We present here the results of an independent approach for examining this problem, where advantage is taken of the Pfeiffer effect displayed by trisphenanthroline complexes of divalent metal ions in the presence of S-$(-)_D$-malic acid. Kirschner et al.[10,11] have reported equilibrium solutions to be enriched in levo and dextro enantiomer (NaD line) for $Ni(phen)_3^{2+}$ and $Fe(phen)_3^{2+}$, respectively. Both isomers have been found to have the Δc_3 absolute configuration from x-ray diffraction studies.[12,13] The complex $Co(phen)_3^{2+}$ also displays the Pfeiffer phenomenon in a malic acid environment,[10] with the levo isomer in excess. Kirschner[10] has suggested that this isomer also has the Δc_3 configuration. Provided this prediction is correct, oxidation of the latter equilibrium mixture should yield the thermally inert Δc_3 isomer of $Co(phen)_3^{3+}$—thus providing the sign of its rotation at the D line.

Experimental conditions involved first preparing a N_2 purged aqueous solution 0.04 M in $Co(phen)_3^{2+}$ and 0.3 M in $(-)_D$-malic acid. The solution was then transferred by syringe to a deaerated aqueous solution of either potassium dichromate or potassium permanganate (with oxidizing agent in 30% excess). In both instances, rapid oxidation to $Co(phen)_3^{3+}$ ensued. The product solution was passed through a Dowex 1-X8 Cl^- exchange resin to remove malic acid and excess MnO_4^- or $Cr_2O_7^{2-}$. Addition of a concentrated $NaClO_4$ solution to the eluate precipitated $[Co(phen)_3](ClO_4)_3$, which was filtered and washed copiously with $NaClO_4$ solution and then ethanol. The relatively insoluble perchlorate salt was converted to the soluble chloride by shaking an aqueous suspension with Dowex 1-X8 (Cl^- form) and filtering. When $KMnO_4$ was used as oxidant, the resultant solution displayed a negative NaD line rotation (−0.0364°, 0.008 M) employing a Bendix automatic polarimeter (Model 1144) with digital readout to ±0.0002°. The corresponding rotation for $K_2Cr_2O_7$ as oxidant was −0.1100° (0.0147 M). It is noteworthy that no rotations were observed if $[Co(phen)_3](ClO_4)_2$ was first precipitated from the Pfeiffer equilibrium mixture, followed by solid state chlorine oxidation of an ethanol suspension. Perchlorate anion most probably removes malic acid from the immediate complex environment prior to precipitation, resulting in racemization of the labile enriched enantiomer. Although this procedure was successful with $Ni(phen)_3^{2+}$,[11] the relative inertness of the latter species would preclude racemization prior to precipitation.

In the present case involving rapid solution oxidation with $KMnO_4$ and $K_2Cr_2O_7$, the induced rotations were lost on addition of a small concentration of $Co(phen)_3^{2+}$. This is consistent with the known rapidity of $Co(phen)_3^{2+/3+}$ self-exchange[14] and fairly rapid racemization of $Co(phen)_3^{2+}$ optical forms.[15] Furthermore, the optically active samples yielded CD spectra enantiomeric to that of a genuine sample of $(+)_D$-$Co(phen)_3^{3+}$.[5,8] The rotations reported above indicated resolutions of 2.0 and 3.3% for $KMnO_4$ and $K_2Cr_2O_7$, respectively,[16] in keeping with that achieved earlier for $Ni(phen)_3^{2+}$. These results, therefore, require a Λc_3 configuration for $(+)_D$-$Co(phen)_3^{3+}$, an observation in agreement with the original assignment[8,9] by Mason and co-workers. The validity of the present approach, however, is dependent on the rate constants for oxidation of levo and dextro isomers of $Co(phen)_3^{2+}$ being very similar in the presence of $(-)_D$-malic acid. This is probably a very reasonable assumption, in view of the reported absence of stereoselectivity in redox reactions involving transition metal systems.[17,18]

We note that the results reported above also have a significant bearing on the origin of the Pfeiffer phenomenon. The isolation of optically active $Co(phen)_3^{3+}$ on oxidation of a $Co(phen)_3^{2+}$-$(-)_D$-malic acid mixture provides further confirmation of a genuine displacement of enantiomer equilibrium in these solutions.

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(15) $t_{1/2}$ = 0.10 sec at 25°C for $Co(phen)_3^{2+}$ racemization (E. Blinn and R. G. Wilkins, unpublished results).
(16) The difference in percent resolution is possibly associated with differences in the respective redox reaction rates, since slow oxidation provides a racemization pathway via $Co(phen)_3^{2+/3+}$ self-exchange. Similar considerations would also account for the optically inactive $Co(phen)_3^{3+}$ product obtained for solution oxidations using $Co(C_2O_4)_3^{3-}$ and $CoEDTA^-$.
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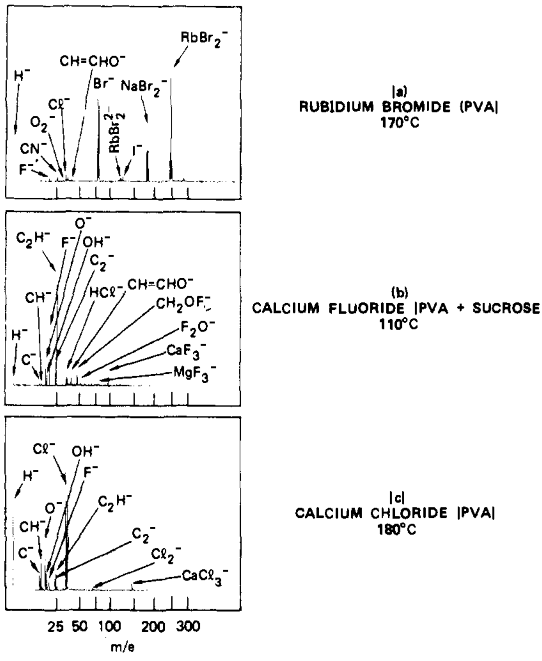
Negative Ion Desorption Mass Spectrometry

Sir:

Application of field desorption mass spectrometry to the mass spectrometric analysis of thermolabile nonvolatile organic compounds[1] has demonstrated fairly high yields of molecular ions. We recently developed a new simpler field desorption source[2] and have demonstrated its use in the analysis of inorganic cations.[3] Field desorption per se is not an ionization process, but involves the desorption of ionic species previously present on a highly curved surface, which allows the buildup of high field gradients (10^7 to 10^8 V/cm). Therefore, it is conceivable that both cations and anions can be desorbed, depending on the polarity of the field desorption source.

This communication presents a series of preliminary results on the mass spectrometry of inorganic *anions* produced by field desorption. The ionization source and the mass spectrometric system have been described previously.[2,3] The desorption takes place from a freshly broken tungsten surface situated about 50 μm from a slit counter electrode (anode in this case). Tungsten rod of $^1/_{16}$-in. diameter was notched at 1-in. intervals on an abrasive wheel and

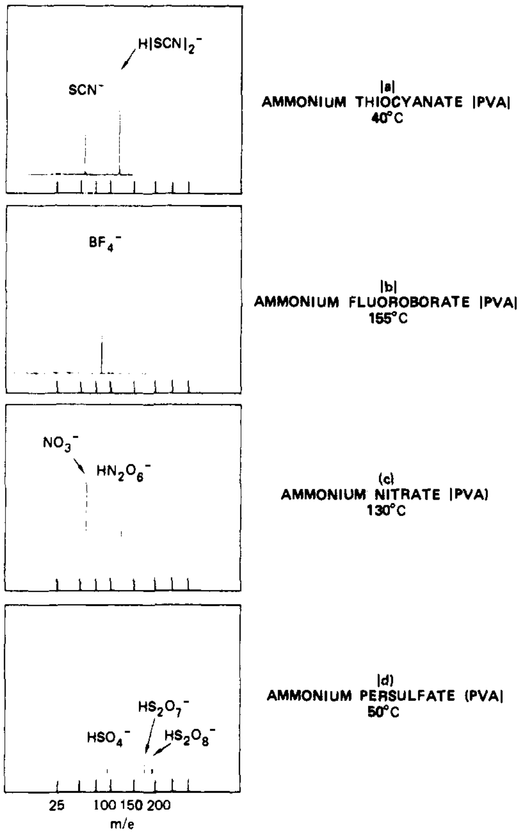


(a) RUBIDIUM BROMIDE (PVA) 170°C

(b) CALCIUM FLUORIDE (PVA + SUCROSE) 110°C

(c) CALCIUM CHLORIDE (PVA) 180°C

Figure 1. Negative ion field desorption spectra: (a) rubidium bromide (PVA) 170°C; (b) calcium fluoride (PVA + sucrose) 110°C; (c) calcium chloride (PVA) 180°C.



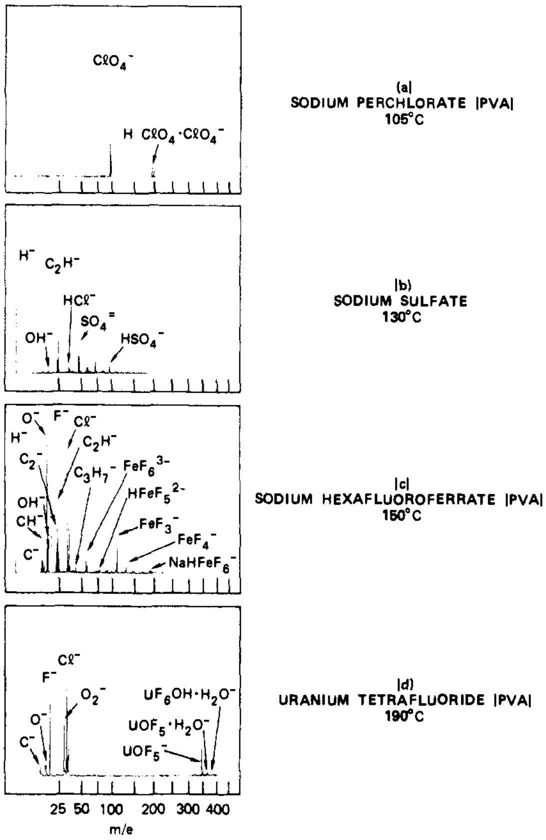
(a) AMMONIUM THIOCYANATE (PVA) 40°C

(b) AMMONIUM FLUOROBORATE (PVA) 155°C

(c) AMMONIUM NITRATE (PVA) 130°C

(d) AMMONIUM PERSULFATE (PVA) 50°C

Figure 2. Negative ion field desorption spectra: (a) ammonium thiocyanate (PVA) 40°C; (b) ammonium fluoroborate (PVA) 155°C; (c) ammonium nitrate (PVA) 130°C; (d) ammonium persulfate (PVA) 50°C.



(a) SODIUM PERCHLORATE (PVA) 105°C

(b) SODIUM SULFATE 130°C

(c) SODIUM HEXAFLUOROFERRATE (PVA) 150°C

(d) URANIUM TETRAFLUORIDE (PVA) 190°C

Figure 3. Negative ion field desorption spectra: (a) sodium perchlorate (PVA) 105°C; (b) sodium sulfate 130°C; (c) sodium hexafluoroferrate (PVA) 150°C; (d) uranium tetrafluoride (PVA) 190°C.

freshly broken for each sample. A potential of 1.5-3 kV is applied between the two electrodes. The mass analyzer used was a low resolution 45° sector magnet, manually scanned. The inorganic substrates were field desorbed from polyvinyl alcohol (PVA), an organic polar polymeric matrix that is an excellent solvent for this purpose.[2,3] In the polymeric matrix the inorganic ions may migrate and be field desorbed when they reach regions of high enough field strengths.

Figure 1 shows representative spectra of alkali metal and alkaline earth halides. In the case of rubidium bromide (Figure 1a) we can observe the Br^- as well as $NaBr_2^-$ and $RbBr_2^-$ ions in complete analogy to the formation of Na^+, Na_2Br^+, and $Na_3Br_2^+$ in the positive ion spectrum.[3] We can also see $RbBr_2^{2-}$ as well as F^-, Cl^-, I^-, and CN^- as trace impurities. O_2^- may be formed from absorbed O_2, originating from the background gas, by electron capture. The peak at mass 42 probably belongs to $CH{=}CHO^-$ originating from the polyvinyl alcohol.

Calcium fluoride, a highly refractory compound, readily produces negative ions under our conditions. CaF_3^- is the most characteristic species, Figure 1b, together with F^-; MgF_3^- is observed as an impurity. The formation of CaF_3^- required higher fields, which resulted in a substantial yield of C^-, CH^-, O^-, OH^-, C_2^-, C_2H^-, as well as $CH{=}CHO^-$ ions from the PVA. We can also observe here the formation of HCl^- in addition to Cl^-. Of special interest are the negative ions of masses 49 and 54, tentatively identified as CH_2OF^- and F_2O^- and probably formed by the interaction of the CaF_2 with the matrix under the high field conditions. Note also the high yield of H^- formed from the matrix.

The formation of $CaCl_3^-$ from $CaCl_2$, Figure 1c, is analogous to the formation of CaF_3^-, but the unique products formed from CaF_2 are evidently absent in this case.

Unlike metallic cations, NH_4^+ does not form anionic complexes and seems to break down to $H^+ + NH_3$ under field desorption. Consequently, ammonium salts seem to be ideal carriers for anions formed by field desorption. Figure 2a is a mass spectrum of ammonium thiocyanate produced under low temperature and low voltage (1.5 kV). The only species of significance here are SCN^- and $H(SCN)_2^-$ ions. Under these mild conditions, no ions originating from the polymeric matrix are observed. Figure 2b is a similar spectrum of ammonium fluoroborate exhibiting only the BF_4^- ion. Ammonium nitrate, shown in Figure 2c, produces only NO_3^- and $HNO_3{\cdot}NO_3^-$ ($HN_2O_6^-$) ions. Ammonium persulfate, Figure 2d, shows, interestingly enough, $HS_2O_7^-$ and HSO_4^- in addition to $HS_2O_8^-$ ions rather than the double charged anions.

The formation of uncomplexed or merely protonated anions is not specific to ammonium salts and seems to occur with oxyanions that do not form complexes with metallic cations. Thus, sodium perchlorate, shown in Figure 3a, shows only ClO_4^- ions plus a few $H(ClO_4)_2^-$ ions, similarly to the ammonium salts described above. Under more drastic conditions (130°C, 2.5 kV), sodium sulfate was shown to produce SO_4^{2-} in addition to HSO_4^-, as shown in Figure 3b. We could not identify some of the additional negative ions formed under these conditions, probably because of the action of sulfuric acid on the polyalcohol. A rather interesting case is the spectrum of Na_3FeF_6 in Figure 3c. Here we were able to identify FeF_6^{3-} in addition to $HFeF_5^{2-}$, FeF_3^-, FeF_4^-, and $NaHFeF_6^-$. Figure 3d shows the spectrum of uranium tetrafluoride suspended in the PVA matrix. The predominant uranium ion formed under fairly mild conditions (~2 kV) is UOF_5^- and its hydrate $UOF_5H_2O^-$. Moreover, $UF_6{\cdot}OH{\cdot}H_2O^-$ ions in a small yield also seem to appear in the spectrum. The latter two spectra suggest that negative ion desorption may be a highly useful tool in the study of the nature of anionic complex ions.

Although the spectra reported in this communication are only preliminary qualitative results, they demonstrate well the potential of negative ion desorption mass spectrometry for the analytical and inorganic chemist.

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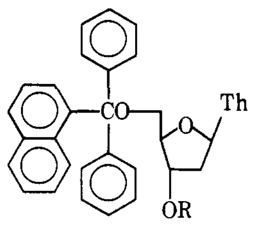
Selective Deprotection by Reductive Cleavage with Radical Anions[1]

Sir:

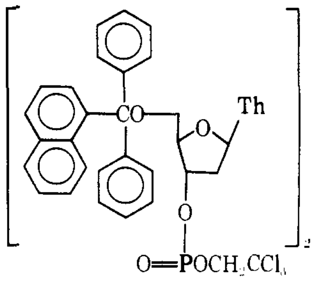
We describe in this communication the selective removal of α-naphthyldiphenylmethyl, a new protecting group, from 5′-*O*-α-naphthyldiphenylmethyl-3′-*O*-*p*-methoxytritylthymidine (**2**) by reductive cleavage with the anthracene radical anion in tetrahydrofuran (THF). This reaction illustrates a technique for selective deprotection which should be generally useful in synthetic work with polyfunctional compounds.

Selectivity in cleaving members of a family of protecting groups has most often depended on differences in rates of reaction with basic, nucleophilic, or acidic reagents. Examples include the sequential hydrolysis of phenoxyacetic, acetic, and trimethylacetic esters[2] under alkaline conditions and the selective hydrolysis of *p*-dimethoxytrityl[3] ethers in the presence of trityl ethers in acidic media. Recently electrolytic reduction has been exploited to discriminate among haloethoxycarbonyl protecting groups.[4]

The successful utilization of the naphthalene radical anion in cleaving methoxytrityl[5] and trichloroethylphosphoryl[6] derivatives of thymidine without reduction of the base ring pointed up the possibility of developing a technique for controlled stepwise removal of protecting groups based on radical anion chemistry. To test this possibility, thymidine derivatives protected at 5′-O by α-naphthyldiphenylmethyl were prepared (compounds **1**–**3**), with the expectation that the naphthalene ring would serve as a better electron acceptor than phenyl or *p*-anisoyl. Compound **1**[7] was obtained (65%) by reaction of α-naphthyldiphenylmethyl chloride[8] with thymidine in pyridine. It was converted to **2**[7] (92%) by reaction with *p*-methoxytrityl chloride in pyridine and to **3**[7] (97%) by successive treatment with trichloroethylphosphorodichloridite in tetrahydrofuran–lutidine and iodine-water.[6,9]



1, R = H
2, R = $CH_3OC_6H_4C(C_6H_5)_2$



3

Solutions differing in reduction potential were prepared by stirring 1.2 mmol of naphthalene, anthracene, or benzophenone with 1 mmol of sodium in 4 ml of tetrahydrofuran (1 hr) or in hexamethyl phosphoric triamide (HMPA) (4 hr)[10] at room temperature. The nucleoside derivative (0.01–0.1 mmol) was added and, after 10 min, the reaction was quenched by addition of water. Following neutralization with acetic acid, the solution was extracted several times with chloroform. Thymidine (aqueous layer) was determined spectrophotometrically. Chloroform-soluble nucleosides and nucleotides were isolated by chromatography on silica plates.

Reaction of the naphthalene radical anion in HMPA afforded, as expected,[5] thymidine from both 5′-*O*-*p*-methoxytritylthymidine (90%) and compound **1** (91%). The yield of thymidine was considerably lower (34–40%) when THF was employed as the solvent. Reduction of the triarylmethyl ethers was complete in THF, as indicated by the absence of products that gave a positive test with perchloric acid; however, additional products resulting from side reactions were observed on the silica plates used for analysis.[11] It was found that the activity of this radical anion in THF could be moderated by adding a small amount of HMPA to the mixture. With a solvent consisting of seven parts THF and one part HMPA (v/v) high conversion to thymidine was realized (92–94% for both **1** and 5′-O-*p*-methoxytritylthymidine).[12]

A solution of the anthracene radical anion in THF proved to be an excellent system for discriminating between the *p*-methoxytrityl and α-naphthyldiphenylmethyl protecting groups. Compound **1** was converted to thymidine in high yield (97%) whereas 5′-*O*-*p*-methoxytritylthymidine was essentially inert under the reaction conditions (2% thymidine). The difference in reactivity of the α-naphthyldiphenylmethyl and the *p*-methoxytrityl protecting groups was confirmed by treating **2** with the anthracene radical anion reagent in THF. 3′-*O*-*p*-Methoxytritylthymidine was isolated from this reaction in 87% yield (cleavage of the α-naphthyldiphenylmethyl group) and the yield of thymidine was only 3% (cleavage of both protecting groups). It may be