new phase, while the second takes place with rising pressure indicating solid solution. The region of constant-pressure sorption is very close to the pressure observed by C. and S. and it seems reasonable to thus interpret their results as arising from the reaction of HCl with the decahydrate rather than with the protein. This conclusion is not certain since C. and S. nowhere state their experimental method explicitly.

In order to then check further we performed an experiment in which the gelatin was first allowed to come to equilibrium with a constant vapor pressure of water. The side arm with decahydrate was then closed off and the sorption of HCl measured directly on this sample. The results of this experiment were similar to those found in the absence of H_2O and showed none of the characteristics reported by C. and S.

While the above experiments do not explain all of the features of the sorption processes observed by C. and S., in particular the results obtained with CO_2 and H_2S (similar to HCl) or the lengths of the isobars (with all gases) they do indicate that their results with HCl and gelatin are inconsistent with results obtained in these and other laboratories, and they indicate a probable source of the anomalies: namely, the reaction of HCl with the $Na_2SO_4 \cdot 10H_2O$–Na_2SO_4 mixtures introduced into the system to maintain constant vapor pressure of water.

[11] These experiments were done by weighing the sample *in situ* using as a balance a helical quartz spring.

[12] The H_2O in reaction 1 may be displaced as a vapor as indicated or may under some conditions be partially bound in the form of hydrates of the NaCl and/or $NaHSO_4$.

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Dielectric Measurement of Heptacosafluorotributylamine

BY FIELDING BROWN

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The dielectric constant and loss tangent of heptacosafluorotributylamine, $C_{12}F_{27}N$, has been measured over the temperature range of 140 to −52°. The measurements were carried out at frequencies of 60 cycles, 1000 cycles, 15 kc., 30 kc., 60 kc. and 100 kc., and the results are shown in the accompanying graph.

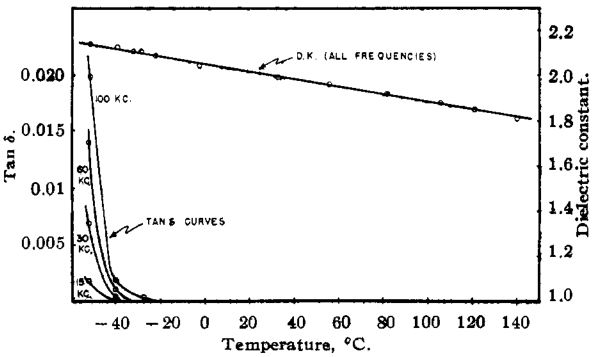

Fig. 1.—Dielectric properties of $C_{12}F_{27}N$.

The liquid was measured in a cell originally described by Horsch and Berberich[1] and the values of capacity and power factor were determined by means of a General Radio 716-C bridge using generators and detectors appropriate to the frequencies in question. A General Radio 716-P2 guard circuit also was employed to balance the guard ring of the measuring cell.

The points on the dielectric constant curve are accurate to ±4% and those of the tan δ curve to ±0.00007. As can be seen, the losses in the liquid are extremely small above −20° but rise sharply below that temperature. The values shown on the graph are further in approximate agreement with those given earlier.[2] Unfortunately it was not possible to carry the measurements low enough in temperature to calculate the electric moment of the molecule. Various members of this laboratory have assisted in performing the measurements.

[1] W. G. Horsch and L. J. Berberich, *Rev. Sci. Instr.*, **5**, 194 (1934).

[2] Technical Report No. 57, Laboratory for Insulation Research, M. I. T.

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Reaction of Methyl *p*-Nitrobenzoate with Phenylmagnesium Bromide

BY DAVID Y. CURTIN AND JAMES C. KAUER

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Phenylmagnesium bromide has been shown to react readily with nitrobenzene to give diphenylamine as the principal product.[1]

$$4C_6H_5MgBr + C_6H_5NO_2 \longrightarrow (C_6H_5)_2NH + C_6H_5C_6H_5 + C_6H_5OH$$

Newman and Smith,[2] however, have found that at −70° the reaction of *m*-nitrobenzaldehyde with phenylmagnesium bromide occurs preferentially at the carbonyl group to give *m*-nitrobenzhydrol in 77% yield.

In connection with other work, we have had occasion to examine the reaction of phenylmagnesium bromide with methyl *p*-nitrobenzoate at −70° and found it leads to *p*-carbomethoxydiphenylamine in a yield of 45% (based on Grignard reagent). None of the product to be expected from reaction at the ester carbonyl could be isolated.

[1] H. Gilman and R. McCracken, THIS JOURNAL, **51**, 821 (1929).

[2] M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948).

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.

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(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).

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The Half-Wave Potential of Lithium

BY WALTER E. CLARK

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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.

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(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).

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The Leuckart Reaction of Some 1,5-Diketones

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

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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]

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