an increase in the energy of ligand field states, this nonproductive deactivation channel is removed and the efficiency of photosensitization is greatly increased.

Using these two criteria, it should be possible to design many Magnus-type materials that will be photoactive. Whether photoactivity is merely a result of light absorbed by surface chromophores or whether cooperative electronic structure allows transfer of excitons (or perhaps conduction-band electrons) from the bulk to the surface is a question of central importance to the study of these materials. From a theoretical viewpoint[32] it is very likely that some variation of an exciton model applies to the d → p states of d^8 linear-chain materials, and therefore bulk excitation is mobile. This study demonstrates that excitation can be harvested at the solid-liquid interface in redox processes. We are currently attempting to grow large single crystals of PBC in order to study the photoconductivity and other electrical properties of this material.

Acknowledgment. We thank Carl Craig and Professor Richard J. Watts at the University of California, Santa Barbara, CA, for lifetime and emission data, Dr. John S. Connolly at SERI for access to equipment in his laboratory and assistance with nanosecond lifetime measurements, Alex Miedaner at SERI for the synthesis of $Pt(bpy)_2^{2+}$ and $Pt(bpy)(MHB)^{2+}$, and Dr. Vincent Miskowski at the Jet Propulsion Laboratory for many helpful discussions. This work was supported by Contract No. 5083-260-0796 from the Gas Research Institute.

Registry No. $[Pt(NH_3)_4][PtCl_4]$, 13820-46-7; $[Pt(bpy)_2][PtCl_4]$, 54822-44-5; $[Pt(bpy)(MHB)][PtCl_4]$, 98064-84-7; $[Pt(bpy)_2][Pt(CN_4)]$, 54806-40-5; $[Pt(bpy)(MHB)][Pt(CN)_4]$, 98064-85-8; H_2O, 7732-18-5; H_2, 1333-74-0; Pt, 7440-06-4.

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Contribution from the Departments of Chemistry, Portland State University,
Portland, Oregon 97207, and University of Idaho, Moscow, Idaho 83843

Synthesis and Spectroscopic Properties of Ethynylsulfur Pentafluoride ($SF_5C\equiv CH$)

JO ANN M. CANICH, MARIA M. LUDVIG, WILLIAM W. PAUDLER, GARY L. GARD,* and JEAN'NE M. SHREEVE*

Received February 25, 1985

Ethynylsulfur pentafluoride, $SF_5C\equiv CH$, has been prepared by the dehydrobromination of $SF_5CH{=}CFBr$ (49%). It also can be obtained in a four-step process by the addition of SF_5Br to acetylene, followed by bromination of the resulting olefin, $SF_5CH{=}CHBr$, to form $SF_5CHBrCHBr_2$, which may be dehydrobrominated with K_2CO_3 to give $SF_5CBr{=}CHBr$. The latter, when treated with Zn, gives $SF_5C\equiv CH$ in an overall yield of 9%.

Introduction

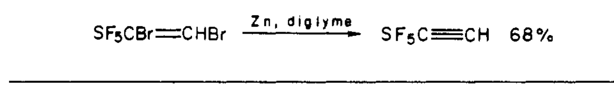
It is known that the introduction of SF_5 groups into molecular systems can bring about significant changes in their physical, chemical, and biological properties. These properties are manifested by various applications, such as solvents for polymers, as perfluorinated blood substitutes, as surface-active agents, as fumigants, and as thermally and chemically stable systems.[1] The synthesis and chemistry of these compounds are the subjects of ongoing studies. One compound of particular interest is ethynylsulfur pentafluoride ($SF_5C\equiv CH$) which has been used as the starting reagent for a number of novel and interesting derivatives that include saturated ethers, vinyl ethers, pyrazoles, cyclic alkenes, and alkyl-substituted phenylsulfur pentafluorides.[2] In addition, $SF_5C\equiv CH$ is found to be useful in preparing a number of SF_5-containing alkenes and alkynes.[2,3]

Results and Discussion

The original synthesis of $SF_5C\equiv CH$ involves four steps, starting with pentafluorosulfur chloride (SF_5Cl) and acetylene.[2] The overall yield for this sequence is only 11%. Since SF_5Br has been under study in our laboratories, an attempt was made to prepare $SF_5C\equiv CH$ in higher yields by the following sequence of reactions.

$$SF_5Br + HC\equiv CH \xrightarrow{57\ °C} SF_5CH{=}CHBr \quad 80\% \qquad (1)$$

$$SF_5CH{=}CHBr \xrightarrow{Br_2,\ h\nu} SF_5CHBrCHBr_2 \quad 46\% \qquad (2)$$



$$SF_5CHBrCHBr_2 \xrightarrow{K_2CO_3,\ 25\ °C} (SF_5)(Br)C{=}C(Br)(H) + (SF_5)(Br)C{=}C(H)(Br) \quad 36\% \qquad (3)$$

$$SF_5CBr{=}CHBr \xrightarrow{Zn,\ diglyme} SF_5C\equiv CH \quad 68\% \qquad (4)$$

Because of the unexpected low yields of reactions 2 and 3, the overall yield was only 9%. It is thought that the yields for reactions 2 and 3 could be improved, but it was found, unexpectedly, that direct dehydrobromination of $SF_5CH{=}CHBr$ gave the acetylene in yields of ~50%.

$$SF_5CH{=}CHBr \xrightarrow[\text{pet. ether}]{KOH} SF_5C\equiv CH \qquad (5)$$

Attempts to dehydrohalogenate $SF_5CH{=}CHCl$ were found to be ineffective and gave a yield of only 1-2% of the desired SF_5 alkyne. The compounds synthesized in reactions 1-3 are new and have been characterized by elemental and spectral analyses.

The common feature of these new compounds and $SF_5C\equiv CH$ is the presence of the SF_5 group. For the compounds reported in this paper, absorption bands in the 845-928-cm^{-1} region are assigned to S—F stretching vibrations. The S—F deformation modes are found near or at 600 cm^{-1}.[4] The infrared spectra of $SF_5CH{=}CHBr$ and $SF_5C\equiv CH$ contain the characteristic absorption band of the olefinic C=C or acetylenic C≡C stretching vibration at 1611 or 2118 cm^{-1}, respectively. For $SF_5CH{=}C(Br)SF_5$, $SF_5CH{=}C(CF_3)Br$, and $CF_3C\equiv CH$, the C=C/C≡C absorption bands are found at 1610, 1630, and 2165 cm^{-1}, respectively.[3,5,6] The C—H stretching vibrations for $SF_5CH{=}C$-

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* To whom correspondence should be addressed: G.L.G., Portland State University; J.M.S., University of Idaho.

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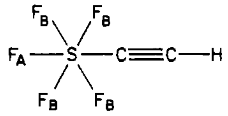
HBr, $SF_5CBr{=}CHBr$, $SF_5CHBrCHBr_2$, and $SF_5C{\equiv}CH$ are located at 3115, 3100, 3022, and 3338 cm^{-1}, respectively. These values are in excellent agreement with similar molecular systems already mentioned.[3,5,6] The C—Br stretching bands in the infrared spectra for fluoroalkyl bromides[7] are reported to be in the 740–770-cm^{-1} range, while for alkyl bromides[8] the range is 515–680 cm^{-1}. For the new compounds described in this paper, the bands in the 774–659-cm^{-1} region may well be due to the C—Br stretching mode.

It should be noted that the stretching frequency for the triple bond in monosubstituted acetylenes, $XC{\equiv}CH$, depends, to some degree, on the nature of the substituent and its corresponding electronegativity; for example, in the series[6,9-11] $FC{\equiv}CH$, $(CF_3)_2NC{\equiv}CH$, $CF_3C{\equiv}CH$, $SF_5C{\equiv}CH$, $ClC{\equiv}CH$, $BrC{\equiv}CH$, and $IC{\equiv}CH$, $\nu(C{\equiv}C)$ is observed at 2255, 2183, 2165, 2118, 2110, 2085, and 2075 cm^{-1}, respectively. This is in agreement with the general order of electronegativity as reported for these substituents. On the basis of the above series, the electronegativity of the SF_5 group is approximately the same as that of chlorine. A previous study with polyfluoroiodides agrees with this conclusion.[12]

For $SF_5C{\equiv}CH$, the proton NMR spectrum is a pentet (J_{F-H} = 3 Hz) at δ 2.25.[2] As expected, the acetylenic proton in $SF_5C{\equiv}CH$ (**1**) resonates at a more shielded position. The fact that it appears as a pentet suggests that it is only coupled significantly to the *equatorial* fluorine atoms (F_B).



1

Of particular interest are the ^{19}F NMR spectral studies for which the AB_4 pattern found for the SF_5 group in $SF_5C{\equiv}CH$ is reversed from that found for ethylenes and saturated hydrocarbons/fluorocarbons that contain the SF_5 group. This behavior is observed also for other SF_5 acetylenic systems.[13] This result can be explained by considering the nature of the anisotropic geometry of the acetylene function. The axial fluorine atom (F_A) is located in the region of maximum shielding while the equatorial fluorine atoms (F_B) are situated in the deshielding region relative to the acetylenic bond. In **1**, the axial fluorine atom resonates at ϕ 72 and the equatorial fluorine atoms resonate at ϕ 80. These values for $SF_5C{\equiv}CH$ are compared with the chemical shifts for the axial S—F values of 80, 77, 77, 76, 80, and 77 ppm and corresponding equatorial SF_4 values of 66, 71, 69, 68, 66, and 68 ppm in the various saturated analogues[14-16] SF_5CH_2CHFBr, $SF_5CH_2CF_2Br$, $SF_5CH_2CF_2Cl$, $SF_5CH_2SF_5$, $SF_5CH_2CHBr(CF_3)$, and $SF_5CH_2CHClBr$. Thus, the transformation of $F_5S{-}CH_2{-}$ to $F_5S{-}C{\equiv}CH$ causes a shielding of 4–8 ppm for the axial fluorine atom while for the equatorial fluorine atoms a deshielding of 9–14 ppm results. It should be noted, that in $SF_5C{\equiv}CSF_5$, the equatorial fluorine atoms are found at 80 ppm while the axial fluorine atoms are at 67 ppm.[3] This shows additional shielding for the axial fluorine atoms when compared to that in $SF_5C{\equiv}CH$. Also, the hybridization change in the carbon to which the SF_5 group is bonded will cause a general, electronegativity-controlled deshielding of both the axial and equatorial fluorine atoms. Thus, the major factors influencing the chemical shifts of the fluorine atoms in **1** are the anisotropic effects and the hybridization state of the carbon.

The proton NMR peaks for monosubstituted acetylenes, $XC{\equiv}CH$, are shifted to high field owing to the diamagnetic anisotropy. Apart from such effects, it is anticipated that a relatively strong deshielding should result if the substituent X withdraws electrons from the π system. Such a deshielding effect does occur in a series of alkyl- and silylacetylenes.[17] It is expected that with more electronegative groups, such as CF_3, $(CF_3)_2N$, and SF_5, electron withdrawal from the π system and increased deshielding will be noted.

By using available data,[18] we see that the proton in $CF_3C{\equiv}CH$ is downfield from $CH_3C{\equiv}CH$ by 0.6 ppm. Coupling this information with the reported values for $(CF_3)_2NC{\equiv}CH$, $SF_5C{\equiv}CH$, and some alkyl- and silylacetylenes, we observe an increase in shielding from CF_3 to CH_2SiR_3 for the acetylenic hydrogen atom in $XC{\equiv}CH$.

X	$(CF_3)_2N$	CF_3	SF_5	SiR_3	CH_3	CR_3	CH_2SiR_3
τ	7.25	7.38	7.75	7.76	7.98	8.08	8.45

The same chemical shifts for $\equiv CH$ when the substituent is SF_5 or SiR_3 must arise from $Si{\leftarrow}C_\pi$ back-bonding with inductive polarization of the SiR_3 group in comparison with the electron-withdrawing effect of the SF_5 group.

Experimental Section

Materials. The compounds used in this work were obtained from commercial sources: $HC{\equiv}CH$ (Airco); dry diglyme, Zn, K_2CO_3, $(CH_3)_2C{=}O$ (Mallinckrodt, AR); KOH, Br_2 (J. T. Baker). All reagents were used without further purification. SF_5Br was synthesized by literature methods.[14]

General Procedure. Gases were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge and a Televac thermocouple gauge. Infrared spectra were obtained by using an 8.25-cm Monel cell with KBr or KRS-5 windows or as solids between KBr, KRS-5, or NaCl disks on a Perkin-Elmer 476 spectrometer. The spectra were calibrated with a polystyrene film. The NMR spectra were recorded with a Varian Model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for fluorine resonances. Tetramethylsilane and trichlorofluoromethane were used as internal standards. The mass spectra were taken with a Hitachi Perkin-Elmer RMU-6E mass spectrometer operating at 15 eV. Perfluorokerosene (PFK) was used as an internal standard. Elemental analyses were obtained by Beller Microanalytical Laboratory, Göttingen, West Germany.

Preparation of $SF_5CH{=}CHBr$. To a 150-mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve were added 27.5 mmol of SF_5Br and 38.5 mmol of $HC{\equiv}CH$. The reaction mixture was maintained at 57 ± 2 °C (3.8 days). The product, 22.0 mmol of $SF_5CH{=}CHBr$, was formed in 80% yield; bp 86 ± 2 °C.

The infrared spectrum of the liquid had the following bands (cm^{-1}): 3115 (wm), 1692 (w), 1611 (m), 1545 (w), 1385 (vw), 1275 (w), 1197 (wm), 1161 (w), 912 (s), 845 (vs, b with sh at 900), 774 (m), 705 (m), 680 (vw), 625 (m), 601 (ms), and 571 (m). The ^{19}F NMR spectrum contained a complex doublet at ϕ 63.3 (SF_4) and a multiplet (nine-line pattern) at ϕ 78.7 (SF) (peak areas 4.1 (SF_4) and 1.0 (SF); coupling constants J_{F-SF_4} = 150.4 Hz and J_{SF_4-CH} = 5.64 Hz). The ^1H NMR spectrum was a multiplet with the band centered at δ 6.8. The mass spectrum for $SF_5CH{=}CHBr$ (15 eV) had the following *m/e* peaks: 232, 234, $(SF_5C_2H_2{}^{79,81}Br)^+$; 215, 213, $(SF_4C_2H_2{}^{79,81}Br)^+$; 153, $(SF_5C_2H_2)^+$; 127, $(SF_5)^+$; 107, 105, $(C_2H_2{}^{79,81}Br)^+$; 106, 104, $(C_2H^{79,81}Br)^+$; 89, $(SF_3)^+$; 44, $(SC)^+$. Anal. Calcd: C, 10.31; H, 0.87; F, 40.8. Found: C, 10.50; H, 0.89; F, 39.4.

Preparation of $SF_5CHBrCHBr_2$. To a 390-mL quartz-Pyrex vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 64.8 mmol of $SF_5CH{=}CHBr$ and 63.9 mmol of Br_2. The bottom portion of the vessel was placed in a water bath at room temperature while the upper half of the vessel was irradiated (17 h) with a 250-W General Electric reflector UV lamp. The product, 29.7 mmol of $SF_5CHBrCHBr_2$,

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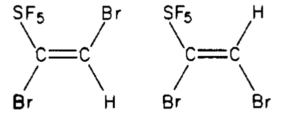
was formed in 46% yield; bp 109 ± 1 °C (50 mmHg).

The infrared spectrum of the liquid had the following bands (cm^{-1}): 3022 (m), 2997 (m), 1386 (vw), 1249 (wm), 1188 (w), 1148 (m), 1015 (mw), 850 (vs, b), 758 (ms), 730 (m), 664 (m), 610 (m), 585 (s, sh, at 574), 561 (ms), 504 (m). The ^{19}F NMR spectrum (AB_4) contained a complex doublet at ϕ 57.0 (SF_4) and a multiplet (nine-line pattern) at ϕ 74.6 (SF). The relative peak areas were 4.0 (SF_4) and 1.0 (SF). The ^1H NMR spectrum contained a doublet at δ 6.29 (band center) and a 20-line multiplet with a band center at δ 5.86 (peak areas 1.0 (SF_5C-H) and 1.0 (Br_2C-H); coupling constants $J_{SF_4-F} = 147$ Hz, $J_{SF_4-CH} = 5.2$ Hz, $J_{SF-CH} = 0.45$ Hz, and $J_{CH-CH} = 1.4$ Hz). The mass spectrum for $SF_5CHBrCHBr_2$ (70 eV) had the following *m/e* peaks: 396, 394, 392, 390, $(SF_5C_2H_2{}^{79,81}Br_3)^+$; 315, 313, 311, $(SF_5C_2H_2{}^{79,81}Br_2)^+$; 269, 267, 265, 263, $(C_2H_2{}^{79,81}Br_3)^+$; 203, 205, 207, $(SF_5C_2H_2{}^{79,81}Br_2)^+$; 188, 186, 184, $(C_2H_2{}^{79,81}Br_2)^+$; 127, $(SF_5)^+$; 107, 105, $(C_2H_2{}^{79,81}Br)^+$; 89, $(SF_3)^+$; 79, 81, $(Br)^+$; 70, $(SF_2)^+$; 45, $(SCH)^+$; 44, $(SC)^+$; 32, $(S)^+$. Anal. Calcd: C, 6.12; H, 0.51; F, 24.2. Found: C, 6.27; H, 0.59; F, 24.2.

Preparation of $SF_5CBr=CHBr$. To a 25-mL round-bottomed vessel equipped with a Teflon stirring bar were added 15.1 mmol of $SF_5CHBrCHBr_2$, 15.4 mmol of K_2CO_3, and 10.0 mL of acetone. The mixture was stirred for 4 h and filtered, and the filtrate was distilled. The product, 5.50 mmol of $SF_5CBr=CHBr$, was formed in 36% yield; bp 55 ± 1 °C (48 mmHg).

The infrared spectrum of the liquid had the following bands (cm^{-1}); 3149 (w), 3100 (mw), 1573 (m), 1253 (w), 1244 (w), 916 (s with sh at 928), 860 (vs, b), 814 (s), 760 (vw), 716 (m), 679 (w), 659 (m), 600 (m), 584 (m), 539 (mw), 527 (vw), 480 (w). The ^{19}F NMR spectrum (AB_4) contained a doublet of multiplets at ϕ 62.0 (SF_4) and a multiplet at ϕ 76.0 (SF) (peak areas 3.9 (SF_4) and 1.0 (SF)). The ^1H NMR spectrum showed a singlet at δ 7.83 and a pentet at δ 7.07 (coupling constants $J_{SF_4-F} = 149$ Hz and $J_{SF_4-CH} = 3.0$ Hz). The following two isomers are present:



pentet singlet

This assignment is based on the greater coupling expected for trans nuclei relative to that for cis groups. This is analogous to the assignments made for the similar dichloro isomers.[2] The mass spectrum for $SF_5CBr=CHBr$ (70 eV) had the following *m/e* peaks: 314, 312, 310, $(SF_5C_2H^{79,81}Br_2)^+$; 233, 231, $(SF_5C_2H^{79,81}Br)^+$; 187, 185, 183, $(C_2H^{79,81}Br_2)^+$; 127, $(SF_5)^+$; 106, 104, $(C_2H_2{}^{79,81}Br)^+$; 89, $(SF_3)^+$; 79, 81, $(Br)^+$; 70, $(SF_2)^+$; 45, $(SCH)^+$; 44, $(SC)^+$; 32, $(S)^+$. Anal. Calcd: C, 7.70; H, 0.32; F, 30.5. Found: C, 7.96; H, 0.35; F, 30.1.

Preparation of $SF_5C\equiv CH$ from $SF_5CBr=CHBr$. A three-necked round-bottomed Pyrex vessel, equipped with a Teflon stirring bar, a separatory funnel, a nitrogen-inlet tube, and a reflux condenser that was connected to a trap cooled to −78 °C (or −196 °C) and protected from the atmosphere by a mercury bubbler, was used for the debromination reaction. To this vessel were added 20 mL of diglyme and 33.0 mmol of zinc. The mixture was heated to 140 °C, and 8.97 mmol of $SF_5CBr=CHBr$ was added over a 0.5-h period. Heating at 140 °C was continued for 1 h under a slow nitrogen flow. The product, 6.05 mmol of $SF_5C\equiv CH$, was formed in 67% yield. The infrared spectrum agreed with that previously reported.[2]

Preparation of $SF_5C\equiv CH$ from $SF_5CH=CHBr$. In the reaction vessel used for the debromination of $SF_5CBr=CHBr$, 80 mL of petroleum ether (90–120 °C fraction) was heated to reflux, and 205 mmol of KOH was added. $SF_5CH=CHBr$ (85.8 mmol) was added slowly over a period of 0.8 h, and 305 mmol of additional KOH was added during this period. The mixture was heated at reflux for 2 h under a slow nitrogen flow. The product, 42.0 mmol of $SF_5C\equiv CH$, was collected in a trap cooled to −196 °C (yield 49%).

The infrared spectrum had the following bands (cm^{-1}); 3338 (ms), 2118 (m), 1613 (vw), 1506 (vw), 1344 (w with sh at 1338), 893 (vs, b), 730 (w), 720 (w), 674 (ms), 620 (m), 590 (ms). ^{19}F NMR spectrum: ϕ 71.8 (SF), ϕ 80.3 (SF_4) (multiplets; $J_{SF_4-F} = 151.8$ Hz). ^1H NMR spectrum: δ 2.76 (pentet; $J_{F-H} = 3.15$ Hz).

Acknowledgment. We express our appreciation to the National Science Foundation (Grant CHE-8404974) and the Gas Research Institute (Grant 5082-260-0654) for support of this research. We thank Dr. Gary D. Knerr for the mass spectra.

Registry No. $SF_5CH=CHBr$, 58636-82-1; SF_5Br, 15607-89-3; $HC\equiv CH$, 74-86-2; $SF_5CHBrCHBr_2$, 87224-28-0; (*E*)-$SF_5CBr=CHBr$, 98050-05-6; (*Z*)-$SF_5CBr=CHBr$, 98103-43-6; $SF_5C\equiv CH$, 917-89-5.

Contribution from the Department of Chemistry,
University of Rajasthan, Jaipur, India

Kinetics and Mechanism of the Uncatalyzed and Silver(I)-Catalyzed Oxidation of Hydrazine with Peroxodiphosphate in Acetate Buffers

ABHAY K. GUPTA, KRISHNA S. GUPTA, and YUGUL K. GUPTA*

Received September 12, 1984

A kinetic study of the title reaction (i) was made in acetate buffers by estimating peroxodiphosphate (pdp) iodometrically. Silver(I)

$$2H_nP_2O_8{}^{n-4} + N_2H_5{}^+ \rightarrow 4H_2PO_4{}^- + N_2 + (2n-3)H^+ \tag{i}$$

catalysis occurs through its complexation with pdp or $N_2H_5{}^+$. The empirical rate law (ii) holds where K_3 is the acid dissociation

$$-d[\mathrm{pdp}]/dt = k_{\mathrm{uncat}}[\mathrm{pdp}][N_2H_5{}^+] + \frac{(A + B[{}^-O_2CCH_3])[Ag(I)][\mathrm{pdp}][N_2H_5{}^+]}{([H^+] + K_3)(1 + K[{}^-O_2CCH_3])} \tag{ii}$$

constant of $H_2P_2O_8{}^{2-}$ and K is the complex formation constant of $Ag(O_2CCH_3)$. A and B are complex rate constants equal to 3.0×10^{-4} M^{-1} s^{-1} and 1.5×10^{-2} M^{-1} s^{-1}, respectively, at 40 °C and $I = 1.0$ M. K_3 was found to be 4.4×10^{-5} M under the same conditions. k_{uncat} is the second-order rate constant for the uncatalyzed reaction and is given by (iii) where k_1' and k_2' are

$$k_{\mathrm{uncat}} = (k_1'[H^+] + k_2'K_3)/([H^+] + K_3) \tag{iii}$$

the rate constants for the ($H_2P_2O_8{}^{2-} + N_2H_5{}^+$) and ($HP_2O_8{}^{3-} + N_2H_5{}^+$) reactions and were found to be 2.25×10^{-3} M^{-1} s^{-1} and 7.5×10^{-3} M^{-1} s^{-1}, respectively, at 40 °C and $I = 1.0$ M.

We reported[1] silver(I)-catalyzed oxidation of water with peroxodiphosphate (pdp) as a sequel to the study of the mechanism of silver(I) catalysis in pdp oxidations. A few investigations[2,3] in our laboratory have revealed that there is no kinetic evidence for a Ag(I)/Ag(II) cycle in Ag(I)-catalyzed reactions. A complex of Ag(I) with either the oxidant or reductant appears to be more reactive. This mechanism is different from that found in peroxodisulfate (pds) oxidations.[4] We thought a few more reactions should be investigated to substantiate the above conclusion about the mechanism.

Toward this aim, hydrazine appeared to be an attractive choice, not only because the reaction of hydrazine and higher valent silver

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