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Reactions of Metals in Fused Nitrate Eutectic

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The reactions of fifteen metals with a 0.1 *M* potassium pyrosulfate solution in lithium–potassium nitrate eutectic have been studied and compared with the reactions in 0.8 *M* potassium dichromate solution and with the reactions in pure nitrate eutectic. The gases formed in these reactions (mainly nitrogen dioxide, nitrous oxide, and nitrogen) and the oxidation products of the metals were identified, and the proportions of the gases and the temperatures required for commencement of reaction determined. With more reducing metals, nitrite and hyponitrite were observed as intermediate reduction products of the nitrate ion. It is suggested that the reactions and products can be considered as resulting from two distinct processes.

Introduction

In recent years, fused alkali metal nitrates have been increasingly used as reaction media, and in the majority of cases studied nitrate ion has been found to be a reactant. A class of reactions not hitherto studied in detail is that of metals with nitrate melts. However, it is significant that in the heat treatment of metals and alloys in nitrate baths it is considered necessary not to exceed certain maximum temperatures in order to avoid serious accidents,[1] and in experimental studies platinum, silver, and mercury (below 235°) are the only metals reported as being used in contact with nitrate melts. In these circumstances, a survey of the extent and type of reactions occurring with a range of metals seemed to be of value.

Many of the reactions previously reported in fused nitrates have been interpreted on the basis of a very small dissociation of the nitrate ion.[2]

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-} \qquad (1)$$

Now since a characteristic reaction of the more electropositive metals is electron transfer to the acidic cation (in this case NO_2^+), the effects of solutes which increase the nitryl ion concentration are evidently of interest. Nitryl compounds themselves cannot be used for this purpose, since even the most stable, nitryl perchlorate, decomposes at 120°, *i.e.*, below the melting point of lithium–potassium nitrate eutectic (132°). However, other solutes react to remove oxide ions and thus increase the nitryl ion concentration. Dichromate has been shown to act in this way as a "weak acid" and pyrosulfate as a "strong acid."[3,4]

Experimental

Lithium–Potassium Nitrate Eutectic.—A.R. potassium nitrate and reagent grade lithium nitrate were dried at 150° for 24 hr., weighed out to give 38 mole % $LiNO_3$, melted, stirred, and filtered through a No. 3 sinter under vacuum in an oven at 150°. On solidification the melt was broken up and stored in a drybox.

Lithium–Potassium Nitrite Eutectic.—Reagent grade potassium and lithium nitrites were treated similarly. The eutectic contained 45 mole % $LiNO_2$.

Metals.—Reagent grades, mainly in thin sheet form, were abraded with emery cloth, degreased with ether, and cut into strips before use to ensure a reasonably high surface area.

Acids.—A.R. potassium dichromate and reagent grade potassium pyrosulfate were dried at 160° to constant weight.

Sodium hyponitrite was prepared using Diver's method as modified by Polydoropoulos.[5]

Procedure.—Approximately 20 g. of purified eutectic was placed in a 22-mm. tube with a closed end which fitted snugly into an electric furnace connected to an Ether Transitrol controller. A B.19 joint at the top of the reaction tube was connected to a vacuum pump *via* a cold trap and a Bourdon pressure gauge, a B.10 outlet being provided for the gas cell or mass spectrometer sample tube.

The melt was evacuated at 350° until the pressure was reduced to 10^{-2} mm. After cooling the melt below the reaction temperature, a weighed quantity of the acid used ($\sim$2.5 g.) and the metal sample ($\sim$1 g.) were added, and then the melt was again evacuated. A stirrer was introduced through the B.19 socket and the temperature increased slowly, the onset of reaction being determined by visual observation.

The temperatures for the commencement of reaction and reaction profiles were also determined by thermogravimetric analysis of the appropriate mixture of melt, acid, and metal, using a Stanton TR-1 thermobalance.

Analysis of Gases.—For gas analysis the stirrer was not used, the temperature being increased slowly until a sufficient rate of gas evolution was obtained (10–40 ml./hr.) to allow the collection of a sufficient sample over the course of 2–6 hr. The reaction rate gradually decreased at a particular temperature, but could be increased again by a 5° rise in temperature. The gases evolved were identified by qualitative tests and by infrared spectroscopy using a 10-cm. cell with potassium bromide windows on two Perkin-Elmer Infracords with sodium chloride and potassium bromide optics. An A.E.1 M.S.3 mass spectrometer was used to confirm the identifications.

Quantitative analysis was carried out by fractional condensation, nitrogen dioxide being condensed in Dry Ice–acetone and nitrous oxide in liquid nitrogen, the percentages quoted in Table I being accurate to ±3%. The proportions of nitrous oxide were also confirmed by quantitative infrared measurements on the 17 mμ peak.

Analysis of Melts.—After reaction the solidified melts and any precipitates were examined by qualitative and quantitative analysis using standard methods. In certain cases, removal of excess melt from a precipitate by washing with water caused further reaction, for example with the calcium oxide precipitate. In these cases the precipitate was separated from the still liquid melt by filtration and the amount of adhering melt, as determined gravimetrically by precipitating potassium as the tetraphenylborate, was subtracted. In the above example, the calcium in the oxide was then determined gravimetrically as tungstate (*Anal.* Calcd. for CaO: Ca, 71.5. Found: Ca, 70.4)

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[1] H. Remy, "Treatise on Inorganic Chemistry," Vol. 1, Elsevier, London, 1956, p. 601.

[2] R. N. Kust and F. R. Duke, *J. Am. Chem. Soc.*, **85**, 3338 (1963).

[3] F. R. Duke and M. L. Iverson, *ibid.*, **80**, 5061 (1958).

[4] F. R. Duke and S. Yamamoto, *ibid.*, **81**, 6378 (1959).

[5] C. N. Polydoropoulos, *Chim. Chronika*, **24**, 147 (1959).

and had 1.47 times its weight of adhering melt. However, in most cases water was not objectionable and the washed and dried precipitate could be analyzed by the usual methods. For example, the chromium in the green chromium oxide (section b) was analyzed volumetrically, after oxidation with potassium persulfate (*Anal.* Calcd. for Cr_2O_3: Cr, 68.4. Found: Cr, 68.1). A further difficulty which occurred in some cases was that, under the experimental conditions used, reactions did not proceed to completion, resulting in small unreacted metal particles persisting in the precipitates. In these cases quantitative analysis became meaningless and the precipitate was identified by qualitative methods and by comparison of properties with known compounds.

Results

(A) Metals with Pure Nitrate Melts. (i) Calcium.—Calcium turnings reacted at temperatures above 230°, the speed of reaction being dependent on the rate of stirring and increasing rapidly with temperature. In some cases with a slow rise of temperature an explosion occurred at 260°. Usually, however, gas was evolved steadily, nitrogen being the major constituent together with nitrous oxide and a trace of nitrogen dioxide, gas analyses being given in Table I. A white precipitate of calcium oxide formed and the melt contained considerable amounts of nitrite and traces of hyponitrite.

TABLE I

ANALYSIS OF GASEOUS PRODUCTS OF REACTION OF METALS WITH MELTS

Metal	Melt	Temp., °C.	% N_2	% N_2O	% NO_2
Ca	Nitrate eutectic	230–240	70	30	<1
Ca	Nitrite eutectic	230–240	70	30	0
Ca	0.8 M $K_2Cr_2O_7$ in nitrate	220	50	47	3
Na–Hg	Nitrate eutectic	250	24	76	0
Mg	Nitrate eutectic	420	7	67	26
Mg	0.8 M $K_2Cr_2O_7$ in nitrate	310	2	44	54
Fe[a]	Nitrate eutectic	400	10	8	<1
Zn	0.8 M $K_2Cr_2O_7$ in nitrate	350	0	6	94

[a] British Drug Houses coarse iron filings.

Despite extensive variation of experimental conditions, the concentration of hyponitrite in both melt and precipitate remained very small and could not be raised much above the limit of chemical identification (1% hyponitrite in melt). This low concentration prevented any spectroscopic evidence being obtained for hyponitrite of either *cis*[6] or *trans*[7,8] forms. Indeed, tests on synthetic mixtures showed that the infrared and ultraviolet absorptions of *trans* hyponitrite could not be observed with concentrations of less than 5 and 50%, respectively in the nitrate melt, owing to the low infrared extinction coefficient and masking by the nitrate bands.

Attempts were made to detect the hyponitrite as it was formed by precipitation as the yellow insoluble silver salt. However when calcium was added to melts containing dissolved silver nitrate, the silver ions were rapidly reduced to a black suspension of metallic silver.

In a comparison experiment the reaction of calcium with nitrite eutectic was studied at the same temperature as for nitrate eutectic. The reaction rate was found to be very similar: calcium oxide was again precipitated and only a trace of hyponitrite found. Nitrogen and nitrous oxide were produced in the same ratio as with the nitrate eutectic.

(ii) **Sodium Amalgam and Magnesium.**—Similar reactions took place in that the metal oxides were precipitated, and much nitrite was produced together with nitrogen and nitrous oxide. However, with magnesium nitrogen dioxide is now a significant product (Table I). The concentration of hyponitrite was again too low for spectroscopic characterization.

(iii) **Iron.**—Iron filings (British Drug Houses) containing the normal 3–5% carbon reacted at 400° (Table I), but the gases evolved were found to contain 82% of carbon dioxide. A purer iron (Johnson Matthey Spec-pure sheet containing less than 300 p.p.m. of carbon) was found to be much less reactive and did not give off sufficient gas for analysis at the maximum temperature investigated (500°). Pure carbon (as granulated charcoal) was found to react at 250° giving off nitrous oxide and nitric oxide together with much carbon dioxide. Free sulfur also reacted at the same temperature, evolving mostly nitrous oxide with a little nitrogen dioxide, sulfate being the oxidation product.

(iv) **Other Metals.**—Manganese and mercury reacted, again in a similar way, giving precipitates of brown manganese dioxide and red mercuric oxide and evolving nitrogen and nitrous oxide. Chromium is unusual in that the oxidation product, dichromate, was completely soluble in the melt. This slowly reacted with more nitrate to form chromate ion. A number of other metals were found to react less readily, the temperatures for commencement of reaction being given in Table II.

(B) Metals with Acidic Melt Solutions.—Reactions were carried out with a number of metals using 0.1 M potassium pyrosulfate and 0.8 M potassium dichromate solutions. Temperatures for commencement of reaction and the oxidation products of the metals are given in Table II. The gaseous products of some metal–dichromate reactions were determined and are listed in Table I.

With one metal, sodium amalgam, dichromate acted as an oxidizing agent, green chromium sesquioxide being formed. This was inert at the reaction temperature (180°) but was oxidized by nitrate at 400° to form chromate and nitrogen dioxide.

(C) Thermal Decomposition of Sodium Hyponitrite.—Because of the possible role of hyponitrite as an intermediate in the reduction of nitrate (see Discussion), the thermal decomposition of pure sodium hyponitrite was investigated. Analysis of the gaseous products of a moderately slow decomposition at 330° showed them to consist of equal parts of nitrogen and

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(6) J. Gaubeau and K. Laitenberger, *Z. anorg. allgem. Chem.*, **320**, 78 (1963).

(7) E. Nachbaur, *Monatshefte*, **93**, 135 (1962).

(8) C. C. Addison, G. A. Gamlen, and K. Thompson, *J. Chem. Soc.*, 338 (1952).

TABLE II

TEMPERATURES FOR COMMENCEMENT OF REACTION OF METALS WITH THREE MELTS AND THE METAL OXIDATION PRODUCT

	Pure nitrate eutectic		0.8 *M* $K_2Cr_2O_7$ in nitrate		0.1 *M* $K_2S_2O_7$ in nitrate	
Metal	Temp., °C.	Product	Temp., °C.	Product	Temp., °C.	Product
Na–Hg	250	Na_2O ppt.	180[a]	Cr_2O_3 ppt.	140	Na^+
Mg	420	MgO ppt.	310	Mg^{2+}	160	Mg^{2+}
Ca	230	CaO ppt.	220	Ca^{2+}	160	Ca^{2+}
Ti	...		...		>250	[c]
V	...		...		140	V_2O_5 ppt.
Cr	300	$Cr_2O_7^{2-}$	...		250	$Cr_2O_7^{2-}$
Mn	300	MnO_2 ppt.	330	Mn^{2+}	180	Mn^{2+}
Fe[b]	>500	[c]	320	Fe^{3+}	180	Fe^{3+}
Co	>500	[c]	390	Co^{2+}	140	Co^{2+}
Ni	>500	[c]	...		160	Ni^{2+}
Cu	>500	[c]	...		160	Cu^{2+}
Zn	450	[c]	350	$ZnCrO_4$ ppt.	160	Zn^{2+}
Hg	400	HgO ppt.	300	Hg^{2+}	150	$HgSO_4$ ppt.
Al	450	[c]	>400	[c]	250	Al^{3+}
Sn	...		...		250	[c]

[a] Direct reaction of Na with $K_2Cr_2O_7$. [b] Johnson Matthey Spec-pure iron sheet. [c] Surface oxidized.

nitrous oxide and the yellow solid residue to contain a large proportion of nitrite.

When suspended in nitrate melt (sodium hyponitrite is less than 1% soluble) decomposition took place more rapidly, at temperatures as low as 225°, the gas produced being found to consist only of nitrous oxide (sample collected at 230–240°). Addition of anhydrous calcium nitrate to the melt did not cause the production of any nitrogen.

Discussion

(A) Pure Nitrate Melts.—With the most reactive metals, such as calcium, the over-all reaction would appear to be

$$14Ca + 6NO_3^- = 14CaO + 3O^{2-} + 2N_2 + N_2O \qquad (2)$$

and the reaction of calcium with nitrite eutectic

$$8Ca + 6NO_2^- = 8CaO + 3O^{2-} + 2N_2 + N_2O \qquad (3)$$

However, these reactions are difficult to take to completion owing to coating of insoluble reaction products on the metal, enabling the intermediate reduction products, nitrite and hyponitrite, to be identified. These suggest that the reduction takes place in the following stages.

(i) Reduction of nitrate ion at the metal surface.

$$Ca + NO_3^- = CaO + NO_2^- \qquad (4)$$

The alternative process of $Ca = Ca^{2+} + 2e$ and $NO_3^- = NO_2^+ + O^{2-}$ followed by $Ca^{2+} + O^{2-} = CaO$ and $NO_2^+ \xrightarrow{e} NO_2 \xrightarrow{e} NO_2^-$ seems unlikely since nitrogen dioxide was produced only in negligible quantities and its electron affinity would be unfavorable.

(ii) Reduction of nitrite ion at the metal surface and dimerization of the hypothetical ion to form hyponitrite.

$$Ca + NO_2^- = CaO + [NO^-] \qquad (5)$$

$$2[NO^-] = N_2O_2^{2-} \qquad (6)$$

(iii) Decomposition of the hyponitrite, which is known to be unstable (the sodium salt is stated to explode at 260°)[9] and has been shown to decompose rapidly in nitrate eutectic at the temperatures of these reductions, with formation of nitrous oxide, *i.e.*

$$N_2O_2^{2-} \longrightarrow N_2O + O^{2-} \qquad (7)$$

Large quantities of this ion would therefore not be expected to be found in the melts.

The nitrogen produced in the presence of strongly reducing metals, like calcium, might be formed either by facilitating an alternative mode of hyponitrite decomposition, *e.g.*, similar to that of sodium hyponitrite at 300° in the absence of melt which was found to correspond to $5Na_2N_2O_2 = 2NaNO_2 + 6Na_2O + 2N_2 + 2N_2O$, or by the direct removal of an oxygen atom from the hyponitrite ion and the immediate decomposition of the hypothetical N_2O^{2-} ion thus formed to nitrogen and oxide ion. The latter process is suggested, since when less strongly reducing metals, as indicated by the free energy of formation of their oxides, were used, nitrous oxide became the dominating product and the proportion of nitrogen fell.

With less strongly reducing metals, nitrogen dioxide also became a more important product. It is suggested that this was produced not by oxygen removal from nitrogen-containing anions similar to those considered above, but by a second type of process involving electron transfer to the nitryl ion, *i.e.*

$$M + NO_2^+ \longrightarrow M^+ + NO_2 \qquad (8)$$

In accordance with this hypothesis the proportion of nitrogen dioxide in the gases formed increased as the nitryl ion concentration was raised by increasing the temperature.

(B) Acidic Melts.—In acidic solutions, the nitryl ion concentrations are much larger,[3,4] and so as would be expected the second, electron-transfer, type of reaction became predominant and the proportion of nitrogen dioxide in the gases produced increased both with temperature and with the acidity of the solution.

With 0.1 *M* pyrosulfate solution the nitryl ion concentration was sufficiently high that the reaction[4]

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[9] N. V. Sidgwick, "Chemical Elements and their Compounds," Vol. 1, Oxford University Press, 1950, p. 693.

$$2S_2O_7^{2-} + 4NO_3^- = 4SO_4^{2-} + 4NO_2 + O_2 \qquad (9)$$

occurred at an appreciable rate even at the melting point of the eutectic. Because of this, the percentages of nitrogen oxides produced were not determined, although it was evident that when metals reacted nitrogen dioxide was evolved at an increased rate. With the less acidic dichromate ion, this reaction was not detectable in 0.8 *M* solutions until 400°. Examination of the gases produced below this temperature (Table I) showed an increasing proportion of nitrogen dioxide with a decreasing proportion of nitrous oxide and a striking decrease in the proportion of nitrogen from reactions with less strongly reducing metals.

The minimum temperatures at which detectable reaction took place (Table II) also indicated the importance of reaction 9, since the temperatures decreased as the acidity of the solutions increased. Although the precise temperatures of reaction depended to some extent on the surface and crystalline condition of the metal, since these factors were held constant valid comparisons could be made between the reactivity of different melt solutions.

The list of oxidation products formed by the metal in these reactions (Table II) shows that oxidation took place to the metal valency normally found with coordinated oxygen, V^{V}, Cr^{VI}, Fe^{III}, Co^{II}, etc. An exception was found with manganese in acidic solutions when Mn^{II} was formed. The reasons for the unexpected stability of this valency state are being further investigated.

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Notes

CONTRIBUTION FROM THE RESEARCH LABORATORIES,
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Chlorodecaborane[1]

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Two patents[4,5] indicate the preparation of a dichlorodecaborane, m.p. 115–122°, and a monochlorodecaborane, m.p. 40–55°. The preparation in both cases involves the unusual use of chloroform or 1,1-dichloroethane in the presence of aluminum chloride as the halogenating agent. Otherwise, nothing has been reported concerning chlorodecaboranes. Bromodecaborane and dibromodecaborane were also prepared by similar reactions using ethylene bromide or bromoform. Wunz[4] mentioned the possibility of preparing iododecaborane using iodoform, but does not give any results. Apparently, fluorodecaborane was neither suggested as a possibility nor prepared. The intent of the present work was to prepare fluorodecaborane and to try to elucidate some of the features of the reaction. This was not realized, for 1,1-difluoroethane reacted with aluminum chloride and decaborane to give a mixture of chlorodecaborane isomers.

Experimental

Preparation of Chlorodecaborane.—In four separate experiments a total of 50 ml. of 1,1-difluoroethane was slowly added to 100 g. of decaborane and 328 g. of aluminum chloride in 1 l. of carbon disulfide. The viscous mixture was stirred with difficulty. After 1 hr., the mixture began to reflux and became less viscous. Refluxing continued for about 2 hr., during which time some HCl was evolved. The reaction mixture was then filtered. Evaporation of the solvent gave 102.5 g. of a liquid. This was distilled, giving 54 g. of a liquid, b.p. 79–85° at 0.3–0.5 mm., and five additional arbitrary fractions of somewhat higher boiling points totaling 19 g. which, by mass spectrographic analysis of the parent peaks and associated isotopic distributions, were found to contain decreasing amounts of chlorodecaborane and increasing amounts of ethylchlorodecaborane, diethylchlorodecaborane, and in the last fraction some triethylchlorodecaborane.

The first and major fraction was cooled to 0° overnight and filtered while cool to give 21 g. of a colorless solid containing 94% chlorodecaborane, 5.7% ethylchlorodecaborane, and 0.3% diethylchlorodecaborane. The filtrate was redistilled. The first two fractions, 13 g., were cooled as above to yield 2.5 g. of additional solid. The filtrate and other distillation fractions were separately combined with an equal volume of pentane, seeded with the solid to give an additional 2 g. of solid. Other distillation fractions were treated by this last method to give another 1.5 g. of solid (total 27 g. containing 92–95% chlorodecaborane). Several crystallizations of the solid from pentane gave two apparently pure fractions, m.p. 73–74 and 58–60°. Infrared spectroscopic analysis of the higher melting isomer as a KBr pellet obtained bands at (cm.$^{-1}$) 702, 715, 736, 820, 850–860 (very strong—at least two bands), 875, 915, 923, 933, 986, 995, 1010, 1025, 1058, 1095, 1470, 1515, 1555, 1905, 1940, 2530, 2580, and several very weak bands. The lower melting isomer, however, appeared to be a mixture of the first isomer and a second isomer with additional bands at (cm.$^{-1}$) 800, 822, 890, 956, 1000, and 1050.

Discussion

That the reaction of a fluoroalkane with decaborane resulted in chlorodecaborane was originally somewhat surprising. However, by means of a mass spectrometric examination, it was found that 1,1-difluoroethane in carbon disulfide was essentially converted to 1,1-dichloroethane by aluminum chloride. Some other

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[2] Brookhaven National Laboratory, Upton, N. Y.

[3] Olin Mathieson Chemical Corporation, New Haven, Conn.

[4] P. R. Wunz, U. S. Patent 3,046,086 (July 24, 1962).

[5] S. L. Clark and D. A. Fidler, U. S. Patent 3,010,783 (Nov. 28, 1961).