oxide was formed when polished copper blocks were heated gently in an electric furnace or exposed to air at ordinary temperatures, but an oxide of unknown structure was obtained by heating the blocks on red hot brass until they were tinted and allowed to cool in air. By electron diffraction studies and chemical tests Murison[18] showed this oxide of unknown structure to be a mixture of cuprous and cupric oxides. When the specimens were heated in air from 300 to 500° the cuprous oxide and the cuprous–cupric oxide patterns were equally probable. If air or oxygen were blown through the furnace tube while the specimen was being heated, the cuprous–cupric oxide pattern invariably was obtained. A cupric oxide pattern was never obtained from the surface films; it was obtained only after heating cuprous oxide powder at temperatures over 600°.

The electrical method has made it possible to measure the respective amounts of the oxides formed on copper under different conditions.[19] The results obtained show that: (1) the oxide films responsible for the early interference colors—and also the still thinner, invisible films—are sometimes entirely and often largely cuprous oxide; (2) sometimes a considerable amount of cupric oxide also is formed on heated copper and its amount increases with film thickness. When copper is heated to tints beyond the middle of the second order, under strongly oxidizing conditions, cupric oxide appears as a separate sooty layer outside the color film, obscuring the later colors.

A film of a given color may contain either no cupric or a considerable amount of this oxide. It thus appears that the cuprous–cupric oxide layer contains either an intimate mixture of the two oxides or even a solid solution possibly with the greater concentration of the cupric oxide toward the outer surface and of the cuprous oxide toward the metal base. Under such conditions light is still reflected mainly from the outer and inner surfaces of the cuprous–cupric oxide film, and normal interference effects are observed until a separate layer of cupric oxide is formed over it.

The author gladly acknowledges his indebtedness to Dr. U. R. Evans for much advice and information, and most valuable suggestions.

Summary

The thicknesses of oxide films produced on heated copper have been estimated by measuring the number of millicoulombs needed for their cathodic reduction. The relations between film thickness and time of heating indicate that the parabolic law $y^2 = kt + A$ is only valid for short periods and that A is not zero for abraded surfaces. The color film on tinted copper may contain cupric as well as cuprous oxide—apparently in intimate admixture—but under strongly oxidizing conditions, a separate sooty film (presumably cupric oxide) obscures the later colors.

CAMBRIDGE, ENGLAND RECEIVED OCTOBER 20, 1937

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[18] Murison, *Phil. Mag.*, **17**, 96 (1934).

[19] The cuprous oxide reduces at a lower potential value than cupric oxide (Fig. 3).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY NO. 626 AND FROM THE LABORATORY OF INORGANIC AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF LEYDEN]

The Electron Diffraction Investigation of Nitrosyl Chloride and Nitrosyl Bromide

BY J. A. A. KETELAAR AND K. J. PALMER

An investigation of the molecular structure of nitrosyl chloride and bromide seemed to be of interest especially with regard to the conclusions which Klinkenberg[1] has drawn from the determination of the crystal structures of some complex compounds formed by nitrosyl chloride and nitrosyl fluoride. He found that the nitrosyl group in many compounds is present in the state of the univalent ON^+ ion. In this respect there may be specially mentioned the case of the compound $2ONCl \cdot SnCl_4$, which is isomorphous with $(NH_4)_2SnCl_6$ and so really has the constitution $(ON)_2SnCl_6$.[2] In the same way he found the compounds $(ON)ClO_4$ and $(ON)BF_4$ to be isomorphous with the corresponding ammonium compounds.

Electron diffraction photographs were prepared in the usual way[3] with a film distance of about 11 cm., the electron wave length being 0.0613 Å. Some ten to fifteen photographs were taken of each compound and several of the best were inter-

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[1] L. J. Klinkenberg, *Rec. trav. chim.*, **56**, 749 (1937).

[2] In course of publication.

[3] L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

preted both by the radial distribution method and by the visual method involving the comparison of calculated curves with the visually estimated intensity curves. Tables I and II contain the values of $s = (4\pi \sin \vartheta/2)/\lambda$ for the apparent maxima and minima together with the estimated intensity values as used in the calculation of the radial distribution curves given in Fig. 1.

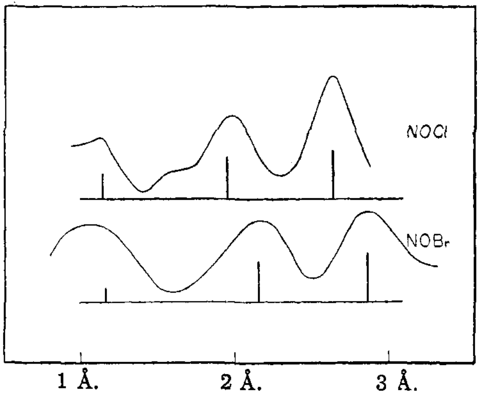

Fig. 1.—Radial distribution curves for nitrosyl chloride and nitrosyl bromide.

In applying the visual method we calculated intensity curves for different models. Some of these are reproduced in Figs. 2 and 3, whereas the data for the models used are found in Tables I and II.

Table I

Nitrosyl Chloride, ONCl

Max.	Min.	I	$s_{\text{obsd.}}$	$s_{\text{calcd.}}$[a]	$s_{\text{calcd.}}/s_{\text{obsd.}}$
1		10	3.19	3.18	0.997
	2		4.28	4.25	.999
2		3	5.23	5.27	1.008
	3		6.32	6.02	(0.953)
3		7	7.58	7.45	.983
	4		8.99	8.95	.996
4		5	10.24	10.33	1.009
	5		11.48	11.47	0.999
5		4	12.66	12.84	1.014
	6		13.71		
6		1	14.67	Shelf	...
	7		15.92	15.77	0.991
7		3	17.06	17.20	1.008
	8		18.45	18.53	1.004
8		2	19.61	19.69	1.004

Average 1.001
Average deviation 0.007

[a] Averaged for models B and C.

Model A: Cl–O = 2.63 Å., Cl–N = 1.97 Å., N–O = 1.14 Å.
B: Cl–O = 2.64 Å., Cl–N = 1.95 Å., N–O = 1.12 Å.
C: Cl–O = 2.65 Å., Cl–N = 1.94 Å., N–O = 1.16 Å.
D: Cl–O = 2.65 Å., Cl–N = 1.92 Å., N–O = 1.16 Å.
E: Cl–O = 2.64 Å., Cl–N = 1.95 Å., N–O = 1.18 Å.

Results: Cl–O = 2.65 ± 0.02 Å. N–O = 1.14 ± 0.04 Å.
Cl–N = 1.95 ± 0.02 Å. Angle Cl–N–O = 116 ± 2°

Table II

Nitrosyl Bromide, ONBr

Max.	Min.	I	$s_{\text{obsd.}}$	$s_{\text{calcd.}}$ (Model B)	$s_{\text{calcd.}}/s_{\text{obsd.}}$
1		8	2.98	2.94	0.997
	2			4.04	
2		1	*4.90*	*4.90*	*1.000*
	3			5.63	
3		10	6.90	6.87	0.997
	4		8.32	8.20	.986
4		6	9.40	9.37	.997
	5		10.67	10.59	.993
5		4	11.71	11.83	1.010

Average 0.997
Average deviation .004

Model A: Br–O = 2.82 Å., Br–N = 2.15 Å., N–O = 1.16 Å.
B: Br–O = 2.86 Å., Br–N = 2.15 Å., N–O = 1.16 Å.
C: Br–O = 2.86 Å., Br–N = 2.10 Å., N–O = 1.16 Å.

Results: Br–O = 2.85 ± 0.02 Å.
Br–N = 2.14 ± .02 Å.
[N–O = 1.15 ± .04 Å.]
Angle Br–N–O = 117 ± 3°

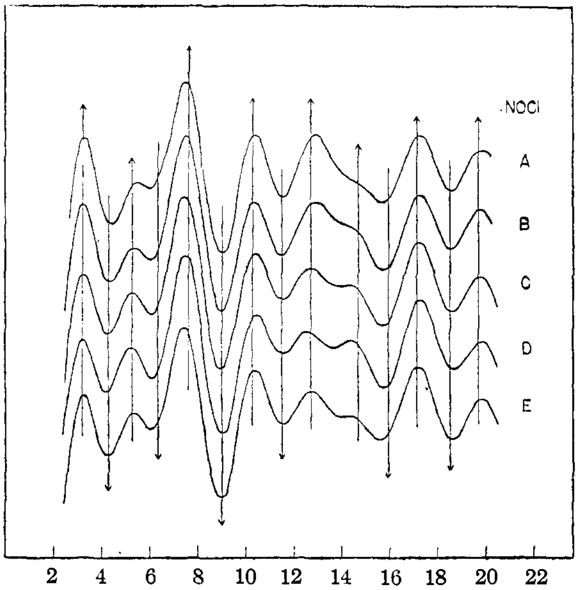

Fig. 2.—Intensity curves for nitrosyl chloride. Models described in Table I.

Curves B and C of Fig. 2 both give a good representation of the appearance of the photographs of nitrosyl chloride. Curve B gives probably a better representation of the intensity ratio of the fourth and fifth maxima, whereas the faint but distinctly visible sixth maximum is perhaps somewhat better represented by curve C. The final distances chosen were assumed to be between those for these two very closely related models, taking into account also the values from the radial distribution curve, *i. e.*, Cl–O = 2.65 Å., Cl–N = 1.94 Å., and N–O = 1.14 Å. The values found are: Cl–O = 2.65 ± 0.01 Å., Cl–N = 1.95 ± 0.01 Å., and N–O = 1.14 ± 0.02 Å. The bond angle Cl–N–O calculated from these distances is found to be 116 ± 2°. The correspondence between calculated curves and the observed intensities is decidedly less satisfactory for the other models especially with regard to the second maximum with the adjacent second and third minima, thus proving the accuracy of the results obtained.

In the case of the calculation of the intensity curves for different models of nitrosyl bromide, the N–O distance, which contributes in this case only very little to the total intensity, was assumed to be about the same as in nitrosyl chloride and taken as 1.16 Å. In this case model B leads to the curve corresponding most satisfactorily with the estimated intensities both with regard to the second maximum and to the part of the curve outside the fifth maximum. The distances for the different models are listed in Table II. The results on nitrosyl bromide are thus: Br–O = 2.85 ± 0.02 Å., Br–N = 2.14 ± 0.02 Å., N–O = 1.15 ± 0.01 Å., and the bond angle Br–N–O = 117 ± 3°.

The interatomic distances and bond angles are provided with estimated probable errors, indicating the extent to which they can be considered as reliable.

The sample of nitrosyl chloride used in this investigation, provided by Professor Don M. Yost of these Laboratories, was considered to be of high purity. A sample of nitrosyl bromide was especially prepared for us by Mr. Carroll Beeson of these Laboratories. In the case of nitrosyl chloride no decomposition of the compound was to be feared, as the values of the dissociation constant determined by Dixon[4] indicate that at room temperature the dissociation is still practically zero. In the case of the less stable nitrosyl bromide a possible decomposition has to be discussed more extensively. The determinations of Blair, Brass, and Yost[5] lead to a decomposition of about 4% at −15° and 200–300 mm. pressure. The sample was prepared by combining bromine with almost four times the necessary amount of nitrous oxide. The extra amount of nitrous oxide was removed later by pumping it off at a temperature of −70°. The sample was kept constantly at low temperature except for about twenty minutes during the exposures when it was at −30 to −15°. From the measurements of Krauss[6] on the velocity of the reaction by which ONBr is formed, combined with the values for the equilibrium, the reaction velocity for the decomposition reaction can be calculated. It is found that even at +15° and a pressure of 200 mm. only 10^{-6} part is decomposed in one second. From these data the conclusion can be drawn that the decomposition of the sample itself at the temperature at which it is kept is negligibly small and also that no decomposition occurs at room temperature during the exposure time of about one-fifth second.

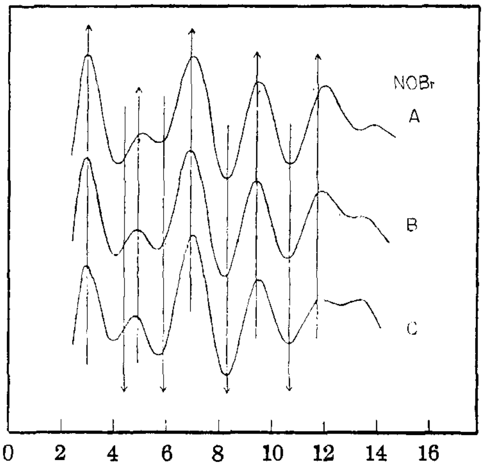

Fig. 3.—Intensity curves for nitrosyl bromide. Models described in Table II.

In the paragraphs above the assumption has been made that the halogen atom in the nitrosyl halides is closer to the nitrogen atom than to the oxygen atom. Because of the small difference in scattering powers of nitrogen and oxygen, the electron-diffraction data do not distinguish between the structures described above and those obtained from them by interchanging the nitrogen and oxygen atoms. We feel, however, that the arrangement ONX is more reasonable from

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(4) J. K. Dixon, *Z. physik. Chem. Bodenstein Festband*, 679 (1931).

(5) C. M. Blair, P. D. Brass and D. M. Yost, THIS JOURNAL, **56**, 1916 (1934).

(6) W. Krauss, *Z. physik. Chem.*, **A175**, 295 (1936).

the standpoint of valence theory than NOX, and so have based our discussion on it, and we have correspondingly used the formulas ONCl and ONBr rather than the conventional NOCl and NOBr in referring to nitrosyl chloride and bromide.

Discussion

As a result of the electron diffraction investigation[7] of ONCl and ONBr it is found that these molecules are non-linear with a bond angle in both cases of 116 ± 3°. The distances between nitrogen and chlorine and bromine are 1.95 and 2.14 Å., respectively, which are much larger than those expected from the sums of single bond radii, these latter being 1.69 and 1.84 Å., respectively. In many cases interatomic distances smaller than the sum of the covalent radii have been observed arising from contributions of structures with double bonds instead of single bonds. Distances appreciably larger than those expected from single bond radii have, however, only been observed in very few cases, *e. g.*, in B_2H_6[8] where the B–B and B–H distances were found to be 5 and 7%, respectively, larger than those calculated for single bond distances.

A possible explanation of this surprising discrepancy is gained from a discussion of the possible structures for the ONCl and ONBr molecules besides the normal structure described by the electronic formula $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:\underset{\cdot\cdot}{N}::\overset{\cdot\cdot}{O}:$. A large contribution of a structure with a double bond between chlorine and nitrogen atoms is excluded as this would result in an even shorter distance than that calculated for a pure single bond. It will be shown, however, that resonance between the normal structure and an ionic structure in which the molecule is built up from a chlorine (or bromine) ion and a nitrosyl ion results in a larger distance between nitrogen and halogen nuclei. An estimate of the distances to be expected for a pure ionic structure can be gained from the following considerations. Klinkenberg has found that the volume of the nitrosyl ion is somewhat less than that of the ammonium ion and about the same as that of the hydronium ion. If we assume a spherical form for the NO^+ ion, this leads to a radius of 1.40 Å. The assumption of spherical symmetry, suggested by the observed isomorphism between K, NH_4, and NO compounds, can be explained easily by the possibility that this high symmetry is caused by the rotation of the group just as, *e. g.*, in the case of the cyanide ion.[9] Taking the radius 1.40 Å. for the nitrosyl ion and setting the nitrogen and oxygen nuclei at equal distances from the center of the ion and at the mutual distance observed in ONCl, *i. e.*, 1.14 Å., we find for the distance from the nitrogen nucleus to the surface 1.40–0.57 = 0.83 Å. With the radius of 1.81 Å. for the chlorine ion we subsequently find 1.81 + 0.83 Å. = 2.64 Å. as the Cl–N distance in a pure ionic structure. We see that the assumption of an appreciable contribution of the ionic structure, as suggested by the above-mentioned results of Klinkenberg on the crystal structure of nitrosyl compounds, indeed leads to the high observed halogen–nitrogen distances. The electronic constitution of the ionic structure could only be $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:^{-}\quad :N:::\overset{+}{O}:$,[10] having a triple bond between nitrogen and oxygen. The distance calculated from covalent radii with the revised value[11] of the double bond factor is 1.18 Å.; similarly the triple bond distance is 1.06 Å. So we see that the observed nitrogen–oxygen distance is somewhat smaller than that calculated for the sum of double bond radii, pointing to some triple bond character just as demanded by a structure resonating between the normal and the ionic structures.

The dependence of the distance on the bond character is not known for the N–Cl bond. Assuming, however, this dependence to be of the same form as that for the C–C bond, we calculate about 50% ionic character for nitrosyl chloride and bromide. This percentage would result in an N–O distance of 1.11 Å., fairly close to the observed value of 1.14 Å. The data obtained from the electron diffraction investigation thus lead to the conclusion that ONCl and ONBr have an appreciable amount of ionic character. Data on their dipole moments are not found in the literature, and one of us (J. A. A. K.) proposes to determine the values of these quantities. The low boiling points suggest, however, that they will be small.

We are indebted to Professor Don M. Yost and

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(7) About two years ago some electron diffraction photographs of ONCl were taken by L. O. Brockway, L. Pauling, and J. Y. Beach in these Laboratories. They arrived at about the same results, especially regarding the large Cl–N distance, as we did from very much better photographs. These results were not published, as the purity of the sample used was doubtful.

(8) S. H. Bauer, THIS JOURNAL, **59**, 1096 (1937).

(9) J. M. Bijvoet and H. J. Verweel, *Rec. trav. chim.*, **54**, 631 (1935).

(10) L. Pauling, THIS JOURNAL, **53**, 3230 (1931).

(11) L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937).

Mr. C. Beeson for samples used in this investigation, and to Professor Linus Pauling for his constant interest and his criticism. One of us (J. A. A. K.) is indebted to the Netherland-America Foundation for a gift enabling him to stay at the California Institute of Technology while carrying out this investigation.

Summary

The arrangements of atoms in the molecules of nitrosyl chloride and nitrosyl bromide have been determined by electron diffraction, the interpretation being made both by the radial distribution method and by the usual visual method. The following results were obtained—nitrosyl chloride: Cl–O = 2.65 ± 0.01 Å., Cl–N = 1.95 ± 0.01 Å., N–O = 1.14 ± 0.02 Å., angle Cl–N–O = 116 ± 2°; nitrosyl bromide: Br–O = 2.85 ± 0.02 Å., Br–N = 2.14 ± 0.02 Å., N–O = 1.15 ± 0.04 Å., angle Br–N–O = 117 ± 3°.

The surprisingly large halogen–nitrogen distances found are explained as caused by resonance between the normal covalent structure and the ionic structure.

LEYDEN, THE NETHERLANDS
PASADENA, CALIF. RECEIVED SEPTEMBER 28, 1937

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

Silver Oxide: Heat Capacity from 13 to 300°K., Entropy, Heat of Solution, and Heat and Free Energy of Formation. The Heat of Formation and Entropy of Silver Ion

BY KENNETH S. PITZER AND WENDELL V. SMITH

A knowledge of the heat capacity of silver oxide makes possible a number of valuable thermodynamic calculations. In the light of our measurements of this heat capacity we have reconsidered the data on the dissociation pressure of silver oxide,[1] obtaining thereby values for both the heat and free energy of formation in which the uncertainties have been largely removed. Also we have calculated the heat of formation and entropy of silver ion, basing them principally on our determinations of the entropy and heat of solution of silver oxide. The results are particularly important because the thermodynamic constants of many silver compounds are dependent either on the constants for silver ion or on those for the oxide.

Material.—The first series of heat capacity measurements was made on a sample of a "reagent" grade of silver oxide which was dried at 110°C. for several days. Analyses for both silver content and acid neutralizing power gave between 99.8 and 100.0% of the theoretical value, while the absence of a hump in the heat capacity curve near the ice-point indicates the absence of a significant amount of water. The subsequent heat capacity measurements and the heat of solution measurements were made on samples prepared by precipitation from a dilute solution of "c. p." silver nitrate with a solution of carbonate-free sodium hydroxide. The sample used for the heat capacity work was washed, then dried and analyzed as above, the results being within 0.5% of the theoretical. In order to increase the rate of solution, the samples for heat of solution measurements were, after repeated washing, left under water until used. The amount of silver oxide was determined by analysis of the resulting solutions.

The Heat Capacity.—The heat capacity measurements were made with a calorimeter and cryostat similar to that described by Latimer and Greensfelder.[2] In the calculation of both heat capacities and heats of solution one calorie was taken equal to 4.1833 int. joules. The absolute temperature of the ice-point was assumed to be 273.10°K.

The first series of measurements, which were made on 179.60 g. of Sample I, showed a region of high heat capacity between 20 and 45°K. In order to confirm and investigate this region further, additional measurements were made on 158.30 g. of a different sample of silver oxide, using a new calorimeter. These results leave no possible doubt concerning the existence of high heat capacities in this region, but also indicate that equilibrium is not obtained readily with respect to the additional heat capacity. The

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(1) (a) Lewis, THIS JOURNAL, **28**, 139 (1906); (b) Keyes and Hara, *ibid.*, **44**, 479 (1922); (c) Benton and Drake, *ibid.*, **54**, 2186 (1932).

(2) Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928).