changing the distribution of Co(III) between the reactant RH_2O^{+++} and the activated complex $R(H_2O)_2^{+++}$. The outer-sphere affinity of these two forms for sulfate ion is expected to be approximately the same, and the present state of understanding of these effects would accommodate a slight preference in either direction.

The conclusions we have reached concerning mechanism for ions of the type $Co(NH_3)_5H_2O^{+++}$ and $Co(NH_3)_5X^{++}$ provide no basis for conclusions in other systems, or for the reactions under widely different conditions. Thus the reactants of the tetrammine series $Co(NH_3)_4X_2^+$ may much more readily adopt S_N1 mechanisms,[19,20] because a means of stabilizing a penta-coördinated intermediate, by making use of unshared electron pairs on the remaining group X, is available.

Acknowledgment.—The research described was supported by the Office of Naval Research under contract N6-Ori-02026. Funds for the purchase of the mass spectrometer were supplied by the Atomic Energy Commission under contract At(11-1)-92.

[19] D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953).

[20] R. G. Pearson, C. R. Boston and F. Basolo, THIS JOURNAL, **75**, 3089 (1953).

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Mechanisms of Electron Transfer in Aquo Cations—The Reaction of RH_2O^{+++} with Cr^{++}

BY R. K. MURMANN, H. TAUBE AND F. A. POSEY

RECEIVED JULY 5, 1956

A kinetic study of the reaction of Cr^{++} with $(NH_3)_5CoH_2O^{+++}$ to form $Cr(H_2O)_6^{+++}$ and Co^{++} has been made, tracer experiments on the transfer of oxygen from $(NH_3)_5CoH_2O^{+++}$ to Cr^{++} have been done, and isotope fractionation effects on the oxygen and nitrogen in $(NH_3)_5CoH_2O^{+++}$ during reaction have been measured. The kinetic data are consistent with the rate law $-d(Cr^{++})/dt = k_1(Cr^{++})((NH_3)_5CoH_2O^{+++}) + k_2(Cr^{++})((NH_3)_5CoOH^{++})$. At 25° and $\mu = 1.$, $k_1 = 19$ l. mole^{-1} min.$^{-1}$, and $k_2 \sim 2 \times 10^7$ mole^{-1} min.$^{-1}$. $E_1 = 8.7$ kcal. mole^{-1} and $a_1 = 10^{8.7}$ l. mole^{-1} min.$^{-1}$. The reaction corresponding to the second term in the rate law proceeds by substantially complete transfer of oxygen from the oxidizing agent to the reducing agent. For the reaction corresponding to the first term, it can be stated that at least partial oxygen transfer is involved. The fractionation factor d ln O^{16}/d ln O^{18} for the oxygen in the bridging ligand OH^- is 1.03_4; and a substantial fractionation for nitrogen is also indicated. The efficiency of Cl^- acting as a bridging ligand and as a simple ligand in the activated complex of composition $Co(NH_3)_5^{+++}\cdot Cl^-\cdot Cr^{++}$ is compared.

In earlier work[1-4] in the general area of interest of this paper, the role of anions as bridging groups in certain electron transfer reactions was demonstrated. None of these observations, however, showed whether molecules of the solvent H_2O, or of the ion derived from it, OH^-, could also function as bridging ligands in a way analogous to that which was demonstrated for Cl^- and a number of other such groups. In the present paper is outlined work done on the reaction

$$RH_2O^{+++} + Cr^{++} + 5H^+ = Co^{++} + Cr(H_2O)_6^{+++} + 5NH_4^+$$

(R represents $Co(NH_3)_5$). The purpose of this work was to learn whether H_2O and OH^- can in fact act as bridging ligands in electron transfer reactions, and to learn other important features of the activated complex for this model reaction involving aquo cations. The considerations which guided the choice of the present system have already been outlined.

Experimental

The preparations $RH_2O(ClO_4)_3$, $RH_2O^*(ClO_4)_3$[5] and Cr^{++} aq.[2] were made following procedures described elsewhere.

The rate of the reaction of Cr^{++} and RH_2O^{+++} was followed by discharging known amounts of the reaction mixture into Fe^{+++} in excess, and determining the amount of Fe^{++} formed, by amperometric titration.

The tracer experiments were done by allowing Cr^{++} to react with RH_2O^{+++} in excess, in perchloric acid solution, precipitating the excess Co(III), the Zn(II) (formed in the reduction of Cr(III)) and Co(II) ions, then precipitating $Cr(H_2O)_6^{+++}$ as the phosphate,[6] heating this precipitate to obtain H_2O, and finally determining the isotopic composition of the H_2O by the CO_2 method.[7] At the concentrations of RH_2O^{+++} and of $HClO_4$ necessary to provide for the formation of $Cr(H_2O)_6^{+++}$ in reasonable quantity, the system contained solid $RH_2O(ClO_4)_3$ during most of the time the reaction proceeded.

For the fractionation work $R(H_2O)^{+++}$ was used in excess. After substantially complete reaction with Cr^{++}, the residual $R(H_2O)^{+++}$ was precipitated as the bromide. This salt was washed, dried and heated to yield water. Comparison of the final oxygen-isotope composition of the RH_2O^{+++}, with that of the salt initially, taking into account the fraction left unreacted, yielded values for the isotope fractionation.[8]

In connection with the experiments on the kinetics, which were completed toward the end of the research, there was evidence that precise stoichiometry in the reaction did not always obtain. Apparently some process for the destruction of Cr^{++} which does not involve Co(III) complex can interfere and the contribution of this additional reaction is not easily controlled. These effects have been more strikingly revealed in recent experiments in which Cr^{++} acts as catalyst rather than by being consumed in the reaction under study, and here the net destruction of Cr^{++}, presumably by ClO_4^-, but catalyzed by adventitious substances could be readily demonstrated. The effect described was almost completely absent in the experiments on the kinetics which have been reported, although it appears to have been present in earlier, preliminary work using a different batch of Cr^{++}. It should be mentioned that different batches of Cr^{++} show the side reactions to a differing extent, but other factors may also influence the extent to which it contributes.

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[1] H. Taube, H. Myers and R. L. Rich, THIS JOURNAL, **75**, 4118 (1953).

[2] H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

[3] H. Taube and E. L. King, *ibid.*, **76**, 4503 (1954).

[4] H. Taube, *ibid.*, **77**, 4481 (1955).

[5] A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 825 (1952).

[6] J. P. Hunt and R. A. Plane, THIS JOURNAL, **76**, 5960 (1954). We wish to express our appreciation to these workers for giving us details of their method for isotopic analyses of $Cr(H_2O)_6^{++}$, prior to the publication of the work.

[7] M. Cohn and H. C. Urey, *ibid.*, **60**, 679 (198).

[8] A. E. Cahill and H. Taube, *ibid.*, **74**, 2312 (1952).

Results

The results obtained in the measurement of the rate of reaction are summarized in Table I.

TABLE I

THE RATE OF REACTION OF Cr^{++} AND RH_2O^{++}

(μ = 1.1 using $NaClO_4$, subscripts o and f refer to initial and final conditions, respectively)

Temp., °C.	($HClO_4$)	$(Cr^{++})_0 \times 10^3$	$(RH_2O^{+++})_0 \times 10^3$	$\frac{(Cr^{++})_0}{(Cr^{++})_f}$	k, l. mole^{-1} min.$^{-1}$
0	0.300	1.00	1.49	3	75
0	1.00	1.25	2.96	5	36
0	1.00	1.01	2.96	10	37[a]
0	1.00	0.80	1.49	3	37
10.3	0.300	1.01	1.49	4	178
10.3	1.00	1.01	1.49	3	78

[a] (Cl^-) = 0.05 *M*.

The specific rates are defined by the relation $-d(Cr^{++})/dt = k(Cr^{++})(RH_2O^{+++})$ and were calculated from the slopes of the lines in graphs of log $(RH_2O^{+++})_t/(Cr^{++})_t$ against time. Significant deviations from the requirements of the second-order law were not observed in the series of experiments reported even for the final points obtained in an experiment.

The experiments on the transfer of oxygen from RH_2O^{+++} to Cr^{++} during the reaction are summarized in Table II. In these experiments, RH_2O^{+++} was used in about 20% excess and the reaction was allowed to proceed until Cr^{++} had been substantially consumed. In calculating the values of % transfer, allowance has been made for the fact that some Cr^{+++} was left in the original Cr^{++} solution (% reduction of Cr^{+++} 96–98), and for the isotope fractionation known to take place (*vide infra*) in the reaction of Cr^{++} and RH_2O^{+++}. No attempt has been made to allow for the other fractionation effects (H_2O is only partially removed from CrH_2O^{+++} on heating $Cr(H_2O)_6PO_4$; H_2O^{18} may be bound in Cr^{+++} in preference to H_2O^{16} when it is formed in the reaction) because they will to some extent cancel, and they can in no event affect significantly the conclusions which can be drawn from the results.

TABLE II

TRANSFER OF OXYGEN FROM RH_2O^{+++} TO Cr^{++}

(At room temperature, in water of ordinary isotopic composition–enrichment ratio = 1.000)

		Oxygen enrichment ratio for		
	($HClO_4$)	RH_2O^{+++}	$Cr(H_2O)^{+++}$ formed	% oxygen transfer
2.01	1.0	5.44	1.31	42
2.02	0.20	5.44	1.59	79
2.03	1.0	4.73	1.38	61
2.04	0.20	4.73	1.51	81
2.05	0.20	5.49	1.42	55
2.06	1.0	5.49	1.57	74
2.07	0.2	6.14	1.80	93
2.08	0.2	2.73	1.19	66

Table IIIA gives a summary of the data on the fractionation of oxygen isotopes (*f* = d ln O^{16}/d ln O^{18}) and IIIB on fractionation of nitrogen isotopes (*f* = d ln N^{14}/d ln N^{15}) in the reaction of RH_2O^{+++} with Cr^{++}. Sulfuric acid rather than perchloric acid was used, because a higher concentration of RH_2O^{+++} in solution is tolerated by $SO_4^{=}$. To get fractionation data which can readily be interpreted, the entire amount of RH_2O^{+++} must be in solution.

TABLE III

ISOTOPIC DISCRIMINATION IN THE REACTION Cr^{++} AND RH_2O^{+++}

(Room temperature. Enrichment ratio of RH_2O^{+++} initially taken as 1.000)

A. Oxygen isotope discrimination

% RH_2O^{+++} left[a]	(H_2SO_4) *M*	Enrichment ratio residual RH_2O^{+++}	
29.2	0.2	1.049	1.041
36.3	0.2	1.045	1.048
19.6	.5	1.062	1.037
29.2	.5	1.045	1.039
36.3	0.5	1.038	1.038

B. Nitrogen isotope discrimination

% RH_2O^{+++} left[a]	(H_2SO_4) *M*	Enrichment ratio residual RH_2O^{+++}	
36.3	0.2	1.003	1.003
36.3	0.5	1.003	1.003

[a] Calculated from initial amounts.

Discussion

The kinetic results show that the reaction of Cr^{++} with RH_2O^{+++} is first order in these reactants and show also, as has been observed in numerous electron transfer reactions between aquo cations,[9] that the rate increases as acidity decreases. The rate law

$$\frac{-d(Cr^{++})}{dt} = \underset{\text{I}}{k_a (Cr^{++})(RH_2O^{+++})} + \underset{\text{II}}{k_h \frac{(Cr^{++})(RH_2O^{+++})}{(H^+)}}$$

has been adopted to interpret the data. The form of the variation with (H^+) is not proven by the present data, but it is reasonable in view of the known behavior of other systems. Making use of the data of Table I, k_a and k_h at 0° are found to be 19 l. mole^{-1} min.$^{-1}$ and 17 min.$^{-1}$, at 10.3, 34 and 44°, respectively. For path I, *E* is calculated as 8.7 kcal. and log *a* as 8.7. Path II can be expressed in the form $k_h/K(Cr^{++})(ROH^{++})$ where *K* is the dissociation constant of RH_2O^{+++}. The value of *K* for the conditions of the experiments is not precisely known, but a value of 10^{-6} at 0° and μ = 1 is probably not in error by more than a factor of 2,[10] so that the 2nd order coefficient for path II is *ca.* 2 × 10^7 l. mole^{-1} min.$^{-1}$. A satisfactory resolution of the specific rate for path II into the exponential and frequency factor terms is not possible until good measurements on the variation of *K* with temperature are made. The estimate of ΔH = 19 for the reaction

$$RH_2O^{+++} = ROH^{++} + H^+$$

which can be made from the data of Brönsted and Volquartz[10] seems unreasonable, both because of the inherent unlikelihood that ΔH for this dis-

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[9] (a) Fe^{++}–Fe^{+++}, J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952); (b) V^{++}–V^{+++}, W. R. King, Jr., and C. S. Garner, THIS JOURNAL, **74**, 3709 (1952); (c) Cr^{++}–Cr^{+++}, A. Anderson and N. A. Bonner, *ibid.*, **76**, 3826 (1954);. (d) Co^{++}–Co^{+++}, N. A. Bonner and J. P. Hunt, *ibid.*, **74**, 1866 (1952); (e) Fe^{+++}–Cr^{++}, ref. 4.

[10] J. N. Brönsted and K. Volquartz, *Z. physik. Chem.*, **134**, 97 (1928).

sociation will be so different from that of $Cr(H_2O)_6^{+++}$ or of Fe^{+++} aq. (10–12 kcal.), and because this value would give a negative temperature coefficient for the bimolecular specific rate in the reaction by path II. While at least for path I, the values of E and a are in the range of those observed in other electron transfer reactions for aquo ions, including Fe^{++}–Fe^{+++}, a quantitative difference between the present system together with certain others on the one hand, and the Fe^{++}–Fe^{+++} system, is great enough to be worthy of note. The ratio of the 2nd-order coefficient of path II to that for path I is 10^6 in the RH_2O^{+++}–Cr^{++} reaction, $> 4 \times 10^4$ in Cr^{++}–$Cr(H_2O)_6^{+++}$,[9c] but only 1.2×10^3 in the Fe^{++}–Fe^{+++} system.[9a] The difference is not peculiar to Cr^{++}, for the ratio of the corresponding rates in the Cr^{++}–Fe^{+++} system is very nearly the same as that for Fe^{++}–Fe^{+++}.

The results in Table II can be taken as establishing *minimum* values for the extent of transfer of oxygen accompanying the reaction of the aquocobaltic ion with Cr^{++}. This follows because the only source of enriched oxygen in the system was RH_2O^{+++}. Contamination or side reactions can only act to reduce the apparent transfer. The irreproducibility of the results can be blamed on the side reactions referred to in the Experimental section as well as the exchange of the enriched $Cr(H_2O)_6^{+++}$ formed as product, catalyzed by Cr^{++}.[11] This reaction is in turn subject to catalysis. These effects are all the more serious when (H^+) is high, corresponding to lower rates of reaction. From experiment 2.07 it can be concluded that path II, the principal path under the conditions of the experiment at low acid, proceeds with substantially complete transfer of OH^- to Cr^{++}. The conclusion for path I is not so definite, but the results show that at least some oxygen transfer by this path occurs. Using the measured rates and temperature coefficients, in 1 M $HClO_4$ and at 25°, 30% of the reaction is expected to take place by the aquo path. Even taking the maximum value observed for transfer by the ROH^{++} path, experiment 2.06 leaves some transfer to be accounted for by the aquo path. Using a more probable value of 70% to 80% for the apparent transfer by the ROH^{++} path, a considerable ($\sim 60\%$) minimum contribution by the RH_2O^{+++} path is suggested.

In considering the function of the bridging ligand in the electron transfer reactions, from one extreme point of view it might be regarded as serving merely to unite oxidant and reductant, while changes elsewhere in the activated complex govern the electron redistribution. From another extreme point of view, the principal act might be conceived as the movement from the oxidizing agent to the reducing agent of the bridging ligand, less one electron. This process would be analogous to that which might reasonably be assumed for the reaction of CH_3Cl with Na. The isotope discrimination experiments serve to make a distinction between these extreme formulations. On the basis of the first point of view, a more rapid rate for $O^{18}H^-$ as bridging group would not be unexpected, for the bond which it makes with Cr^{++} is stronger than that made by $O^{16}H^-$; on the basis of the second point of view, since the Co–O bond is stretched in the activated complex, a substantial preference in reaction for O^{16} compared to O^{18} would be expected. Before the data on oxygen fractionation in Table III can be applied to the problem at hand, the fractionation factors must be resolved into the kinetic and equilibrium components. This is necessary because, although ROH^{++} provided the path for most of the reaction under the conditions of the experiment, RH_2O^{+++} was by far the dominant form. Thus to factor out the equilibrium fractionation implied, the relative acidity of RH_2O^{16+++} compared to RH_2O^{18+++} must be known. This has been determined as 1.009,[12] and therefore the kinetic fractionation factor by path II is $1.04_3/1.009 = 1.03_4$. A factor of this magnitude is consistent with the view that the Co–O bond is considerably weakened in the activated complex. Since the oxygen is not completely freed from Co, a very large factor cannot be expected. At high acid, a greater fraction of the reaction proceeds by the aquo path. The decrease in the values of f may be caused by the increasing contribution of side-reactions at the lower rates obtaining, rather than by a marked change in fractionation factor. The fractionation data on nitrogen show a substantial effect on the Co–N bond also. It must be remembered that the isotopic effect of the single $N^{15}H_3$ which will on the average be present in each labeled molecule is diluted by the presence of 4 others of ordinary mass. The rate factor on complete substitution could therefore be expected to be $(1.003)^5$ or 1.015 to 1.02. The effect is too small to be consistent with complete rupture of the $Co–NH_3$ bond (the frequency for the breathing mode in $Co(NH_3)_6^{+++}$ is probably[13] in the range 450–500 mμ) but it does indicate that stretching of these bonds is required.

Another feature of interest in the present data is the comparison of the rates by the two distinct paths having activated complexes of composition R^{+++} aq $\cdot Cl^- \cdot Cr^{++}$

$[(NH_3)_5CoClCr]^{+4}$	$[(NH_3)_5CoH_2OCrCl]^{+4}$
III, Chloride as bridge	IV, Chloride as ligand

The data of Table I concerned with the effect of Cl^- on the rate of the reaction of Cr^{++} with $(NH_3)_5CoH_2O^{+++}$ make it possible to set an upper limit on the coefficient of the rate term $(RH_2O^{+++})(Cl^-)(Cr^{++})$ which corresponds to the reaction by path IV. Any effect which chloride ion exerts includes that corresponding to the activated complex IV. At 0.05 M Cl^-, the 2nd-order specific rate k is not noticeably different from that when no Cl^- is present. Thus the upper limit of 37-36/0.05 = 20 on the coefficient of the rate function $(RH_2O^{+++})(Cl^-)(Cr^{++})$ can be set by the data. The coefficient for the rate term $(RCl^{++})(Cr^{++})$ which governs the reaction by path III appears to be at least 10^3 (unpublished observations). In order to convert this rate law to the same form as that used for path IV, the equilibrium relation

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[11] R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

[12] R. H. Hunt, R. K. Murmann and H. Taube, to be published.

[13] J. P. Mathieu, *J. Chem. Phys.*, **36**, 300 (1939).

$(RCl^{++})/(RH_2O^{+++})(Cl^-) = 1.2$[14] can be used. When this is done, the coefficient multiplying the rate function $(RH_2O^{+++})(Cl^-)(Cr^{++})$, now corresponding to reaction by the activated complex III in which chloride is a bridging group, is found to be at least 10^3. Thus, Cl^- appears in this system to be at least 50 times more effective as a bridging ligand than as a simple ligand on Cr^{++} in promoting electron transfer. It should be pointed out that the form $(RH_2O^{+++})(Cl^-)(Cr^{++})$ for expressing the rate by path III is artificial, because in actually starting with $RH_2O^{+++} + Cl^-$, the rate-determining step would be the formation of RCl^{++} from RH_2O^{+++} and Cl^-. This does not invalidate the comparison made. The calculation does show what the value of the rate coefficient for the kinetic function $(RH_2O^{+++})(Cl^-)(Cr^{++})$ would be for path III, if the substitution equilibrium were established rapidly.

A general and important implication of the present observations is this: OH^- (and probably H_2O) can transfer from oxidant to reductant during electron transfer in water, so that this mechanism must be considered a distinct possibility also for other aquo-cations undergoing electron transfer. Furthermore, at least for path 1, log a and E are similar in magnitude to values which have been observed in other systems, and therefore the agreement in the magnitude of these quantities for a variety of systems cannot be taken as diagnostic of a hydrogen atom transfer mechanism,[15] or in general of mechanisms which exclude close approach of oxidant and reductant.

It would be dangerous to generalize from the fractionation effects observed for the bridging group in the present system to other oxidizing agents. A consideration of the electron structure of Co(III), which shows that all stable orbitals are occupied, makes the existence of a marked fractionation effect in the bridging group appear reasonable, because an orbital about Co(III) must be vacated before the electron released by Cr^{++} can be accommodated. With oxidizing agents having stable orbitals vacant, the bridging group may function more nearly simply as a cement. Unfortunately, few systems of this kind can be suggested which are as amenable to direct study of fractionation effects as that chosen for the present work.

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[14] F. J. Garrick, *Trans. Faraday Soc.*, **33**, 486 (1937); $K = 1.8$ at $\mu = 0.3$. Corrected to $\mu = 1$, using variation of $K_{FeCl^{++}}$ with μ (E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942)).

[15] W. I. Reynolds and R. W. Lumry, *J. Chem. Phys.*, **23**, 2460 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

A New Method for the Preparation of Sodium and Calcium Nitrites

BY JAMES D. RAY AND RICHARD A. OGG, JR.

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Sodium nitrite was prepared by the reaction of nitric oxide with a mixture of sodium ferrate(III) and sodium nitrate at 400° in a vacuum system. The nitrite product was at least 99.9% pure. The reaction is quantitative with respect to nitrate, but a small percentage of nitric oxide must be recycled. Calcium nitrite was similarly prepared at 275°.

Introduction

Although the reversible reaction involving pyrolysis of sodium nitrate produces a melt containing a large proportion of nitrite contaminated with sodium oxide and peroxide,[1] isolation of pure nitrite is difficult. Even the exothermic irreversible reduction of nitrate with lead gives a product contaminated with sodium oxide.

This paper describes a method whereby very pure sodium nitrite may be prepared by means of the reversible exothermic reaction represented by the equation

$$NaNO_3 + Na_2Fe_2O_4 + 2NO = 3NaNO_2 + Fe_2O_3 \quad (1)$$

Preparation of Materials.—Nitric oxide was quantitatively prepared from potassium nitrate by a modification of the method discovered by Wagner[2] in accordance with eq. 2

$$K_2CO_3 + 2KNO_3 + Cr_2O_3 = 2K_2CrO_4 + 2NO + CO_2 \quad (2)$$

A twofold excess of chromic oxide which had been calcined at 950° under vacuum to remove higher oxides was used. The thoroughly mixed reactants were heated in a Pyrex side arm of a vacuum system to evolve the gases through a tube containing "Ascarite" in order to remove the carbon dioxide. The nitric oxide was collected in a trap cooled with liquid nitrogen for subsequent use in making nitrite. A pressure of less than 60 mm. during the course of nitric oxide and carbon dioxide evolution was not exceeded, since the Pyrex would soften at temperatures required for higher pressures.

Sodium ferrate(III) was prepared in a vacuum furnace at 850° from sodium carbonate and an excess of ferric oxide (precipitated powder). This temperature was employed since it gives the optimum rate for the reaction,[3] and a product of small particle size. It was found difficult to remove the last traces of carbon dioxide, hence the mixture was removed from the furnace twice for regrinding. A final heating with a vacuum of 10^{-3} mm. for 24 hours gave a product free of carbonate. This great care was necessary since subsequent methanol extraction of sodium nitrite from the products of its use (eq. 1) would also extract the carbonate to give an impure sodium nitrite product.

Experimental

Reaction 1 was carried out by placing a mixture of sodium

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[1] K. Leschewski and W. Degenhard, *Z. anorg. Chem.*, **239**, 21 (1938).

[2] A. Wagner, *Z. Anal. Chem.*, **18**, 552 (1879).

[3] V. R. Terashkevich, R. E. Shtok and E. G. Gurova, *C. A.*, **35**, 3775 (1941).