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Dissociative Chlorination of Nitrogen Oxides and Oxy Anions in Molten Sodium Chloride–Aluminum Chloride Solvents

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Nitrosyl cation has been found to undergo reversible one-electron reduction–oxidation in molten NaCl–$AlCl_3$ mixtures (175°) at vitreous C electrodes. The NO^+ ion half-wave potential in normal pulse voltammograms occurs at $E_{1/2} \approx +1.86$ V vs. Al reference electrode in $NaAlCl_4$(NaCl saturated) and a diffusion coefficient for NO^+ ion in acidic melts ($AlCl_3$ rich) is estimated to be 1.8×10^{-5} cm^2 sec^{-1} (175°). Nitrite ion reacts with fused NaCl–$AlCl_3$ mixtures to produce high yields of NO^+ ion, which is separable from the solvent phase as nitrosyl chloride. Nitryl ion, nitrogen dioxide, and nitrate ion are reduced in these molten salts, to varying extents, whereas nitrous oxide and nitric oxide remain unaffected in 24 hr. Possible mechanisms are discussed for these dissociative chlorination processes.

Introduction

Interpretations of potentiometric data[1-6] and of Raman spectral data[7] with ionic equilibria models have advanced the understanding of the structures of molten alkali metal chloride–aluminum chloride mixtures. Their acid–base characteristics, using Lux–Flood theory terminology, vary with both the alkali metal chloride:aluminum chloride molar ratio and the nature of the alkali metal cation. These chloroaluminate solvents are known to be effective chlorinating agents for a number of oxides and oxy anions,[8-12] e.g., H_2O, TiO_2, TiO_3^{2-}, GeO_2, GeO_3^-, As_2O_3, AsO_2^-, SnO_2, SnO_3^{2-}, and Sb_2O_5. In this regard, they behave similarly to aluminum chloride in its high-temperature (150–500°) reactions with many oxygen-containing compounds[13-18] (e.g., MgO, γ-AlOOH, γ-Al_2O_3, SO_2, CaO, TiO_2, V_2O_5, Fe_2O_3, FeOCl, ZnO, As_2O_3, Nb_2O_5, $NbOCl_3$, MoO_3, Sb_2O_5, Sb_2O_3, Ta_2O_5, and Bi_2O_3). Aluminum oxychloride and the corresponding chlorides or oxychlorides are obtained as products, e.g.

$$2H_2O + Al_2Cl_6 \overset{\Delta}{\rightarrow} 2AlOCl + 4HCl$$

$$WO_3 + Al_2Cl_6 \overset{\Delta}{\rightarrow} 2AlOCl + WOCl_4$$

In this study, selected nitrogen oxides and oxy anions have been allowed to react with NaCl–$AlCl_3$ melts at 175° to examine further the chlorination capabilities of these fused-salt media. Chemical analysis and electroanalytical techniques were used in conjunction to identify the major intermediates and products of reactions.

Experimental Section

Chemicals. Matheson gases nitric oxide (CP grade), chlorine (Research grade), nitrosyl chloride (97% minimum purity), and nitrogen dioxide (99.5% minimum purity) were redistilled several times before being weighed and condensed in reaction vessels. Sodium tetrachloroaluminate melt preparation, purification, and analysis methods were similar to those described in earlier publications.[19,20] To obtain samples of sodium tetrachloroaluminate for vacuum-line experiments, the molten salt was filtered through a fritted-glass disk into a Pyrex tube to remove any aluminum particles which readily dislodge from the cathode during and after melt purification. Sodium nitrite (Baker Analyzed) and sodium nitrate (Mallinckrodt, analytic) were stored in a desiccator over P_2O_5, in the drybox. Nitrosyl and nitryl tetrafluoroborates (Research Organic/Inorganic Chemical Corp.) and nitrous oxide gas (98.0% minimum purity) were used as supplied. Air-sensitive compounds always were handled under vacuum or dried nitrogen atmospheres.

Apparatus. Volatile products were condensed from the reaction vessels in cold traps at liquid nitrogen temperature. Subsequently, the condensates could be analyzed conveniently by infrared spectroscopy and/or gas chromatography of the gaseous constituents. Solid reactants in glass vials were added from side arms and gases were introduced into the reaction vessels, after vacuum degassing the $NaAlCl_4$ melts. Suitable glassware was heated to 500° for several hours immediately before being transferred into the drybox. Vacuum joints were coated lightly with Dow Corning Silicone High Vacuum grease. Quantitative ir spectral data were collected on a Beckman IR 12 spectrophotometer operated in the single-beam mode. For calibration and analysis purposes, gases were expanded into a 5-cm glass cell fitted with Irtran-2 plates (Barnes Engineering Co.); a linear Beer–Lambert plot of the $2\nu_1$ band center (3563.3 cm^{-1} [21]) was obtained for nitrosyl chloride gas pressures in the experimental range. Nitric oxide, nitrous oxide, and chlorine were analyzed on a Carle Model 8000 gas chromatograph, fitted with a mini single-loop sampling valve and a Polypak 1 column (3 ft × 1/8 in. o.d., S/S), which was operated at ambient temperatures with He carrier gas (20 psi).[22] The apparatus used for the uv measurement was similar to that previously described.[23] Samples of solidified melts were extracted with liquid sulfur dioxide to remove the soluble $NaAlCl_4$, using the

Table I. Product Analyses and Conditions for Reactions[d]

Entry	Starting materials	Cell type[a]	Period of reacn,[b] hr	Yield[c] (mol %)
A	N_2O (0.570 mmol in 23.9 g of melt)	I	24	95% N_2O recovered
B	NO (0.570 mmol in 14.2 g of melt)	I	24	98% NO recovered
C	ONCl (0.595 mmol in 12.5 g of melt)	I	24	86% ONCl, HCl trace in ir spectrum
D	$NOBF_4$ (0.420 mmol in 18.4 g of melt)	I	*e*	93% ONCl, BF_3 and HCl traces in ir spectrum
E	$NaNO_2$ (1.092 mmol in 36.4 g of melt)	II	24	89% ONCl, traces of N_2O, NO, and HCl in ir spectrum
F	NO_2 (1.093 mmol in 30.5 g of melt)	I	15	20% ONCl, NO_2, and O_2NCl in ir spectrum
G	NO_2 (0.902 mmol in 48.3 g of melt)	II	72	41% ONCl, N_2O and HCl traces in ir spectrum
H	$NaNO_3$ (0.922 mmol in 41.1 g of melt)	II	24	<5% ONCl, N_2O and HCl traces in ir spectrum
I	NO_2BF_4 (0.294 mmol in 20.3 g of melt)	II	*e*	97% ONCl, BF_3 and HCl traces in ir spectrum

[a] Two designs of reaction vessels were used: type I, small melt surface area, gaseous region mainly at room temperature; type II, large melt surface area, gaseous region mainly at 175°. [b] Products condensed by liquid nitrogen for ~1 hr. [c] Based on conversion from stated formulas of reactants. [d] All $NaAlCl_4$ solvents were saturated in NaCl at 175 ± 2°. [e] Product condensations commenced with additions of reactants.

experimental techniques described by Kühnl and Geffarth,[12] and the insoluble fractions were finely ground in the drybox. For X-ray diffraction, the samples were sealed into soft-glass capillaries using paraffin wax. All molten salt experiments were thermostated to 175 ± 2°.

Electrochemical measurements were made under a purified nitrogen atmosphere in a Vacuum Atmospheres Co. drybox in cells similar to those previously described.[20] Cyclic voltammograms were recorded on a PAR Model 170 electrochemistry system (Princeton Applied Research Corp.) with *IR* compensation for fast voltage scans or with a Tacussel Electronique Model UAP 4 research polarograph control unit and potentiostat, Model PRT 30-0.1. The current–voltage curves were photographed from a Tektronix Model 564 storage oscilloscope. Normal-pulse voltammograms were obtained using a PDP 12 or 8/e digital computer system, the details of which are available elsewhere.[24]

Results

I. Chemical Analyses. Details of the reaction conditions and the product analyses are summarized in Table I. The yields of gaseous product often could be improved slightly by continuing condensation while the reaction mixtures were permitted to cool, solidify, and outgas. Oxidation states of nitrogen compounds investigated are from +1 to +5.

(i) N_2O and NO Reactions with $NaAlCl_4$. Neither nitrous oxide nor nitric oxide reacted to any measurable extent with the molten sodium tetrachloroaluminate under the conditions outlined in Table I.

(ii) ONCl Reaction with $NaAlCl_4$. Colorless sodium tetrachloroaluminate solvents became yellow when nitrosyl chloride gas was introduced into the reaction vessels. A uv spectrum taken of a very dilute sample of the solution had a broad absorption band, λ_{max} 255 nm, which is analogous to the absorption spectra for the nitrosyl cation in aqueous acid solutions (λ_{max} 260 nm).[25,26] Nitrosyl chloride could be recovered in high yields from $NaAlCl_4$(NaCl saturated) melts after 24 hr, Table I-C (cf. ref 27). Product mixtures of NO, HCl, and ONCl initially condensed in a red-violet form, followed by a yellow more copious solid. The red-violet coloration is thought to be due to a low-temperature NO·HCl "addition compound".[28,29] Traces of HCl contaminant appeared in spite of precautions taken to dry the glassware and chemicals. These residual concentrations of HCl may account in part for the persistent aluminum corrosion previously found in highly purified sodium tetrachloroaluminate electrolytes.[20]

(iii) NO_2^- Ion Reaction with $NaAlCl_4$. High yields of nitrosyl chloride resulted from the reaction between sodium nitrite and the sodium tetrachloroaluminate melt, Table I-E. This result is consistent with the electrochemical evidence for the dissociation of sodium nitrite to nitrosyl cation in acidic $NaAlCl_4$ melts (vide infra). A residue remained in the $NaAlCl_4$(NaCl saturated) solvent during the reaction with sodium nitrite. After decantation and extraction of the residue with liquid SO_2, X-ray powder diffraction analysis of it revealed an intense sodium chloride band pattern. Attempts to confirm the presence of aluminum oxychloride by extraction of the solidified melt were unsuccessful with both basic and acidic melt compositions.

(iv) NO_2 Reaction with $NaAlCl_4$. Since NO_2 remained present in the gas phase in contact with $NaAlCl_4$ melt after 15 hr (Table I-F), it may be concluded that the reaction of NO_2 with the melt is not rapid. After 72 hr, a 41% yield of nitrosyl chloride, together with some chlorine and nitrous oxide, was obtained. It is not possible to distinguish between solvent-phase, gaseous-phase, and surface-catalyzed reactions in these experiments and no reasons will be evoked to explain the appearance of nitrous oxide as product. At 175°, nitrogen tetroxide is completely dissociated to the nitrogen dioxide monomer which, of course, may be the species involved in the $NaAlCl_4$ melt reaction. In contrast, the reaction of aluminum chloride with liquid nitrogen tetroxide has a solid product whose analyses conform to a mixture of $Al(NO_3)_3$ and $NO[Al(NO_3)_4]$.[30]

(v) NO_3^- Ion Reaction with $NaAlCl_4$. Sodium nitrate crystals added to $NaAlCl_4$(NaCl saturated) melt slowly effervesced and only small amounts of ONCl were formed (Table I-H). An undissolved white solid, shown by X-ray diffraction patterns to contain NaCl and $NaNO_3$, remained present in the melt for several days. Probably, the crystal surfaces quickly became passivated with a NaCl coating and little further reaction ensued. In agreement with this suggestion, a far more vigorous reaction took place between $NaNO_3$ and acidic melts. Chlorine was identified qualitatively in the evolved gases. It can be noted that this behavior of nitrate ion is comparable to its behavior in nitromethane solvent containing dissolved aluminum chloride; Bauer and Foucault[31] have reported that nitrosyl ion and chlorine gas are obtained as products when potassium nitrate is dissolved in this medium.

(vi) $NOBF_4$ and NO_2BF_4 Reactions with $NaAlCl_4$. Nitrosyl and nitryl tetrafluoroborates decomposed rapidly when added to molten $NaAlCl_4$ to give ONCl and some BF_3 as the major ir-active gases (Table I-D,I). Similarly, readily available nitrosyl salts have been used to prepare nitrosyl fluoride by their reactions with alkali metal fluorides at high temperatures,[32] e.g.

$$NOBF_4 + F^- \xrightarrow{200-300^\circ} ONF + BF_4^-$$

Nitryl salts of polyfluoro[33] and polychloro[34] anions and nitryl chloride have low thermal stabilities; noticeable decomposition of the latter has been found at 120° in the gas phase.[35] Interestingly, Drago and Whitten[36] were able to isolate nitryl chloride from the reaction of potassium nitrate with aluminum chloride in an equimolar LiCl–NaCl–KCl mixture. However, they cautioned that in order to obtain reasonable yields by this preparative method, the temperature should be slowly raised and a large excess of aluminum chloride has to be avoided. Also, a 52% molar conversion of potassium nitrite into nitrosyl chloride was obtained using this aluminum chloride–chloride

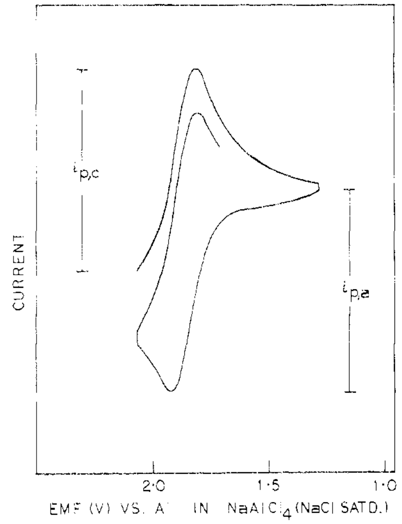

Figure 1. Cyclic voltammogram of ONCl in $NaAlCl_4$(NaCl saturated), at 175° and $\nu = 0.500$ V sec^{-1}. Apparent area of vitreous C electrode is 0.07 cm^2.

Table II. Cyclic Voltammetric Curve Data for 0.72 mmol of $NOBF_4$ Added to 37.0 g of $NaAlCl_4$(NaCl saturated)[a]

ν, V sec^{-1}	$i_{p,c}$, mA	$i_{p,a}$, mA	$i_{p,c}/i_{p,a}$	$i_{p,c}/\nu^{1/2}$	$i_{p,a}/\nu^{1/2}$
0.050	0.250	−0.218	−1.15	1.12	−0.97
0.100	0.346	−0.326	−1.06	1.09	−1.03
0.200	0.495	−0.489	−1.01	1.11	−1.09
0.500	0.754	−0.738	−1.02	1.07	−1.04
1.000	1.031	−1.061	−0.97	1.03	−1.06

[a] Temperature 175°; apparent area of vitreous C electrode 0.07 cm^2.

mixture and, as for the nitryl chloride synthesis, they observed that too rapid a heating rate resulted in contamination of the product with large amounts of the oxides of nitrogen. The chlorination conditions described for these syntheses seem to be milder per se than sodium tetrachloroaluminate melt at 175°.

II. Electroanalytical Investigations. A typical cyclic (triangular wave) voltammogram recorded after release of nitrosyl chloride gas above a sodium tetrachloroaluminate (sodium chloride saturated) melt is shown schematically in Figure 1. The predominant feature of the current–voltage curve is the apparently reversible couple at + 1.86 V vs. aluminum wire electrode in $NaAlCl_4$(NaCl saturated). Cyclic voltammograms recorded a few minutes after the additions to melts of a small quantity (~5–40 mmol) of one of the solids sodium nitrite, sodium nitrate, nitrosyl tetrafluoroborate, and nitryl tetrafluoroborate, or nitrogen dioxide gas each contained an anodic and cathodic wave at peak potentials identical with those obtained with ONCl. Positions of the peaks and their separation values, $\Delta E_p = 100 \pm 10$ mV, were independent of sweep rates (ν) throughout the range from 0.010 to 100 V sec^{-1}. As the theoretical peak separation for an *n*-electron, reversible charge-transfer reaction at 175° is 85.7/*n* mV, the experimental ΔE_p approximates the theoretical value for a one-electron, reversible system. Measurements of cyclic voltammetric curves that were recorded in rapid succession indicate the $i_{p,c}/i_{p,a}$ ratios are approximately 1 and the $i_p/\nu^{1/2}$ values remain essentially constant; e.g., see Table II. These data satisfy the diagnostic criteria for reversible charge transfer.[37]

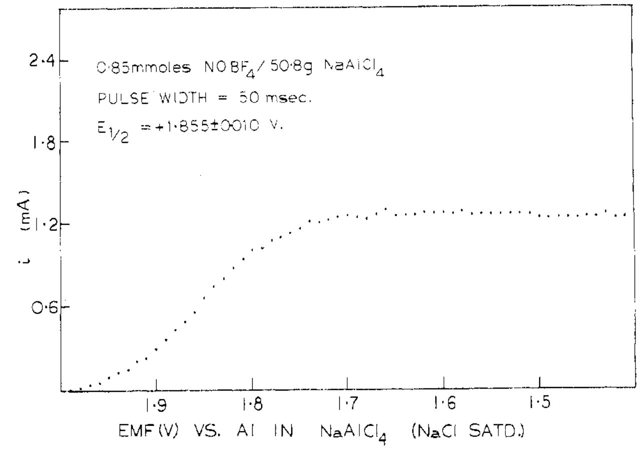

Figure 2. Normal-pulse voltammogram of NO^+ ion reduction in $NaAlCl_4$(NaCl saturated) at 175°. Apparent area of vitreous C electrode is 0.07 cm^2.

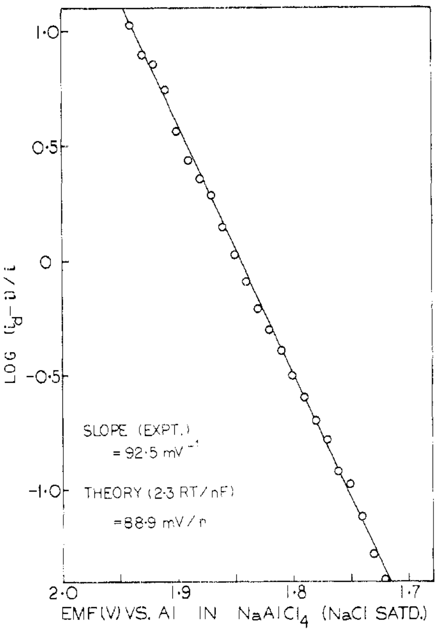

Figure 3. Plot of log $(i_d - i)/i$ vs. potential for the electrode reaction, $NO^+ + e^- \rightarrow NO$, in $NaAlCl_4$(NaCl saturated) at 175°.

Table III. Normal-Pulse Diffusion Currents for NO^+ Ion (i_d) × (Pulse Width)$^{1/2}$

Expt no.	Pulse width *t*, msec	i_d, mA	$i_d t^{1/2}$
1	50	0.983	6.95
2	100	0.685	6.85
3	30	1.245	6.82
4	20	1.534	6.86
5	80	0.749	6.70
6	50	0.958	6.77

An example of a normal-pulse voltammogram for the reduction of nitrosyl cation in $NaAlCl_4$ melt is illustrated in Figure 2. When pulse voltammograms were obtained within a short period (<10 min), reasonably constant values for the product diffusion current (i_d) × (pulse width)$^{1/2}$ resulted (Table III). Experimental slope values of the voltammetric wave equation agree well with the theoretical value for a one-electron process (e.g., Figure 3)

$$NO^+ + e^- \rightarrow NO$$

This assignment of the wave is in contrast to the irreversible, two-electron process suggested by Leroy[38] for a reduction wave at $E_{1/2} \approx + 1.35$ V vs. Al in KCl-NaCl-$AlCl_3$ (14–26–60 mol %)

$$NO_2 + 2e^- \rightarrow NO + O^{2-}$$

Leroy contended that nitrite ion dismutes into nitric oxide and

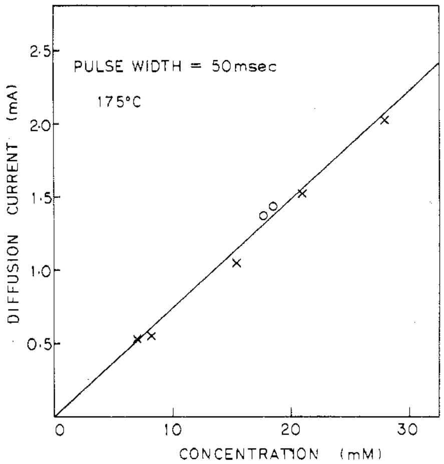

Figure 4. Normal-pulse diffusion current (i_d) vs. added quantities of $NOBF_4$ (×) and $NaNO_2$ (○) to the nominal 1:2 NaCl–$AlCl_3$ melt. Apparent area of vitreous C electrode is 0.07 cm^2.

nitrogen dioxide in the ternary eutectic KCl–NaCl–$AlCl_3$ and, apparently, the presence of nitrosyl cation as a feasible solution species was not considered. Supposedly, the NO_2 was strongly retained in the melt and responsible for a yellow coloration. As the Al reference electrode in $NaAlCl_4$(NaCl saturated) is approximately 0.5–0.6 V negative of the reference electrode employed by Leroy, it is probable that the reduction of NO^+ ions was observed in this earlier work rather than the reduction of a stable, electroactive NO_2 species.

In a nominal 1:2 NaCl–$AlCl_3$ melt, for NO^+ ion concentrations of similar magnitude to those added to NaCl-saturated melts, the rest potential was shifted $\gtrsim$100 mV in the positive direction. A rest potential of +2.0 V vs. Al in $NaAlCl_4$(NaCl saturated) is approximately the positive limit of the accessible potential range for a NaCl-saturated electrolyte. The change in the rest potential values with solvent acidity could reflect a readjustment of the mixed equilibria NO–NO^+ and Cl^-–Cl_2 at the surfaces of the electrodes, as dissolved nitric oxide and chlorine will both be present in the electrolyte. The dissociation of molecular ONCl in the gas phase at 175° to produce nitric oxide and chlorine is appreciable; Beeson and Yost,[39] for example, have determined an equilibrium constant for the gas-phase composition at 179°

$$K = p_{NO}^2 p_{Cl_2}/p_{ONCl}^2 = 0.210$$

A rough estimate of undissolved gases was made in a sealed, two-bulb apparatus of total volume 107.7 ml. After 3 hr equilibration of 0.64 mmol of ONCl + 45.3 g of $NaAlCl_4$(NaCl saturated) at 175°, approximately 12 mol % of ONCl, measured at room temperature, remained in the gas phase (g). The equilibria involved may be summarized by the equations

$$2ONCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

$$NO(g) \rightleftharpoons NO_{solv}$$

$$Cl_2(g) \rightleftharpoons Cl_{2\,solv}$$

$$NO_{solv} + Cl_{2\,solv} \rightleftharpoons ONCl_{solv}$$

$$ONCl_{solv} \rightleftharpoons NO^+{}_{solv} + Cl^-{}_{solv}$$

Since gases were lost at appreciable rates from the loosely sealed electrochemical cell, especially when using NaCl-saturated electrolytes, attempts to measure the diffusion currents of NO^+ species formed from dissociations gave inconsistent results. More complete retention seemed to occur in acidic melts and some observed diffusion currents are given in Figure 4. If the assumption is made that added nitrosyl cation is retained completely in an ionized form by the acidic solvent, the diffusion coefficient calculated from the gradient of Figure 4 using the Cottrell equation is $D_{NO^+} = 1.8 \times 10^{-5}$ cm^2 sec^{-1} (175°).

Discussion

Molten sodium tetrachloroaluminate may be a convenient chlorinating mixture for the synthesis of nitrosyl chloride from nitrite ion because high yields of reasonably pure product can be obtained. Formation of nitrosyl chloride by the chlorination of nitrite ion with either aluminum chloride, phosphorus pentachloride, or phosphoryl trichloride are well-known preparative routes.[40] The chlorination of the nitrite ion in these processes does not involve a net change in the oxidation state of the nitrogen and it is interesting to speculate about the dissociation mechanism. Acknowledging the affinity of the aluminum chloride molecule for oxygen, Drago and Whitten[36] have proposed an ionic mechanism for chlorination processes in which a complex intermediate, containing an Al···O bond, participates in the first stage of the process. Abstraction of an oxide ion from nitrite ion would give a nitrosyl cation directly

$$O\text{-}N\text{-}O^- + AlCl_3 \rightarrow O\text{-}N\text{-}O^-\cdots AlCl_3 \rightarrow NO^+ + AlOCl + 2Cl^-$$

The preparation of nitryl chloride from nitrate ion and aluminum chloride, with mild chlorination conditions,[36] may be taken to imply that the net displacement of an oxide ion occurs generally in these processes in an uncomplicated single step. However, alternative routes can be distinguished that involve reduction–oxidation processes of cleaved oxy atoms or molecules and the aluminum chloride (or active chlorinating species).

For example, the first reaction step might involve scission of nitrite ion to give a peroxide ion–aluminum chloride complex intermediate

$$O\text{-}N\text{-}O^- + AlCl_3 \rightarrow O\text{-}N + O^-\cdots AlCl_3$$

The separation of a singly charged negative ion from a neutral molecule is entailed in this mechanism, whereas the immediate loss of an oxide ion involves the removal of a doubly charged negative ion from a singly charged positive ion. Subsequently, oxidation of the solvent by fast reduction–oxidation reactions, to produce chlorine, would enable the nitric oxide and chlorine to combine and then to ionize to the nitrosyl cation and chloride anion. Although kinetic studies by Jordan, Zambonin, et al., for example ref 41 and 42, have aided in the understanding of the roles of O_2, O_2^-, and O_2^{2-} species in molten nitrites and nitrates, no information is available on the behavior of these species in chloroaluminate solvents. The nitrogen reduction in the reactions of nitrogen dioxide, nitryl ion, and nitrate ion can be accomplished either by evolution of oxygen or by direct oxidation of the chloroaluminate solvent. Undoubtedly the reaction pathways for these chlorination processes are complex; nonetheless because side reactions, as exemplified by the nitrogen dioxide product analyses, can contribute to the difficulties to elucidate the basic mode of reactions.

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Registry No. N_2O, 10024-97-2; NO, 10102-43-9; ONCl, 2696-92-6; $NOBF_4$, 14635-75-7; NO_2^-, 14797-65-0; NO_2, 10102-44-0; NO_3^-, 14797-55-8; NO_2BF_4, 13826-86-3; $NaAlCl_4$, 7784-16-9; NaCl, 7647-14-5; $AlCl_3$, 7446-70-0; NO^+, 14452-93-8.

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Chemistry of (Triphenylphosphoranylidene)sulfamoyl Chloride. I. Reaction with Amines and Alcohols

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Compounds of the type Ph_3PNSO_2OR and Ph_3PNSO_2NHR (R = Me, Et, *n*-Pr, *n*-Bu, and *o*-, *m*-, *p*-BrC_6H_4) have been prepared in good yield by the reaction of (triphenylphosphoranylidene)sulfamoyl chloride, Ph_3PNSO_2Cl, with alcohols in pyridine or with amines in chloroform; derivatives of secondary amines may also be prepared by the latter method. Heating the methyl ester in pyridine to moderately high temperatures produces a compound containing the $Ph_3PNSO_2O^-$ ion which yields the free acid upon acidification. The infrared spectra of the title compound and the alkyl esters in the 1100–1300-cm^{-1} region are presented and discussed.

Introduction

The reaction of dry sulfamic acid with dichlorotriphenylphosphorane in refluxing acetonitrile[1] or benzene yields the novel compound (triphenylphosphoranylidene)sulfamoyl chloride, Ph_3PNSO_2Cl (**1**), the first known representative of a series of compounds of general formula Ar_3PNSO_2Cl. As part of a general investigation of the chemistry of these compounds, the reaction of the sulfamoyl chloride **1** with selected alcohols and primary and secondary amines has been studied.

Experimental Section

Reagents. Gaseous dimethylamine (Matheson) was used as received; methylamine was used as a 40% aqueous solution while all other amines and the three isomeric bromophenols were reagent grade materials (Eastman) and used without further purification. Aliphatic alcohols (reagent grade) were dried over Drierite for several days, filtered from the desiccant, and distilled from the corresponding magnesium alkoxide. Pyridine was dried by distillation from KOH pellets; chloroform was the commercially available "anhydrous" reagent and was used without further treatment.

The synthesis of **1** has been described previously;[1] however, a significant improvement results if benzene is substituted for acetonitrile as solvent. In a number of runs using 1.00 mol of sulfamic acid, 2.05 mol of dichlorotriphenylphosphorane, and 1.5–2.0 l. of dry benzene, yields of 91–94% were consistently obtained. The product precipitates as small, white crystals during the course of the reaction which is essentially complete after 24 hr at reflux (a small amount of HCl can still be detected after this time, but it probably results from traces remaining dissolved in the solvent). The analytically pure product is obtained directly from the reaction mixture by filtering the golden brown solution, washing the product several times with dry benzene, and drying in vacuo; mp 213.0–216.0°. *Anal.* Calcd for $C_{18}H_{15}ClNO_2PS$: C, 57.54; H, 4.08; N, 3.86. Found: C, 57.54; H, 3.99; N, 3.73.

Procedure. One of two general procedures was followed depending upon whether chloroform or pyridine was used as solvent. Examples of each of these procedures are given along with additional comments concerning other compounds whose syntheses are not described in detail. It should be noted that for the reactions run in chloroform, no special effort was made to exclude atmospheric moisture; on humid days, the transfer of pyridine to the reaction flask was done in a nitrogen-filled glove bag.

***N*-Methyl-*N*'-(triphenylphosphoranylidene)sulfamide.** A 7.52-g (20.0-mmol) amount of **1** was added in small portions to a mechanically stirred mixture of 100 ml of chloroform and 10.00 ml of a 40% aqueous solution of methylamine contained in a 300-ml, two-necked flask (the flask was kept stoppered between additions). The chloride reacted immediately as evidenced by its dissolution in the reaction mixture; external cooling was not necessary. After all of the sulfamoyl chloride had been added, the clear solution was stirred for 1 additional hr, transferred to a separatory funnel, and washed with water until the water extract was just faintly basic to litmus. After drying of the solution overnight with anhydrous sodium sulfate, the solvent was removed in vacuo using a rotary evaporator to yield a white solid which was finally dried in vacuo at 40°.