

Figure 2. Product ions detected when ionized benzene- d_6 (m/z 84) collides with an ethanethiol/gold surface at a collision energy of 30 eV. The ions higher in mass than the colliding projectile ion are the result of reactions at the surface.

Figure 1b illustrates that the use of a self-assembled monolayer of ethanethiol on gold, rather than bare gold, greatly reduces chemical sputtering. This spectrum was obtained by allowing ionized ethanol- d_6 (m/z 52) to collide with an ethanethiol/gold surface at a collision energy of 60 eV. The spectrum is simple and consists mainly of peaks corresponding to combinations of C, D, and O, as expected from fragmentation of a $C_2D_6O^{+}$ ion.^{23,24} For ethanethiol-modified gold, this decrease in chemical sputtering was observed for time periods as long as 1 month, even after the surface had been bombarded with numerous projectile ions (alcohols, benzene, pyridine, peptides) and continuously bathed with isobutane (10^{-5} Torr) for 72 h. When long-chain alkanethiols, such as octadecanethiol, are used to prepare the self-assembled monolayers, sputtering products ($C_nH_m^+$) are detected in the surface-induced dissociation spectrum of ethanol- d_6 , although they are of decreased abundance compared to the sputtering products obtained from untreated gold.²⁵ In future work, a series of alkanethiols of varying chain length or deuterated²⁶ alkanethiols will be used to determine whether the sputtering products result solely from ionization and fragmentation of the long alkanethiolate chain or also from ionization and fragmentation of hydrocarbons adsorbed on the monolayer surface.

Although *chemical sputtering* is greatly reduced at the ethanethiol-modified gold surface, *ion/surface reactions*¹⁹ such as addition of hydrogen or methyl still occur, as they do from the untreated metal surfaces on which hydrocarbons are adsorbed. This type of reaction would account for the product ion of m/z 21 (HD_2O^+) in Figure 1b.²⁴ Another example of an ion/surface reaction product is the ion of m/z 91 that results upon collision

(23) On the basis of comparison of the ionic products formed from both ethanol and ethanol- d_6 , the major fragmentation pathways indicated in Figure 1 correspond to (i) α -cleavage by methyl radical loss (product ion at m/z 34; CD_2OD^+) and (ii) formation of $C_2D_3^+$ (m/z 30).

(24) Ions of odd m/z ratios (21, 29, 33) that do not decrease in abundance when results from the untreated gold surfaces are compared with those from the self-assembled monolayer on gold are ascribed to dissociation of an initial H addition product, ($CD_3CD_2OD + H^+$), or to H/D scrambling at the surface.

(25) Projectile ions, such as CF_3^+ , with a strong propensity for charge transfer to hydrocarbon adsorbates, produce sputtering spectra even on the ethanethiol/gold surface. However, the total ion current detected is significantly lower than that produced when CF_3^+ is allowed to collide with adventitious hydrocarbons on a metal surface.

(26) See the accompanying paper: Winger, B. E.; Julian, R. K., Jr.; Cooks, R. G.; Chidsey, C. E. D. *J. Am. Chem. Soc.*, preceding paper in this issue.

of ionized benzene with untreated metal surfaces. This product has been suggested^{19,20} to arise from addition of methyl followed by loss of H_2 . Our results for benzene- d_6 both on untreated metal surfaces and on alkanethiol surfaces (Figure 2) support this view, because ions corresponding to addition of methyl followed by loss of H_2 and loss of HD are detected (m/z 97 and m/z 96, respectively). For the self-assembled monolayer surfaces of ethanethiol on gold, *ion/surface reaction products* are detected even when *chemical sputtering* products are not detected. This suggests that the ion/surface abstraction reactions may involve the alkanethiolate.²⁶

The reactions between self-assembled monolayers and ions with kinetic energies in the electronvolt range may be related to neutral molecular beam work at single crystal surfaces,²⁷ since our reactions of projectile ions with alkanethiol-treated surfaces show a similar dependence on collision energy (i.e., highly unsaturated adducts containing an increasing number of carbon atoms are detected as the collision energy is increased). By using model systems in which the exposed tail group (terminal functional group remote to the sulfur) of the alkanethiolate is varied (e.g., substitute OH for CH_3),²⁸ it should be possible to systematically explore both charge transfer and reactive ion/surface collisions as a function of projectile ion, collision energy, and surface type. These experiments could be useful in the characterization of both projectile ion and surface properties.²⁶

Acknowledgment. We thank Jeanne E. Pemberton for helpful discussions and John K. Cullison for cyclic voltammetry experiments.^{4,9} This work was supported by the Office of Naval Research, the Society for Analytical Chemists of Pittsburgh, and the Thomas F. and Kate Miller Jeffress Memorial Trust.

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Use of Intramolecular Coulombic Interactions To Achieve "Impossible" Reactions. Photochemical Cleavage of 4-Nitrophenyl Ethers

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Received March 29, 1991

Revised Manuscript Received September 6, 1991

Reactive intermediates electronic distribution largely determines the outcome of a chemical or photochemical reaction. Therefore, its coulombic disturbance can lead to previously unknown processes of wide importance. This approach has been tested with success in the present work achieving the photoreductive cleavage of some 4-nitrophenyl ethers, circumventing the spin regioconservation principle.¹

The reductive cleavage of diaryl ethers and alkyl aryl ethers is well-known.² Nevertheless 4-nitrophenyl ethers are not active in this kind of reaction.^{1,3-5} We advanced that by altering (through coulombic interactions)⁶ the electronic density of the

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Table I. Photoreactions of 4-Nitrophenyl Piperidinoalkyl Ethers

Exp.	Substrate ^a	Conditions ^b	Photoproducts ^c	Yield (%) ^d
1		hv 400w 15'	 	88 traces
2		hv 400w 10'	 	50 10
3		hv 400w 10'	 	>95
4		hv 125w 20' (anhydrous methanol)	 	85 5
5		hv 400w 20'	Very complex mixture ^d	..
6		hv 400w 15'		>95

^aThe new products and reagents gave correct analyses. Their full characterization will be reported elsewhere. The indicated photoproducts were the only identified ones in each photoreaction except in experiment 1 (see text). ^bMedium-pressure Hg lamp. Room temperature. H₂O/MeOH or H₂O/CH₃CN (70:30) as solvent (pH 12) except in experiment 4 where anhydrous methanol and sodium methoxide was used. Pyrex filter ($\lambda > 290$ nm) in all cases. ^cAbsolute preparative yields based on nonrecovered starting material. Conversion in all cases was more than 80%. ^dVery complex mixture of products where no traces of the corresponding *p*-phenol could be detected.

intermediate aryl ether radical anions,⁷ forcing the electronic excess to be located in the ether linkage, a previously unknown fragmentation could be obtained. Thus, the semiempirical AM1⁸ method, implemented in the AMPAC program,⁹ was used to perform a "theoretical experiment". We calculated the excess net charge distribution, based on a Mulliken's analysis, for the 4-nitroanisole radical anion and for the ion pair formally obtained when a 1 au positive charge is placed at a distance of 1 Å from the atoms forming the alkyl ether linkage in the radical anion. Our results show that this specific placement of the counterion is translated in a dramatic migration of the electronic excess toward the alkyl ether bond, thus significantly weakening the alkyl ether bond (calculated bond orders for the radical anion and the ion pair are 0.99 and 0.62, respectively). This is due to the fact that the additional positive charge lowers the energy of a molecular orbital (MO) that contains an important σ^* C-O contribution, in such a way that MO becomes monooccupied.

In order to test our theoretical predictions we decided to explore the photochemistry of some 4-nitrophenyl ethers linked through a methylene chain to a tertiary amine. We expected that a topologically controlled coulombic interaction, similar to the one in our starting theoretical experiment, would be created after a photoinduced intramolecular electron-transfer process. Our results are reported in Table I. Thus, when 1-piperidino-5-(2-methoxy-4-nitrophenoxy)pentane is irradiated in basic medium (experiment 1), the usual¹⁰ meta-substituted photoproduct is obtained. Things change considerably when the linker chain length is reduced to three methylene units (experiment 2) and dramatically for the cases we use the substrate with only two methylene units in the linker (experiments 3 and 4). Now, 2-methoxy-4-nitrophenol is the main product in all the cases. The same photoreaction is observed for experiment 6 (two methylene units linker) where the

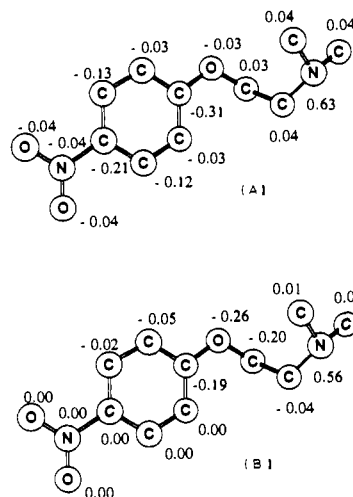


Figure 1. Intramolecular electron transfer excited states. Net charge differences between S₁ (A) (alkyl ether linkage bond order 0.95) and the σ^* excited state (B) (alkyl ether linkage bond order 0.70) with respect to the ground state, calculated for 1-(dimethylamino)-2-(4-nitrophenoxy)ethane. (Only values for heavy atoms are shown.)

substrate lacks a good leaving group in the meta position with respect to the nitro group, even though the corresponding photoreaction (experiment 5) with a longer linker substrate (five methylene units) leads to a complex mixture where no 2-methoxy-4-nitrophenol could be detected.

Comparison of the experiments reported in Table I with the general photobehavior of 4-nitrophenyl ethers in front of high ionization potential nucleophiles^{3,10} and also consideration of the result of experiment 3 (carried out in the absence of water) strongly suggest the photocleavage of the alkyl ether linkage when the substrate has a short (two or three methylene units) linker between the donor and the acceptor. Experiment 2 (three methylene units substrate) indicates a continuous change of properties with the linker length and strongly argues against those mechanistic hypothesis like 1,4-diradical-type fragmentation (after hydrogen atom migration) or a six-member cyclic transition state which would properly explain photofragmentation only for the two methylene units linker cases. The basic fraction of the reaction crudes show in all the cases extensive decomposition and polymerization. However for experiment 1, and when the photoreaction was carried out in extremely diluted conditions, 3-methoxy-4-(2-piperidinoethoxy)phenyl-2-piperidinoethyl nitroxide (relatively persistent radical) could be detected, in trace amounts, and tentatively identified by its UV, ESR, and MS spectra. This result suggests the presence of the piperidinoethyl radical in solution.

UV/vis spectroscopy of 1-piperidino-2-(2-methoxy-4-nitrophenoxy)ethane, -propane and -pentane shows the presence of a $\lambda \approx 430$ nm shoulder, not present in the isolated chromophores ($\lambda_{\max} = 350$ nm for 4-nitroveratrole), and that we attribute to a transition to a low-lying intramolecular electron-transfer excited state. Configuration interaction AM1 calculations were carried out for the optimized conformations of 1-(dimethylamino)-2-(4-nitrophenoxy)ethane and -pentane, as simpler models of our extreme substrates support the existence of such a low-lying excited states. In all cases, the lowest singlet excited state (S₁) results from an intramolecular electron-transfer transition, from the amine to the nitrophenyl group (Figure 1A). In the long spacer case, the first singlet excited state with the ether linkage σ^* character appears 1.8 eV higher in energy than S₁ (in the gas phase). On the other hand, in the short spacer case, a strong coulombic stabilization of this σ^* excited state (Figure 1B) is observed being now the state (alkyl ether bond order 0.70) almost degenerate (0.17 eV above in the gas phase) with respect to S₁ (alkyl ether bond order 0.95). Population of such a low-lying fragmentative state would weaken the alkyl ether linkage thus justifying the experimentally observed photocleavage of substrates with short acceptor-donor linkage. In summary, the short methylene chain keeps the positive end of the electron-transfer excited state in such

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a way that it tends to stabilize an "anomalous" electronic distribution of the negative moiety, probably responsible for the "new" observed photoreactivity.

Acknowledgment. We thank Professor M. Moreno-Mañas for stimulating discussions. Financial support from DGICYT ("Ministerio de Educación y Ciencia" of Spain) through project No. PB87-0032 is gratefully acknowledged.

Registry No. 1-Piperidino-5-(2-methoxy-4-nitrophenoxy)pentane, 136616-33-6; 1-piperidino-3-(2-methoxy-4-nitrophenoxy)propane, 136616-34-7; 1-piperidino-2-(2-methoxy-4-nitrophenoxy)ethane, 136616-35-8; 1-piperidino-5-(2-hydroxy-4-nitrophenoxy)pentane, 136616-36-9; 1-piperidino-5-(4-nitrophenoxy)pentane, 136616-37-0; 1-piperidino-2-(4-nitrophenoxy)ethane, 92033-76-6; 1-piperidino-3-(2-hydroxy-4-nitrophenoxy)propane, 136616-38-1; 2-methoxy-4-nitrophenol, 3251-56-7; 1,2-dimethoxy-4-nitrobenzene, 709-09-1; 4-nitrophenol, 100-02-7; 1-(dimethylamino)-2-(4-nitrophenoxy)ethane, 51344-13-9; 1-(dimethylamino)-5-(4-nitrophenoxy)pentane, 91905-11-2.

Electrophilic Substitutions on η^2 -Coordinated Arenes: An Unprecedented Michael Addition for Phenol and Aniline

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Symmetrically bound arenes, such as in $[\text{Mn}(\text{CO})_3(\eta^6\text{-benzene})]^+$, are activated toward nucleophilic attack, and the utility of these complexes in organic synthesis has been widely demonstrated.¹ Although η^2 -arene species have been reported for several transition metals,² their propensity to dissociate or undergo oxidative addition usually precludes an investigation of the arene chemistry. $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-benzene})]^{2+}$ and its derivatives are stable in this regard,³ and their facile hydrogenation recently has been demonstrated.⁴ Presently, we report a dramatic enhancement of electrophilic reactivity at the para position for anisoles, phenols, and anilines upon their η^2 -coordination.

Crystallographic data have shown that arenes which are η^2 -coordinated have partially localized π -electron systems.⁵ Pentaammineosmium(II) forms complexes with anisole (**1**), phenol (**2**), and *N,N*-dimethylaniline (**3**) in which the metal is coordinated across C_2 and C_3 .^{3,6} Thus, the uncoordinated portion of the arene resembles a dienyl ether, a dienol, or a dieneamine, respectively (Scheme I), and would be expected to undergo electrophilic substitution under milder conditions than the corresponding arene.

Treatment of $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-anisole})](\text{OTf})_2$ (**1**; 0.06 M) with CH_3OTf (~ 1 M) in acetonitrile⁷ yielded in a new species, **4**, whose ^1H and ^{13}C NMR,⁸ NOE, and $^1\text{H}, ^1\text{H}$ -COSY data support the assignment of **4** as $[\text{Os}(\text{NH}_3)_5[(2,3-\eta)\text{-4-methoxy-}N\text{-methylacetophenone imine}]]^{2+}$, the direct reaction product of *N*-methylacetanilium addition to C_4 of anisole followed by deprotonation (Scheme I). Exposure of an acetone solution of **4** to air and trace acid resulted in the decomposition of this complex to yield *p*-methoxyacetophenone in 93% yield.^{9,10} Although nitrilium additions have been demonstrated for arenes containing electron-donating groups, these reactions are sluggish at room temperature, even at molar concentrations, and are reported to occur in low yield.¹¹ An acetonitrile solution of anisole (0.3 M) and CH_3OTf (1.5 M) showed less than 5% reaction after 2 weeks.

An acetonitrile solution of the phenol complex (**2**) reacted with maleic anhydride to form **5** (85%),¹² a species whose ^1H NMR, ^{13}C NMR, and DEPT spectra reveal four olefinic methine, one methylene, and two aliphatic methine carbons. Cyclic voltammetric data of this product showed a reversible couple at 0.85 V (NHE), consistent with an electron-deficient olefinic ligand on pentaammineosmium(II).¹³ Infrared data confirmed the integrity of the anhydride linkage and in addition revealed a band at 1641 cm^{-1} consistent with other 2,5-dienone complexes of pentaammineosmium(II).¹⁴ Judging from these data, we assign **5** as the (2,5-cyclohexadienonyl)succinic anhydride species shown in Scheme I, the product of a net Michael addition of the coordinated phenol at C_4 .¹⁵ ^1H and ^{13}C data suggest the formation of a single diastereomer ($>10:1$), although the presence of a second isomer has not been ruled out. The small coupling constant between H_3 and H_4 ($J = 3$ Hz) suggests a $\text{H}_4\text{-C}_4\text{-C}_3\text{-H}_3$ dihedral angle approaching 90° and the occurrence of Michael addition anti to the osmium, as shown in Scheme I. Refluxing **5** in acidic methanol resulted in the formation of the free diester, **6**,¹⁶ as shown in Scheme I. A retro-Michael reaction hampered efforts to obtain **6** or its anhydride precursor in high yield as the crude organic product was accompanied by varying amounts of phenol and *O*-alkylated phenols not present prior to attempted esterification.¹⁷

(7) An acetonitrile (1.10 g) solution of **1** (56.0 mg; 0.082 mmol) is treated with CH_3OTf (300 mg; 1.83 mmol) and the solution allowed to stand for 10 min. Addition of Et_2O precipitates **4**.

(8) Characterization of **4**: ^1H NMR (acetone- d_6): δ 7.86 (dd, 1 H, CH), 6.10 (dd, 1 H, CH), 5.86 (dd, 1 H, CH), 5.34 (dd, 1 H, CH), 5.02 (br, 3 H, *t*- NH_3), 3.95 (s, 3 H, OCH_3), 3.64 (br s, 12 H, *c*- NH_3), 3.36 (s, 3 H, NCH_3), 2.69 (s, 3 H, COCH_3). ^{13}C NMR: δ 184.1, 178.4, 142.5, 125.0, 95.6, 57.1, 53.2, 52.0, 33.0, 16.5. CV (CH_3CN ; TBAH; 100 mV/s): $E_{1/2} = -0.10$ V.

(9) The ^1H NMR spectrum matches that of an authentic sample.

(10) No attempt has been made to recover the osmium in the present study, although an osmium(III) pentaammine precursor has been recovered in high yield for a related system. See ref 4.

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(12) An acetonitrile (1.10 g) solution of $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-phenol})](\text{OTf})_2$ (**2**) (148 mg; 0.22 mmol) and maleic anhydride (100 mg; 1.02 mmol) is allowed to stand for 20 h. Upon addition of ether (15 mL), an orange precipitate, **5**, is formed (85%). ^1H NMR (acetone- d_6): δ 6.60 (br d, 1 H), 6.05 (d, 1 H), 5.1 (br s, 3 H, *trans*- NH_3), 4.59 (d, 1 H), 4.42 (d, 1 H), 4.16 (m, 1 H), 3.78 (br s, 13 H, *cis*- NH_3 , allylic CH), 3.32 (dd, 1 H), 2.83 (dd, 1 H). ^{13}C NMR: δ 198.8, 173.4, 170.7, 143.6, 134.1, 52.5, 51.6, 45.6, 40.0, 31.3. IR (KBr, cm^{-1}): 1865, 1782 [$(\text{CO})_2\text{O}$], 1641.5 (CO). CV (CH_3CN , TBAH, 100 mV/cm): $E_{1/2} = +0.85$ and $+1.04$ V (NHE).

(13) For the complex $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-cyclohexenone})]^{2+}$, $E_{1/2} = +0.88$ V (NHE, CH_3CN).

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(15) The mechanism for this reaction is currently under investigation.

(16) Characterization of **6**: ^1H NMR (CDCl_3) δ 7.12 (d, 2 H, CH), 6.75 (d, 2 H, CH), 6.23 (br, 1 H, OH), 4.02 (dd, 1 H, CH), 3.16 (dd, 1 H, CH_2), 2.66 (dd, 1 H, CH_2); ^{13}C NMR δ 174.6, 172.9, 156.0, 129.3, 116.2, 52.9, 52.5, 46.7, 38.1; mp 68–69 °C; $M^+ = 238$; lit. mp 76–77 °C. Swain, G.; Todd, A. R.; Waring, W. S. *J. Chem. Soc.* **1944**, 548.

(17) Compound **5** was refluxed in methanol (variable reaction times and $[\text{H}^+]$) and the mixture partitioned between water and CH_2Cl_2 . The crude organic product was eluted down silica with 1:3 ethyl acetate/ether. Overall yield (**6**): 20–40%.

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(6) The synthesis of $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-phenol})]^{2+}$ is carried out in a manner similar to that of anisole and aniline as specified in ref 4. ^1H NMR (acetone- d_6): δ 8.65 (br, 1 H), 6.59 (t, 1 H), 6.36 (t, 1 H), 5.70 (d, 1 H), 5.32 (t, 1 H), 5.03 (d, 1 H), 4.70 (br, 3 H), 3.45 (br, 12 H). Anal. ($\text{C}_8\text{H}_2\text{O}_2\text{Os}_2\text{F}_6\text{O}_7\text{N}_5 \cdot 1/4\text{DMA}$) C, H, N (DMA = *N,N*-dimethylacetamide).