As a first approximation *R* seems to be independent of HCl concentration and the same for all elements.

The extent of fluoride complexing was estimated for various metal systems according to eq. 1 with log $R = -0.2$ and the computed fractions F' are summarized in Table I. The values listed should be considered approximate though they are useful for demonstrating semi-quantitatively the wide differences in complexing properties of the elements. The method is of course adaptable to more precise determination of the extent of fluoride complexing though it requires more accurate measurement of D_F/D_{Cl} and of the factor *R*.

In the computation of F' according to eq. 1, adsorption of fluoride containing complexes is considered negligible. This seems to be the case for those elements which in HCl–HF are negligibly adsorbed at low HCl concentrations. For the other elements this condition is only met at very high HCl concentration.

Negatively charged fluoride complexes seem to be only moderately strongly adsorbed and their adsorption apparently becomes appreciable only at chloride concentrations less than *ca.* 3 *M*, where their presence is revealed by an increase of D_F with decreasing *M* HCl. In view of this low intrinsic adsorbability of negatively charged fluoride complexes, it is extremely difficult to establish their existence at high ionic strength. Thus even for the elements whose adsorbability in concentrated HCl essentially vanishes on addition of substantial amounts of HF, one can only conclude that they are essentially completely converted to fluoride complexes; a decision regarding the sign of the charge of these fluoride complexes at high *M* HCl must be deferred.

Acknowledgment.—We are indebted to Mrs. Donna Michelson and Dr. R. A. Day for permission to include some of their adsorption data for V(IV), Ti(IV) and Fe(III) in HCl–HF solutions.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, VICTORIA UNIVERSITY OF WELLINGTON]

The Composition of the Nitric Oxide Complexes of Cupric Halides[1]

BY R. T. M. FRASER[2] AND W. E. DASENT

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The formation of a blue complex when nitric oxide is absorbed by solutions of cupric bromide or chloride is due to the presence of covalent molecules such as $CuBr_2 \cdot NO$. In ethanol, dissociation to colorless, ionic species takes place and these are shown to be responsible for erroneous reports of ion migration experiments. Reduction to cuprous bromide occurs upon reaction of nitric oxide with solutions containing less than two equivalents of bromide ion per cupric ion.

Absorption of nitric oxide by cupric salts in non-aqueous solvents with the simultaneous formation of deep blue solutions was first observed by Kohlschütter.[3] Several workers[4–8] have subsequently studied the complexes, but because the solid compounds have not been isolated from solution, and indeed are unstable even in solution, their composition and structure have usually been argued by analogy with the nitric oxide complexes of ferrous salt.[9]

The results of ion migration experiments[3] have been confusing and have led to the proposal of formulas such as $CuNo \cdot X_n^{(n-2)-}$, $CuX_2 \cdot NO$ and $Cu(EtOH)_3 \cdot NO^{++}$ (X = Br or Cl). Since the nitric oxide is coördinated in the +I state (as the nitrosonium ion),[8] the complexes are important because of their possible relationship to the carbon monoxide–cuprous chloride complex.

This study was undertaken to define the stoichiometry of the complexes and to reinterpret the ion migration experiments.

Experimental

Reagents.—All chemicals were of analytical reagent grade unless stated and were stored in sealed bottles in vacuum desiccators until required. Ethyl alcohol was refluxed over magnesium turnings in the presence of a trace of iodine to yield "super dry alcohol."[10] Acetonitrile was distilled twice and stored in a brown bottle away from light.[11] Formic acid was distilled and then fractionally crystallized.

Cupric bromide was prepared from cupric oxide and hydrobromic acid.[12] The brown crystals were dried in a desiccator, finely powdered, then returned to the desiccator for a week before use. Anhydrous cupric chloride was prepared from the hydrate by warming in a stream of dry hydrogen chloride.[12] The cupric salts were analyzed frequently; no change in the copper or halide content occurred during the course of experiments.

Nitric oxide was prepared from ferrous sulfate, sulfuric acid and sodium nitrite.[13] As evolution of gas was slow, powdered pumice or calcium sulfate was added to the mixture (1 g. to 25 ml. of solution). Calcium sulfate was the more efficient and evolution of gas was complete within one min.

Gas Absorption Measurements.—The nitric oxide was stored in a reservoir until needed, then slowly forced through scrubbers containing successively concentrated sodium hydroxide solution and concentrated sulfuric acid. The scrubbers were cleaned and refilled after every twenty absorption measurements. The gas then passed to a buret connected to a manometer and to the absorption flask. Before each measurement the absorption flask was carefully

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(1) From a dissertation submitted by R. T. M. Fraser in partial fulfillment of the requirements for the degree of Master of Science. Nov., 1957.

(2) Department of Chemistry, The University of Chicago.

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freed from traces of moisture, as the volume of nitric oxide absorbed by the cupric salts is greatly reduced by traces of water and neglect of this fact is responsible for many of the low values recorded in the literature. During reaction the absorption flask was maintained at a constant temperature (±0.50) in a thermostat. Blank runs established the volume of nitric oxide absorbed by the solvent at each temperature for which measurements were made. All volumes recorded are corrected for this absorption, and corrections have also been applied for the effect of dissolved salts upon nitric oxide absorption.

Measurement of Optical Spectra.—Special cells were constructed to fit the Unicam S P 500 Spectrophotometer used. These cells were blown in a half-inch square, two opposite faces were cut off and replaced with plane glass such that the optical path length was 1.0 cm. The neck of each cell was ground to take glass stoppers, one of which was fitted with a capillary bubbler and exit tube; reactions could thus be carried out directly in the cell. The bubbler was bent out of the path of the light beam. A thermocouple composed of thin copper and constantan wires sealed into a glass capillary was used to measure the temperature within the cell (the accuracy was about ±0.25°). Connection to the thermocouple was made through the exit tube in the stopper.

The cells were calibrated against 1 cm. silica cells: variation in the transmission was within 1% at all wave lengths. The spectra were plotted manually from 400–800 mμ.

Apparatus for Ion Migration Measurements.—A U-shaped absorption vessel was constructed: platinum electrodes were sealed into a 2 cm. diameter glass tube fitted at one end with a stopcock, and joined through a 1 cm. diameter tube at the other end to a bulb having a capacity equal to that of the rest of the apparatus. To form the complexes, the cupric solutions were run back into the bulb, the apparatus flushed with nitrogen and then nitric oxide was admitted until absorption of the gas was complete. Measurements of the migration of the color were made overnight.

Results

As the results reported in the literature are inconclusive, it was necessary to establish from the outset the maximum value for the nitric oxide copper ratio.

A. Solutions where Halide/Copper[14] $\geqslant 2.0$.—The volume of nitric oxide absorbed by cupric bromide or chloride in a number of organic solvents was measured. The results for ethyl alcohol are shown in Table I.

TABLE I

SUMMARY OF VOLUME OF NITRIC OXIDE ABSORBED BY CUPRIC HALIDES IN ETHYL ALCOHOL AT ATMOSPHERIC PRESSURE, 0°

[$CuBr_2$] × 10^3, mole/l.	Vol. NO, mole/mole Cu	[$CuCl_2$] × 10^3, mole/l.	Vol. NO, mole/mole Cu
3.74	0.995	4.18	0.79
6.11	0.970	7.40	.92
11.3	1.00	12.6	.83
15.5	1.00	16.7	.77

Cupric bromide was only very slightly soluble in acetonitrile, the salt did not absorb nitric oxide and the optical spectrum of the solution did not change. Cupric chloride, however, was readily soluble and the volume of nitric oxide absorbed ranged from 0.97 to 1.01 mole/mole copper at 0°. The color of the solution changed from a pale green to pink after reaction.

In formic acid the solubility of cupric bromide was too low to allow measurements of nitric oxide absorption; cupric chloride, however, was soluble up to 0.005 mole/l., and reacted readily with the gas to yield deep purple solutions. Absorptions were made at 5–8°, the volume of the nitric oxide absorbed ranged from 0.96 to 0.98 mole/mole copper. The nitrosyl formed was particularly stable, even on exposure to air (its behavior is similar in this respect to the copper nitrosyl complex formed in concentrated sulfuric acid). If a stream of oxygen was blown through the solution after reaction, the nitrosyl color faded; the color returned rapidly when the flow of oxygen was stopped, and this process could be repeated many times, although the intensity of the nitrosyl coloration slowly faded. If nitrogen was blown through the solution, the color faded and did not return after the gas flow was stopped.

Cupric sulfate dissolved in formic acid also formed a complex with nitric oxide but this decomposed almost immediately with the evolution of carbon dioxide.

The volumes of gas absorbed when the halide content of the solutions was increased by the addition of tetraethylammonium bromide or lithium bromide or chloride are shown in Table II.

TABLE II

EFFECT OF ADDED HALIDE CONCENTRATION UPON NITRIC OXIDE ABSORPTION

[$CuBr_2$] × 10^3, mole/l.	Br/Cu	Vol. NO, mole/mole Cu	[$CuCl_2$] × 10^3, mole/l.	Cl/Cu	Vol. NO, mole/mole Cu
		Ethanol solutions			
4.22	2.46	0.99	7.40	2.00	0.92
9.38	3.05	.98	12.6	3.13	.96
6.48	4.28	.97	7.40	6.30	.95
11.1	5.88	.99	1.89	8.62	.98
10.6	10.65	1.01	4.15	11.72	.99
10.6	12.30	1.01	1.89	27.3	1.08
		Acetonitrile solutions			
[$CuCl_2$] × 10^3, mole/l.	Cl/Cu	Vol. NO, mole/mole Cu	[$CuCl_2$] × 10^3, mole/l.	Cl/Cu	Vol. NO, mole/mole Cu
10.7	2.0	1.00	10.7	6.7	0.99
10.7	2.6	1.00	6.72	7.6	1.00
6.72	3.4	0.99	10.7	10.8	1.00

B. Halide/Copper Ratio <2.0.—By adding ethyl alcohol containing anhydrous silver perchlorate to the alcoholic solutions of the cupric halides and filtering off the silver halide formed, the ratio of halide to copper was decreased from 2.0 to 0.1. The variation of absorption of nitric oxide as this ratio was changed is shown in Fig. 1.

In solutions containing cupric bromide, as the reaction proceeded a white precipitate of cuprous bromide also was formed; this increased to a maximum at Br/Cu = 1.0, at which point all the copper in solution was precipitated and then decreased as the bromide concentration was lowered further. The optical density of the complex formed decreased linearly to zero as the Br/Cu ratio was lowered from 2.0 to 1.0. The relationship is shown in Fig. 2. The amounts of $CuBr_2 \cdot NI$, CuBr and NO^+ at each Br/Cu ratio were determined as follows: the nitrosyl complex was estimated by measurement of the optical density of the solutions at 575 mμ; the precipitate of cuprous bromide was dried and weighed; NO^+,

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[14] The terms "Halide/Copper," "Bromide/Copper" and the symbols "Br/Cu" etc., refer to the ratio of total concentrations, whether combined or as simple ions in solution.

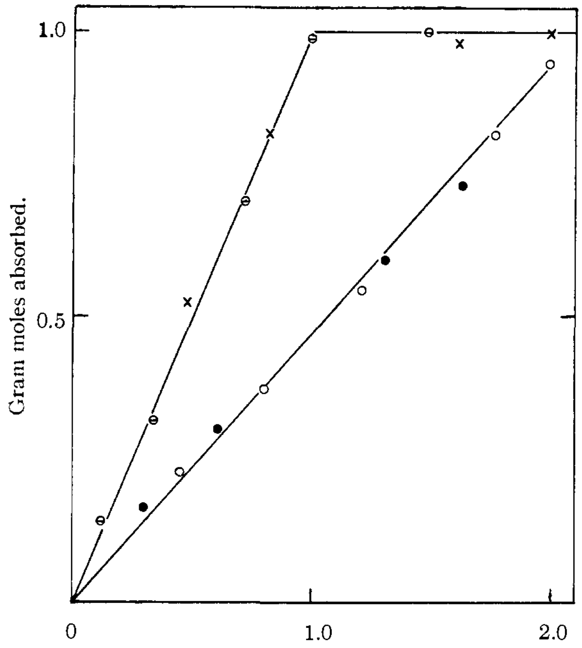


Fig. 1.—Relation between the volume of nitric oxide absorbed and the halide/copper ratio: ×, 0.0119 *M* $CuBr_2$; ⊖, 0.0132 *M* $CuBr_2$; ○, 0.0110 *M* $CuCl_2$; ●, 0.0137 *M* $CuCl_2$.

present as ethyl nitrite, was estimated in the filtered solutions by addition of potassium iodide and subsequent titration of the liberated iodine with standard sodium thiosulfate solution.

C. Spectrophotometric Measurements.—The absorption spectra of the complexes from 400–800 mμ in a number of solvents were redetermined using the new cells. In these cells the color of the nitrosyl persisted for periods up to 40 minutes without change. The spectra are shown in Fig. 3.

The effect of addition of carbon tetrachloride or cyclohexane to alcohol solutions upon the apparent molar extinction coefficient of the cupric bromide–nitric oxide complex is shown in Table III.

Discussion

Gas Absorption Measurements.—In alcoholic solutions where the halide/copper ratio is 2.0, the effect of traces of water upon the cupric chloride reaction is evident; even when super-dry alcohol is used, the volume of nitric oxide absorbed is much less than corresponding measurements with cupric bromide. Recent experiments seem[8] to indicate an equilibrium between nitric oxide and cupric chloride, although the present authors found that change in pressure or temperature (up to 39°) had no effect upon the volume of gas absorbed by cupric bromide.

The solution of cupric chloride in formic acid presents an interesting side reaction: some oxidation of the species containing the nitric oxide apparently occurs and the product is reduced back by the solvent. Carbon dioxide is one of the end products.

Table III

Increase in Apparent Molar Extinction Coefficient of Cupric Bromide–Nitric Oxide Solutions at 575 mμ with Decrease in Ethyl Alcohol Content of Solvent

% cyclohexane,[a] v./v.	Apparent ε	% CCl_4, v./v.[b]	Apparent ε
10	234	10	285
20	270	20	316
30	306	30	380
40	335	40	441
50	398	50	521
60	466	60	539
70	548	70	625
80	620	80	620
85	625		
90	627		

[a] [$CuBr_2$] 1.71 × 10^{-3}, mole/l. [b] [$CuBr_2$] 2.48 × 10^{-3}, mole/l.

If the absorbing species forming the nitrosyls in the solvents studied were complex cupric anions, the absorption of nitric oxide should have risen above 1.0 mole/mole Cu as the halide concentration was increased. This is not so (Table II). Values as high as 3.6 equivalents of gas absorbed[3] apparently cannot be obtained in non-aqueous solvents.

Upon decreasing the halide/copper ratio of the solutions, there is a marked difference in the behavior of the chloride and the bromide. In the solutions of cupric chloride, the absorbing species is the neutral $CuCl_2$, shown by the fact that both the volume of gas absorbed and the intensity of the color of the nitrosyl (measured at 425 and 550 mμ) decrease linearly to zero as the Cl/Cu ratio falls. Although it would appear (Fig. 1) that the absorbing species in the bromide solutions is $CuBr^+$, it is apparent from the observed stoichiometry plotted on Fig. 2 that this is incorrect. If the copper and bromide ions are present as

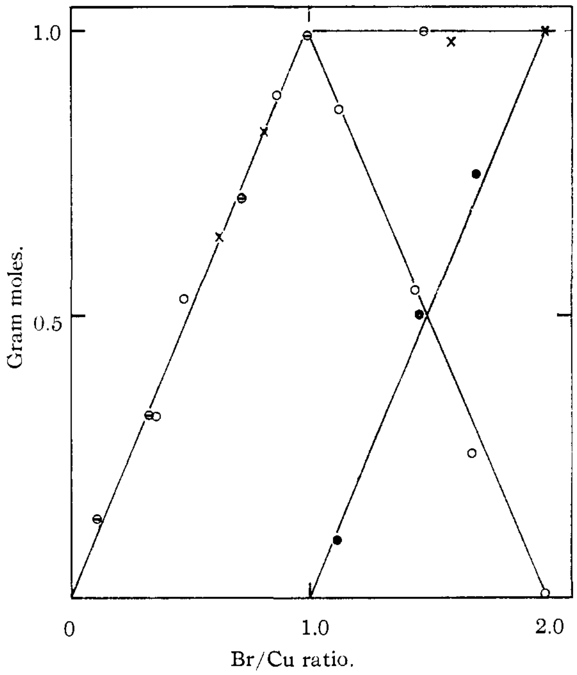


Fig. 2.—Relation between nitric oxide absorbed (× and ⊖), nitrosyl formed (●) and the cuprous bromide precipitated (○).

species such as $CuBr^+$ and $CuBr_2$,[15] the uptake of nitric oxide can be accounted for satisfactorily by a combination of the two reactions

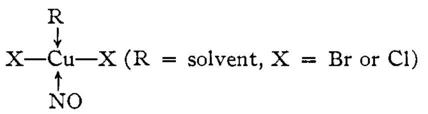
$$CuBr_2 + NO \rightleftarrows CuBr_2{\cdot}NO$$

$$CuBr^+ + NO \rightleftarrows CuBr + NO^+$$

(It is not suggested that the nitrosonium ion remains as such in ethyl alcohol.) The reversibility of the first reaction is well known[6]; the reversibility of the second was shown by passing a stream of oxygen-free nitrogen through the mixture: as the nitric oxide was removed, the cuprous bromide redissolved. The species forming the nitrosyl is $CuBr_2$, similar to $CuCl_2$.

As acetonitrile is capable of solvating the nitrosonium ion without reacting with it, it was hoped to repeat the cupric bromide system in this solvent. Unfortunately there does not appear to be any reaction between nitric oxide and the bromide in acetonitrile.

Spectrophotometric Measurements.—All the optical spectra exhibit the same general pattern, indicating that the complexes possess similar constitutions. The double maximum near 560 mμ has not been reported before. From the shift in position of the maximum as the composition of a mixed solvent (ethyl alcohol and ethyl acetate) was changed, Mahon[16] assumes that a molecule of the solvent participates in the formation of the complex, occupying the fourth coördination position about the central copper atom. This view is supported by the fact that the nitrosyls are formed in solvents with donor properties, such as ketones, alcohols and esters, and not in carbon tetrachloride or cyclohexane. A structure such as



$$\begin{array}{c} R \\ \downarrow \\ X\text{—}Cu\text{—}X \\ \uparrow \\ NO \end{array} \quad (R = \text{solvent}, X = Br \text{ or } Cl)$$

accounts satisfactorily for the blue color observed but does not explain the ion migration experiments[3] which recently have been confirmed.[17] On the other hand, dissociation into NO^+ and $CuBr_2^-$ (giving in ethyl alcohol EtONO, H^+, $CuBr_2^-$) does not explain the color, since none of the ions absorb in the visible region of the spectrum.

It is possible that both forms are present in equilibrium, as suggested for $AlCl_3{\cdot}NOCl$[18]; in which case, decrease of the dielectric constant of the solvent brought about by addition of carbon tetrachloride or cyclohexane to the alcohol should result in an increase in the concentration of the colored covalent species over the ionic form. This is so, shown by the fact that as the dielectric constant decreases, the apparent molar extinction coefficient measured at 575 mμ tends toward a limit of 625 (Table III), although the volume of nitric oxide absorbed by the cupric bromide remains constant at one equivalent. The value 625 disagrees with a recent figure of 309 determined for the nitric oxide complex of cupric chloride in ethyl alcohol,[8] where the possibility of such an equilibrium was ignored. The cupric bromide is more satisfactory for study, since the gas absorption is always complete even at temperatures as high as 39°, contrary to previous opinion. Preliminary spectrophotometric measurements made at a series of temperatures indicate that the dissociation constant for the blue nitrosyl of cupric bromide is 3.7×10^{-3} (ΔH = 9 kcal./mole, ΔS = 19 e.u.); thus the extinction coefficient is much greater than previously realized.

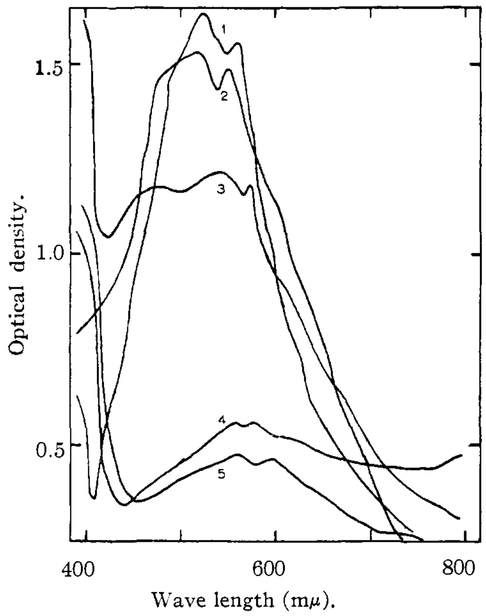


Fig. 3.—The optical spectra of the nitrosyl complexes: 1, $CuCl_2{\cdot}NO$ in formic acid; 2, $CuSO_4{\cdot}NO$ in concentrated sulfuric acid; 3, $CuCl_2{\cdot}NO$ in acetonitrile; 4, $CuCl_2{\cdot}NO$ in ethanol; 5, $CuBr_2{\cdot}NO$ in ethanol.

Ion Migration Measurements.—Because of the confusion caused by early reports[3] of ion migrations using these complexes, the measurements were repeated. A distinct movement of the color does occur, but instead of explaining this in terms of an ionic complex, the colorless ions CuX_2^- and NO^+ (H^+ in alcohol) may be considered to move. The CuX_2^- moves to the anode, becomes neutral CuX_2 and immediately combines with nitric oxide dissolved in the solvent to form the blue nitrosyl around the anode. The positive ion moves to the cathode and is discharged as a gas. Although this formation of gas apparently was neglected by early workers, enough is formed overnight to be visible to the eye. It is interesting to note that in those cases where the complex has been described as a cation, ion migration could not be detected upon repetition.

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