[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Anodic Oxidation of Aluminum in Liquid Ammonia[1]

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In the electrolysis, between an aluminum anode and a platinum cathode, of a variety of electrolytes in liquid ammonia solutions, initial valence numbers lower than 3 for aluminum are not observed except when nitrate ion is present in the electrolyte. In simple nitrate media the apparent initial valence number of aluminum is in the neighborhood of 2.7, with little dependence on the nature of the cation. In nitrate–halide mixtures, the initial valence number is found to vary regularly with the ratio of concentrations of nitrate and halide, a minimum value close to 1.5 being found for mixtures containing about 2 moles of nitrate to 1 of bromide. These results show no dependence upon anodic current density, nor upon change in total concentration of the solutes, so long as the nitrate–halide ratio remains constant. No compound of lower valent aluminum could be isolated from the product of electrolysis. Evidence has been presented in support of the hypothesis that such aluminum is oxidized by nitrate ion to the tripositive state, the nitrate being reduced to elementary nitrogen.

In a recent communication from this Laboratory[2] on the anodic oxidation of the elements of the aluminum family in anhydrous acetic acid solutions, it was demonstrated that, on the basis of Faraday's law, the mean oxidation state of the cations formed when aluminum was used as anode in an electrolyte of ammonium or sodium acetate, was *always* appreciably lower than 3. In most instances, the anolyte showed but little reducing power upon termination of electrolysis; and, although considerable amounts of hydrogen were liberated from the solution, presumably as a result of the secondary reduction of acetic acid, it was not possible to account quantitatively for the oxidation of the lower valent species of aluminum.

The present paper deals with the behavior of aluminum as anode in a variety of electrolytes in liquid ammonia solution. Ammonia was chosen as solvent because of the possibility of isolation, in a medium so stable toward reduction, of any compound of lower valent aluminum which might be formed. It appears to be a somewhat unfortunate circumstance—although probably not a fortuitous one—that, in the work herein described, low initial valence numbers were observed only when the electrolyte contained the readily reducible nitrate ion.

Experimental

Materials.—The aluminum used as anode was of 99.996% purity, and was obtained from the Aluminum Company of America[3] in the form of rods 0.63 cm. in diameter. The cathode consisted of a strip of bright platinum, approximately 10 sq. cm. in area. The electrolytes were C.P. products which were carefully freed of water before use, in some cases by conversion to ammoniates. The nitrogen employed to provide an inert atmosphere was dried by successive passage through drying towers containing sodium hydroxide, calcium chloride and magnesium perchlorate. Since the presence of traces of oxygen was found not to affect the results, no precautions were taken for the removal of this substance. The liquid ammonia was taken directly from commercial cylinders of the anhydrous substance.

Apparatus and General Procedure.—The source of direct current was a full-wave rectifier, the voltage output of which could be controlled to deliver any desired voltage from 0 to 750 by means of a potential divider located at the alternating current input. The quantity of electricity passed through the circuit was determined by means of a silver coulometer. The simple electrolytic cell employed in the earlier expts. has been described in a previous communication.[4] A second type of cell will be discussed later.

Prior to each electrolysis, the aluminum anode was cleaned with concentrated sodium hydroxide solution, rinsed with distilled water, dried in an oven, and weighed. The electrolyte was weighed and placed in the thoroughly dried cell; dry nitrogen was passed through the system until all oxygen and traces of moisture had been removed. The cell was then placed in a cooling bath consisting of a Dry Ice–isopropyl alcohol mixture, and about 60 ml. of ammonia was condensed in it. Solution of the electrolyte was hastened either by permitting the ammonia to boil or by the use of a magnetic stirrer. The cell was then connected in series with the current source, the silver coulometer, and an ammeter. After electrolysis, the anode was thoroughly cleaned with distilled water, dried in an oven, and weighed.

Before its application with an aluminum anode, the experimental procedure was checked by the determination of the valence number attained in the anodic oxidation of zinc, since it was to be expected that in this case only the dipositive ion would be formed. The electrolyte used was a liquid ammonia solution of tetrammine zinc nitrate. This salt was prepared by bubbling ammonia through a saturated aqueous solution of the hydrate until the precipitate initially formed had dissolved; treatment of the resulting cooled solution with ethanol gave a precipitate of the ammoniate. In five electrolyses with a zinc anode, the calculated valence number deviated from the expected value of 2 by only about 2%.

In the experiments with aluminum as anode, the apparent initial valence number, V_i, of the aluminum ion formed was calculated by means of the equation

$$V_i = \frac{\text{wt. of Ag deposited in coulometer} \times 26.97}{107.88 \times \text{wt. of Al lost from anode}}$$

Results of Electrolysis in Simple Electrolytes.—In the oxidation of aluminum at −33° in solutions of simple electrolytes, valence numbers close to 3 (±3%) were obtained with cupric bromide, ammonium bromide, aluminum iodide,[5] aluminum acetylacetonate, sodium thiocyanate and potassium iodate; in these media, then, the aluminum is apparently oxidized solely to the tripositive state. Abnormally high apparent valence numbers, indicative of the phenomenon of passivity, were calculated for electrolyses with ammonium acetate, ammonium salicylate, sodium nitrite, sodium cyanide and potassium permanganate; here, anodic reactions other than the dissolution of aluminum must be taking place.

Data for solutions of several nitrates are summarized in Table I.

Thus, of all the simple electrolytes tested, only in the case of nitrates were valence numbers appreciably lower than 3 attained. The values all fell

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[1] From part of a thesis submitted by William E. Bennett in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Kansas, 1951.

[2] A. W. Davidson and F. Jirik, THIS JOURNAL, **72**, 1700 (1950).

[3] The authors hereby express their appreciation for this courtesy.

[4] A. D. McElroy, J. Kleinberg and A. W. Davidson, THIS JOURNAL, **72**, 5178 (1950).

[5] In the electrolyses with aluminum iodide as electrolyte, the formation of blue solutions of metallic aluminum at the cathode was observed. This phenomenon was investigated further, and has been the subject of a recent report from this Laboratory (*cf.* ref. 4).

TABLE I

ANODIC OXIDATION OF ALUMINUM IN NITRATE SOLUTIONS

Electrolyte	Initial concentration, g./l.	Time, hr.	Current density amp./cm.^{2}	V_i
$Cu(NO_3)_2$	10	3	0.01	2.71[a]
$Cu(NO_3)_2$	10	3	.02	2.68
$Cu(NO_3)_2$	10	$1^{1}/_{2}$	.03	2.62
$Zn(NO_3)_2$	7	$2^{1}/_{2}$	.008	2.85
$Zn(NO_3)_2$	17	3	.01	2.66
$Al(NO_3)_3$	17	1	.03	2.73
NH_4NO_3	50	$1^{1}/_{2}$	.01	2.71

[a] The values obtained with $Cu(NO_3)_2$ as electrolyte are not in accord with that of del Boca (*Helv. Chim. Acta*, 16, 565 (1933)), who found in a single expt. an initial valence number for aluminum of 1.48.

in the neighborhood of 2.7, with little apparent dependence upon the nature of the cation.

Electrolysis in Mixed Electrolytes

From the results just given, it was apparent that the presence of nitrate ion was the determining factor in bringing about the dissolution of aluminum in amounts larger than would be predicted according to the hypothesis of a uniformly tripositive aluminum ion. It therefore promised to be of interest to determine to what extent this property of nitrate ion would persist in mixtures of nitrates with salts containing other anions. Accordingly, preliminary expts. were carried out in the simple cell previously described, on electrolytes consisting of nitrate–halide mixtures.

Preliminary Experiments.—In the first of such experiments, the solute consisted of a mixture of cupric nitrate and cupric bromide. It was ascertained that a 5-g. sample of aluminum, on immersion for an hour in 20 ml. of a solution containing 0.2 g. of each of the cupric salts, underwent no detectable decrease in weight. On electrolysis, however, in a mixture of the two salts at a total concentration of about 17 g. per liter, the surprising result was an initial valence number of only 1.55—a value considerably *lower* than had been found with any single salt as electrolyte.

A series of electrolyses was next undertaken with various sodium nitrate–sodium halide mixtures. Initial valence numbers lower than 3 were obtained in mixtures containing either chloride or bromide, but not in those containing iodide. In the nitrate–bromide mixtures, a minimum V_i value of 1.43 was found for a solution of about 0.3 molar total concentration, containing 3 moles of nitrate to 1 of bromide. In the nitrate–chloride mixtures, the minimum value found was 1.63, for a 0.4 molar solution containing nitrate and chloride in about a 4:3 ratio.

In all of these experiments, the original nitrate–halide ratio was subject to distortion in the course of electrolysis, due to electrode reactions to be described later. In order to minimize this effect by the use of a relatively large volume of electrolytic solution, as well as to facilitate the separate study of anodic and cathodic processes, most of the subsequent expts. were carried out in a 180-ml. cell, the anode and cathode of which were separated by a sintered Pyrex disk. This cell, together with the gas burets and scrubbers used for the collection and washing of the effluent gases, is illustrated in Fig. 1.

Results of Electrolysis in the Divided Cell.—The data for a number of electrolyses carried out in the cell just mentioned with sodium bromide–sodium nitrate mixtures are given in Table II, while Table III shows the results of a similar series with ammonium bromide–ammonium nitrate mixtures. In each case, it was shown that aluminum was not attacked, in the absence of electrolysis, by the mixed electrolyte.

TABLE II

ANODIC OXIDATION OF ALUMINUM IN $NaNO_3$–NaBr MIXTURES

Mole of $NaNO_3$	Mole of NaBr	Mole % NaBr in solute	Time, hr.	Current density, amp./cm.^{2}	V_i
0.00647	0.00287	30.4	$^{3}/_{4}$	0.02	1.63
.00636	.00301	32.2	$^{3}/_{4}$	.02	1.63
.00646	.00327	33.6	$^{3}/_{4}$	.02	1.51
.00630	.00340	35.1	$^{3}/_{4}$	.02	1.49
.00624	.00373	37.4	$^{3}/_{4}$	.02	1.53
.00588	.00419	41.6	$^{3}/_{4}$	.02	1.58
.00531	.00571	51.8	$^{3}/_{4}$	.05	1.78
.02400	.01986	45.3	$2^{3}/_{4}$	.007	1.61
.02367	.01623	41.4	$6^{1}/_{2}$	.008	1.58
.02498	.01400	36.0	5	.015	1.49

TABLE III

ANODIC OXIDATION OF ALUMINUM IN NH_4NO_3–NH_4Br MIXTURES

Mole of NH_4NO_3	Mole of NH_4Br	Mole % NH_4Br in solute	Current density, amp./cm.^{2}	V_i
0	0.0633	100	0.01	2.94
0.0217	.0360	61.4	.01	1.94
.0286	.0298	51.2	.01	1.77
.0296	.0262	45.3	.01	1.65
.0358	.0228	39.8	.01	1.56
.0363	.0212	37.0	.01	1.52
.1250	.0614	33.0	.01	1.54
.0606	.0266	31.6	.015	1.53
.0375	.0160	30.0	.002	1.52
.0325	.0124	27.6	.002	1.58
.0465	.0115	19.9	.01	2.27
.1000	0	0	.01	2.71

In Fig. 2, typical data on sodium chloride–nitrate, sodium bromide–nitrate and ammonium bromide–nitrate mixtures are plotted on a single diagram. It is evident that the general trend of the data is independent of the identity both of the cation and of the halide; it is the halide–nitrate ratio that appears to be the significant factor. It appears further that a minimum valence number of about 1.5, which corresponds to a ratio of 3 unipositive aluminum ions to 1 tripositive ion, is obtained for mixtures containing approximately 2 moles of nitrate to 1 of halide. No satisfactory explanation of this phenomenon is as yet available.

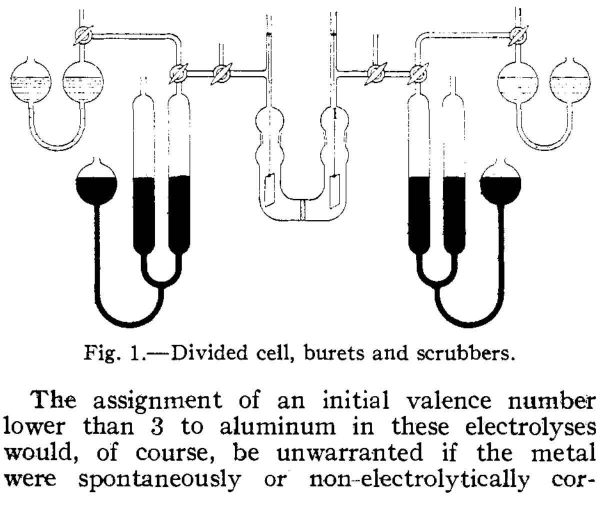

Fig. 1.—Divided cell, burets and scrubbers.

The assignment of an initial valence number lower than 3 to aluminum in these electrolyses would, of course, be unwarranted if the metal were spontaneously or non-electrolytically cor-

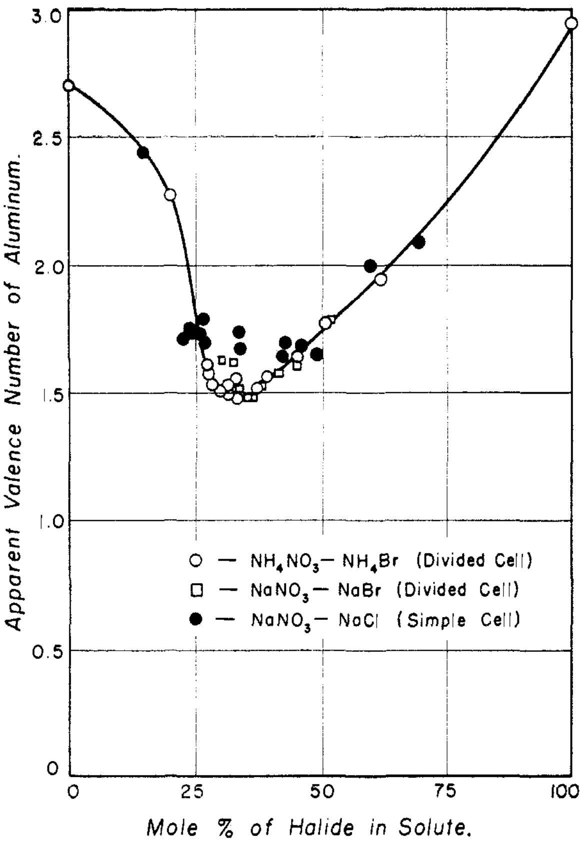

Fig. 2.—Variation of V_i with composition of electrolyte.

roded either by the original electrolyte or by some product of electrolysis. As has already been stated, the original mixtures were found to be without action upon test strips of aluminum. In order to investigate the possible effects of products of electrolysis, the following additional tests were carried out.

In a simple cell with an ammonium bromide–ammonium nitrate mixture (about 33 mole % bromide) as electrolyte, an aluminum rod was used as *cathode*. Although the usual low initial valence number was obtained by anodic oxidation, the cathode underwent no detectable loss in weight during the electrolysis.

In two electrolyses with the same bromide–nitrate mixture as electrolyte, the rectifier was modified in such a manner as to yield an intermittent direct current; *i.e.*, current flowed for periods of $^1/_{120}$ second, separated by $^1/_{120}$ second intervals. The aluminum anode was thus exposed to the possibility of non-electrolytic corrosion for half the duration of the electrolysis. Yet the initial valence numbers, 1.57 and 1.59, were essentially the same as when a continuous current was used with the same electrolyte.

Products of Electrolysis in Ammonium Nitrate–Ammonium Bromide Mixtures

Gaseous Products.—When the amount of gas evolved during electrolysis was to be measured, the cell was maintained, before electrolysis was started, at a known constant temperature until the gaseous contents had become saturated with ammonia; the gas in the cell and the attached mercury burets was then brought to atmospheric pressure. After completion of the electrolysis, the system was again equilibrated to atmospheric pressure, and the temperature was adjusted to the same point as before. The gas from each compartment of the cell was washed free of ammonia in the scrubber, and the residual volume was measured in the corresponding buret. The hydrogen content of each sample was then determined from the volume change which took place upon combustion, initiated by a platinum filament in air or oxygen. The gas remaining after combustion and removal of the water vapor was taken to be nitrogen.

In order to recover any gas which may have been dissolved in the liquid ammonia, as well as gas liberated by secondary reactions, the solution after electrolysis was evaporated to dryness, the gaseous ammonia was absorbed in dilute sulfuric acid, and the residual gases were analyzed for hydrogen and nitrogen as before.

These analyses showed the following results: (1) no trace of oxides of nitrogen could be detected; (2) the quantity of hydrogen obtained from the cathode compartment was somewhat less than that calculated from coulometric data, on the assumption of hydrogen liberation as the sole cathode reaction; (3) appreciable quantities of nitrogen were found in the gas from both compartments.

Solid and Dissolved Products. Cathode.—There was always formed at or near the cathode a black finely divided deposit, in an amount which increased with increasing cathodic current density and with decreasing concentration of electrolyte. On analysis, this substance proved to be metallic platinum. The origin of this deposit, *i.e.*, whether from mechanical disintegration or from a cathode reaction, remains unknown; however, since no loss in weight of the cathode greater than 0.00006 gram-atom of platinum was ever observed, this need not be regarded as a quantitatively significant cathode process.

Nevertheless, the deficiency in the amount of cathodic hydrogen clearly indicated a competing cathode reaction, probably involving the reduction of nitrate. Since no more than a trace of nitrite ion could be found in the catholyte after electrolysis, it may be concluded that the reduction product was free nitrogen.

Anode.—In all of the electrolyses, a white to gray deposit, usually non-adherent, was formed at the anode. Analysis of this deposit showed it to contain from 17 to 24% of aluminum and about 10% of bromide. Upon treatment with sodium hydroxide solution, ammonia was evolved to the extent of about 23% of the weight of the original sample. Nitrate ion, and a trace of nitrite, were found to be present also. The deposit, then, was obviously a mixture, to which no simple formula can be assigned.

In view of the low initial valence number indicated by the coulometric data, it was to be expected that either a strong reducing agent, or a product of reduction of the electrolyte or of the solvent, would be found in the anode deposit, the anolyte, or the gas evolved from the anode compartment. Yet neither the solid nor the dissolved anode products reduced iodine solution. Only a small amount of hydrogen was present in the anode gas, and no hydrogen was evolved when the solid was treated with sodium hydroxide solution. Furthermore, since no reduction was observed when the gases evolved during electrolysis were passed through Tollens reagent, it was concluded that neither hydrazine nor hydroxylamine was present.

Reduction of Nitrate.—The only remaining possibility appeared to be that at least a portion of the nitrogen evolved must have been a product of the reduction of nitrate by the lower valent aluminum ion formed in electrolysis. In order to test this hypothesis, experiments were carried out to determine the amount of nitrate ion lost from the entire solution during electrolysis. For this purpose, the method given by Furman[6] was used for the determination of nitrate ion; this consists essentially in the reduction of nitrate with an excess of standard ferrous ammonium sulfate solution, followed by titration of the excess ferrous ion with potassium dichromate solution.

Qualitative experiments showed that considerable reduction of nitrate did indeed occur during electrolysis. In order to determine, however, whether or not such loss corresponded to the expected reducing power of the lower valent alumi-

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(6) N. H. Furman, "Scott's Standard Methods of Chemical Analysis," 5th edition, Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1936, p. 644.

num, it was necessary to take into consideration the fact that some reduction of nitrate to nitrogen undoubtedly occurred at the cathode. A quantitative check of the hypothesis of reduction by lower valent aluminum was made in the following manner.

The postulated reactions occurring at the electrodes are

$$\text{Cathode}\quad \begin{aligned} &2NH_4^+ + 2e^- = 2NH_3 + H_2 \\ &2NO_3^- + 12NH_4^+ + 10e^- = N_2 + 12NH_3 + 6H_2O \end{aligned}$$

$$\text{Anode}\quad \begin{aligned} &Al = Al^{+++} + 3e^- \\ &Al = Al^+ + e^- \\ &5Al^+ + 2NO_3^- + 12NH_4^+ = 5Al^{+++} + N_2 + 12NH_3 + 6H_2O \end{aligned}$$

Since all of the aluminum dissolved is eventually oxidized to the tripositive state, and since this oxidation is accompanied either by the liberation of hydrogen or by the reduction of nitrate to nitrogen, we may write the equation

$$\text{g.-atoms of Al dissolved} = \frac{(5 \times \text{moles of } NO_3^- \text{ lost}) + \text{equiv. of } H_2}{3}$$

from which it follows that

$$\text{moles of } NO_3^- \text{ lost} = \frac{3 \times \text{g.-atoms of Al dissolved} - \text{equiv. of } H_2}{5}$$

Three quantitative experiments designed to test the foregoing hypothesis were carried out in a simple cell of 25-ml. capacity. The results are given in Table IV.

TABLE IV

REDUCTION OF NITRATE DURING ELECTROLYSIS

(A)	Faraday	0.003783	0.004460	0.003593
(B)	G.-atom of Al dissolved	.001928	.002080	.002002
(C)	V_i, from (A) and (B)	1.96	2.14	1.79
(D)	Equiv. of H_2 evolved	0.002513	0.002560	0.001955
(E)	Mole of NO_3^- reduced (calcd. from (B) and (D))	.000654	.000736	0.000810
(F)	Mole of NO_3^- lost (from NO_3^- analysis)	.000641	.000751	.000773

The agreement between the calculated quantity of nitrate reduced (E) and the observed loss of nitrate (F) is in accord with our assumptions as to the course of both the primary electrode reactions and the secondary reduction of nitrate by incompletely oxidized aluminum ion.

Another possible means of testing the hypothesis is by comparison of the calculated quantity of nitrogen produced by the reduction of nitrate with the amount observed to be evolved. This method, however, is considerably less accurate than the preceding one, since the small volume of nitrogen can be determined only as the difference between the total volume of gas evolved and the volume of hydrogen as determined by combustion. The equation that may be used for such a calculation is

$$\text{moles of } N_2 \text{ evolved} = \frac{3 \times \text{g.-atoms of Al dissolved} - \text{equiv. of } H_2}{10}$$

Two experiments, the first carried out in a 60-ml. divided cell, the second in the 25-ml. simple cell, gave the results shown in Table V.

TABLE V

LIBERATION OF NITROGEN FROM REDUCTION OF NITRATE

(A)	Faraday	0.004917	0.002573
(B)	G-atom of Al dissolved	.003235	.001354
(C)	V_i, from (A) and (B)	1.52	1.90
(D)	Equiv. of H_2 evolved	0.00424	0.00245
(E)	Mole of N_2 (calcd. from (B) and (D))	.000547	.00161
(F)	Mole of N_2 evolved	.000478	.00165

These results again support the hypothesis of nitrate reduction to nitrogen as a primary cathodic and a secondary anodic reaction.

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