thermal degradation at room temperature. This decomposition behavior appears to be rather general for pentaammineosmium(II) complexes containing organic ligands which include a carbonyl group.

$$[Os(NH_3)_5(RCOR')]^{2+} \rightarrow [Os(NH_3)_5CO]^{2+} + \text{organic fragments}$$

Details of these reactions and structural and spectroscopic properties of other pentaammineosmium(II) complexes of η^2-bound unsaturated ligands will be described separately.

To our knowledge, $[Os(NH_3)_5((CH_3)_2CO)]^{2+}$ is the first example of a carbonyl-bound η^2 in a pentaammine complex. The reactions of pentaammineosmium(II) and unsaturated organic ligands promise to expand substantially the interface between organometallic and traditional coordination chemistry.

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Registry No. I, 105164-48-5; $I \cdot {}^1/_2(CH_3)_2CO$, 105164-49-6; 1 ($^{18}O$ labeled), 105164-54-3; $[Os(NH_3)_5(TFMS)](TFMS)_2$, 83781-30-0; $[Os(NH_3)_5((CH_3)_2CO)]Cl_4$, 105164-50-9; $[Os(NH_3)_5(PhCN)]^{3+}$, 105164-51-0; $[Os(NH_3)_5(PhCN)]^{2+}$, 105164-52-1; $[Os(NH_3)_5Co]^{2+}$, 70528-08-4.

Supplementary Material Available: Listings of bond lengths, bond angles, and plane calculations (9 pages); tables of structure factors (13 pages). Ordering information is given on any current masthead page.

Mechanistic and Kinetic Studies of the Thiodediazoniation Reaction

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Abstract: Treatment of the diazonium salt, **1**, with sodium benzenethiolate in Me_2SO affords mixtures of uncyclized (**4**) and cyclized (**5**) products. Formation of the latter involves ring closure of the substituted aryl radical, **2**. The variation in the relative yields of **4** and **5** with reactant concentration shows that thiodediazoniation involves two key propagation steps: coupling of aryl radicals with thiolate anions to give radical anions, and electron transfer from the latter to the diazosulfide formed in a fast initial equilibration. The rate constant, k_N, for the reaction of **2** with PhS^- is given by $\log k_N = (9.57 \pm 0.28) - (1.74 \pm 0.37)/2.3RT$ where E_{act} is in kcal mol^{-1}.

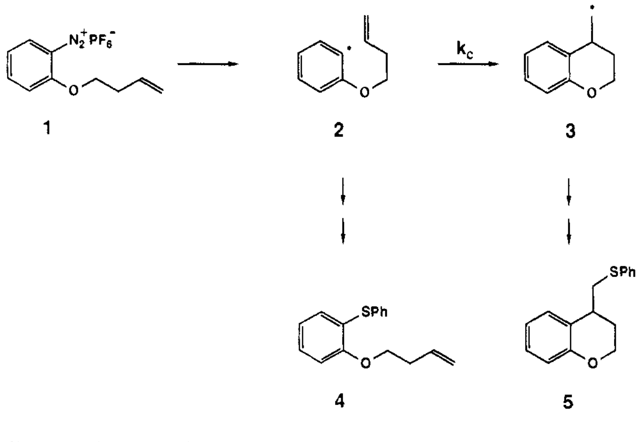
The reaction between arenediazonium salts and arenethiolate ions is a well-known and convenient means of preparing diaryl sulfides[1,2] (eq 1). However, mechanistic information on such thiodediazoniation reactions is surprisingly limited. Several workers dating back to the 19th century have suggested that the reaction proceeds via an intermediate diazosulfide (eq 2) which

$$ArN_2^+ + Ar'S^- \rightarrow ArSAr' + N_2 \qquad (1)$$

$$ArN_2^+ + Ar'S^- \rightarrow ArN{=}NSAr' \qquad (2)$$

undergoes decomposition, liberating nitrogen to yield the diaryl sulfide.[1a,c,i,2] A number of such diazosulfides have indeed been isolated and characterized.[3] A recent report[2] postulates that electron transfer from arenethiolate ions to the diazosulfide may be the key activation step in the decomposition of the latter species. On the other hand, Beckwith and Meijs,[4] whose preliminary studies have demonstrated the intermediacy of aryl radicals in thiodediazoniation reactions, have suggested that such reactions may be initiated by electron transfer from thiolate ions to diazonium cations (eq 3).

Scheme I



$$ArN_2^+ + Ar'S^- \rightarrow Ar^\bullet + Ar'S^\bullet + N_2 \qquad (3)$$

In order to resolve these questions, we decided to study the reaction between benzenethiolate ions and *o*-(but-3-enyloxy)benzenediazonium ions in Me_2SO solution. It was expected that the intermediate *o*-(but-3-enyloxy)phenyl radical, **2** (Scheme I), the rate of cyclization of which has recently been determined,[5]

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Table I. Variation of Product Ratio with [ArN=NSPh] and [PhS$^-$][a]

run	[ArN$_2^+$],[b] M	[PhS$^-$],[b] M	[ArN=NSPh],[c] M	[PhS$^-$]$_{\text{excess}}$,[c] M	[4]/[5][d]
1	0.4	0.4	~0.4	~0.0	0.07
2	0.2	0.6	~0.2	~0.4	0.39
3	0.1	0.7	~0.1	~0.6	0.48
4	0.1[e]	0.7[e]	~0.1	~0.6	0.51

[a] All reactions carried out at 20 °C in Me$_2$SO solvent. Reaction times 5–6 h. [b] Initial concentrations of added reactants. [c] Concentrations of species assuming complete and rapid conversion of ArN$_2^+$ to Ar—N=N—SPh. [d] Determined by GC. [e] Contained added PhSSPh (0.1 M).

would act as a kinetic and mechanistic probe for the reactions between the aryl radicals and other chemical species present.

Treatment of the diazonium salt, **1**, with PhS$^-$Na$^+$ in Me$_2$SO solution afforded a mixture of compounds **4** and **5**. The formation of **5** via the diagnostic ring closure **2** → **3** confirmed the involvement of aryl radical intermediates. Significant amounts of the corresponding reduction products, i.e., *o*-(but-3-enyloxy)benzene and 3,4-dihydro-2*H*-1-benzopyran, were not observed. In addition to compounds **4** and **5**, varying amounts (5–20%) of diphenyl disulfide were also found among the reaction products. The large variation in the amount of the latter product suggests that it is at least partly formed by atmospheric oxidation of unreacted thiophenol during the workup stage. Careful monitoring of the reaction mixture by TLC showed the rapid appearance of an intermediate compound which gradually disappeared during the course of the reaction and was accompanied by the formation of products **4** and **5**. This intermediate was identified as the diazosulfide on the basis of previous reports,[2,3] as well as by the large increase observed in UV absorption at 364 nm[3b] when solutions of the diazonium salt and PhS$^-$Na$^+$ were combined. The rapid appearance of the diazosulfide is in keeping with the very large rate constant (~10^9 M^{-1} s^{-1}) reported for the bimolecular reaction between diazonium cations and benzenethiolate anions.[6]

It is possible to envisage three main species with which the aryl radical intermediates could interact to yield the final diaryl sulfide products (eq 4, 5, and 6). The first is the benzenethiolate ion,

$$\text{Ar}^\bullet + \text{PhS}^- \rightarrow \text{ArSPh}^{\bullet -} \tag{4}$$

$$\text{Ar}^\bullet + \text{ArN}{=}\text{NSPh} \rightarrow \text{ArSPh} + \text{Ar}^\bullet + \text{N}_2 \tag{5}$$

$$\text{Ar}^\bullet + \text{PhSSPh} \rightarrow \text{ArSPh} + \text{PhS}^\bullet \tag{6}$$

which is already known from studies of the S$_{\text{RN}}$1 reaction and similar processes[7] to react readily with aryl radicals to give a sulfide radical anion (eq 4). Another is the diazosulfide, ArN=NSPh, which might reasonably be expected to undergo homolytic substitution by aryl radicals at sulfur. Somewhat similar intramolecular reactions of aryl radicals with sulfide sulfur have recently been described.[8] Finally, there is the disulfide, PhSSPh, which could also undergo fast S$_\text{H}$2 attack at sulfur by aryl radicals.[9]

In order to investigate the relative importance of these possible alternative routes, thiodediazoniation reactions were carried out at several different concentrations of ArN$_2^+$ and PhS$^-$ (Table I). Since both the forward rate constant and the equilibrium constant (K ~ 10^{10} M^{-1})[6] for the reaction in eq 2 are so large, it may be assumed that in the presence of an excess of PhS$^-$ all of the ArN$_2^+$ will be immediately converted into the diazosulfide. Consequently, the effective concentrations of the reagents very shortly after mixing will be as listed in Table I. It can be seen that down the series of runs, 1–3, the concentration of PhS$^-$ increases while that of ArN=NSPh decreases. Since each of the bimolecular reactions in eq 4, 5, and 6 must compete with the unimolecular ring closure of the aryl radical, **2**, the increase in the [**4**]/[**5**] ratio for runs 1–3 suggests that the product **4** is formed predominantly via a pathway (eq 4) in which PhS$^-$ is kinetically significant but not one involving the diazosulfide. Moreover, in the presence of a large excess of PhS$^-$ the reaction between aryl radicals and diphenyl disulfide (eq 6) must be of minor importance. This is demonstrated by the observation that thiodediazoniation of **1** in the presence of an equivalent amount of PhSSPh resulted in only a small increase in the [**4**]/[**5**] ratio (cf. runs 3 and 4). Further studies involving various concentrations of excess benzenethiolate ions confirmed that the [**4**]/[**5**] ratio was approximately proportional to [PhS$^-$] (Table II), in conformity with a reaction step in which aryl radicals couple with benzenethiolate ions. The dependence of the product ratio on the bulk concentration of PhS$^-$ also acts as evidence against a mechanism in which the diazosulfide collapses to the products within a solvent cage[10] (eq 7).

Table II. Kinetic Data[a] for Reaction Ar$^\bullet$ + PhS$^-$ → Ar–SPh$^{\bullet -}$

run	temp, °C	[PhS$^-$],[b] M	[4]/[5][c]	k_N/k_c, M^{-1}	log k_N/k_c	$10^{-8}k_N$, M^{-1} s^{-1}
1	17	0.37	0.29	0.78	-0.108	2.03
	17	0.48	0.41	0.85	-0.071	2.21
	17	0.68	0.52	0.77	-0.114	2.00
2	35	0.37	0.27	0.73	-0.137	2.73
	35	0.48	0.36	0.75	-0.125	2.81
	35	0.68	0.46	0.68	-0.167	2.54
3	55	0.37	0.20	0.54	-0.268	2.89
	55	0.48	0.27	0.56	-0.252	3.00
	55	0.68	0.39	0.59	-0.229	3.16
4	80	0.37	0.18	0.48	-0.319	3.79
	80	0.48	0.23	0.48	-0.319	3.79
	80	0.68	0.29	0.43	-0.367	3.40

[a] All reactions carried out in Me$_2$SO solvent. Reaction times range from 15 min (80 °C) to 5–6 h (17 °C). [b] Used in 10-fold excess compared to the diazonium salt. [c] Determined by GC.

$$\text{ArN}{=}\text{NSPh} \rightarrow [\text{Ar}^\bullet\ \text{N}_2\ {}^\bullet\text{SPh}] \rightarrow \text{ArSPh} + \text{N}_2 \tag{7}$$

Thus, it appears that the predominant, although possibly not exclusive, mechanistic route followed by the thiodediazoniation process (Scheme II) involves initial formation of diazosulfide and two chain-propagation steps in which a sulfide radical anion is formed by the coupling of PhS$^-$ with Ar$^\bullet$ and converted into product by electron transfer to diazosulfide. Chain initiation possibly occurs by thermal or photochemical homolysis of the diazosulfide.

Scheme II

$$\text{ArN}_2^+ + \text{PhS}^- \rightarrow \text{ArN}{=}\text{NSPh}$$

$$\text{ArN}{=}\text{NSPh} \rightarrow \text{Ar}^\bullet + \text{N}_2 + \text{PhS}^\bullet$$

$$\text{Ar}^\bullet + \text{PhS}^- \rightarrow \text{ArSPh}^{\bullet -}$$

$$\text{ArN}{=}\text{NSPh} + \text{ArSPh}^{\bullet -} \rightarrow \text{Ar}^\bullet + \text{N}_2 + \text{PhS}^- + \text{ArSPh}$$

In the case of the aryl radical, **2**, the bimolecular reaction with PhS$^-$ must compete with the unimolecular ring closure **2** → **3**. Application of the usual steady-state theory shows that when PhS$^-$ is in large excess, k_N/k_c = [**4**]/[**5**][PhS$^-$], where k_c is the rate constant for ring closure and k_N the rate constant for the reaction between aryl radicals and PhS$^-$. Thus, the results in Table II allow the relative rate constant k_N/k_c to be estimated at several different temperatures. Substitution of the values[5] of k_c allows the absolute rate constants (k_N) themselves to be evaluated (Table II).

It is seen that k_N = 2–4 × 10^8 M^{-1} s^{-1} in the temperature range of the present study. These values fall within the general range of 10^7–10^{10} M^{-1} s^{-1} observed by Saveant and co-workers,[11] who measured the rate of reaction between PhS$^-$ and a number of aryl radicals by using electrochemical methods. For reaction of the phenyl radical itself, Saveant reports[11b] a value of 2.6 × 10^7 at

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−38 °C. Since it appears that k_N is markedly influenced by substrate structure, an exact comparison of the present results must be made with independent measurements for *o*-alkoxy aryl radicals.

When the variation of k_N/k_c with temperature was studied, it was found that there was an approximately linear correlation between log k_N/k_c and $1/T$. The resulting Arrhenius plot was used to estimate the relative activation parameters log A and E_{act}. Combination of these (eq 8) with the known[5] Arrhenius equation for k_c (eq 9) gave the activation parameters for the reaction between the aryl radicals, **2**, and phenylthiolate ions (eq 10), where $\theta = 2.3RT$ and E_{act} is in kcal mol^{-1}.

$$\log k_N/k_c = (-1.55 \pm 0.25) + (1.85 \pm 0.33)/\theta \qquad (8)$$

$$\log k_c = (11.12 \pm 0.12) - (3.59 \pm 0.16)/\theta \qquad (9)$$

$$\log k_N = (9.57 \pm 0.28) - (1.74 \pm 0.37)/\theta \qquad (10)$$

In the above discussion we have reasonably assumed that the mechanism of the reaction of diazonium salt **1** with sodium benzenethiolate is an appropriate general model for the thiodediazoniation reaction. We now address the question of the mechanism for formation of the cyclized sulfide, **5**. Clearly it must be derived from radical **3** by an analogue of one of the reactions in eq 4, 5, or 6 but involving an *alkyl* rather than an aryl radical. Although clear-cut evidence is not available, we prefer the first. While relatively rare, a similar nucleophilic attack has been invoked as an intermediate step in the conversion of 1-iodoadamantane to its 1-phenylthio analogue by the $S_{RN}1$ mechanism.[12] Since it has been suggested that radical anions of the type $RSPh^{\bullet-}$ are more likely to undergo fragmentation to $R^{\bullet}$ and PhS^- when R is alkyl rather than aryl,[12] it is possible to envisage the formation of additional products via the alkyl radical **3**. However, the absence of the cyclized hydrocarbon 3,4-dihydro-2*H*-1-benzopyran or its dimer suggests that the rate constant for the fragmentation reaction is much smaller than the rate constant for electron transfer from $RSPh^{\bullet-}$ to ArN=NSPh (or ArN_2^+).

Conclusion

The above experiments show that thiodediazoniation of arenediazonium salts involves three key mechanistic steps: (i) initial formation of diazosulfide, ArN=NSAr′, (ii) coupling of aryl radicals with thiolate to give radical anions, $ArSAr'^{\bullet-}$, and (iii) chain propagation by electron transfer from the latter to the former. Initiation probably occurs by thermal or photochemical homolysis of ArN=NSAr′. The coupling reaction has a low activation energy and approaches the diffusion-controlled limit. This study demonstrates the utility of aryl radical "clock" reactions as kinetic yardsticks and mechanistic probes.

Experimental Section

General Methods. Analytical grade dimethyl sulfoxide was dried over calcium hydride and distilled under reduced pressure. Thiophenol was distilled from sodium hydroxide pellets under reduced pressure. Diphenyl disulfide (Fluka, 99%) was used without further purification.

^{1}H and ^{13}C NMR spectra were recorded on a Jeol FX-200 spectrometer operating at 199.50 and 50.10 MHz, respectively. All chemical shifts are in parts per million (ppm) relative to internal Me_4Si. Ultraviolet spectra were recorded on a Hewlett-Packard 8450A spectrophotometer. Gas chromatographic analyses were performed on Varian 3400 and 6000 chromatographs equipped with flame ionization detectors and coupled to Hewlett-Packard 3390A recorder/integrators. Glass columns (6 ft) packed with either 3% SE-30 on 100/120-mesh Chromosorb W or 2% OV-17 on 60–80-mesh Gaschrom Q were employed with helium as the carrier gas. GC/MS analyses were carried out using a Varian 1440 gas chromatograph coupled to a VG micromass 7070F mass spectrometer. Thermostated baths accurate to ±0.3 °C were used for temperature control.

***o*-(But-3-enyloxy)benzenediazonium Hexafluorophosphate (1).** This compound was prepared by the treatment of diazotized *o*-(but-3-enyloxy)aniline[13] with hexafluorophosphoric acid according to standard procedures.[14] Further purification by dissolving in acetone and reprecipitating with dry ether gave **1** as an almost colorless powder in 72% yield: mp 104 °C dec; ^{1}H NMR (acetone-d_6) δ 2.72 (q, 2, $CH_2CH=$), 4.65 (t, 2, OCH_2), 5.12–5.30 (m, 2, $=CH_2$), 5.88–6.05 (m, 1, $CH=$), 7.54 (t), 7.79 (d), 8.33 (t), 8.61 (d) (aromatics).

***o*-(But-3-enyloxy)phenyl Phenyl Sulfide (4) and 4-((Phenylthio)methyl)-3,4-dihydro-2*H*-1-benzopyran (5).** A solution of the diazonium salt (0.32 g, 1 mmol) in Me_2SO (2 mL) was added to a solution of PhS^-Na^+ (5 mmol) in Me_2SO (3 mL) at 20 °C and the mixture stirred under a nitrogen atmosphere for 6 h. The reaction was quenched with a saturated solution of NaCl and the mixture extracted with ether. The extracts were washed with 10% NaOH solution and dried (Na_2SO_4), and the solvent was evaporated. The crude residue was subjected to medium-pressure liquid chromatography on a LiChroprep Si 60 (40–63-μm) column (purchased from Merck) using 5% ethyl acetate/95% hexane as the eluent. The desired compounds were obtained as colorless liquids. Compound **4**: 0.78 g (30%); ^{1}H NMR ($CDCl_3$) δ 2.47 (q, 2, $CH_2CH=$), 4.02 (t, 2, OCH_2), 5.01–5.15 (m, 2, $=CH_2$), 5.70–5.87 (m, 1, $CH=$), 6.82–7.47 (m, 9, aromatics); ^{13}C NMR ($CDCl_3$) δ 33.55 (t), 68.09 (t), 112.07 (d), 116.97 (t), 121.21 (d), 126.96 (d), 127.54 (s), 128.18 (d), 129.03 (d), 131.51 (d), 134.29 (d), 134.78 (s), 156.72 (s). Anal. ($C_{16}H_{16}OS$) C, H. Compound **5**: 0.86 g (34%); ^{1}H NMR ($CDCl_3$) δ 2.10–2.18 (m, 2, SCH_2), 2.98–3.01 (m, 2, CCH_2), 3.37–3.53 (m, 1, CH), 4.03–4.26 (m, 2, OCH_2), 6.79–7.44 (m, 9, aromatics); ^{13}C NMR ($CDCl_3$) δ 25.70 (t), 33.12 (t), 40.27 (d), 62.81 (t), 117.01 (d), 120.28 (d), 124.42 (s), 126.26 (d), 127.93 (d), 129.01 (d), 129.10 (d), 129.59 (d), 136.16 (s), 154.62 (s). Anal. ($C_{16}H_{16}OS$) C, H.

Stock Solutions. Each stock solution of PhS^-Na^+ was prepared by carefully adding an accurately measured amount of thiophenol to an ice-cooled slurry of NaH (1.05 equiv) and Me_2SO (~3 mL) in a 10-mL volumetric flask maintained under an argon atmosphere. After the vigorous exothermic reaction had subsided, a further 2–3 mL of Me_2SO was added and the mixture held at ambient temperature until the evolution of hydrogen had ceased completely. The flask was then evacuated to 0.1 mm to remove any dissolved gases and finally made up to the required 10-mL volume.

Stock solutions of the diazonium salt were freshly prepared in 1.0-mL volumetric flasks prior to kinetic measurements. It was found that such solutions darkened in color over a period of time even when stored at low temperature.

Preliminary Studies. Thiodediazoniation experiments using a 10-fold excess of PhS^-Na^+ relative to the diazonium salt were carried out at several temperatures over the range 17–80 °C, and the progress of these reactions was monitored by TLC. The initially formed diazosulfide was found to disappear gradually with the formation of **4** and **5**. The time required for the complete disappearance of the intermediate varied between 5–6 h at 17 °C and 15–20 min at 80 °C.

Solutions of $ArN_2^+PF_6^-$ (0.8 M) and PhS^-Na^+ (0.8 M) in Me_2SO were mixed in the ratios 1:1, 1:3, 1:7, and 1:7 (with added PhSSPh) for runs 1–4, Table I, and stirred under an argon atmosphere at 20 °C for 5 h. The reactions were then quenched with NaCl solution and the products extracted with ether as previously described and analyzed by GC.

Kinetic Measurements. To 1.0 mL of a solution of PhS^-Na^+ (of known molarity) in Me_2SO was added 100 μL of a solution of the diazonium salt (of identical molarity) in Me_2SO with the aid of a microsyringe whose needle tip was held below the liquid surface. After the mixture was stirred at constant temperature under an argon atmosphere for an appropriate length of time (as estimated from preliminary studies), a measured amount of hydrocarbon standard was added and the reaction quenched with saturated NaCl solution. The mixture was extracted with ether, washed with 10% NaOH solution, dried (Na_2SO_4), and analyzed by GC.

Note Added in Proof. Dr. K. U. Ingold in a private communication has indicated that the value of k_H, the rate constant for the reaction of aryl radicals with Bu_3SnH, upon which the value of k_c rests, may be in error. However, an independent determination of k_c by a trapping technique using nitroxide radicals has shown that the rate constants presented here are approximately correct.

Registry No. 1, 104994-79-8; **2**, 56182-34-4; **3**, 25087-57-4; **4**, 104994-80-1; **5**, 104994-81-2; *o*-$CH_2=CH(CH_2)_2OC_6H_4N=NS-Ph$, 104994-82-3; PhSNa, 930-69-8.

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