alcohol and propionyl chloride in the presence of dimethylaniline, essentially according to the procedure of Norris and Rigby[5] for the preparation of *t*-butyl acetate.

Anal.[4] Calcd. for $C_7H_{14}O_2$: C, 64.6; H, 10.84. Found: C, 65.1; H, 11.20.

t-Butyl propionate (107 cc., 92 g., 0.708 mole) was added to sodium triphenylmethyl[2] (1700 cc., 0.708 mole), the color being discharged within thirty seconds, and after two minutes 86 cc. (83.5 g., 0.708 mole) of ethyl carbonate was added. Stirring was continued for one and one-half hours longer. Glacial acetic acid (60 cc.) was added and the mixture worked up. After distilling off the solvent the residue gave 55.2 g. of a mixture (b. p. 35–77° at 40 mm.) of *t*-butyl propionate and ethyl carbonate, and 66.2 g. of material (b. p. 77° at 40 mm. to 150° at 12 mm.). Redistillation of the latter fraction through a twelve-inch Vigreux column at 14 mm., yielded 13.0 g. of a fore-fraction (b. p. 49–94°) and 48.7 g. (72% yield based on the sodium triphenylmethyl) of ethyl *t*-butyl-α-methylmalonate (b. p. 94–95°).

Anal.[4] Calcd. for $C_{10}H_{18}O_4$: C, 59.4; H, 8.97. Found: C, 60.0; H, 9.10.

Diethyl *t*-Butylmalonate.—Ethyl *t*-butyl acetate (38.2 g., 0.266 mole) prepared by the method of Homeyer, Whitmore and Wallingford,[6] was added with shaking to an ether solution of 0.266 mole of sodium triphenylmethyl and, after standing for ten minutes, 31.4 g. (0.266 mole) of ethyl carbonate was added. After twenty-four hours the reaction mixture was acidified with dilute acetic acid, the ether solution dried and the solvent distilled. The residue yielded 30 g. of recovered esters (b. p. 67–78° at 100 mm.) and 13.3 g. (47%) of diethyl *t*-butylmalonate (b. p. 102–104° at 11 mm.).

Anal.[7] Calcd. for $C_{11}H_{20}O_4$: C, 61.10; H, 9.32. Found: C, 61.24; H, 9.20.

Summary

The anions of ethyl *t*-butyl acetate, *t*-butyl acetate and *t*-butyl propionate (prepared by means of sodium triphenylmethyl) have been acylated with ethyl carbonate to form, respectively, diethyl *t*-butylmalonate and the "mixed" malonic esters, ethyl *t*-butylmalonate and ethyl *t*-butyl-α-methylmalonate.

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[5] Norris and Rigby, THIS JOURNAL, **54**, 2097 (1932).

[6] Homeyer, Whitmore, and Wallingford, *ibid.*, **55**, 4209 (1933).

[7] Analysis by William Saschek, 630 W. 168 St., New York, N. Y.

DURHAM, N. C.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A Study of the Products Obtained by the Reducing Action of Metals upon Salts in Liquid Ammonia Solution. VIII. The Reduction of Complex Cyanides

BY JOHN W. EASTES AND WAYLAND M. BURGESS[1]

Introduction

The unusual result obtained by the action of alkali metals on the complex cyanides of nickel in liquid ammonia solution,[2] as contrasted to that obtained through the use of simple nickel salts,[3] prompted the examination of the behavior of the complex cyanides of other metals, some of whose simple salts are also known to give the free metal when reduced by alkali metals in liquid ammonia solution. For this purpose the complex cyanides of cadmium, copper, silver and zinc were chosen. Also the action of calcium on potassium cyanonickelate was investigated. The reactions were carried out as described in previous articles.[2]

Preparation of Complex Cyanides

The complex potassium cyanides of silver, copper and zinc were prepared in the way previously described for the nickel compound.[2] All were markedly more soluble in hot than cold water. Inasmuch as cadmium cyanide is soluble in water, the complex cyanide was prepared by crystallization from a solution containing the stoichiometric quantities of cadmium sulfate and potassium cyanide. The product was recrystallized until free of sulfate ion and then dried at 110°.

All of these complex cyanides were very soluble in liquid ammonia, giving clear colorless solutions.

Potassium Cyanocadmiumate, $K_2Cd(CN)_4$, and Potassium.—Pieces of potassium, when added to a liquid ammonia solution of potassium cyanocadmiumate (in excess), slowly react in such a way that each piece is replaced by a clump of metallic cadmium. No hydrogen gas is given off during the reaction. The black metallic cadmium is not reactive with water, but is highly pyrophoric.

Potassium Cyanocopperate, $K_3Cu(CN)_4$, and Potassium.—Potassium, when added to a solution of potassium cyanocopperate in liquid ammonia, reacts to give a finely divided black precipitate of pyrophoric copper. At the instant the solution turns blue, due to reaction of all of the complex cyanide and solution of the excess potassium, a beautiful copper mirror forms on the surface of the reaction tube in contact with the solution.

Potassium Cyanosilverate, $KAg(CN)_2$, and Potassium.—When pieces of potassium are added to a liquid ammonia

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by John W. Eastes in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1936.

[2] Eastes and Burgess, THIS JOURNAL, **64**, 1187 (1942).

[3] Burgess and Eastes, *ibid.*, **63**, 2674 (1941).

solution of potassium cyanosilverate, each piece reacts slowly to be replaced by a clump of black pyrophoric silver. Only a trace of hydrogen gas is given off before the solution becomes blue with excess potassium after reaction of all the complex cyanide. Thereafter hydrogen is very, very slowly given off until the blue color of the dissolved potassium disappears. Thus the clumps of silver are very poor catalysts for the formation of potassium amide and hydrogen. The silver was not reactive with water.

Potassium Cyanozincate, $K_2Zn(CN_4)$, and Sodium.—Sodium reacts rapidly with a liquid ammonia solution of potassium cyanozincate to give a finely divided precipitate of metallic zinc. This precipitate is not reactive with water nor is it pyrophoric. No hydrogen gas is given off during its formation nor after the solution has become blue with excess sodium. Thus the precipitate is not a catalyst for the amide formation. At the instant the solution becomes blue with excess sodium, a beautiful silvery mirror is formed on the walls of the reaction tube exposed to the solution. This mirror was not reactive with water.

The formation of zinc instead of $NaZn_4$ is comparable to the case wherein Burgess and Rose[4] observed the formation of metallic zinc by reaction of sodium with a 20% excess of zinc cyanide.

Potassium Cyanonickelate, $K_2Ni(CN)_4$, and Calcium.—Calcium, when added to a solution of potassium cyanonickelate in liquid ammonia, gives the same type of reaction as does sodium and potassium,[2] but with the difference that hydrogen gas is given off throughout the course of the reaction. The insoluble reaction products are soluble in water to give the characteristic red solutions.

Summary

Unlike that of nickel, the complex cyanides of cadmium, copper, silver and zinc are reduced to the free metal by alkali metals in liquid ammonia solutions. Under the conditions used all of the precipitated metals but zinc were pyrophoric.

Calcium, in liquid ammonia solution, reduces alkali metal cyanonickelates to give the same type of products as obtained by reduction with alkali metals

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[4] Burgess and Rose, THIS JOURNAL, **51**, 2127 (1929).

[COMMUNICATION NO. 871 FROM THE KODAK RESEARCH LABORATORIES]

The Viscosity of Dilute Solutions of Long-Chain Molecules. IV. Dependence on Concentration[1]

BY MAURICE L. HUGGINS

In the first[2] and second[3] papers of this series an equation was derived for the specific viscosity (η_{sp}) of dilute solutions of randomly-kinked chain compounds. At the limit of infinite dilution this equation reduces to

$$\left(\frac{\eta_{sp}}{c}\right)_{c=0} = \frac{\eta-\eta_0}{\eta_0} = K_0 + K_n n = K_0 + K_M M \quad (1)$$

where η and η_0 are the viscosities of the solution and of the pure solvent, c is the concentration in submoles per liter (or any units proportional to these), n is the number of submolecules per molecule, M is the molecular weight, and K_0, K_n and K_M are constants.

In deriving this expression, Stokes' law

$$\text{Force} = 6\pi\eta a u \quad (2)$$

was assumed in computing the frictional force acting on each submolecule as a result of its velocity (u) relative to the liquid immediately surrounding it. The insertion of η_0 for η in (2) leads to the limiting Equation (1) just given. If, instead, one inserts into (2) the value of the viscosity of the *solution*

$$\eta = \eta_0(1 + \eta_{sp}) \quad (3)$$

the expression

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0}(1 + \eta_{sp}) \quad (4)$$

is obtained.[4]

For small concentrations, (4) is equivalent to

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c=0} + \left(\frac{\eta_{sp}}{c}\right)^2_{c=0} c \quad (5)$$

At first sight, it might seem that this should give the initial variation of η_{sp}/c with concentration. The application of Equation (2) to the solutions under discussion is, however, very questionable. Strictly speaking, this equation would be applicable only if each submolecule were isolated from all others, so that the liquid streaming past one

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[1] Presented before the Division of Colloid Chemistry at the Buffalo Meeting of the American Chemical Society, Sept. 9, 1942. Some of the material contained herein was previously presented at the Symposium on "Viscosity, Molecular Size and Molecular Shape," held under the sponsorship of the Society of Rheology at the Polytechnic Institute of Brooklyn on Feb. 20, 1942.

[2] M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938).

[3] M. L. Huggins, *ibid.*, **43**, 439 (1939).

[4] This is equivalent to Eq. (25) of ref. 2 and, except for the Einstein term in the numerator, to Eqs. (123) and (126) of ref. 3. If Einstein's derivation (which also depends on (2)) is similarly modified, to make it applicable to solutions of finite concentration, by the use of η instead of η_0 for the frictional coefficient in Stokes' law, Eqs. (123) and (126) of ref. 3 also become equivalent (as regards the concentration dependence) to (4) above.