Anal. Calcd. for $C_5H_9NO_5$: C, 41.14; sapn. equiv., 88.6. Found: C, 41.75; sapn. equiv., 86.8.

Polymerization of 2-Nitratoethyl Esters.—A 1-g. sample of 2-nitratoethyl methacrylate and 10 mg. of benzoyl peroxide on heating in a watch glass at 100° for twenty minutes gave a hard polymer. This compound also polymerized to a hard polymer after standing at 25° for a few days in the absence of a catalyst. 2-Nitratoethyl acrylate, 1 g., and 10 mg. of benzoyl peroxide on heating at 100° for one hour gave a soft, tacky polymer. The 2-nitratoethyl crotonate did not polymerize under these conditions.

Reaction with Alkali.—Mixtures of weighed samples of the 2-nitratoethyl esters (0.3 g.) and a measured excess of 0.1 *N* aqueous sodium hydroxide were shaken until they became homogeneous (5 minutes). Back-titration with standard hydrochloric acid gave for the equivalent weight for 2-nitratoethyl acrylate 164 (calcd. for one equivalent per molecular weight 161.2), for 2-nitratoethyl methacrylate 179 (calcd. 175.3), for 2-nitratoethyl crotonate 179 (calcd. 175.3) and for 2-nitratoethanol *ca.* 600 (calcd. 107.2).

The cleavage that occurred here was indicated to be that of the nitratoalkyl group from the unsaturated acid. A sample of 2.4 g. of 2-nitratoethyl crotonate was shaken with 2 g. of sodium hydroxide in 50 cc. of water until the mixture became homogeneous. Ethereal extracts of the solution on distillation gave 0.7 g. of 2-nitratoethanol, b. p. 95° (8 mm.), $n^{25}D$ 1.4366 and the saponification equivalent determined in the manner given below was 111 (calcd. 107).

Saponification equivalents for the three esters were determined in the following manner. A 0.3-g. sample was added to 25 ml. of 0.2 *N* alcoholic potassium hydroxide and the mixture refluxed for thirty minutes. Back-titration with standard acid gave the following equivalent weights: for 2-nitratoethyl acrylate, 80.5 (calcd. for two equivalents per molecular weight, 80.6), for 2-nitratoethyl methacrylate 88.4 (calcd. 88.5), for 2-nitratoethyl crotonate 86.8 (calcd. 88.5) and for 2-nitratoethanol 111 (calcd. 107).

A sample of 0.3 g. of 2-nitratoethyl crotonate was soluble on addition to 25 ml. of 0.2 *N* alcoholic potassium hydroxide. After standing for five minutes the solution was back-titrated with standard hydrochloric acid to give an equivalent weight of *ca.* 600. The experiment repeated with 2-nitratoethyl acrylate gave an equivalent weight of *ca.* 600.

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Some Properties of Pure γ-Butyrolactone

BY CLYDE MCKINLEY AND JOSEPH P. COPES

A highly purified sample of γ-butyrolactone has been prepared[1] and certain of its physical properties determined. Vapor pressures, using an isoteniscope, were determined and are presented in the table. Freezing point was determined using apparatus patterned after that in use by the National Bureau of Standards[2] and T_{f_0} was found to be −43.53°[3] by Mr. L. J. Lohr of this Laboratory. The refractive index, using an Abbe refractometer, was $n^{25}D$ 1.4348 and the density, using a pycnometer, was found as d^{25}_4 1.1254.

P, mm.	Temp., °C.
50.1	119
79.4	132
125.9	145
199.6	159
316.3	174
501.2	189
708.0	201
760 (extrap.)	204 (extrap.)

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[1] For method see PB 60902.

[2] Research paper 1937.

[3] Calculations as in Bureau of Standards Technical Paper No, 1596, Research paper 1676.

Dipositive Silver as an Intermediate in Coulometric Analysis

BY DALE J. MEIER AND ERNEST H. SWIFT

Electrolytically generated bromine has been shown to be a satisfactory intermediate oxidant in coulometric titrations of arsenic(III), antimony(III) and thiodiglycol.[1] At the concentration of bromine and bromide ion existing in these titrations the use of bromine as the intermediate is limited by equilibrium considerations to the determination of reductants with half-cell potentials (Red. = Ox. + e^-) more positive than approximately −0.78 v. This value is obtained by assuming that the final approximate concentrations of bromide and tribromide were 10^{-1} and 10^{-6} *M*, respectively, and that the final ratio of $M_{ox.}$ to $M_{red.}$ was 1000. The negative limit of the oxidation potential can be extended somewhat by the use of chlorine as the intermediate, and Farrington and Swift[2] have described the use of chlorine for the determination of arsenic(III). In an effort to further extend the permissible negative limit of the half-cell potential of the reductant being determined, and also to find non-halide intermediates, we have investigated dipositive silver as an intermediate oxidant for coulometric titrations. The Ag(I)–Ag(II) formal potential has been determined by Noyes and his co-workers to be −1.98 v. in perchloric acid solutions.[3,4]

It has long been known that higher oxidation states of silver can be obtained by anodic oxidation, and although solid compounds can be precipitated which contain silver in a tripositive state, Noyes and his co-workers[5] have shown in

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[1] R. Myers and E. H. Swift, THIS JOURNAL, **70**, 1047 (1948); R. A. Brown and E. H. Swift, *ibid.*, **71**, 2717 (1949); J. W. Sease, C. Niemann and E. H. Swift, *Ind. Eng. Chem., Anal. Ed.*, **19**, 197 (1947).

[2] P. S. Farrington and E. H. Swift, *Anal. Chem.*, **22**, 889 (1950).

[3] A. A. Noyes, D. DeVault, C. D. Coryell and T. J. Deahl, THIS JOURNAL, **59**, 1326 (1937).

[4] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 181.

[5] A. A. Noyes, J. L. Hoard and K. S. Pitzer, THIS JOURNAL, **57**, 1221 (1935); A. A. Noyes, K. S. Pitzer and C. L. Dunn, *ibid.*, **57**, 1229 (1935); A. A. Noyes and A. Kossiakoff, *ibid.*, **57**, 1238 (1935).

several ways that in nitric acid solutions the oxidized silver is, within their experimental error, completely in the dipositive state. The concentration of dipositive silver in our solutions did not exceed 10^{-4} formal, which is much below its known solubility in similar solutions. Several requirements have to be met in order for the argentous–argentic system to be useful in secondary coulometric titrations. First, the current efficiency for the production of dipositive silver would have to be 100%; second, the rate of oxidation of reductants would have to be rapid, and, third, in order for an amperometric end-point to be used, the Ag(I)–Ag(II) couple would have to be reversible at the indicator electrodes.

Experiments were carried out with the apparatus described by Meier, Myers and Swift.[6] Argentic silver was anodically generated both in silver perchlorate solutions 1 to 6 formal in perchloric acid and in silver nitrate solutions 1 to 10 formal in nitric acid and it was found that the couple setup on the smooth platinum indicator electrodes was reversible, in that indicator currents were observed. It appeared that the anodic oxidation occurred with nearly 100% current efficiency, since after a brief initial delay period, the plot of the indicator current *vs.* generation time was linear.

Noyes, Coryell, Stitt and Kossiakoff[7] found that the rate of reduction of dipositive silver by water varied inversely with the concentration of nitric acid, and followed the rate law $\frac{-\mathrm{d}[\mathrm{Ag(II)}]}{\mathrm{d}t} = k_2 \frac{[\mathrm{Ag(II)}]^2}{[\mathrm{Ag(I)}]} + k_4 \frac{[\mathrm{Ag(II)}]^4}{[\mathrm{Ag(I)}]}$, with the second order term predominating at low dipositive silver concentrations. However, we found that if the indicator current was assumed to be proportional to the dipositive silver concentration, the rate of decomposition was first order with respect to the dipositive silver, and was many orders of magnitude faster than that observed by Noyes, *et al.* It can be shown that if the indicator current is proportional to any power of the dipositive silver concentration the observed first order decay ($\mathrm{d}i/\mathrm{d}t = ki$) of the indicator current requires the reduction of the dipositive silver to be first order. We also observed that the rate of decomposition varied directly as the acid concentration. These facts indicated that the mechanism of decomposition was different from that reported by Noyes, *et al.* We suspected that the decomposition was catalyzed by the platinum electrodes in the cell, and this was shown to be true by varying the electrode surface area; the rate of decomposition was directly proportional to the surface area of the platinum. This also explained the first order dependence on the dipositive silver concentration, in that the rate of decomposition was proportional to the rate at which the dipositive silver diffused to the platinum surface, and this rate was proportional to the concentration of dipositive silver in the cell.

In addition to the fairly rapid decomposition, another difficulty was encountered when it was found that an indicator current was not observable until after approximately four or five seconds of generation. At first it was thought that this was due to impurities in the solution which were being oxidized, but this was shown to be not true by varying the concentrations of the reagents, and also by generating a large amount of dipositive silver in the solution and then allowing it to decompose overnight. When this solution was again anodically oxidized, the same delay in obtaining an indicator current was noticed. The cause of this initial delay is uncertain. The period of delay was not constant, which would introduce a large uncertainty in the end-point corrections when using this system as a means of analysis.

Noyes, Hoard and Pitzer[5] reported that argentic silver solutions rapidly oxidized such substances as Mn(II), Cr(III), As(III) and Ce(III). However, we found that the rates of oxidation of all reducing agents tried, including Mn(II), As(III) and Ce(III), were much too slow to enable the coulometric method to be developed, since large indicating currents were observed before the equivalence point. The slow rates of oxidation were observed in both nitric and perchloric acid solutions of widely varied concentrations. This apparent anomaly is attributed to the extremely large Ag(I)/Ag(II) ratio in our solutions which would give a very low concentration of Ag(III) which was postulated to be the kinetically active specie by Noyes, Coryell, Stitt and Kossiakoff.[7]

The slow rate of oxidation of the above species, the variation in the initial delay of the indicator current, and the fairly rapid decomposition of the dipositive silver by water caused discontinuance of further work on the use of dipositive silver as a coulometric intermediate.

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[6] D. J. Meier, R. Myers and E. H. Swift, THIS JOURNAL, **71**, 2340 (1949).

[7] A. A. Noyes, C. D. Coryell, F. Stitt and A. Kossiakoff, *ibid.*, **59**, 1316 (1937).

An Improved Synthesis of 10-Thiaxanthenol

BY H. F. OEHLSCHLAEGER[1] AND IAN R. MACGREGOR

10-Thiaxanthenol is a somewhat unstable compound which has been prepared by reduction of thiaxanthone with zinc dust and alcoholic sodium hydroxide[2] or potassium hydroxide.[3,4] Hilditch and Smiles[5] reported erratic results, an impure

[1] Laws Fellow 1949–1950, University of Cincinnati.

[2] Werner, *Ber.*, **34**, 3310 (1901).

[3] Mayer, *ibid.*, **42**, 1133 (1909).

[4] Finzi, *Gazz. chim. ital.*, **62**, 211–218 (1932).

[5] Hilditch and Smiles, *J. Chem. Soc.*, **99**, 145 (1911).