

**Acknowledgments.**—This work was supported in part by the National Science Foundation under Grant GP-7510. The authors are grateful to Dr. B. N. Figgis for helpful discussions.

CONTRIBUTION FROM THE SCIENTIFIC RESEARCH STAFF,  
FORD MOTOR COMPANY, DEARBORN, MICHIGAN 48121

## The Preparation of Nitrosonium $\beta$ -Alumina

BY R. H. RADZIŁOWSKI AND J. T. KUMMER

Received June 30, 1969

In a previous paper<sup>1</sup> sodium  $\beta$ -alumina with the stoichiometric formula  $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$  has been reported to exchange completely its  $\text{Na}^+$  ions for other cations ( $\text{Ag}^+$ ,  $\text{Tl}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{NH}_4^+$ ) in molten salts. The products of such ion exchanges have been used similarly to prepare other ion-substituted  $\beta$ -aluminas<sup>1,2</sup> ( $\text{Ga}^+$ ,  $\text{Li}^+$ ,  $\text{In}^+$ ) which could not be made directly from sodium  $\beta$ -alumina. In all cases, the ion-substituted  $\beta$ -aluminas are isomorphous with the starting material, sodium  $\beta$ -alumina, and the exchanges are reversible. This paper reports the preparation of nitrosonium  $\beta$ -alumina by an ion-exchange method in which  $\text{Ag}^+$  ions in silver-substituted  $\beta$ -alumina are replaced mole for mole by  $\text{NO}^+$  ions in a  $\text{NOCl} \cdot \text{AlCl}_3$  melt.

### Experimental Section

The ionic compound  $\text{NOCl} \cdot \text{AlCl}_3$ <sup>3,4</sup> was prepared by placing 0.03 mol of  $\text{AlCl}_3$  (Baker and Adamson Quality) into a quartz tube (60 cm long and 0.5 cm in diameter) and subliming it under an atmosphere of dry Ar to a cooled section of the tube. After sealing the tube under the sublimed  $\text{AlCl}_3$ , the tube was lowered into a Dry Ice-trichloroethylene bath. Nitrosyl chloride gas (The Matheson Co. Inc., East Rutherford, N. J.) was bled from a lecture bottle through Teflon and glass tubing into a Dry Ice cold trap where  $\sim 0.03$  mol of  $\text{NOCl}$  was collected. The liquid  $\text{NOCl}$  was warmed gently until it distilled into the tube containing  $\text{AlCl}_3$ . After 1 hr in an ice bath and occasional agitation, the contents of the tube were heated gently to  $200^\circ$  in order to form the light yellow-brown melt of  $\text{NOCl} \cdot \text{AlCl}_3$ .

Silver-substituted  $\beta$ -alumina was made from 75–150- $\mu$  size single crystals of sodium  $\beta$ -alumina<sup>5</sup> that were heated in an  $\text{NaCl}$  melt at  $810^\circ$  for 16 hr. These crystals were washed with distilled water and heated to  $400^\circ$  before being placed in an  $\text{AgNO}_3$  melt. Two exchanges in an  $\text{AgNO}_3$  melt removed all but 0.08 wt % sodium.

The silver-substituted  $\beta$ -alumina crystals, preheated to  $400^\circ$  under Ar to remove any moisture, were inserted into the  $\text{NOCl} \cdot \text{AlCl}_3$  melt and the tube was sealed with a small amount ( $\sim 0.008$  mol) of  $\text{NOCl}$  above the melt. The tube was heated at  $197^\circ$  for 23 hr. The melt to crystal volume ratio was  $\sim 20:1$ . Since  $\text{NOCl} \cdot \text{AlCl}_3$  hydrolyzed readily, it was important that all materials were kept under anhydrous conditions. At the end of a run the melt was dissolved in distilled water giving off yellow-brown fumes and leaving a white precipitate and the transparent, yellow cast crystals of nitrosonium  $\beta$ -alumina. The precipitate

was dissolved in ethylenediamine and reprecipitated as  $\text{AgCl}$ . This precipitate was reduced on strong heating with  $\text{Na}_2\text{CO}_3$  to Ag metal and then weighed. Although it was difficult to recover all of the silver due to the large amount of  $\text{Cl}^-$  ion in solution, the silver that was recovered showed that an essentially complete exchange occurred. After one exchange only  $< 0.05$  wt % Ag was detected in the crystals by X-ray fluorescence analysis.

It should be noted that larger silver  $\beta$ -alumina crystals ( $\sim 1.5$ – $2.5$ -mm diameter) could not be converted completely to nitrosonium  $\beta$ -alumina after one exchange even after 7 days in the melt. The melt to crystal volume ratio in these cases was  $\sim 80:1$ . When these 40%-exchanged crystals were sanded lightly on the edges and placed into a new melt, however, only 20% more of the  $\text{Ag}^+$  ions left in the crystals could be exchanged for  $\text{NO}^+$  ions. Apparently, the surface of the  $\beta$ -alumina crystals was attacked by the melt,  $\text{NOCl}$ , or  $\text{AlCl}_3$ , and the exchange was inhibited. The much smaller crystals could exchange their  $\text{Ag}^+$  ions for  $\text{NO}^+$  ions before their surfaces were corroded.

The crystals were analyzed for silver and sodium by atomic absorption spectroscopy using a Techtron AA (Cary Instruments Inc., Monrovia, Calif.). Infrared spectra of single crystals (0.75–1-mm diameter) of silver  $\beta$ -alumina and nitrosonium  $\beta$ -alumina were obtained on a Perkin-Elmer 457 grating infrared spectrophotometer using a beam condenser with KBr optics at  $24^\circ$ . X-Ray powder diffraction data were obtained with a Debye-Scherrer 114.59-mm camera. The samples were ground to 44- $\mu$  size, sieved, and packed into 0.3-mm glass capillaries. Samples were exposed to Ni-filtered Cu  $K\alpha$  radiation for 0.7–6 hr on a Norelco X-ray generator. Intensities of reflections were measured on a double-beam recording microdensitometer (Joyce, Loebel and Co., Ltd., Gateshead, England). Thermogravimetric analyses were made on a 950 thermogravimetric analyzer (Du Pont, Wilmington, Del.). The density was determined by weighing a 0.5-g sample in air and in freshly distilled chlorobenzene. The X-ray fluorescence analysis for silver was performed on a Norelco Universal vacuum X-ray spectrograph (Phillips Electronics Instruments, Mount Vernon, N. Y.).

### Discussion

Nitrosonium  $\beta$ -alumina is isomorphous with the hexagonal layer structure of  $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$  which has the space group  $P6_3/mmc$ , with one molecule per unit cell. The lattice constants of  $(\text{NO})_2\text{O} \cdot 11\text{Al}_2\text{O}_3$  containing 6.13 wt % NO are  $a_0 = 5.597$  and  $c_0 = 22.711$  Å as determined from a Debye-Scherrer powder pattern and refined by a least-squares method. The powder diffraction pattern for nitrosonium  $\beta$ -alumina is given in Table I.

The variation of silver in silver-substituted  $\beta$ -alumina from sample to sample was in agreement with the 4.3–5.0 wt % sodium variation found in the starting material, sodium  $\beta$ -alumina. The amount of nitrosonium ion in the  $\beta$ -alumina structure was calculated from the chemical analysis for silver based on a mole for mole exchange for  $\text{NO}^+$  ions since an accurate direct method of determining the nitrosonium ion content was not available. The calculated density and nitrosonium ion content of the stoichiometric  $(\text{NO})_2\text{O} \cdot 11\text{Al}_2\text{O}_3$  are 3.22 g/cm<sup>3</sup> and 5.012 wt % NO, respectively. The measured density of nitrosonium  $\beta$ -alumina containing  $6.13 \pm 0.05$  wt % NO is  $3.22 \pm 0.02$  g/cm<sup>3</sup>.

The infrared spectra of single crystals of silver-substituted  $\beta$ -alumina and the nitrosonium  $\beta$ -alumina made from it are shown in Figure 1. A Nujol mull of a finely ground sample gave a much weaker absorption band

(1) Y. F. Yu Yao and J. T. Kummer, *J. Inorg. Nucl. Chem.*, **29**, 2453 (1967).

(2) R. H. Radziłowski, *Inorg. Chem.*, **8**, 994 (1969).

(3) H. Gerding and H. Houtgraaf, *Rec. Trav. Chim.*, **72**, 21 (1953).

(4) H. Houtgraaf and A. M. DeRoos, *ibid.*, **72**, 963 (1953).

(5) The  $\beta$ -alumina used was obtained from fused cast bricks (Monofrax H, 31 lb each) made by the Harbison Carborundum Co., Falconer, N. Y.

TABLE I  
POWDER PATTERN FOR  $(\text{NO})_2\text{O} \cdot 11\text{Al}_2\text{O}_3$   
(FORWARD-REFLECTED REGION)

$I/I_0$	$d_{\text{obsd}}, \text{\AA}$	$d_{\text{calcd}}, \text{\AA}$	(hkl)
100	11.3	11.36	002
25	5.66	5.68	004
29	4.45	4.46	102
9	4.08	4.08	103
4	3.69	3.69	104
2	2.984	2.983	106
4	2.839	2.839	008
27	2.796	2.799	110
38	2.697	2.696	107
36	2.510	2.510	114
4	2.449	2.450	108
26	2.409	2.410	201
14	2.371	2.370	202
4	2.308	2.308	203
4	2.271	2.271	0, 0, 10
16	2.251	2.250	116
9	2.229	2.229	204
26	2.139	2.138	205
26	2.041	2.041	206
15	1.943	1.942	207
6	1.844	1.843	208
1	1.780	1.781	213
2	1.765	1.764	1, 1, 10
2	1.744	1.744	214
3	1.658	1.657	2, 0, 10
5	1.621	1.622	0, 0, 14
24	1.597	1.600	302
		1.595	217
12	1.571	1.572	2, 0, 11
		1.568	1, 1, 12
9	1.555	1.554	304
4	1.540	1.539	218
		1.538	1, 0, 14
6	1.486	1.486	306
14	1.418	1.419	0, 0, 16
		1.417	2, 0, 13
45	1.400	1.399	220
8	1.389	1.389	222
6	1.360	1.359	224
12	1.349	1.348	2, 0, 14

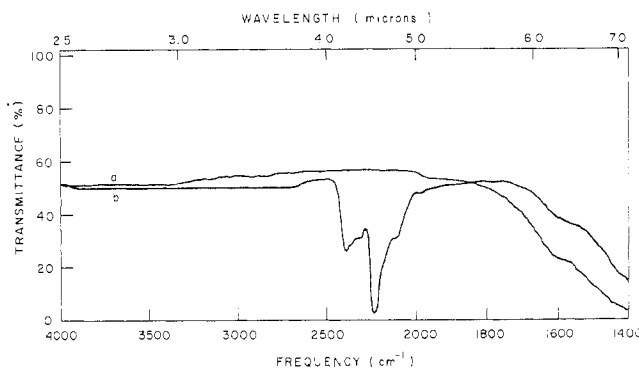


Figure 1.—Infrared spectra of (a) silver  $\beta$ -alumina and (b) nitrosonium  $\beta$ -alumina crystals.

at  $2245 \text{ cm}^{-1}$  than did the single crystals. The principal absorption band at  $2245 \text{ cm}^{-1}$  is believed to be due to the N-O stretching motion which is reported<sup>6,7</sup> to be in the  $2200\text{--}2480\text{-cm}^{-1}$  frequency range for the

nitrosonium ion. The origin of the weaker absorption bands at  $2390, 2355, 2300,$  and  $2110 \text{ cm}^{-1}$  is not known.

The thermogravimetric behavior of nitrosonium  $\beta$ -alumina as shown in Table II is dependent on particle size. The largest weight loss for the thermal decomposition of nitrosonium  $\beta$ -alumina crystals was obtained

TABLE II  
THE THERMAL DECOMPOSITION OF NITROSONIUM  $\beta$ -ALUMINA<sup>a</sup>

Run no.	Particle size, $\mu$	Heat-ing rate, deg/min	Atm	Temp at which wt loss began, $^{\circ}\text{C}$	Final wt % loss from sample
1	150-250	20	Dry $\text{N}_2$ (760 mm)	$\sim 400$	5.4
2	75-150	10	Dry $\text{N}_2$ (760 mm)	$\sim 325$	5.7
3	75-150	(16 hr at $800^{\circ}$ in an evacuated quartz tube)			5.2
4	$\leq 45$	10	Dry $\text{N}_2$ (760 mm)	185	7.0
5	$\leq 45$	10	Air (760 mm)	160	7.3
6	$\leq 45$	10	Vacuum ( $\sim 10^{-3}$ mm)	$\sim 150$	7.7

<sup>a</sup> Sample size: 6-30 mg for all runs except no. 3 which contained 197 mg. Sample holder: platinum. Temperature range:  $25\text{--}1000^{\circ}$ ; in runs 4 and 5, the temperature was held for  $\sim 20$  min at  $520$  and  $470^{\circ}$ , respectively, before continuing on to  $1000^{\circ}$ .

when the particle size was  $\leq 45 \mu$ . When heating this compound the  $\beta$ -alumina structure was altered as evidenced by the absence of the characteristic  $d$  spacings of  $\beta$ -alumina in the X-ray powder pattern of the decomposition product. A yellow-brown gas which turned colorless in the presence of platinum at  $800^{\circ}$  was observed above the sample. The behavior of the yellow-brown gas is indicative of  $\text{NO}_2$ .

Based on the above observations and the known crystal structure of sodium  $\beta$ -alumina,<sup>8,9</sup> a mechanism for the thermal decomposition is proposed. The  $\text{NO}^+$  ions which reside in "mirror" planes of the  $\beta$ -alumina lattice can react with oxygen ions near or in these planes by the reaction



Although there are many oxygen ions available to react with the  $\text{NO}^+$  ions, it is believed, tentatively, that many of the oxygens belonging to the Al-O-Al bridges which hold the "mirror" planes apart react with adjacent  $\text{NO}^+$  ions and cause these planes to collapse. In the large crystals the collapse of the lattice may trap the gaseous products thus resulting in a lower weight loss than anticipated. For the above reaction a 7.78% weight loss was expected for 6.13 wt %  $\text{NO}^+$  in nitrosonium  $\beta$ -alumina. Such a weight loss was observed for the  $\leq 45\text{-}\mu$  crystals when heated *in vacuo* to  $1000^{\circ}$ .

There was no evidence from ir or weight loss data that water was absorbed by the nitrosonium  $\beta$ -alumina which stood in air for 3 months. No attempts were

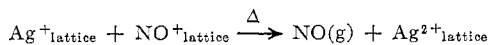
(6) T. C. Waddington and F. Klanberg, *Z. Anorg. Allgem. Chem.*, **304**, 190 (1960).

(7) D. W. A. Sharp and J. Thorley, *J. Chem. Soc.*, 3557 (1963).

(8) C. A. Beevers and M. A. S. Ross, *Z. Krist.*, **97**, 59 (1937).

(9) J. Felsche, *ibid.*, **127**, 94 (1968).

made to reexchange the  $\text{NO}^+$  ions in nitrosonium  $\beta$ -alumina with  $\text{Ag}^+$  or  $\text{Na}^+$  ions; however, a partially exchanged silver  $\beta$ -alumina crystal (1.5-mm diameter) containing 37 mol %  $\text{NO}$  was heated *in vacuo* at  $490^\circ$  for 1 hr in order to see whether  $\text{Ag}^{2+}$  ions could be produced by the reaction

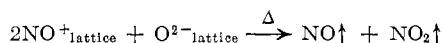


The crystal was examined by electron spin resonance spectroscopy at room temperature but no absorption peaks were found which would indicate that a paramagnetic species such as the  $\text{Ag}^{2+}$  ion was present. The crystal remained colorless and transparent after the heat treatment, but absorption bands between 1700 and  $4000\text{ cm}^{-1}$  were no longer present in the ir spectrum. This latter work was not pursued any further.

### Conclusions

Silver ions in silver-substituted  $\beta$ -alumina are completely exchanged for  $\text{NO}^+$  ions in a  $\text{NOCl}\cdot\text{AlCl}_3$  melt without altering the  $\beta$ -alumina structure.

The proposed reaction in the thermal decomposition of nitrosonium  $\beta$ -alumina is



This reaction is based on (1) the amount of weight loss from the sample, (2) the evolution of a yellow-brown gas believed to be  $\text{NO}_2$ , and (3) the alteration of the  $\beta$ -alumina crystal structure.

The ir spectrum of nitrosonium  $\beta$ -alumina contains a strong absorption band at  $2245\text{ cm}^{-1}$ , a frequency indicative of the N-O stretching motion of the nitrosonium ion.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
REED COLLEGE, PORTLAND, OREGON 97202

## The Preparation of Copper(I) Trifluoroacetate Carbonyl<sup>1</sup>

By ARTHUR F. SCOTT, LAUREL L. WILKENING,  
AND BYRON RUBIN

Received May 30, 1969

In a variety of different environments,<sup>2</sup>  $\text{Cu(I)}$  ion binds carbon monoxide, the limiting ratio  $\text{CO}:\text{Cu}$  being 1:1. This note describes the preparation of the carbonyl derived from copper(I) trifluoroacetate, with and without a molecule of solvent trifluoroacetic acid (TFA). The novel observations encompass the usefulness of TFA as a solvent for the dissolution of  $\text{Cu(I)}$  in the presence of carbon monoxide, the usefulness of trifluoroacetic anhydride (TFAA) to simplify the handling of the  $\text{Cu(I)}$  salt, and the fact that pumping away the

carbon monoxide from the complex leaves a stable<sup>3</sup>  $\text{Cu(I)}$  salt.

### Experimental Section

The reaction system is sensitive to air oxidation.  $\text{Cu(I)}$  complexes were prepared and handled under dry, oxygen-free nitrogen or carbon monoxide.

**Materials.**—Carbon monoxide (The Matheson Co.) was deoxygenated by alkaline pyrogallol, dried over Drierite, and stored over 1-butyl phthalate. Cuprous oxide was prepared by reduction of cupric sulfate by sucrose in basic solution. *Anal.*  $\text{Cu}$ , 89.1. Trifluoroacetic acid (Matheson Coleman & Bell) was distilled through a bubble-plate column. Trifluoroacetic anhydride was prepared from the acid and phosphorus pentoxide under reflux. It was then distilled through the bubble-plate column.

**Copper(I) Trifluoroacetate Carbonyl—Trifluoroacetic Acid. Method A.**—Cuprous oxide (2.0318 g) under carbon monoxide was covered with 13.95 ml of trifluoroacetic acid, and the dark brown slurry was stirred magnetically. Over 2 hr it absorbed 775 ml (0.0346 mol) of carbon monoxide and colorless crystals had separated from the then blue-green solution. The crystals were filtered, dried, and transferred under nitrogen; yield, 3.20 g (35.3%). *Anal.* Calcd for  $\text{C}_5\text{HCuF}_6\text{O}_5$ :  $\text{Cu}$ , 19.94. Found:  $\text{Cu}$ , 18.75.

**Method B.**—Cuprous oxide (2.0476 g) under carbon monoxide was covered with 15.82 ml of freshly prepared trifluoroacetic anhydride and the slurry was stirred magnetically. It absorbed no carbon monoxide. Water (0.60 ml, 0.056 mol) was injected; the mixture became warm and rapidly absorbed carbon monoxide. After 0.5 hr the colorless crystals were filtered and dried; yield, 4.95 g (54.2%). *Anal.* Calcd for  $\text{C}_5\text{HCuF}_6\text{O}_5$ :  $\text{Cu}$ , 19.94;  $\text{C}_2\text{HF}_3\text{O}_2$ , 35.79. Found:  $\text{Cu}$ , 19.93;  $\text{C}_2\text{HF}_3\text{O}_2$ , 35.78,<sup>4</sup> 36.39;<sup>5</sup> weight loss *in vacuo*, 39.30%.  $\nu_{\text{max}}^{\text{nujol}}$ : 2155, 1667, 1212, 1164, 854, 792, 735  $\text{cm}^{-1}$ .

**Copper(I) Trifluoroacetate Carbonyl.**—The solvated complex (3.3725 g) was subjected to oil pump vacuum for 45 min at room temperature. In other experiments all condensable liquid was collected by pumping for 45 min or less. Essentially 1 equiv of TFA is lost (see analysis above) to give colorless crystals of the unsolvated complex. *Anal.* Calcd for  $\text{C}_5\text{CuF}_6\text{O}_5$ :  $\text{Cu}$ , 31.06. Found:  $\text{Cu}$ , 31.9.  $\nu_{\text{max}}^{\text{nujol}}$ : 2155  $\text{cm}^{-1}$ .

Prolonged pumping on the solvated complex left a colorless product with a composition approaching that of cuprous trifluoroacetate. The characteristic absorption of  $\text{CO}$  was absent. *Anal.* Calcd for  $\text{C}_2\text{CuF}_3\text{O}_2$ :  $\text{Cu}$ , 35.9. Found:  $\text{Cu}$ , 34.8.  $\nu_{\text{max}}^{\text{KBr}}$ : 1670, 1438, 1220, 1201, 1150  $\text{cm}^{-1}$ .

The X-ray crystal structure determination of copper(I) trifluoroacetate carbonyl is in progress.

### Discussion

Earlier experiments in this laboratory<sup>6</sup> had indicated the suitability of TFA as a solvent in facilitating the reaction of  $\text{Cu(I)}$  with carbon monoxide. Owing to the extraordinary sensitivity of the complexes to oxygen and the difficulty of obtaining it free of the solvent TFA, since pumping rather readily removes the carbon monoxide as well, we had only rough indications<sup>6</sup> of the stoichiometry of the complex prior to preparing it in TFAA.

The preparation in the anhydride as a solvent, however, affords a number of cogent observations. There is no absorption of carbon monoxide by the stirred mixture

(1) This work was supported by Grant G-18827 from the National Science Foundation.

(2) (a) R. Stewart and D. G. Evans, *Anal. Chem.*, **35**, 1315 (1963); (b) summarized in "Gmelin Handbuch der Anorganischen Chemie," Kupfer Teil B, Lieferung 1, 1958, pp 223-237; (c) C. W. Alegranti and E. L. Muertteries, private communication.

(3) Other simple salts such as  $\text{Cu}^+\text{NO}_2$  cannot ordinarily be obtained unsolvated; they disproportionate.

(4) By titration.

(5) Based on the weight of trapped liquid, assuming it to be pure TFA.

(6) A. F. Scott and J. Colony, results unpublished except as reported (1960) to the Atomic Energy Commission.