

while the CO groups *cis* to the ligand (force constant k_2) may interact with both the metal d_{xz} and d_{yz} orbitals. Hence if π bonding with the ligand is involved, k_1 and k_2 should increase and Δk_2 should be approximately $2\Delta k_1$ as is observed for $M(\text{CO})_4(2,2'\text{-bipy})$ compounds.⁸ That $\Delta k_1 \cong \Delta k_2$ for $M(\text{CO})_4(\text{py})_2$ was attributed to a nonplanar arrangement of the ligand rings.⁸

From Table I it is found that the complexes $M(\text{CO})_4(\text{II})$ all exhibit $\Delta k_2 \cong 2\Delta k_1$ which by the above argument suggests π interaction. It is surprising to find that $\Delta k_1 \cong \Delta k_2$ for the analogous complexes wherein the ligand is I or phenanthroline. Since these ligands are restricted to a planar configuration, this would appear to imply that neither of them participates appreciably in π bonding in the $M(\text{CO})_4\text{L}$ compounds. The inconsistency arising from interpreting both the change in force constant magnitude and the total force constant magnitude to infer π -bonding interaction suggests caution in the use of such arguments.

Several authors^{9,14,15} have observed that the position of the CO stretching frequency is directly dependent on the basicity of the ligand and thus have questioned the relation to π -bonding ability. Angelici and Graham⁹ reported a linear relation between $\text{p}K_a$ and CO stretching frequency for the complexes of the type $M(\text{CO})_4\text{L}$ where $M = \text{Cr}, \text{Mo},$ or W and $\text{L} =$ eight different substituted 1,10-phenanthrolines. From Table I it is found that analogous complexes of II follow very roughly this relationship; however, one finds little correlation when ligands such as I, pyridine,^{8,15} and 2,2'-bipyridine^{8,16} are considered. Apparently such correlations are extremely dependent on the basic geometry of the ligand system and to a lesser extent on steric factors with respect to coordination.

The two methyl groups of II are found to hinder coordination with transition metal salts.^{17,18} If, on coordination to form $M(\text{CO})_4(\text{II})$, there is also a steric problem, such is not in evidence from a comparison of the CO stretching frequencies with less hindered phenanthroline ligands.⁹ That the air and thermal stabilities of complexes of I are almost as great as five-member ring chelates and the similar high CO force constants suggests little steric problem due to the two methyl groups.

Preliminary investigations of substitution reactions of $M(\text{CO})_4(\text{I})$ with various monodentate ligands indicate that the reaction rate is similar to that reported for complexes containing five-member chelate rings and thus suggests similar "labilizing" properties.^{8,12} Studies of the coordination properties of the naphthyridine ligand system with transition metal salts, metal alkyls, and alkyl halides, as well as other carbonyls, are in progress.

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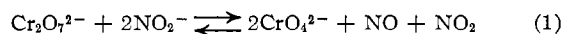
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The Dichromate–Nitrite Reaction in Fused Sodium Nitrite

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In a manner analogous to the behavior of the nitrate ion, the nitrite ion could be expected to act as a Lux base. Attack on Pyrex glass by molten KNO_2 suggests that nitrite is indeed a relatively strong base. Brough, *et al.*,¹ have reported that a brisk reaction occurs when dichromate and nitrite are fused. The reaction



has been proposed² for the reaction of dichromate with nitrite in a sodium nitrate–potassium nitrate eutectic melt, but no accurate determination of the moles of gaseous products produced per mole of dichromate consumed or of the relative proportion of NO to NO_2 in the gaseous products has been made.

Of further interest is the observation that dichromate, a relatively strong oxidizing agent, is not reduced to lower valence chromium species and that in turn nitrite is not oxidized to nitrate (at least directly) by dichromate but undergoes a complex reaction to give NO and NO_2 .

This paper is a report of a study to assess the stoichiometry indicated in eq 1 in order to elucidate the basic nature of the nitrite ion.

Experimental Section

Chemicals.—Reagent grade sodium nitrite was recrystallized from aqueous solution and dried under reduced pressure at 130° . Primary standard grade potassium dichromate was used after drying without further purification.

Procedures.—An accurately weighed sample of $\text{K}_2\text{Cr}_2\text{O}_7$ and a large excess of NaNO_2 were placed in a reaction vessel of known volume and connected to a mercury manometer and a vacuum manifold. After evacuation, the dichromate–nitrite mixture was fused at about 300° . Gaseous products were rapidly evolved. When the reaction subsided, the melt was allowed to cool and solidify. The reaction vessel was then submerged in a 96° water bath, and the pressure in the reaction vessel was measured. The number of moles of gaseous products was then calculated. The gaseous products were identified from their infrared spectra.

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(1) B. J. Brough, D. H. Kerridge, and S. A. Tariq, *Inorg. Chim. Acta*, **1**, 267 (1967).
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To determine the relative amounts of nitric oxide and nitrogen dioxide produced, a quantitative method of analyzing mixtures of NO and NO₂ as described by Whitnack, *et al.*,³ was used with minor modifications. One modification was the incorporation of a reaction vessel in which the reaction generating the NO and NO₂ mixture could be carried out and which could be isolated from the remaining part of the gas analysis system in order that the reaction chamber could be evacuated. Dry nitrogen gas was used as a carrier gas to sweep the NO and NO₂ into the absorption vessels. Trace quantities of oxygen were removed from the nitrogen by passing the nitrogen through a solution of sodium dithionite in a 10% potassium hydroxide solution. The analysis of the absorption solutions was done volumetrically using standard Ce(IV) solutions rather than permanganate solutions.

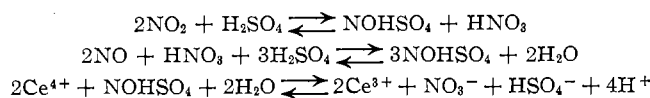
Weight loss experiments were done using a weighed tube containing the reactants and a glass wool plug to prevent loss of solids. The reaction could be carried out under atmospheric pressure or under a dynamic vacuum.

Results

The manometric experiments were made to help determine the over-all stoichiometry of eq 1. The reaction studied was that between potassium dichromate and sodium nitrite in pure fused sodium nitrite. After the reaction had taken place by fusing the mixture in the reaction vessel, the vessel was brought to a constant temperature of 96°. This temperature was selected because at this temperature the amount of nitrogen dioxide, an obvious product of the reaction, that would be dimerized to N₂O₄ would be small, less than 1%. Also the amount of dissociation of NO₂ into NO and O₂ would be negligible. The pressures developed when equilibrium was attained were in the range of 20–60 Torr. The calibrated volume of the system was 423 cm³. Although there was some attack on the mercury by the gaseous products, the errors introduced appeared negligible if the time of observation was kept to less than 0.5 hr. In the calculation of the number of moles of gas present, the gaseous products were assumed to behave ideally at 96° and reduced pressure. The results for nine experiments are listed in Table I. On the average, 98% of the moles of gaseous products calculated on the basis of eq 1 were obtained.

These gaseous products were identified as nitric oxide and nitrogen dioxide by comparison of their infrared spectra with published spectra.⁴ No other nitrogen oxides were detected.

To determine the ratio of NO and NO₂ present, the product gases were absorbed in sulfuric acid and sulfuric acid–nitric acid solutions. These solutions were analyzed for oxidizable nitrogen oxide species by titration with Ce(IV) solutions. The following reactions are pertinent



The results of these gas absorption experiments are given in Table II. Although equal moles of NO and

TABLE I
MILLIMOLES OF GASEOUS PRODUCTS PRODUCED PER MILLIMOLE OF DICHROMATE CONSUMED IN THE REACTION OF POTASSIUM DICHROMATE WITH MOLTEN SODIUM NITRITE AT 300°

Expt. no.	mmol of K ₂ Cr ₂ O ₇	ΔP, ^a Torr	mmol of gaseous products	Ratio ^b
1	0.258	27.3	0.502	1.94
2	0.290	31.1	0.572	1.97
3	0.329	33.7	0.620	1.88
4	0.330	35.6	0.655	1.98
5	0.383	41.5	0.763	1.99
6	0.396	42.1	0.774	1.95
7	0.417	44.6	0.820	1.97
8	0.460	49.6	0.913	1.98
9	0.501	53.4	0.983	1.96
				Av 1.96

^a ΔP observed at 96° in a volume of 423 cm³. ^b Ratio of millimoles of gaseous product to millimoles of K₂Cr₂O₇ consumed.

TABLE II
MILLIMOLES OF NO AND NO₂ ABSORBED AS GASEOUS PRODUCTS OF REACTION BETWEEN DICHROMATE AND NITRITE IN MOLTEN SODIUM NITRITE AT 300°

Expt no.	mmol of K ₂ Cr ₂ O ₇	mmol of NO	mmol of NO ₂	Ratio ^a
1 ^b	3.33	5.54	1.15	4.77
2 ^b	3.60	5.90	1.31	4.52
3 ^c	3.40	4.08	2.73	1.50
4 ^c	3.41	4.21	2.61	1.61
5 ^d	4.35	6.27	2.43	2.58
6 ^c	3.55	4.41	2.70	1.64
7 ^d	3.57	5.31	1.84	2.88
8 ^d	10.45	15.06	5.85	2.58

^a Ratio of millimoles of NO to millimoles of NO₂. ^b Experiment carried out under atmospheric pressure. ^c Experiment carried out under vacuum; gaseous products trapped at –78°. ^d Experiment carried out under reduced pressure; gaseous products not trapped.

NO₂ were predicted by eq 1, the relative amounts of NO and NO₂ present varied considerably. Nitric oxide was present in larger quantities than nitrogen dioxide in all experiments, the nearest ratio to the predicted ratio of 1:1 being 1.5:1 (60% NO, 40% NO₂), obtained when the reaction was carried out under vacuum and the product gases were trapped at –78°.

The weight loss experiments were done to check the results of the gas absorption measurements. Other investigators² have implied that their thermogravimetric experiments indicated that equal moles of NO and NO₂ were lost in the reaction of potassium dichromate with a sodium nitrite–potassium nitrite eutectic. Our weight loss experiments were done using purified sodium nitrite alone with potassium dichromate. Consequently the temperature at which the reaction was allowed to take place was about 300°. The experiments were performed under both atmospheric pressure and under a dynamic vacuum. The results are shown in Table III. Here again the relative proportion of NO to NO₂ is variable. The closest ratio to equimolar is 1.11 (52.5% NO, 47.5% NO₂) and this also was obtained when the reacting system was kept under vacuum.

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TABLE III
LOSS IN WEIGHT OF THE $K_2Cr_2O_7$ - $NaNO_2$ SYSTEM WHEN HEATED TO 300°

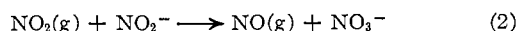
Expt no.	mmol of $K_2Cr_2O_7$	Wt loss, mg	Ratio ^a
1 ^b	1.73	112	5.46
2 ^b	1.69	109	6.68
3 ^c	1.73	124	1.91
4 ^c	1.82	136	1.20
5 ^c	1.70	126	1.29
6 ^c	1.75	132	1.11

^a Ratio of millimoles of NO to millimoles of NO_2 . ^b Experiment done under atmospheric pressure. ^c Experiment done under dynamic vacuum.

Discussion

The manometric studies support the stoichiometry of eq 1 in that 2 mol of gaseous products is produced per mole of dichromate which reacts with the nitrite, a reaction which proceeds to completion within the limits of the experimental observations. Although dichromate is generally considered to be a strong oxidizing agent, there was no indication of oxidation of nitrite by dichromate since no visually observable chromium(III) species were detected.

The variation in the relative proportion of NO to NO_2 in the gaseous products indicated by the gas absorption and weight loss experiments can best be explained by considering the oxidation of NO_2^- by NO_2 gas according to the reaction



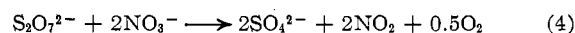
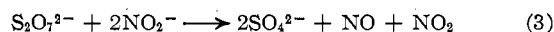
This reaction has been suggested by other workers.² Verification was obtained by placing NO_2 gas in a closed tube with molten sodium nitrite at 300° . The brown color of NO_2 disappeared in about 0.5 hr with no change in pressure. When oxygen gas was added to the system, the brown color reappeared. This indicated that NO_2 had been reduced to NO which was subsequently reoxidized by oxygen.

Apparently in both the gas absorption and weight loss experiments, some of the NO_2 produced reacted with the molten nitrite and as a result the ratio of NO to NO_2 increased. Furthermore, the departure from an equimolar ratio of NO to NO_2 was least when the weight loss and gas absorption experiments were performed under vacuum. This suggests that the less contact the gaseous products have with the melt, the less the conversion of NO_2 to NO occurs.

The results of the manometric experiments are insensitive to the relative amounts of NO and NO_2 produced. Since 1 mol of NO is produced for every mole of NO_2 which reacts with the sodium nitrite, the number of moles of gaseous products remains constant and consequently the pressure measurement will not indicate to what extent this secondary reaction takes place.

Topol, Osteryoung, and Christie² reported that in reactions between nitrite and different acids in an alkali metal nitrate melt, the relative amounts of NO and NO_2 formed varied with the acid. $K_2Cr_2O_7$ gave a

mixture of about 90% NO and 10% NO_2 whereas $K_2S_2O_7$ gave a mixture of about 50% NO and 50% NO_2 . In view of the strong-base behavior of nitrite as compared to nitrate, it would seem reasonable that the primary reaction in the case of dichromate is directly with nitrite according to reaction 1, followed by the reaction of NO_2 gas with nitrite to form NO as in reaction 2. The reaction of dichromate with the nitrate melt would be negligible. In the case of pyrosulfate, however, the increase in the relative amount of NO_2 produced is most likely the result of several factors. Because of the strong acidic nature of pyrosulfate as compared to dichromate, the reactions of pyrosulfate directly with nitrite and with nitrate are probably both important, *i.e.*



Also, the oxygen produced in (4) would react with the NO produced in (3) to produce more NO_2 . The decrease in NO_2 due to reaction 2 would be offset to some degree by this reaction.

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Spectral Properties of Oxovanadium(IV) Complexes. III. Salicylaldimines

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Previous papers have dealt with the β -ketimine complexes of the oxovanadium(IV) ion.^{1,2} To add data for our model compound studies of naturally occurring vanadium complexes, we report here some new work on the electronic absorption and esr spectra of some oxovanadium(IV) salicylaldimine complexes (Figure 1). Ligands^{3,4} and coordination compounds were prepared as previously described.⁵ Elemental analyses, mass spectral molecular weight, and effective magnetic moments agree with the formulation given. Spectroscopic methods used have been completely described elsewhere.¹

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