Chemical and Electrochemical Oxidation of Solutions of Silver Nitrate in Acetonitrile

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In anhydrous acetonitrile the unstable, brown species $Ag(NO_3)_4^{2-}$, I, can be produced either by the electrolysis of silver nitrate or by the equilibrium reaction $N_2O_5 + Ag^+ + 3NO_3^- \Rightarrow I + NO_2$, for which the concentration quotient is 8.0 M⁻³. The ESR spectrum of I at 77 K is that of a Ag(II) ion in a field with pronounced axial distortion. Its resonance Raman spectrum indicates square-planar coordination of the metal ion by unidentate nitrate ligands. The complex decomposes to form cyanomethyl nitrate and nitric acid by the rate law $-d[I]/dt = k[I]/[NO_3^-]$. In the presence of *p*-xylene a major organic product is *p*-methylbenzyl nitrate. Equilibrium and electrochemical studies lead to estimated ΔG°_{298} values for the free radical and ionic dissociation pathways of N_2O_5 in acetonitrile solution of +38 and -26 kJ, respectively.

Introduction

A number of years ago, Schmidt and Stange¹ reported that, when a solution of silver nitrate in acetonitrile was oxidized electrochemically, a deep brown color developed near the platinum anode. The brown color disappeared when the solution was stirred, and the medium became acidic with a 1:1 ratio of coulombs passed to titratable acidity. The electrolysis of cadmium nitrate led also to an acidic solution, and, in addition, oxygen was detected above the anolyte. These authors proposed that nitrate ions were oxidized to nitrogen trioxide at the electrode and that these species ultimately formed dinitrogen pentoxide and oxygen. In the presence of silver ion the brown-colored species was presumed to form in a subsequent reaction between the N₂O₅ and Ag⁺. In separate experiments authentic samples of N₂O₅ were found to react with silver nitrate in acetonitrile to produce the brown coloration.

Rao and co-workers² studied the electrochemical oxidation of lithium, cadmium, tetrabutylammonium, and silver nitrates in this solvent. In the oxidized silver solutions they found an ESR signal that they attributed to a Ag(II) species. Since the anodic discharge potential of all the solutions was independent of the cation, they concluded that nitrate ions were the first species to be oxidized.

Mishima et al.³ also investigated the electrochemical behavior of silver nitrate in acetonitrile. They reached the conclusion that the brown Ag(II) transient species was formed in a reaction between Ag(I) ions and nitrogen trioxide radicals bound to the electrode.

In all the work to date no attempt seems to have been made to identify the Ag(II)-containing species, nor has there been any discussion of its ultimate fate. In this paper we address both of these questions.

Experimental Section

Materials. Burdick and Jackson UV grade acetonitrile with manufacturer's water analyses of between 0.016 and 0.004% was stored under nitrogen and used without purification. Silver nitrate (Mallinckrodt) was dried at 80 °C and stored in a desiccator. Lithium nitrate (Mallinckrodt) was dried and stored in an oven at 140 °C. Nitronium tetrafluoroborate, 98% (Aldrich), was dried overnight in vacuo and used without further purification.

Silver perchlorate (G. F. Smith) was dissolved in benzene and azeotropically distilled to remove water, and then filtered hot. Upon cooling, a crystalline benzene solvate formed. After the benzene was removed by gentle heating in vacuo, the product was dissolved in acetonitrile and azeotropically distilled to remove the last traces of water and benzene. The silver content of the stock solution in acetonitrile was assayed by a reverse Fajans titration with KBr. Silver tetrafluoroborate was prepared by neutralizing aqueous HBF_4 (Mallinckrodt) with Ag_2O and then filtering. The concentrated aqueous $AgBF_4$ solution was dissolved in acetonitrile and then azeotropically distilled to remove the water. The silver content was assayed by a reverse Fajans titration.

Tetrapropylammonium nitrate was prepared by reacting equimolar amounts of silver nitrate and recrystallized tetrapropylammonium bromide (Eastman) in water, filtering out the AgBr, and evaporating to dryness in vacuo at room temperature to avoid thermal decomposition. The crude product was recrystallized three times from acetone/hexane or acetone/ethyl acetate and vacuum dried.

Tetraethylammonium perchlorate crystallized when a hot aqueous solution containing equimolar amounts of sodium perchlorate (G. F. Smith) and tetraethylammonium chloride (Eastman) was allowed to cool. The material was recrystallized from hot water and then vacuum dried overnight.

Dinitrogen pentoxide was generated by the gas-phase ozonolysis of NO₂ in a stream of oxygen⁴ and condensed into a receiver at -78 °C. The condensate was dissolved in about 15 mL of acetonitrile and the solution was chilled. Aliquots of 0.75 mL were sealed in ampules and stored in dry ice until they were needed. The N₂O_x content was determined by titration of a hydrolyzed sample with NaOH. This assay does not distinguish N₂O₄ from N₂O₅.

Cyanomethyl nitrate and prepared by reacting silver nitrate with iodoacetonitrile in acetonitrile according to the procedure of Ferris et al.⁵

Instrumentation. UV/visible spectra were recorded by a Hewlett-Packard Model 8450A spectrophotometer using 0.010-, 0.10-, 0.20-, or 1.00-cm silica cells as appropriate. Raman spectra were recorded on a Spex Ramalab spectrometer using Ar^+ 488-nm exciting radiation from a Spectra-Physics Model 164-02 laser. ESR spectra were obtained with a Varian Model E-4 spectrometer. Proton NMR spectra were recorded with a Varian Model EM-360 60 MHz spectrometer.

The electrolyses were performed in a thermostated, twochamber electrolysis cell constructed of 1.5-cm-i.d. glass tubing clamped horizontally. The 10-mL anode compartment was separated from the cathode compartment by a coarse frit filter. The 4×10 mm Pt mesh anode and the coiled Ag wire cathode were held 8 cm apart. The anode compartment was fitted with an outlet tube near the anode and an inlet tube near the divider frit so that the solution could be peristaltically pumped past the anode and through a spectrophotometer cell and then either discarded or re-electrolyzed.

Constant current electrolyses in the range 1-4 mA were used to measure the molar absorptivity of the colored species (vide

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infra). Preliminary cyclic voltammetric studies on AgNO₃ solutions confirmed the finding of others^{2,3} that only one anodic process occurs up to at least 2.2 V vs. Ag/AgNO₃ (0.1 M in CH₃CN). Over the course of a constant current experiment the applied voltage and the IR drop calculated from an ac measurement of the cell resistance never differed by amounts that would imply the possible oxidation of other species.

Results and Discussion

In agreement with previous workers we find that a brown color does develop, either in the anode compartment when AgNO3 solutions in acetonitrile are electrolyzed, 1-3 or homogeneously when such solutions are mixed with an acetonitrile solution of N_2O_5 .¹ We have also observed the brown color, together with the precipitation of AgCl, when gaseous chlorine is bubbled into solutions of AgNO₃ in this solvent. In other experiments we found that the color is discharged if NO_2 is added to solutions of the brown species.

Irrespective of the method of preparation, the same electronic spectrum at ambient temperature and ESR spectrum at 77 K are found for the colored species (vide infra). Nitrate ion is essential for its formation, since neither the color nor the characteristic ESR spectrum are observed when AgBF₄ solutions in acetonitrile are treated with N_2O_5 . If tetrapropylammonium nitrate is added to such a mixture, however, the color forms rapidly.

As all the previous investigators have also noted, the colored species disappears with time-quite rapidly if impure reagents or water are present, but more slowly if carefully purified materials are used. In the following paragraphs we present experimental results that establish the identity of the colored species, the kinetic rate law by which it decays, and its decay products.

ESR Confirmation of Ag(II). Rao et al.² reported finding an ESR signal in solutions of the colored species at room temperature that are consistent with Ag(II). At 77 K we find two doublets: $g_{\perp} = 2.052, |A| = 27 \text{ G}; \text{ and } g_{\parallel} = 2.261, |A| = 38 \text{ G}; \text{ a spectrum}$ characteristic of Ag(II) in a field with pronounced axial distortion. Po⁶ has collected ESR results for a large number of square-planar complexes of Ag(II) with nitrogen-heterocyclic ligands, and for these he gives typical values of $g_x = g_y = 2.03-2.06$; $g_z =$ 2.09-2.18. For aqueous Ag(II) in nitric acid McMillan and Smaller⁷ reported $g_x = g_y = 2.065$, |A| = 32 G; and $g_z = 2.265$, |A| = 48 G.

Among the ⁶⁰Co radiolysis products formed in acetonitrile solutions of AgNO₃ frozen at 77 K, Brown et al.⁸ reported finding a Ag(II) species having $g_x = g_y = 2.058$, |A| = 30 G; and $g_z =$ 2.283, |A| = 42 G. Neither Brown et al. nor we find any superhyperfine structure that would indicate the presence of a coordinated nitrogen atom.

UV/Visible Spectrum. Electrochemical experiments were used to obtain the molar absorptivity of the Ag(II) species at its 422-nm absorption maximum. Constant-current circulating electrolysis was performed with continuous stirring of the anolyte until the absorbance of the solution in a 0.20-cm flow-through spectrophotometer cell reached a steady-state value. Both the flow and the electrolysis were then halted and the pseudo-first-order decay of the species was monitored.

The decay rate at any time is given by k(concentration) = $k(A/\epsilon l)$, where A is the instantaneous absorbance, ϵ is the molar absorptivity, and l is the path length in cm. We assume that the formation rate from the electrolysis is i/VF, where i is the current, V is the volume of the electrolyzed solution in liters, and F is the Faraday constant. In the steady state these two rates are equal, and hence we find $\epsilon = AkFV/il$.

Three independent determinations with V = 6.5 mL gave A_1 = 0.163, k_1 = 4.08 × 10⁻² s⁻¹, i_1 = 3.0 mA; A_2 = 0.245, k_2 = 2.52 $\times 10^{-2} \text{ s}^{-1}$, $i_2 = 3.0 \text{ mA}$; and $A_3 = 0.103$, $k_3 = 3.27 \times 10^{-2} \text{ s}^{-1}$, $i_3 = 1.5$ mA. From these data we find $\epsilon = 6800 \pm 350$ M⁻¹ cm⁻¹ at 422 nm $(2.37 \times 10^4 \text{ cm}^{-1})$.



Figure 1. Logarithmic plots of equilibrium $[Ag(NO_3)_4^{2-}]$ against formal $[NO_3^-]$ with constant $[Ag^+] = 0.10$ M (triangles), and against formal [AgNO₃] (circles). The upper and lower curves are the calculated values for the respective experiments based on $K_1 = 8.0 \text{ M}^{-3}$.

The electronic spectrum of the brown species shows a long tail extending well into the visible (hwhm = 4360 cm^{-1}), a barely discernable shoulder at 340 nm, and another intense absorption $(\epsilon \approx 1.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$ at about 260 nm that appears as a shoulder on the long-wavelength side of the nitrate ion peak in the ultraviolet.

Stoichiometry of the Ag(II) Species. The composition of the absorbing species was determined in a series of experiments in which various solutions containing AgNO₃ and tetrapropylammonium nitrate were oxidized by mixing them with thawed solutions containing both N_2O_5 and its decay product, NO_2 . The total acidity of a representative sample of the oxidizing stock solution was also assayed.

The solutions of interest were mixed in a spectrophotometer cell and the absorbance at 422 nm was followed with time. The resulting pseudo-first-order decays, with rate constants of about 10^{-5} s⁻¹ (characteristic of the behavior of N₂O₅ in aprotic media⁹), were extrapolated to zero time to obtain the initial absorbance (and hence concentration) of the colored species.

In one series of runs the initial Ag(I) concentration was held constant at 0.10 M, the NO₃⁻ concentration was varied from 0.15 to 0.62 M, and the titratable acidity was 0.220 M. In a second series of runs the concentration of AgNO₃ was varied between 0.068 and 0.335 M and the titratable acidity was 0.042 M.

For each of these series the extrapolated initial concentrations of the colored species were in good agreement with calculated values based on the hypothesis that it formed in solution by the equilibrium reaction

$$N_2O_5 + Ag^+ + 3NO_3^- = Ag(NO_3)_4^{2-} + NO_2$$
 (1)

Figure 1 shows both the experimental initial concentrations of the colored species and theoretical formation curves for [Ag- $(NO_3)_4^{2-}$ calculated on the basis of reaction 1 with a concentration quotient of 8.0 M⁻³. The upper curve in Figure 1 describes the runs in which [Ag⁺] was held constant at 0.10 M. For these the best-fit calculated initial concentrations of N_2O_5 and NO_2 were found to be 0.10 and 0.02 M, respectively. The lower curve describes the runs in which the initial AgNO3 concentration was varied. These data were fitted with initial N_2O_5 and NO_2 con-

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TABLE I: Raman Spectra of Ag(NO₂),²⁻ and KAu(NO₂)

	provina or 1.9(1.03)	4
$Ag(NO_3)_4^{2-a}$	KAu(NO ₃) ₄ ^b	probable assignment ^b
1576 (1)	1588 (w)	$A' [\nu_{as}(NO_2)]$
	1555 (w)	
1308 (5)	1311 (s)	A' $[\nu_{s}(NO_{2})]$
1276 (4)		
1018 (7)	963 (s)	A' $[\nu_{\rm s}(\rm NO)]^{c}$
956 (3)	925 (w)	
780 (1)	784 (vs)	$A' [\delta_{s}(NO_{2})]$
734 (5)	768 (s)	
708 (5)	708 (w)	$A' [\delta_{as}(NO_2)]$
458 (1)		
432 (1)		
385-350 (2)		
	360 (vvs)	$[\nu(M-O)]^c$
320 (2)		1
268 (3)	266 ^d	}
238 (1)		skeletal motions
228 (1)		
198 (1)	202^{d})
·/		

^a Resonance-enhanced spectrum; position ± 2 cm⁻¹; numbers in parentheses are relative intensities in arbitrary units. ^b From ref 11; crystalline sample except as noted. ^c Coordinated oxygen. d In nitromethane solution.

centrations of 0.010 and 0.022 M, respectively.

In contrast to our results, the aqueous Ag(II) nitrate system studied by Honig and Kustin¹⁰ formed only AgNO₃⁺, with no evidence for more highly coordinated species. This complex has an absorption maximum at 390 nm ($\epsilon = 3200 \text{ M}^{-1} \text{ cm}^{-1}$) and a formation constant from Ag²⁺_{aq} and NO_{3 aq} of 0.72 M⁻¹ in 3.12 M HClO₄.

Probable Structure of $Ag(NO_3)_4^{2-}$. The resonance Raman spectrum of Ag(NO₃)₄²⁻ excited by 488-nm Ar⁺ radiation was recorded by circulating an elecrolytically generated, intensely colored solution of it in 1.3 M AgNO3 through a glass capillary tube mounted in the spectrometer. Under these conditions the nonenhanced solvent and bulk nitrate ion spectra are almost completely suppressed. The resulting spectrum in the 200-1600-cm⁻¹ region is listed in Table I together with the conventional Raman spectrum of KAu(NO₃)₄.¹¹

All the isolated NO_3^- stretching and in-plane bending modes have counterparts in the Raman spectra of both $Ag(NO_3)_4^{2-}$ and $KAu(NO_3)_4$. The out-of-plane bend is found at 793 and 802 cm⁻¹ in the IR spectrum of solid KAu(NO₃)₄ but does not appear in its Raman spectrum.¹¹ In the gold compound the nitrate ligands show square-planar, unidentate oxygen coordination to the central metal ion, with the planes of the ligands essentially perpendicular to the coordination plane.¹² Addison et al.¹³ have given several empirical spectroscopic criteria for distinguishing unidentate from bidentate nitrate coordination. One of these is that for bidentate nitrate ions the conventional Raman band at ca. 1300 cm⁻¹ is weak relative to those at about 1000 and 1600 cm⁻¹, whereas for unidentate coordination this band is intense. We find that this intensity behavior is also manifest in the resonance Raman spectrum of $Ag(NO_3)_4^{2-}$. This and other spectral similarities apparent in Table I suggest that the Ag(II) and Au(III) species have similar structures. The ESR results are also compatible with this conclusion.

Thermodynamic Considerations. A solution having [Ag- $(NO_3)_4^{2-}$] = 1 × 10⁻⁴ M, [Ag⁺] = [NO₃⁻] = 0.25 M, was found to generate a galvanic cell potential of 1.08 V vs. a Ag|AgNO₃ (0.25 M) electrode in acetonitrile. If the half-reaction involving Ag(II) is assumed to be

$$Ag(NO_3)_4^{2-} + e^- \rightarrow Ag^+ + 4NO_3^-$$
(2)

the observed cell voltage leads to an apparent E° for this half-

reaction of ± 1.15 V vs. the Ag|AgNO₃ (0.10 M) electrode that is one of the reference standards commonly used with this solvent.¹⁴ Activity coefficients were ignored in making this estimate of E° .

Bontempelli et al.¹⁵ have conducted voltammetric studies of the behavior of nitrogen oxides in acetonitrile. Against the Ag|Ag⁺ (0.10 M) electrode they found apparent half-wave potential values of

$$NO_2^+ + e^- \rightarrow NO_2 \qquad E_{1/2} = +0.93 V$$
 (3)

$$NO_3 + e^- \rightarrow NO_3^- \qquad E_{1/2} = +1.60 V$$
 (4)

With the realization that the resulting conclusions are only semiquantitatively correct, the potentials and species for reactions 2-4 may be combined with reaction 1 by using $K_1 = 8.0$ to yield

$$N_2O_5 \rightarrow NO_2 + NO_3$$
 (5)

$$\Delta G^{\circ}$$
, $\approx +38$ kJ, $K_5 \approx 1.9 \times 10^{-7}$

$$N_2O_5 \rightarrow NO_2^+ + NO_3^- \tag{6}$$

$$\Delta G^{\circ}_{6} \approx -26 \text{ kJ}, \quad K_{6} \approx 3.9 \times 10^{4}$$

The estimated magnitude of K_5 is large enough to ensure that an N_2O_5 solution contains an ample concentration of the NO₃ radical that is presumably the actual oxidizing agent in both the chemical and the electrochemical formation of $Ag(NO_3)_4^{2-}$. Equation 6 suggests that the kinetic barrier for the ionic dissociation of N_2O_5 must be substantial since the Raman spectrum we have observed for it in acetonitrile is the same as that reported by Chedin¹⁶ for the molecular form in carbon tetrachloride. Equations 5 and 6 also explain our observation that $Ag(NO_3)_4^{2-}$ cannot be formed by adding NO_2BF_4 to a solution of silver nitrate in acetonitrile.

Our results furthermore demonstrate that one of the conclusions reached by Bontempelli et al. cannot be correct. These authors assigned a voltammetric feature at +0.39 V vs. Ag|Ag⁺ (0.10 M) in solutions containing NO_2^+ and NO_3^- to the reaction

$$N_2O_5 + e^- \rightarrow NO_2 + NO_3^- \tag{7}$$

Reactions 2 and 7 combine to produce reaction 1, ΔG° for which is slightly negative by experiment. Thus, the apparent E° for reaction 7 must be slightly more positive than 1.15 V.

The gas-phase analogue of reaction 5 has been studied very recently by Tuazon et al.,¹⁷ who reports for it a K_{298} value of (2.91 \pm 0.69) \times 10¹⁰ molecule cm⁻³. From this result we calculate a ΔG°_{298} value of 58.9 ± 0.6 kJ for reaction 5 in the gas phase using 1 mol· L^{-1} standard states. When this value is combined with the newly reported 9.790 \pm 0.001 eV ionization potential of NO₂¹⁸ and the 3.77 \pm 0.25 eV electron affinity of NO₃¹⁹ we find a ΔG°_{298} value for reaction 6 in the gas phase (1 mol·L⁻¹ standard states) of 640 \pm 25 kJ. The overwhelming majority of the discrepancy between this value and the one reported above for the same reaction in acetonitrile solution must arise from the Gibbs energy of transfer of the two ions from the gas phase to a medium of dielectric constant $37.^{20}$ If the transfer of N_2O_5 from the gas phase to acetonitrile solution is assumed to have $\Delta G^{\circ} = 0$, although it is probably slightly negative, the Born equation²¹ then shows that the transfer thermochemistry can be reconciled if the average

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Figure 2. Logarithmic plot of observed pseudo-first-order rate constant against formal [AgNO₃] for the spontaneous decomposition of Ag- $(NO_3)_4^{2-}$.

radius of the two ions is 2.1 ± 0.1 Å. For comparison purposes we note that the Stokes law radius²² of NO₃⁻ in acetonitrile is 2.2 Å, calculated from its average limiting equivalent conductance of 107 cm²·eq⁻¹·ohm⁻¹ and a solvent viscosity of 0.345 cP.²⁰

Decay Kinetics and Products. Whether chemically or electrolytically produced, $Ag(NO_3)_4^{2-}$ decays spontaneously by pseudo-first-order kinetics. Since the decay of chemically generated $Ag(NO_3)_4^{2-}$ is linked to the slow decay of N_2O_5 , detailed kinetic studies were made only for the behavior of electrolytic $Ag(NO_3)_4^{2-}$. The decay constants were observed to vary somewhat from one batch of solvent and reagents to another, but within a given formulation a dependence on the silver nitrate concentration was also evident. Figure 2 shows a log-log plot of the apparent rate constants for the decay of electrolytic $Ag(NO_1)_4^{2-}$ vs. the respective AgNO₃ concentrations over the range of 0.10–0.40 M. A similar unit negative slope was also found in another series of runs in which [AgNO₃] was varied from 0.5 to 1.1 M.

A pairwise set of four experiments using constant ionic strength mixtures of AgNO₃, AgClO₄, and tetraalkylammonium nitrates and perchlorates in which the concentrations of both Ag⁺ and NO₃⁻ were varied by factors of two was performed. It was found that when aliquots of an electrolytic Ag(II) solution were added to these mixtures, the decay rate of the Ag(II) species was independent of [Ag⁺] but had an inverse first-power dependence on [NO₃⁻].

The decay products of electrolytic $Ag(NO_3)_4^{2-}$ were identified from infrared, proton NMR, and Raman spectroscopic evidence. New IR absorptions in the decayed solutions at 3140, 2910, and 2340 cm⁻¹ were found to match peaks in the spectrum of nitric acid (made by adding water to an N_2O_5 solution) in acetonitrile containing AgNO₃. Raman spectral matches for these two solutions occurred at 1325 and 1020 cm⁻¹. If AgNO₃ was absent from the comparison solution no such correspondences were found, and therefore $H(NO_3)_2^-$ is the most likely absorbing species.²³

New IR absorptions in the decayed solutions at 2560 and 1670 cm⁻¹, Raman shifts at 1280, 840, and 600 cm⁻¹, and a broadened NMR singlet at $\delta = 5.2$ all had counterparts in the spectra of authentic samples of cyanomethyl nitrate in acetonitrile. The NMR spectra also showed a sharp singlet with variable position in the range 11-18 ppm that we attribute to HNO₃ complexed with NO₃⁻. The relative areas of the HNO₃ and cyanomethyl

nitrate NMR peaks gave a product ratio of 4:1, respectively. Rao et al.² reported finding gaseous nitrogen as a product of the electrolysis of silver nitrate in acetonitrile, whereas Mishima et al.³ stated that no gases were evolved. To resolve this conflict we allowed relatively concentrated electrolytic $Ag(NO_3)_4^{2-}$ solutions to decay in a 5-mL flask connected to one side of a miniaturized differential mercury manometer. The reference side contained an unelectrolyzed sample of the same AgNO₃ solution. No significant pressure changes accompanied the decay of the Ag(II) species. Further to confirm that gaseous products are unimportant, an AgNO3 solution was heavily electrolyzed under an argon atmosphere. While still under argon, an aliquot of the anolyte was allowed to decay in a 10-mL tube that was connected to an evacuated mass-spectrometer sampling bulb. The mass spectrum of the gas above the decayed solution showed no enrichment above the background O_2/N_2 ratio. A trace of NO_2 was detected in this experiment.

A mechanism that is generally consistent with the kinetic and chemical facts is

 $Ag(NO_3)_4^{2-} + NCCH_3 \rightleftharpoons Ag(NO_3)_3(NCCH_3)^- + NO_3^-$ (8)

Ag

$$(NO_3)_3(NCCH_3)^- + HR \rightarrow Ag^+ + 2NO_3^- + CH_3CN + HNO_3 + \dot{R} (9)$$

$$\dot{R} + Ag(NO_3)_4^{2-} \rightarrow Ag^+ + 3NO_2^- + RONO_3$$
 (10)

where HR is any suitable hydrogen atom donor, in this instance acetonitrile. The initial equilibrium 8 is suggested by the observed rate law dependence on $[NO_3^-]^{-1}$ and independence of $[Ag^+]$. Reaction 9, which is probably rate determining, accounts for the formation of nitric acid. Reaction 10 accounts for the formation of nitrate esters. Although an N-coordinated species is postulated in reaction 8, if this reaction is endothermic, no significant amount of it could persist at 77 K where the ESR spectra were measured. Also the value of K_8 must be small at 298 K since only a single Ag(II) species need be invoked to produce the agreement shown in Figure 1.

In strictly anhydrous acetonitrile the only hydrogen source available is the solvent, and hence one would expect to find equivalent amounts of HNO3 and products derived from ·CH2CN. We take the experimental product ratio as evidence that there must be other reactions in addition to the ones postulated. One such reaction that could account for up to a 30% enhancement in the HNO₃ yield is one between a Ag(II) species and residual water, which is present in the solvent at the 2-8 mM level. An obvious possibility is the dimerization of cyanomethyl radicals to succinonitrile. In a search for this substance the solvent was stripped from a decayed Ag(II) solution; no evidence for succinonitrile could be found in the NMR spectrum of the residue dissolved in D_2O . A third possibility is that the cyanomethyl nitrate is also a hydrogen atom donor and is thereby reduced in concentration.

In order to assure that cyanomethyl nitrate is a decay product of $Ag(NO_3)_4^{2-}$ rather than a product of some independent reaction between NO3 and acetonitrile, a saturated solution of lithium nitrate was extensively electrolyzed. The NMR spectrum of the anolyte showed that it contained four times more HNO3 than was found for a typical AgNO₃ electrolysis, but there was no evidence whatever for cyanomethyl nitrate formation, nor could succinonitrile be found.

To further confirm reactions 9 and 10 in the mechanism, a small amount of *p*-xylene was introduced into a solution of electrolytic $Ag(NO_3)_4^{2-}$. Since the abstraction of a methyl hydrogen is more facile for xylene than for acetonitrile, a much faster reaction would be expected for the former: the observed reaction was immediate. The corresponding organic product of reaction 10, p-methylbenzyl nitrate, was detected in the NMR spectrum of the reaction mixture (7.25 and 5.40 ppm, ratio 2:1).

Registry No. Ag(NO₃)₄²⁻, 94993-23-4; N₂O₅, 10102-03-1; NO₃⁻, 14797-55-8; Ag, 7440-22-4; cyanomethyl nitrate, 95017-67-7; nitric acid, 7697-37-2; p-xylene, 106-42-3; p-methylbenzyl nitrate, 13527-05-4; silver nitrate, 7761-88-8; tetrapropylammonium nitrate, 1941-28-2.

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