66. *The Action of Nitrosyl Chloride on Certain Silicates.*

By I. R. BEATTIE.

The action of nitrosyl chloride on silver analcite and sodium metasilicate is described. The experimental results are explained in terms of an ion-exchange process involving nitrosonium cations. Nitrosyl analcite is stable at room temperature.

THE existence of the nitrosonium cation in the solid state and in solution is well established.[1] However, despite the stability of this ion, together with the fact that its maximum radius lies between that of the ammonium and the hydroxonium ion,[2] there has been no attempt to study the possibility of ion-exchange reactions with nitrosyl compounds.

Nitrosyl perchlorate has the same crystal structure as ammonium or hydroxonium perchlorate.[2] This indicates either that the nitrosonium group rotates freely, or that there is a degree of randomness in the crystal. The approximate dimensions of the nitric oxide radical are shown in Fig. 1(*a*), while those of nitrosyl chloride are shown in Fig. 1(*b*). Spectroscopic evidence [3] indicates that the nitrogen–oxygen distance in NO^+ differs only slightly from that in nitric oxide. From Fig. 1(*a*) it is therefore clear that the maximum dimension of the nitrosonium ion must be less than 2·6 Å. However, where ion exchange is occurring, the ion will be oriented into the most favourable position to pass through an energy barrier, giving an effective radius which may be as low as 0·7 Å.

Certain aluminosilicates undergo ion exchange readily with univalent cations. It was therefore decided to study the possibility of nitrosonium-ion exchange in the zeolites analcite and chabazite, and in anhydrous sodium metasilicate. The nitrosyl compound selected was the chloride, which is gaseous at room temperature.

EXPERIMENTAL

Preparation of Reactants.—Nitrosyl chloride was prepared by the passage of dry nitrogen dioxide over potassium chloride containing 2% of water by weight.[4] The product was dried over anhydrous calcium chloride and distilled *in vacuo* into ampoules which were then sealed. The nitrogen dioxide was obtained by heating previously dried " AnalaR " lead nitrate.

We also prepared ion-exchanged forms of analcite ($Na_2O,Al_2O_3,4SiO_2,2H_2O$) and chabazite ($CaO,Al_2O_3,4SiO_2,6H_2O$) as described elsewhere.[5]

Crystalline sodium metasilicate nonahydrate [6] was dehydrated and melted in a platinum basin. It was then held just below its m. p. for one day, the anhydrous salt crystallising.

Procedure.—The apparatus is shown in Fig. 2. Sealed ampoules containing the appropriate silicate, which had been previously outgassed at 400°, were placed at *A* and *B*, and a tube containing nitrosyl chloride was placed in *C*, all together with iron-in-glass magnetic breakers. The apparatus was then evacuated through tube *E*, and sealed off at that point. The zero reading

---

[1] For a recent review of the chemistry of the nitrosyl group see Addison and Lewis, *Quart. Rev.*, 1955, **9**, 115.

[2] Klinkenberg, *Rec. Trav. chim.*, 1937, **56**, 74.

[3] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1944, p. 267.

[4] Whittaker, Lundstrom, and Merz, *Ind. Eng. Chem.*, 1931, **23**, 1410.

[5] Beattie, *Trans. Faraday Soc.*, 1954, **50**, 581.

[6] Harman, *J. Phys. Chem.*, 1925, **29**, 1155.

of the spiral gauge *F* was noted, the nitrosyl chloride ampoule smashed, and the equilibrium pressure measured, the spiral gauge being used as a null-point instrument. The ampoules in *A* and *B* were then broken and readings of pressure noted at appropriate times. When no further change occurred in the pressure readings, one of the ampoules *D* was used to remove the residual gases for analysis. Sample *A* was then heated at 400° for 3 hr., one of the remaining ampoules *D* being continuously immersed in liquid air to remove any released gases immediately. At the end of the heating period, this ampoule also was removed for subsequent analysis of the contents. Tubes *A* and *B* were also drawn off from the apparatus.

The weights of nitrosyl chloride and of the residual and released gases, and the changes in weight of the heated and the unheated silicate were noted.

Analysis.—The ampoule was placed in a flask which was then evacuated and cooled in liquid air. By shaking the flask it was possible to break the ampoule. Then 50 ml. of air-free N-sodium hydroxide were allowed to run into the flask and react with the contents. The flask was opened to the atmosphere and the contents were analysed.

(a) *Nitrite*. The solution was run slowly from a pipette dipping under warm acidified potassium permanganate solution. Excess of sodium oxalate solution was then added, to be back-titrated against the permanganate solution.

FIG. 1(*a*). *Dimensions of* NO *radical.*

(~0·7—N—1·14—O—~0·7)

FIG. 1(*b*). *Dimensions of nitrosyl chloride*

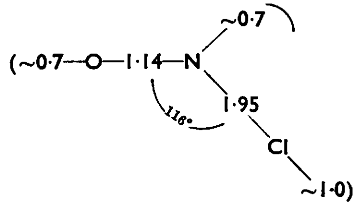
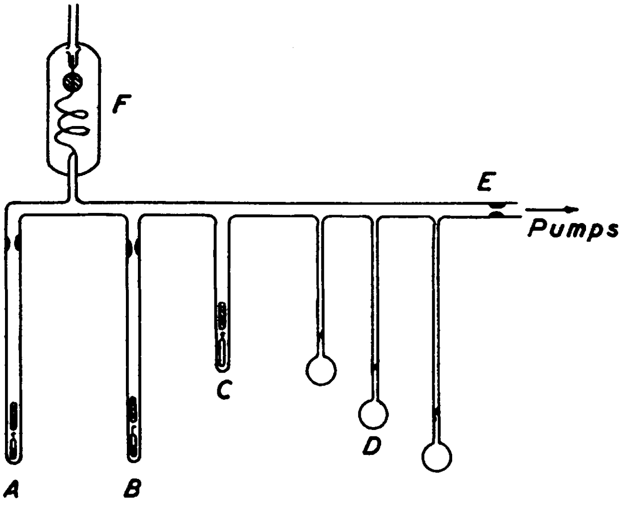


FIG. 2. *The apparatus.*



(b) *Chloride*. The solution was acidified with dilute nitric acid, boiled, and cooled, and excess of silver nitrate solution was added. After the addition of nitrobenzene the excess of silver nitrate was back-titrated with the standard thiocyanate solution.

RESULTS

In all cases where reaction occurred the pressure readings were dependent on the square root of the time, suggesting that a diffusion process was operative. These results are shown in Fig. 3. The products of reaction and the *X*-ray spectra of the unheated solids are shown in the Table. With sodium and thallium forms of analcite no reaction occurred, while with a glass of the composition CaO 6%, Na_2O 22%, SiO_2 72% (by wt.) there was only a slight reaction.

The action of nitrosyl chloride on certain silicates.

Compound	*X*-Ray identification of unheated product	Residual gases	Gases evolved on heating product	Notes on the exchange
Na_2SiO_3	NaCl	NOCl + 50 mol. % N_2O_3	Pure N_2O_3	20—30% exchange
Ag analcite	AgCl	Pure NOCl	NOCl + 15—25 mol.% N_2O_3	Nearly complete exchange
Na or Tl chabazite	Typical chabazite spectrum	Pure NOCl	NOCl + trace N_2O_3	One NOCl molecule sorbed per univalent cation

DISCUSSION

Sodium Metasilicate.—The fact that nitrosyl chloride with sodium metasilicate yields sodium chloride and some dinitrogen trioxide is difficult to explain without the assumption of nitrosonium ion exchange. Further, pure dinitrogen trioxide is obtained when the solid product of reaction is heated. The kinetics of the reaction indicate that a diffusion mechanism is probably operative. The reaction may then be represented :

$$Na_2SiO_3 + 2NOCl \longrightarrow (NO)_2SiO_3 + 2NaCl \longrightarrow N_2O_3 + SiO_2 + 2NaCl$$

The nitrosyl metasilicate is unstable even at room temperature and rapidly decomposes when heated. It is extremely unlikely that nitrosyl chloride could diffuse molecularly into sodium metasilicate, and further, the sodium chloride is *extra*crystalline.

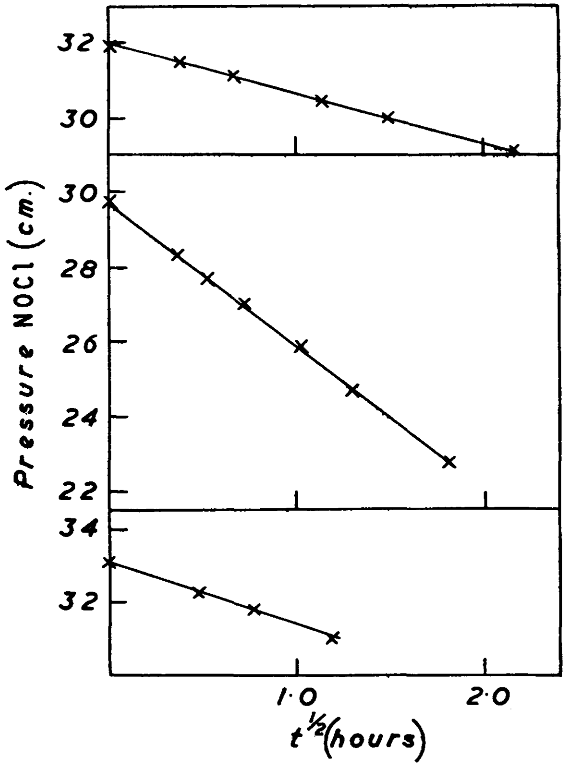


FIG. 3. *Relation between the nitrosyl chloride pressure and the square root of the time. The top curve refers to anhydrous metasilicate, the middle one to silver analcite, and the bottom one to thallium chabazite.*

Silver Analcite.—The reaction between silver analcite and nitrosyl chloride is particularly interesting. The solid product is stable and has a very low vapour pressure. As an example, an initial nitrosyl chloride pressure equal to 30 cm. Hg decreased to less than 1 cm. during two days (excess of silver analcite being present). No increase in pressure was observed during several days. Again, considering the dimensions of the nitrosyl chloride molecule, it is unlikely that physical sorption could occur. This is supported by the lack of reaction with the sodium form of analcite, which is isostructural with silver analcite. The appropriate equation in this instance appears to be :

$$NOCl + Ag\ analcite \longrightarrow NO\ analcite + AgCl$$

However, there is a number of points to be considered. The product of heating the solid reaction product is predominantly nitrosyl chloride, containing only a small percentage of dinitrogen trioxide. Also, the product of the initial reaction, containing *extra*crystalline silver chloride, is unaffected by light even after the removal of the residual nitrosyl chloride. The heated product is, however, affected by light. An estimation of the silver chloride from the unheated sample indicated complete exchange, in agreement with the decrease in nitrosyl chloride pressure.

These factors may be explained in the following manner. Silver chloride sorbs a small quantity of nitrosyl chloride, and in these circumstances is not discoloured by the action of sunlight. This was experimentally verified by placing dry, partially photolysed, silver chloride in the apparatus shown in Fig. 2, evacuating the whole, and introducing nitrosyl chloride. The silver chloride rapidly whitened, and did not become discoloured on removal of the excess of nitrosyl chloride. There is no compound formation, as the change in pressure of the nitrosyl chloride was very slight.

The release of nitrosyl chloride on heating of the solid product of the reaction between nitrosyl chloride and silver analcite is readily explained by the reversal of an equilibrium. At room temperature the equilibrium lies on the side of the nitrosyl analcite, but as the temperature is raised so the equilibrium shifts towards the release of gaseous nitrosyl chloride. The percentage of dinitrogen trioxide obtained will be variable and dependent on the rate of heating.

Sodium and Thallium Chabazite.—It is probable that in these two systems physical sorption alone occurred. This is, however, difficult to prove in view of the possibility of equilibria such as that indicated above. The products are *intra*crystalline, and hydrothermal extraction would be an essential for further study. This would clearly alter any nitrosyl products.

APPENDIX

The demonstration of nitrosonium ion exchange in silicates indicates that a glass electrode might respond to change of nitrosyl concentration in a non-hydroxylic solvent. The following cells were constructed :

(*a*) Ag,AgCl	NOCl in nitromethane C_2	Glass	NOCl in nitromethane C_1	NOCl in nitromethane C_2	Ag,AgCl

C_1 was varied, while C_2 was kept constant. It was not found possible to obtain reproducible results with this system.

(*b*) Ag,AgCl	N-HCl	Glass	$NOClO_4$ $+AgClO_4$ in nitromethane	Ag

The nitrosyl perchlorate concentration was varied, but again reproducible results were not obtained.

The author thanks Dr. V. Gold for helpful discussion.

KING'S COLLEGE, STRAND, LONDON, W.C.1.

[*Received, August 29th,* 1956.]