20 ml. of water had been used. Finally, refluxing was continued for an additional hour.

Recovery of Products.[2]—For the isolation of the reduction products, different procedures were found to be necessary: (a) In those preparations in which the product was soluble in benzene and was isolated as the hydrochloride, the reaction mixture was freed of iron by filtration, and dry hydrogen chloride was passed through the benzene solution; the insoluble hydrochloride precipitated and was collected by filtration. (b) In other instances where the amine which was formed in the course of the reduction was soluble in benzene, the reaction mixture was filtered while still hot, and the iron residue was extracted three times with hot benzene. The extracts were combined with the original filtrate. The crude free amine was obtained by removal of the benzene by distillation, and purification was effected by recrystallization from a suitable solvent. (c) With one amine which was insoluble in benzene, the solvent was removed from the reaction mixture by distillation from a steam-bath, the desired product was extracted from the residue with hot methanol, and the iron compounds which were dissolved by the hot solvent were removed by precipitation with hydrogen sulfide. Purification was accomplished by recrystallization.

Identifications of Products.—Identifications of the reaction products were made by means of melting points of: (a) the free amines, (b) the acetyl derivatives, or (c) the hydrochlorides.

Results.—The results which were obtained when various nitro compounds—a number of them bifunctional in character—were reduced by the method outlined above are summarized in Table I.

Summary

Seventeen nitro compounds were reduced by the use of activated iron, and products were obtained, for the most part, in good yields. In contrast to methods involving more severe conditions, there was no evidence of undesired introduction into or removal from the amines of halogen. Preliminary results suggested the possible use of this method for the reduction of esters of nitro substituted acids and similar compounds which would be subject to hydrolysis if reduced in acidic or basic aqueous media; this end was realized in several cases.

Pullman, Washington Received June 26, 1944

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[2] Any deviations from these general procedures are indicated as notes to Table I.

[Contribution from the School of Chemistry of the University of Minnesota]

A New Method for the Polarographic Determination of Nitrate

By I. M. Kolthoff, W. E. Harris and G. Matsuyama

The reduction of nitrate at the dropping mercury electrode in the presence of various cations has been studied by Tokuoka and Ruzicka.[1,2] They observed that in the presence of a large excess of lanthanum, the diffusion current of nitrate was proportional to the nitrate concentration. Scott and Bambach[3] applied these results to the determination of nitrate in blood and urine. It is found, in this Laboratory, that the proportionality holds only over a narrow range of nitrate concentrations.

One of the authors, in his work on the polarography of uranium, observed the reduction of nitrate at the dropping mercury electrode in the presence of small amounts of uranyl ion. The nitrate wave appears at a more positive potential and is more normal in appearance than that observed in the presence of lanthanum. Furthermore, this wave is subject to less interference by other anions.

A method for determining small amounts of nitrate, based on its reduction in the presence of uranyl ion, with some observations on the nitrate wave obtained in the presence of lanthanum are described in this paper.

Experimental

Qualitative observations were made with a Heyrovsky Type VIII Polarograph, and quantitative measurements, with a manual apparatus[4] at 25°. All chemicals used were of "reagent quality," and conductivity water was used in the preparation of all solutions.

Comparison of the Nitrate Waves in the Presence of Lanthanum and of Uranyl Ions.—The nitrate wave in the presence of lanthanum is peculiar in the abruptness at which the current increases at the start of the wave, and in the irregularities and large oscillations in the current at the rising and limiting portions of the wave. These irregularities are largely eliminated by adding a trace of the sodium salt of methyl red to the solution. The half-wave potential varies between −1.3 and −1.5 volt against the saturated calomel electrode (hereafter abbreviated to S.C.E.) with variations in the concentrations of lanthanum and nitrate. When the wave is determined backward, *i. e.*, by gradually decreasing a large negative applied potential, the wave does not coincide with that found by gradually increasing the potential (see Fig. 1).

In moderate concentrations of hydrochloric acid (0.001 to 0.1 *N*), uranyl chloride gives two reduction waves at the dropping mercury electrode (see curve 2, Fig. 2). The first wave of uranium corresponds to a reduction to pentavalent uranium while the second corresponds to the two consecutive reductions of pentavalent uranium to tetravalent and trivalent uranium.

When the solution contains some nitrate in

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[1] M. Tokuoka, *Coll. Czechoslov. Chem. Commun.*, **4**, 444 (1932).

[2] M. Tokuoka and J. Ruzicka, *ibid.*, **6**, 339 (1934).

[3] E. W. Scott and K. Bambach, *Ind. Eng. Chem., Anal. Ed.*, **14**, 136 (1942).

[4] I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

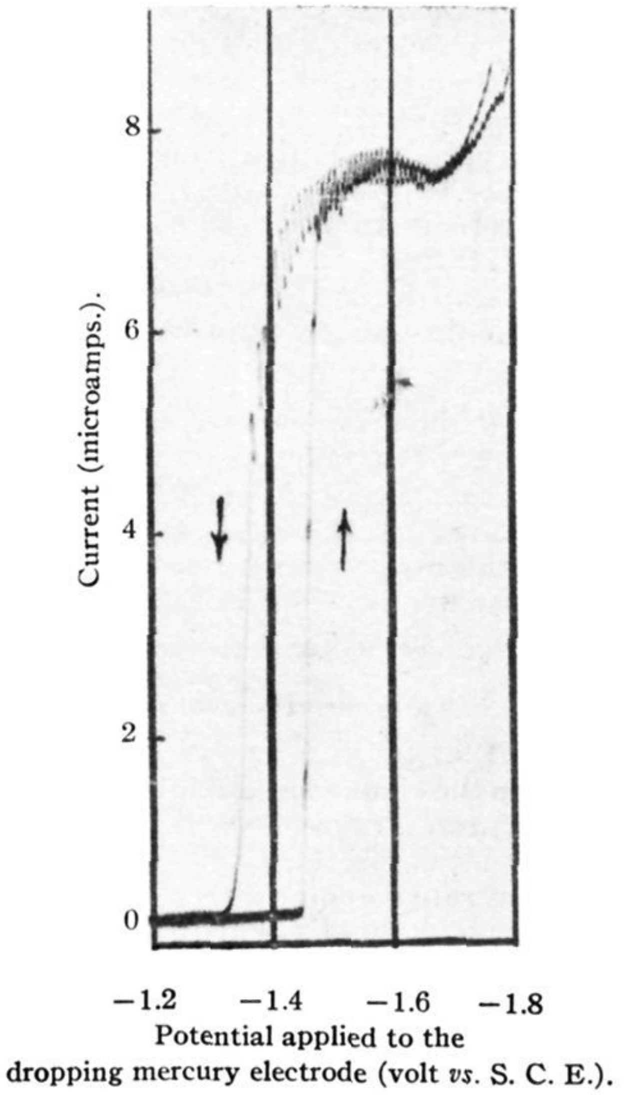

Fig. 1.—Polarogram of a solution which is 2×10^{-4} M in potassium nitrate and 10^{-2} M in lanthanum chloride, showing the difference in the curve obtained by gradually increasing the applied potential and that obtained by gradually decreasing the applied potential.

addition to the uranyl, the nitrate is reduced at potentials where the second uranium wave occurs. The half-wave potential of the nitrate wave is around −1.0 volt (*vs.* S. C. E.) using as the supporting electrolyte a solution which is 0.1 M in potassium chloride, 0.01 M in hydrochloric acid, and 2×10^{-4} M in uranyl chloride. The half-wave potential varies with the nitrate concentration as shown in Table I.

TABLE I

VARIATION OF THE NITRATE HALF-WAVE POTENTIAL WITH NITRATE CONCENTRATION

0.1 M in KCl, 0.01 M in HCl, and 2.00×10^{-4} M in UO_2Cl_2.

Concn. of nitrate, moles/liter	Half-wave potential, volt *vs.* S. C. E.
4.00×10^{-5}	−0.91
1.00×10^{-4}	− .90
2.00×10^{-4}	− .95
4.00×10^{-4}	− .98

Application of the Nitrate Diffusion Current to the Determination of Nitrate.—Tokuoka and Ruzicka[1,2] reported that the height of the limiting current due to the reduction of nitrate was not attained until the equivalent concentration of lanthanum was around 50 times that of nitrate. Using 0.01 M lanthanum chloride solutions containing varying amounts of nitrate, we find that the diffusion current for nitrate is not proportional to the nitrate concentration except within a narrow range of concentrations, even if the equivalent concentration ratio of lanthanum to nitrate is kept greater than 50 (see Table II). The quotient $i_d/[NO_3^-]$ increases through a maximum and then decreases with increasing nitrate concentrations. The deviation is greater than is desirable for an accurate quantitative determination of nitrate.

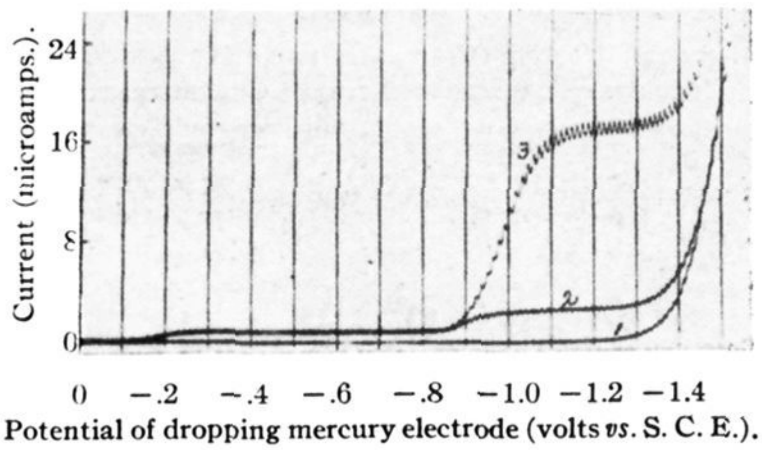

Fig. 2.—Polarograms in 0.01 M hydrochloric acid, 0.1 M potassium chloride: (1) 4×10^{-4} M potassium nitrate; (2) 2×10^{-4} M uranyl chloride; (3) 4×10^{-4} M potassium nitrate, 2×10^{-4} M uranyl chloride.

TABLE II

DIFFUSION CURRENT OF NITRATE IN THE PRESENCE OF LANTHANUM AS A FUNCTION OF THE NITRATE CONCENTRATION

($m^{2/3}t^{1/6}$ of the capillary = 1.742 mg.$^{2/3}$sec.$^{-1/2}$, residual current = 0.26 micro amp. at −1.6 v. *vs.* S. C. E. *Concentration of lanthanum* = 1.00×10^{-2} molar.)

Concn. of nitrate, moles/liter	Nitrate diffusion current, microamp.	$k = i_d/[NO_3^-]$ microamp./millimole/liter
2.00×10^{-5}	0.52	26.0
3.98×10^{-5}	1.06	26.6
8.19×10^{-5}	2.26	27.6
1.21×10^{-4}	3.28	27.1
1.59×10^{-4}	3.96	24.9
2.35×10^{-4}	5.46	23.2
4.75×10^{-4}	10.18	21.4

With uranyl as an "activator" in the reduction of nitrate, it is possible to obtain a satisfactory proportionality between the nitrate concentration and the diffusion current when the ratio of uranyl to nitrate is above a certain minimum. With greater amounts of uranyl, the proportionality still holds, but the "residual" current due to the reduction of the uranyl ion increases, making measurements of the nitrate diffusion current less accurate. With amounts of uranyl less than the minimum, the nitrate diffusion current ceases to be proportional to the nitrate concentration. The minimum concentrations of uranyl are given for a few nitrate concentrations in Table III. Table IV shows the extent to which

TABLE III

MINIMUM URANYL CONCENTRATIONS AT WHICH i_d IS PROPORTIONAL TO THE NITRATE CONCENTRATION

Nitrate ion concn., moles/liter	Minimum uranyl ion concn. moles/liter
1.00×10^{-5}	2.00×10^{-5}
1.00×10^{-4}	1.00×10^{-4}
5.00×10^{-4}	2.00×10^{-4}

TABLE IV

DIFFUSION CURRENT OF NITRATE AGAINST CONCENTRATION OF NITRATE

Solutions containing 0.1 M KCl, 0.01 M HCl, and 2.00×10^{-4} M UO_2Cl_2 at the dropping mercury electrode; $\pi = -1.2$ volt *vs.* S. C. E.; $m^{2/3}t^{1/6} = 2.58$ mg.$^{2/3}$sec.$^{-1/2}$ at -1.2 volt; $t = 25.0°$; residual current at -1.2 volt = 2.94 microamperes.

Concn. of nitrate, moles/liter	Diffusion current of nitrate, microamperes	$K = i_d/C$ microamp./millimole/liter
7.9×10^{-6}	0.32	(40)
1.004×10^{-5}	.36	(36)
2.002×10^{-5}	.61	(31)
2.71×10^{-5}	1.06	39
4.00×10^{-5}	1.42	35.6
4.75×10^{-5}	1.74	36.6
6.004×10^{-5}	2.13	35.5
7.22×10^{-5}	2.54	35.2
8.00×10^{-5}	2.86	35.7
2.002×10^{-4}	7.14	35.7
3.00×10^{-4}	10.84	36.1
4.00×10^{-4}	14.4	36.0
5.00×10^{-4}	17.6	35.2
8.00×10^{-4}	26.2	32.8
2.00×10^{-3}	48.6	24.3
8.00×10^{-3}	82.6	10.3

the proportionality of the nitrate diffusion current to the nitrate concentration holds for solutions which are 0.1 M in potassium chloride, 0.01 M in hydrochloric acid, and 2.00×10^{-4} M in uranyl chloride and which contain varying amounts of potassium nitrate. Under these conditions, the optimum nitrate concentration range is 5×10^{-5} to 4×10^{-4} molar.

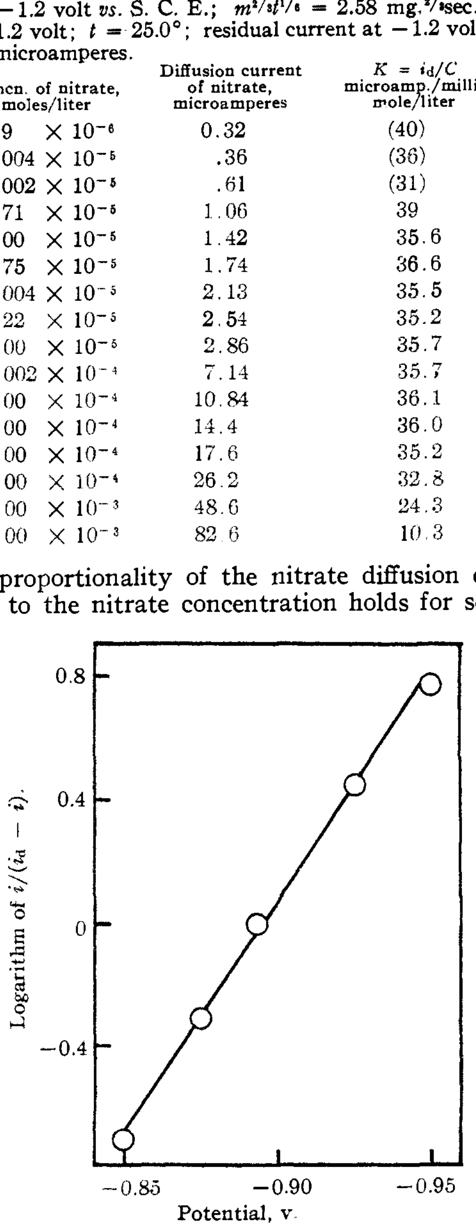

Fig. 3.—Analysis of nitrate reduction wave in 0.1 M potassium chloride, 0.01 M hydrochloric acid, 2×10^{-4} M uranyl chloride.

Number of Electrons Transferred in the Reduction of Nitrate.—The theoretical equation, derived by Ilkovič, for the diffusion current obtained at the dropping mercury electrode is

$$i_d = 605nD^{1/2}Cm^{2/3}t^{1/6} = KC$$

where i_d is the average current in microamperes, n is the number of faradays transferred per mole, D is the diffusion coefficient in cm.^{2} sec.$^{-1}$, C is the concentration of the reduced ion in millimoles per liter, m is the rate of flow of mercury from the dropping mercury electrode in mg. sec.$^{-1}$, t is the drop time in seconds, and K is the proportionality constant

$$K = 605nD^{1/2}m^{2/3}t^{1/6}$$

The value 1.92×10^{-5} cm.^{2}sec.$^{-1}$ for D^0, calculated from the equivalent conductance of nitrate ions at infinite dilution at 25°,[5] is taken as the diffusion coefficient of the nitrate ion.

For the nitrate wave in the presence of uranyl ions, $m^{2/3}t^{1/6}$ for the capillary used was 2.58 mg.$^{2/3}$-sec.$^{-1/2}$ at -1.2 volt (*vs.* S. C. E.) and thus the proportionality constant is calculated to be $K = 6.85\,n$. Comparison of this calculated value with the observed values in Table IV yields a value for n of approximately 5; *e. g.*, $n = 35.7/6.85 = 5.2$ This indicates that nitrate ions are reduced to nitrogen in the presence of uranyl ions at potentials where the second reduction wave of uranyl ions occurs.

For the nitrate wave in the presence of lanthanum ions, $m^{2/3}t^{1/6}$ for the capillary used was 1.742 mg.$^{2/3}$sec.$^{-1/2}$ at -1.6 volt (*vs.* S. C. E.), and the proportionality constant is calculated to be $K = 4.62\,n$. Comparison of this calculated value with the observed values in Table II gives n a value of 6. Tokuoka and Ruzicka[2] claim that the reduction of nitrate in the presence of lanthanum corresponds to an 8 electron reduction. This is not confirmed by the present authors. Our results correspond to a reduction of nitrate to hydroxylamine in the presence of lanthanum.

Analysis of the wave (slope of the line obtained by plotting $\log i/(i_d - i)$ against π, see Fig. 3) gives a value of $n = 1$ for the nitrate reduction in the presence of uranyl ions. A similar value of n has been found by Orlemann and Kolthoff[6] in the irreversible reduction of iodate and bromate. Although the over-all reduction involves 6 electrons, the analysis of the waves corresponded to an apparent electron transfer of one. A similar result is found now in the irreversible reduction of nitrate at the dropping mercury elec-

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[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 45.

[6] E. F. Orlemann and I. M. Kolthoff, THIS JOURNAL, **64**, 1044 (1942).

trode in the presence of uranium. A straight line yielding a value of $n = 1$ does not indicate that the reaction is reversible. Analysis of the nitrate wave in the presence of lanthanum did not give a straight line.

The Polarographic Determination of Nitrate.—For the determination of nitrate in solutions where the nitrate concentration, after dilution as given in the procedure, is between 5×10^{-5} and 4×10^{-4} *M*, the following procedure is recommended.

Prepare a stock uranyl chloride solution which is 10^{-3} *M* in uranyl chloride, 0.5 *M* in potassium chloride, and 0.05 *M* in hydrochloric acid.

Procedure.—Dilute 5.00 ml. of the stock uranyl chloride solution to 25.00 ml. with conductivity water, bubble with nitrogen or hydrogen gas to make air-free, and measure the apparent diffusion current due to the reduction of uranium at a potential of -1.2 volt *vs.* S. C. E. This current is taken as the "blank" or "residual" current for the nitrate wave.

Measure a suitable volume of an unknown nitrate solution into a 25-ml. volumetric flask, add 5.00 ml. of the stock uranyl chloride solution and dilute to volume with conductivity water. Make the resulting solution air-free and measure the apparent diffusion current at a potential of -1.2 volt *vs.* S. C. E. Subtract the "residual" current due to the reduction of uranium from the diffusion current to obtain the nitrate diffusion current. The amount of nitrate in the solution can be found from this diffusion current by referring to a standard curve or the proportionality constant, $K = i_d/C_{NO_3^-}$. These can be obtained as follows.

The diffusion current is obtained for a known nitrate solution treated in the same manner as the unknown. The nitrate concentration in the known solution, after dilution to 25 ml., should be between 5×10^{-5} and 4×10^{-4} *M* in which range the nitrate diffusion current is proportional to the nitrate concentration. The standard curve is constructed by plotting the value of the diffusion current of the known solution against its concentration and drawing a straight line through the origin and this point.

For the determination of nitrate in solutions where the nitrate concentration is less than 5×10^{-5} *M* after dilution, the uranyl chloride concentration may be reduced to allow for a more accurate determination of the nitrate diffusion current. The extent of this reduction in concentration is limited and can be found from Table III.

Interferences.—Basic solutions precipitate the uranium, and highly acid solutions (greater than 0.1 *M*) cause the reduction of hydrogen before -1.2 volt. These interferences may be eliminated readily by making the solution just acid to methyl red, the indicator causing no interference. The adjustment of the acidity is demonstrated in the following experiment: 4.992 ml. of a solution which was 8.00×10^{-4} *M* in potassium nitrate and 1.086 *M* in hydrochloric acid was transferred to a 25-ml. volumetric flask. One drop of 0.1% methyl red was added, followed by saturated sodium hydroxide added dropwise until the indicator turned yellow. One molar hydrochloric acid was added dropwise until the color of the indicator just changed to acid or became intermediate. Five milliliters of the stock uranyl solution was added and the solution was diluted to volume. The diffusion current for the nitrate at -1.2 volt was determined, from which the nitrate concentration in the original solution was found to be 8.00×10^{-4} molar.

Sulfate interferes strongly in the polarographic determination of nitrate according to the lanthanum procedure. In the new uranyl procedure, sulfate interferes only when present in large excess to nitrate. For example, when working with 4×10^{-5} *M* potassium nitrate, the sulfate concentration was varied between 0 and 8×10^{-3} *M* and no interference was found. Thus a sulfate concentration 200 times as great as that of nitrate did not interfere. Working with 4×10^{-4} *M* potassium nitrate solutions, the sulfate concentration could be as large as 4×10^{-3} *M* without interference. With increasing concentrations of sulfate, the nitrate diffusion current was reduced slightly. When the sulfate concentration was 1.1×10^{-2} *M*, the error amounted to -2.2%. When excessive amounts of sulfate are present, a separation by precipitation of strontium sulfate is necessary. The separation should not be carried out as barium sulfate because serious errors arise as the result of coprecipitation of nitrate with barium sulfate.

Chlorate does not interfere. In a solution which was 2×10^{-4} *M* in nitrate and 6×10^{-2} *M* in potassium chlorate, no interference was found. It may be mentioned that the new procedure is suitable for the determination of traces of nitrate in commercial potassium chlorate products. In a "C. P." product of potassium chlorate labelled to contain less than 0.001% of nitrogen, we found a nitrate wave corresponding to 0.0048% nitrogen. By recrystallization of the product from water, the nitrate wave disappeared.

Oxalate, which does not give a well-defined wave under the conditions of the procedure, is reduced at the same potential as nitrate in the presence of uranyl and must be removed or destroyed.

Phosphate precipitates uranyl and must be removed. This can be done simply by precipitation of the phosphate with alkali-earth metals.

Substances present in large amounts which give reduction waves before the nitrate wave interfere and must be removed. For example, copper and lead in large amounts should be removed by precipitation with sodium carbonate.

Uranous sulfate instead of uranyl chloride showed the same catalytic effect on the nitrate reduction. The use of uranous has the advantage that the residual current due to uranium is one-third that of uranyl chloride. However, uranous sulfate solutions are oxidized slowly by air. Therefore, in general, the use of a stable uranyl chloride solution is preferable in routine work.

Investigations are being carried out to find out if the catalytic effect of uranium on nitrate reduction can be used for the detection and determination of traces of uranium.

Acknowledgment is made to the Graduate School of the University of Minnesota for a grant which enabled us to carry out a part of this work.

Summary

1. In the presence of uranyl ions, nitrate in dilute solutions of hydrochloric acid is reduced at potentials where the second uranium wave occurs. The diffusion current of nitrate is well defined and is proportional to the nitrate concentration when the ratio of uranyl to nitrate is above a certain minimum. This ratio depends upon the nitrate concentration and has been given in the paper. The reduction of nitrate under the above conditions involves five electrons, indicating a reduction to nitrogen. The high electron consumption allows the quantitative determination of very dilute nitrate solutions. In a solution which is 0.01 *M* in hydrochloric acid and 0.1 *M* in potassium chloride the half-wave potential is of the order of -0.9 to -1.0 volt (*vs.* S. C. E.).

2. The proposed method has many advantages over the procedure in which the nitrate reduction wave is determined in the presence of a large excess of lanthanum chloride. The half wave potential of nitrate in the presence of much lanthanum varies between -1.3 and -1.5 volts (*vs.* S. C. E.), dependent on nitrate and lanthanum

concentrations. The diffusion current is found proportional to the nitrate concentration over a very narrow range of nitrate concentrations only. It is found that the reduction involves 6 electrons and not 8 electrons as claimed by Tokuoka and Ruzicka.

3. Small amounts of sulfate do not interfere in the uranyl procedure but they do interfere in the lanthanum procedure.
4. Uranous instead of uranyl salt can be used in the catalytic polarographic reduction of nitrate.

MINNEAPOLIS, MINNESOTA RECEIVED JULY 5, 1944

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

The Catalytic Isomerization of Paraffin Hydrocarbons. II. Promoters for Catalysis by Aluminum Bromide

BY JULIUS D. HELDMAN[1]

Although aluminum halides, as ordinarily prepared and handled, are catalysts for the isomerization of paraffin hydrocarbons, it has been shown that the pure bromide, in the absence of moisture, has no effect on the butanes[2,3] or *n*-heptane,[4] and that anhydrous aluminum chloride does not cause any reaction of *n*-butane,[2,5] *n*-pentane,[6] *n*-hexane, *n*-heptane, and 2,2,4-trimethylpentane.[5] Presumably, therefore, the dry aluminum halides are inert to all paraffins at relatively low temperatures.

Addition of a hydrogen halide or water to the aluminum halide gives rise to an active isomerization catalyst. On the basis of kinetic experiments, Leighton and Heldman[2] postulated this substance to be $HAlBr_4$ in the case of hydrogen bromide–aluminum bromide mixtures.

It is known that other substances besides hydrogen halides may function as "promoters" for aluminum halide catalysis.[7] To determine the role of the promoter and hence to gain an insight into the mechanism of halide-catalyzed isomerization, *n*-butane has been subjected to the action of carefully purified, anhydrous aluminum bromide with various promoters added. The results of these experiments are here reported.

Experimental

Aluminum bromide was prepared and handled as in previous work[2,3] except in a few cases, in which it was finally distilled *in vacuo* into thin capsules and sealed. The capsules could be broken open in a reaction tube when desired by action of a glass-enclosed iron core activated either by a solenoid or shaking.

Two *n*-butane preparations were employed, part of both having been used in earlier work.[2,3] These were stored over phosphorus pentoxide at 0°.

The sodium chloride and sodium bromide were Merck reagent grade. Hydrogen bromide was prepared as previously described,[2] and hydrogen chloride was made by heating potassium acid sulfate with sodium chloride and purified by dry ice to liquid air distillations. Boron trifluoride was taken from an Ohio Company cylinder.

Eastman Kodak "practical" methyl bromide was subjected to fractionation on the column described below, and the heart cut was stored at 0° over Drierite in the dark. The product was colorless. The methylene dibromide was a Kahlbaum sample, and the *n*-butyl bromide was Eastman Kodak Co. "white label."

All volatile materials were introduced into the reaction tubes containing aluminum bromide essentially in the manner previously described.[2] In the cases of sodium chloride and sodium bromide, the salts were weighed in the tubes before these were sealed to the manifolds (or before a capsule was introduced).

No manifold was used after *n*-butyl bromide or boron trifluoride had been distilled into a reaction tube on it.

Since exclusion of moisture and hydrogen bromide was of the utmost importance in this work, and since activity of the "anhydrous" aluminum bromide as a catalyst is a test for very small traces of these promoters, blanks were run on all manifolds of tubes used, and also on a capsule from the same batch as those used here. Two of these blanks have been previously reported,[8] while others were run under different conditions and for much longer times. In one blank experiment, which was run at 25.0° for 3.0 days with shaking, the charge of aluminum bromide far exceeded its solubility in *n*-butane.[3]

In none of these blanks was there any reaction, recovery of the original *n*-butane being practically quantitative. This result cannot be stressed too strongly, since the validity of the results and the conclusions to be drawn therefrom would be vitiated if the aluminum bromide itself were not completely inactive.

After reaction and freezing of the sealed tube in liquid air, residual pressure was estimated from the Tesla coil glow, except in one experiment with air. No tubes tested showed appreciable amounts of permanent gas formation.

The aluminum bromide content in the tubes was determined after reaction either by direct weighing after removal of all volatile material or by analysis as aluminum oxide. In experiments where capsules of the halide were used, the weight had been determined previously from the known length density of the glass tubing leading to the capsule and the weight of the capsule plus a measured length of tubing before and after distilling in the aluminum bromide.

Before analysis, the volatile material from an experiment was passed through potassium hydroxide pellets and phosphorus pentoxide. With the organic bromides, the charge was first treated with ethanolamine.

Four methods of analysis were employed: low temperature fractional distillation using a manually operated 3 mm. i. d. Podbielniak micro-precision type R column,[9] dew pressure,[3,10] "float point,"[2] and aniline point.[11]

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[7] For a review of work in this field, see Egloff, Hulla and Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corporation, New York, N. Y., 1942.

[8] Ref. 2, Experiments 41 and 42.

[9] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931); **5**, 119 (1933).

[10] Savelli, Seyfried and Filbert, *ibid.*, **13**, 868 (1941).

[11] Ludemann, *ibid.*, **12**, 446 (1940).