state with respect to Mn(II), and electron-donating substituents on the porphyrin periphery further stabilize the oxidized form.[22] Table II compares the potentials of $ClMn^{III}P$–$Mn^{II}P$ (measured in acetonitrile) with the rate of reduction of the manganese(III) porphyrins in 4 *M* pyridine. Since both $Mn^{II}P$ and $Mn^{III}P$ are high spin with or without nitrogen donor ligands,[11] no change in the relative order of the oxidation potentials is expected due to the differing types of solvents. Table II shows that the more negative the $ClMn^{III}P$-$Mn^{II}P$ couple, the slower the rate of reduction to the divalent state by dithionite. Thus electrochemical and kinetic stabilities parallel one another in both the cobalt and the manganese porphyrin series. These are a number of cases where the driving force of a reaction contributes to its rate.[23]

Since K_D is unknown under the reaction conditions, the results are reported in terms of $(k_0/[S_2O_4^{2-}]^{1/2})$. With $K_D^{1/2}$ *ca.* 10^{-5} $M^{1/2}$, the rates for $Mn^{III}P$ are *ca.* 10^6 M^{-1} sec^{-1} and those for Co(III) approximately 10^4 M^{-1} sec^{-1}. This can be explained in part by the greater ligand field stabilization energy of a formal d^6 Co^{3+} configuration *vs.* d^4 for Mn(III). In addition, bis(pyridine)manganese(III) hematoporphyrin is reduced at potentials 86 mV more positive[16] than hematoporphyrin of $(py)_2Co^{III}$ in line with their relative reactivities toward dithionite.

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Registry No. Etioporphyrin(III), 531-16-8; mesoporphyrin DME, 1263-63-4; deuteroporphyrin DME, 10589-94-3; hematoporphyrin DME, 33070-12-1; protoporphyrin DME, 5522-66-7; diacetyldeuteroporphyrin DME, 52760-90-4; dibromodeuteroporphyrin DME, 14196-91-9; tetrapyridylporphine, 16834-13-2; Mn(III), 14546-48-6; Co(III), 22541-63-5; $S_2O_4^{2-}$, 14844-07-6.

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Reactions of Fluorosulfuryl Isocyanate With Metal Oxides[1]

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Fluorosulfuryl isocyanate, FSO_2NCO,[2,3] has been found to react with various metal fluorides to form addition products which were characterized as salts of (fluoroformyl)fluorosulfurylimide, $M^+[N(SO_2F)C(O)F]^-$.[4,5] In these reactions which involved addition of fluoride ion, the carbon–nitrogen bond in FSO_2NCO remained intact. Therefore, it was of interest to examine reactions of FSO_2NCO with a stronger base which could effect cleavage of the carbon-nitrogen bond and lead to the synthesis of new sulfur-nitrogen compounds. FSO_2NCO was found to react with red mercury(II) oxide (HgO) and silver(I) oxide (Ag_2O) *via* elimination of CO_2 to form the compounds mercury(II) fluorosulfurylamide, mercury(II) *N,N'*-bis(fluorosulfuryl)ureide, and disilver(I) *N,N'*-bis(fluorosulfuryl)ureide which were isolated as the solvates from acetonitrile.

Experimental Section

Materials. FSO_2NCO was prepared by the method of Roesky and Hoff.[6] The infrared spectrum, ^{19}F nmr spectrum, and vapor density (mol wt calcd, 125; found, 124) agreed with those previously reported.[6,7] HgO and Ag_2O were obtained from Baker and Adamson and Fisher Scientific, respectively. CH_3CN was Fisher Certified reagent grade and distilled from CaH_2 prior to use.

Preparation of $HgNSO_2F \cdot CH_3CN$. In a typical run, HgO (0.4474 g, 2.06 mmol) was placed in a preweighed 30-ml Pyrex bulb equipped with a Fischer and Porter Labcrest 4-mm bluntnose Teflon–glass valve. The reaction vessel was evacuated and flamed gently to remove residual moisture. CH_3CN (4.1888 g) was condensed into the reaction vessel under high-vacuum conditions from a reservoir which contained CaH_2 to ensure that the solvent was dry. A stoichiometric amount of FSO_2NCO with respect to HgO (1:1) was measured out by volume and condensed into the reaction mixture. The actual amount of FSO_2NCO transferred (0.2661 g, 2.13 mmol) was determined by weighing. As the reaction mixture approached room temperature, a slow evolution of gas (CO_2) was observed. The mixture was stirred for several days, and the orange color of HgO slowly disappeared as a white solid formed. CO_2 was periodically removed from the reaction mixture by holding the vessel at −78° and condensing the material volatile at that temperature into a trap held at −196°. The volatile material obtained in this way was subjected further to fractional condensation at −78 and −196° to rid the CO_2 of traces of CH_3CN that had condensed in the original separation. Infrared analysis showed that the material which had condensed in the trap held at −196° was pure CO_2.[8] The molecular weight was obtained by vapor density measurements: calcd for CO_2, 44.0; found, 43.7. Weight: calcd for CO_2, 0.0906 g; found, 0.0880 g, 97.1% on basis of original amount of HgO. The solvent was removed from the solid residue by pumping on the reaction vessel through a trap cooled to −196°. Infrared analysis of the material which condensed at this temperature showed the presence of CH_3CN only.[9] The white solid which remained in the reaction vessel was pumped until the weight loss did not exceed several milligrams per hour and chemically analyzed. Weight: calcd for $HgNSO_2F \cdot CH_3CN$, 0.6994 g; found, 0.6989 g. *Anal.* Calcd for $HgNSO_2F \cdot CH_3CN$: C, 7.09; H, 0.89; N, 8.27; S, 9.45; F, 5.61. Found: C, 6.63; H, 0.88; N, 7.71; S, 8.73; F, 5.5.

If a molar ratio of FSO_2NCO to HgO greater than 1:1 was allowed to react, it was noticed in several instances that the weight of the white residue was higher than that calculated for $HgNSO_2F \cdot CH_3CN$. This result suggested that reaction of HgO with 2 equiv of FSO_2NCO could occur and this hypothesis was verified. For a typical run, the composition of the product was calculated assuming that the excess FSO_2NCO reacted with $HgNSO_2F \cdot CH_3CN$ to form $Hg[N(SO_2F)C(O)NSO_2F] \cdot CH_3CN$. Amounts: HgO, 0.5276 g, 2.44 mmol; FSO_2NCO, 0.3281 g, 2.62 mmol; CO_2 produced, 0.1035 g, 2.35 mmol; calcd for mixture of 2.26 mmol of $HgNSO_2F \cdot CH_3CN$ + 0.18 mmol of $Hg[N(SO_2F)C(O)NSO_2F] \cdot CH_3CN$, 0.8487 g; found for same mixture, 0.8599 g. Other runs gave similar results.

Preparation of $Hg[N(SO_2F)C(O)NSO_2F] \cdot CH_3CN$. The general procedure is described above. HgO (0.4065 g, 1.88 mmol) reacted with FSO_2NCO (0.2394 g, 1.92 mmol) in CH_3CN (2.8475 g) to produce CO_2 (0.0819 g, 1.86 mmol) and a white solid ($HgNSO_2F$) insoluble in the CH_3CN solvent. Another portion of FSO_2NCO (0.2429 g, 1.94 mmol) was added to the reaction vessel such that the overall ratio of FSO_2NCO to HgO was 2:1. When the reaction mixture was warmed to room temperature and stirred, the white solid immediately dissolved to give a clear colorless solution. No gases were evolved when this reaction took place. The solvent and excess FSO_2NCO were removed from the reaction vessel by pumping through a trap cooled to −196°. Infrared analysis revealed that only CH_3CN[9]

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and a trace of FSO_2NCO[6,7] were present in the volatile material. The white solid remaining in the reaction vessel was pumped until the weight loss did not exceed several milligrams per hour. Weight of residue: calcd for $Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$, 0.8700 g; found, 0.8691 g. *Anal.* Calcd for $Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$: C, 7.77; H, 0.65; N, 9.06; S, 13.83; F, 8.19. Found: C, 8.87; H, 0.67; N, 8.87; S, 13.53; F, 8.20. Similar results were observed in other runs.

Preparation of $Ag_2[N(SO_2F)C(O)NSO_2F]\cdot XCH_3CN$. Reactions were run as described above. When Ag_2O (0.7345 g, 3.17 mmol) was stirred in the presence of CH_3CN (2.5134 g) and a large excess of FSO_2NCO (1.6510 g, 13.21 mmol) at room temperature, a reaction took place in which CO_2 was produced and most of the Ag_2O went into solution. However, continued stirring did not result in the dissolution of all of the Ag_2O indicating that the reaction was incomplete. The solution was separated from the unreacted solid by centrifugation under vacuum and the supernate was pumped to dryness under high-vacuum conditions. When the weight loss over several hours reached a value below 3 mg, the sample was analyzed. *Anal.* Calcd for $Ag_2[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$: C, 7.52; H, 0.63; N, 8.77; S, 13.40; F, 7.93. Found: C, 8.24; H, 0.75; N, 9.53; S, 14.85; F, 8.1. In another case, $Ag_2[N(SO_2F)C(O)NSO_2F]$ was prepared as described above, but the volatile material was quickly pumped away until the white solid remaining in the reaction vessel appeared dry and the pressure of CH_3CN above the product was not measurable on a mercury manometer. The white free-flowing solid was then analyzed. *Anal.* Calcd for $Ag_2[N(SO_2F)C(O)NSO_2F]\cdot 2CH_3CN$: C, 11.55; H, 1.16; N, 10.77; S, 12.33; F, 7.31. Found: C, 12.72; H, 1.43; N, 11.21; S, 12.52; F, 8.2.

Reaction of $HgNSO_2F$ with Cl_2. A sample of $HgNSO_2F\cdot CH_3CN$ was pumped at high vacuum at 100° for 3 hr to remove CH_3CN. The sample (0.7476 g of $HgNSO_2F\cdot 0.22CH_3CN$) did not lose weight appreciably on further pumping for 2 hr at 100°. Cl_2 (0.2070 g, 2.92 mmol) which had been dried over P_4O_{10} was added and its characteristic color disappeared in 30 min indicating that reaction had taken place. The volatile materials were removed and shown by infrared spectrometry to be Cl_2NSO_2F[10] and a trace of FSO_2NCO.[6,7] Another quantity of Cl_2 (0.1475 g, 2.08 mmol) was added and the mixture was allowed to stand overnight. The characteristic color of Cl_2 did not completely disappear during this time. The volatile materials were removed and shown to be Cl_2NSO_2F[10] and SO_2ClF[11] by infrared spectroscopy. In addition, a noncondensable gas (N_2) and a green-yellow condensable gas (Cl_2) were present. Any CH_3CN liberated from the reactant was probably present in too small a quantity to be detected by infrared spectroscopy under the conditions employed. An ^{19}F nmr spectrum of the higher boiling fraction of these volatile materials exhibited an intense singlet resonance at −27.3 ppm (lit.[10] for Cl_2NSO_2F −26.5 ppm). A white sublimable solid remained in the vessel. Weight of residue: calcd for $HgCl_2$, 0.6618 g; found, 0.6800 g.

Reaction of $Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$ with Cl_2. A sample of the product (1.3083 g) produced by the reaction of FSO_2NCO and HgO in a 2:1 molar ratio was pumped at 25° until the weight was nearly constant. Cl_2 was added until its characteristic yellow-green color did not disappear by reaction with the white solid. The volatile material was removed and subjected to fractional condensation at −78 and −196°. The yellow-green material (Cl_2) which passed the trap held at −78° showed no absorption bands in the infrared region. The material which condensed at −78° showed absorption bands characteristic of a mixture of CH_3CN,[9] FSO_2NCO[6,7] and FSO_2NCl_2.[10] The most intense bands of CH_3CN overlap those of FSO_2NCO and FSO_2NCl_2 in the region 1500–1400 cm^{-1} and are difficult to detect in the presence of these species. A white solid remained in the reaction vessel. Weight: calcd for $HgCl_2$, 0.8402 g; found, 0.9327 g.

Reaction of $Ag_2[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$ with Cl_2. A sample of $Ag_2[N(SO_2F)C(O)NSO_2F\cdot xCH_3CN$ (0.6295 g) was pumped to constant weight at room temperature under high vacuum in 100 hr. The final composition was close to that for $x = 1$. Dry Cl_2 gas (total amount 0.1983 g, 2.80 mmol) was added in increments until the yellow-green color of the gas failed to disappear. After each addition of Cl_2, the volatile products were removed.

The volatile products were examined by infrared spectroscopy and found to be FSO_2NCl_2,[10] FSO_2NCO,[6,7] and a small amount of CH_3CN.[9] ^{19}F nmr spectroscopy of the product mixture confirmed the presence of FSO_2NCl_2[10] and FSO_2NCO (−61.3 ppm, singlet; lit.[6,7] −61.1 ppm). The white residue in the reaction vessel was identified as AgCl by chemical tests. Weight of AgCl: calcd, 0.3768 g; found, 0.3696 g.

Stability of $Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$ and $Ag[N(SO_2F)C(O)NSO_2F]\cdot xCH_3CN$. A sample of $Hg[N(SO_2F)C(O)NSO_2F]\cdot xCH_3CN$ was pumped at 25° until the weight loss did not exceed 2 mg hr^{-1}. The observed material balance indicated that the composition was close to that for $x = 1$: calcd, 3.8592 g; found, 3.8334 g.

The vessel containing the dry white product was heated to 50° under dynamic vacuum for 13 hr during which time the weight loss decreased to a rate of about 3 mg hr^{-1}. The volatile material which had evolved was collected in a trap held at −196° and shown to be a mixture of CH_3CN[9] (0.0763 g, 1.86 mmol) and FSO_2NCO[6,7] (0.0375 g, 0.30 mmol) by infrared spectroscopy and vapor density measurements. Further heating of the white residue to 100° for 18.5 hr and 150° for 3.5 hr resulted in the evolution of CH_3CN (0.1177 g (2.87 mmol) and 0.0284 g (0.69 mmol), respectively) and FSO_2NCO (0.2688 g (2.15 mmol) and 0.3969 g (3.18 mmol), respectively). At 215° a volatile mixture which attacked glass and contained CH_3CN,[9] CO_2,[8] FSO_2NCO,[6,7] and SiF_4[12] was collected. The white solid residue (2.7821 g) in the reaction vessel was a free-flowing powder.

A sample of $Ag_2[N(SO_2F)C(O)NSO_2F]\cdot xCH_3CN$ (1.0229 g) was pumped to constant weight at room temperature. The substance was heated to various temperatures under dynamic vacuum while volatile materials were collected as described above. At 40° in 12.8 hr, only CH_3CN[9] (0.0877 g) was liberated and no further evolution occurred until the temperature reached 60°. At 60–80°, CH_3CN[9] (0.0613 g) was liberated in 14.5 hr, but less than 5 mg of volatile material evolved as the temperature was increased to 110°. At 145–150° the white solid began to turn brown and melted to a dark brown viscous liquid over the temperature range 160–170°. Volatile material collected at 170° proved to be CH_3CN[9] (0.0010 g) and FSO_2NCO[6,7] (0.0148 g). Above 170° SO_2F_2,[12] SO_2,[8] and FSO_2NCO[6,7] appeared in the volatile products indicating that further decomposition had taken place.

Spectral Data. A Varian A-56/60 nmr spectrometer was used to obtain chemical shifts, relative to CCl_3F as an external reference. $Hg[N(SO_2F)C(O)NSO_2F]$ and $Ag_2[N(SO_2F)C(O)NSO_2F]$ were run in CH_3CN solution and exhibited sharp singlet resonances at −50.8 and −46.0 ppm, respectively. Infrared spectra were taken on a Perkin-Elmer Model 621 infrared spectrophotometer. The bands listed here are for the solvated or partially solvated products pressed between AgCl plates. $HgNSO_2F\cdot CH_3CN$: 3005 (w), 2940 (vw), 2290 (w), 2255 (s), 2195 (w), 1312 (vs), 1153 (vs), 1035 (vs), 925 (mw), 815 (vs), 710 (vs), 618 (vs), 544 (s), 390 (w), 380 (w) cm^{-1}. $Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$: 3000 (vw), 2940 (w), 2300 (s), 1615 (vs), 1400 (vs), 1180 (vs), 1030 (vw), 965 (s), 925 (m), 795 (vs), 640 (vs), 615 (w), 588 (vs), 568 (vs), 543 (vs), 512 (m), 388 (w), 380 (w) cm^{-1}. $Ag_2[N(SO_2F)C(O)NSO_2F]\cdot xCH_3CN$: 3010 (w), 2940 (vw), 2300 (m), 2280 (w, sh), 1560 (vs), 1362 (vs), 1310 (sh), 1180 (vs), 1152 (sh), 1120 (m), 1030 (m), 942 (vs), 853 (vs), 820 (sh), 760 (vs), 622 (vs), 572 (vs), 552 (sh), 545 (vs), 507 (s), 480 (w), 420 (w), 386 (w), 376 (w) cm^{-1}.

Results and Discussion

Fluorosulfuryl isocyanate reacts with red mercury(II) oxide and silver(I) oxide in the presence of acetonitrile. The reactions proceed *via* elimination of carbon dioxide and formation of the solvated products according to the equations

$$HgO + FSO_2NCO \xrightarrow{CH_3CN} HgNSO_2F\cdot CH_3CN + CO_2$$

$$HgO + 2FSO_2NCO \xrightarrow{CH_3CN} Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN + CO_2$$

$$Ag_2O + 2FSO_2NCO \xrightarrow{CH_3CN} Ag_2[N(SO_2F)C(O)NSO_2F]\cdot xCH_3CN + CO_2$$

The preparation of these compounds has not been reported previously although Roesky and Hoff have synthesized compounds containing the *N,N'*-bis(fluorosulfuryl)ureide group by the reaction of *N,N'*-bis(fluorosulfuryl)urea with alkali or alkaline earth metal carbonates.[6] Breitinger, *et al.*,[13] have

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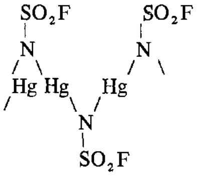
extended Roesky's method to include dimercury(I) *N,N'*-bis(fluorosulfuryl)ureide.

The new compounds are white solids which are stable at room temperature but slowly lose CH_3CN when held under reduced pressure. Upon heating under high vacuum, CH_3CN is lost more rapidly, but in the case of $Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$ removal of the solvated CH_3CN is accompanied by decomposition *via* elimination of FSO_2NCO at temperatures below 100°. This result may be due to the high stability of $HgNSO_2F$ compared to Ag_2NSO_2F for which no evidence of formation was observed.

Infrared spectral data provide evidence for the proposed structure of the new compounds although some of the bands were broad, and exact assignment of some absorption frequencies is uncertain. In all cases, strong absorption bands appear in the region of 1400-1150 cm^{-1} indicating that the sulfuryl group ($-SO_2-$) is present.[14] Strong bands near 800 cm^{-1} indicate the presence of the S-F linkage.[14] For $Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$ and $Ag_2[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$ strong absorptions at 1615 and 1560 cm^{-1}, respectively, are assigned to the amide I band.[13] The spectra of these substances also exhibit strong, sharp bands near 2300 cm^{-1} (ν(CN)) which indicates coordination of acetonitrile to the central Hg atom through the lone pair of electrons on nitrogen.[15] Sharp bands at 965 and 942 cm^{-1} (ν(C-C)), respectively, support this conclusion. However, in the case of $HgNSO_2F\cdot CH_3CN$, it appears that coordination of acetonitrile through the lone pair on nitrogen is either very weak or absent. The strongest band in the $-C\equiv N$ stretching region appears at 2255 cm^{-1} which is close to that reported for free CH_3CN (2250, 2251 cm^{-1}).[16-18] Another weaker absorption at 2290 cm^{-1} may be a combination band ($\nu_3 + \nu_4$) of free CH_3CN.[18] The presence of a weak third band at 2195 cm^{-1} is not understood. These results are in agreement with the observation that prolonged pumping at 100° results in removal of about 80% of the CH_3CN from $Hg[NSO_2F]\cdot CH_3CN$.

In view of the tendency for N-Hg-N bonds to be linear,[19] it is probable that unsolvated $HgNSO_2F$ exists as a chain polymer with a backbone formed of linear N-Hg-N bonds



A similar structure has been proposed[20,21] for the related compound $Na[SO_3NHg]$. The results of a vibrational and X-ray spectroscopic study performed by Breitinger, *et al.*,[13] suggested that dimercury(I) *N,N'*-bis(fluorosulfuryl)ureide exists in a polymeric chain structure in the solid state. It is likely that unsolvated $Hg[N(SO_2F)C(O)NSO_2F]$ also exists in a chain structure. However, if CH_3CN is coordinated to Hg, as the infrared spectral data appear to indicate, the N-Hg-N bond system would not be linear. Further work will be necessary to determine whether this is the case.

The ^{19}F nmr spectra of $Hg[N(SO_2F)C(O)NSO_2F]$ and $Ag[N(SO_2F)C(O)NSO_2F]$ in CH_3CN solution exhibit a singlet resonance in the region expected for fluorine on sulfur in a fluorosulfuryl group.[14] This result agrees with the proposed structure of the *N,N'*-bis(fluorosulfuryl)ureide group which contains two equivalent F atoms. ^{19}F nmr spectra for $HgNSO_2F$ were not obtained due to the insolubility of the substance.

The new compounds react vigorously with chlorine to produce mainly the metal chloride and *N,N*-dichlorofluorosulfurylamine according to the equations

$$HgNSO_2F + 2Cl_2 \rightarrow HgCl_2 + Cl_2NSO_2F$$

$$Hg[N(SO_2F)C(O)NSO_2F] + 2Cl_2 \rightarrow HgCl_2 + Cl_2NSO_2F + FSO_2NCO$$

$$Ag_2[N(SO_2F)C(O)NSO_2F] + 2Cl_2 \rightarrow 2AgCl + Cl_2NSO_2F + FSO_2NCO$$

The weight of the solid residue remaining in the reaction vessel was slightly greater than that expected for complete conversion to the metal chloride for the first two reactions listed above. This result suggests the occurrence of side reactions or incomplete reaction of Cl_2 with the substrate.

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Registry No. $HgNSO_2F\cdot CH_3CN$, 52500-56-8; $Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$, 52555-16-5; $Ag_2[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN$, 52555-15-4; HgO, 21908-53-2; Ag_2O, 12249-86-4; FSO_2NCO, 1495-51-8; $Ag_2[N(SO_2F)C(O)NSO_2F]\cdot 2CH_3CN$, 52555-17-6.

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Kinetics of Ligand Substitution on Ferric Horse Heart Myoglobin

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Numerous kinetic studies of ligand interactions with ferric myoglobin have been reported.[1-3] Blanck, *et al.*,[1] studied the kinetics of anation and aquation of ferric myoglobin, reaction 1. The ligand L was CN^-, N_3^-, OCN^-, SCN^-, NO_2^-, etc. The kinetics were followed at 21-23° in phosphate-borate buffers covering the pH range 6-9.

$$Mb\text{-}OH_2 + L \rightleftharpoons Mb\text{-}L + H_2O \qquad (1)$$

The mechanism of these anation and aquation reactions is generally considered to be dissociatively activated,[3] as is the

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