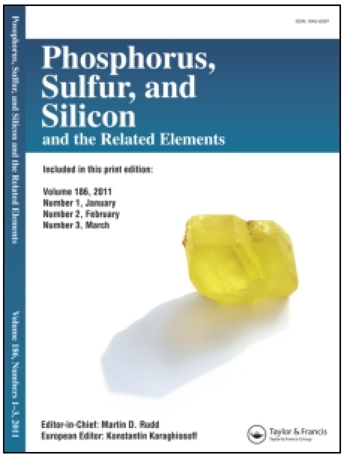

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STUDIES ON THE DEUTERATION OF AROMATIC ORGANOSULFUR COMPOUNDS USING AQUEOUS TRANSITION METAL SPECIES

Peter D. Clark[a]; Alex Primak[a]
[a] Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada

To cite this Article Clark, Peter D. and Primak, Alex(1993) 'STUDIES ON THE DEUTERATION OF AROMATIC ORGANOSULFUR COMPOUNDS USING AQUEOUS TRANSITION METAL SPECIES', Phosphorus, Sulfur, and Silicon and the Related Elements, 84: 1, 149 — 157

To link to this Article: DOI: 10.1080/10426509308034326

URL: http://dx.doi.org/10.1080/10426509308034326

Phosphorus, Sulfur, and Silicon, 1993, Vol. 84, pp. 149–157
Reprints available directly from the publisher
Photocopying permitted by license only

STUDIES ON THE DEUTERATION OF AROMATIC ORGANOSULFUR COMPOUNDS USING AQUEOUS TRANSITION METAL SPECIES†

PETER D. CLARK‡ and ALEX PRIMAK
Department of Chemistry, The University of Calgary, 2500 University Drive N.W., Calgary, Alberta, Canada, T2N 1N4

(Received June 30, 1993; in final form August 25, 1993)

Reaction of benzenethiols and benzo[*b*]thiophene (BT) with D_2O solutions of trichlorides of Ru, Fe or Cr at elevated temperatures (200–315°C) constitutes a simple method for the preparation of per-deuterated derivatives. Substitution patterns observed for partially deuterated products imply that D-incorporation occurs by standard electrophilic processes. Reactions with benzenethiols produced diaryl sulfides as by-products although these compounds were deuterated to the same extent as the thiols. Experimental observations and the known behaviour of aqueous transition metal species indicate that D^+ is furnished by the hydrolysis of D_2O molecules in the solvation sphere of the metal ion. Complete deuteration of the organosulfur substrates was achieved using a 100:1 organosulfur/metal chloride mole ratio. Hydrodesulfurization of per-deuteroBT under standard conditions afforded perdeuteroethylbenzene in good yield.

Key words: Aromatic organosulfur compounds; deuteration; aqueous transition metal salts.

INTRODUCTION

A variety of studies have been published on the deuteration of aromatic hydrocarbons using acidic D_2O[1–6] but a lesser amount of work has been described concerning H-D exchange in heterocyclic and heteroatom substituted compounds. Deuteration of phenol, aniline and benzoic acid has been examined by Werstiuk and co-workers[7] and H-D exchange of pyridine and its alkyl derivatives has been studied by Werstiuk *et al.*[8] and by Fischer and Puza.[9] Although a vast amount of effort has been devoted to the gas phase deuteration of thiophene and related sulfur heterocycles with D_2 in relation to establishing the mechanism of hydrodesulfurization of these compounds,[10] very little work has examined H-D exchange in sulfur compounds using D_2O. Karakhanov and co-workers have studied H-D exchange in some thiophenes using homogeneous Pt(II) complexes[11] and extended this work to benzothiophene (BT), indoles and benzofurans.[12] These workers found that thiophene derivatives were deuterated readily using Pt complexes and postulated coordination of the sulfur compound to the metal centre to explain the apparent activation of the substrate. In contrast, very little exchange was observed with BT. To date, the most successful method for deuteration of BT has been D_2O quenching of lithio-derivatives derived from bromo-substituted compounds. However, this method is restricted to deuteration of BT at selected positions.[13]

---

†Presented in part as a communication to the 15th International Symposium on the Organic Chemistry of Sulfur, Caen, France, June 28–July 3, 1992.

‡Author to whom correspondence may be addressed.

In the course of other work, we observed rapid deuteration of BT by heating it with a solution of $RuCl_3$ in D_2O at 350°C.[14] Per-deuteration was achieved within 3 h and it was postulated that coordination of BT to Ru(III) was responsible for the facile H-D exchange. Since hydrodesulfurization of the per-deuterated BT would constitute a simple synthesis of per-deuteroethylbenzene (a useful NMR solvent), we have extended the study to examine the deuteration of benzenethiol (PhSH) and toluenethiols (TolSH), which, if per-deuterated, could yield per-deuterobenzene and per-deuterotoluene after desulfurization. In addition to using Ru-compounds, we have examined the use of Fe and Cr trichlorides and compared their ability to promote H-D exchange to standard acid/D_2O conditions. Some competitive experiments with aromatic hydrocarbons were carried out to deduce kinetic and mechanistic information.

EXPERIMENTAL

Reagents. All reagents except iron and chromium trichlorides (Fisher Chemical Company) were obtained from the Aldrich Chemical Company and had purities >99.5%. D_2O had 99.9% D-content. 2,3-DihydroBT was prepared by $LiAlH_4$ reduction of the dihydro-sulfone derivative using the procedure of Bordwell and McKellin.[15]

Reagent Solutions. Since the pH of metal chloride solutions is dependent on the amount of metal salt present, one batch of metal chloride/D_2O solution was prepared for use in all experiments. The ruthenium solution was prepared by stirring as received $RuCl_3 \cdot 3H_2O$ (0.029 g) and D_2O (20.0 g) for 16 h under an argon atmosphere. The pH of this solution was found to be 1.47 and a reference DCl/D_2O solution of the same pH was prepared by adding DCl (99.9% D) to D_2O until the desired pH was obtained. Solutions of $FeCl_3$ and $CrCl_3$ in D_2O were prepared similarly using 30.2 mg of $FeCl_3 \cdot 6H_2O$ and 29.7 mg of $CrCl_3 \cdot 6H_2O$. DCl/D_2O reference solutions of pH 2.14 and 2.97 were prepared for iron and chromium respectively.

H-D Exchange Procedures. In a typical experiment 1.26 mL (ca. 70 mmol) of either D_2O, a metal chloride reagent solution, or a reference DCl/D_2O solution and an organosulfur compound (1.0–1.2 mmol) were placed in a clear fused quartz tube (General Electric Type 214, i.d. 6 mm, o.d. 10 mm and ca. 250 mm in length). When a metal reagent solution was used, these quantities result in a D_2O/organosulfur/metal mole ratio of 67:1:0.01. The H/D content of all reagents allows a theoretical maximum deuterium exchange of ca. 96%. The contents of the tubes were degassed using freeze-thaw cycles (liquid N_2 and 1 mm Hg) and the tubes were flame sealed with the contents cooled by liquid N_2. The tubes were placed in cap enclosure autoclaves (containing water to minimize the pressure differential across the tube walls) and were heated by placing the autoclaves in ovens held at the desired temperature (± 5°C). The internal temperature of the autoclaves was monitored for short residence time experiments by comparing the steam pressure attained inside the autoclave to standard steam pressure tables. For long duration experiments, it was assumed that the internal temperature of the autoclave was that of the oven. Based on steam pressure measurements, it required approximately 4–4.5 h for the autoclaves to attain 250°C. Whenever possible, comparative experiments were conducted in the same autoclave so that each tube was subjected to the same warm-up and cool down times. Experiments done together are arranged in groups in Tables I and II.

Reaction products were isolated by breaking the tubes cooled to room temperature and extracting the contents with pentane (3 × 10 mL). (Note: although no excessive pressure build-ups were observed in these experiments, opening of the tubes can be performed safely by placing the scored tube inside a flexible steel tube and bending the tube to break the quartz.) The pentane extracts were filtered through a small plug of chromatography grade silica to remove inorganic residues, were dried over $MgSO_4$ and were concentrated by rotary evaporation until ca. 2 mL of solution remained. Deuterium incorporation was determined by analysis of the mass spectrum obtained from the GC-MS analysis of the reaction mixtures using a Hewlett-Packard 5970/5809 system. The chromatography was performed using a SPB5 0.25 mm × 30 M column ramped from 50–200°C with He carrier gas at a flow rate of 25 cm/s. The average molecular weight of the deuterated products and reactants was calculated using

TABLE I

H-D Exchange in BT and DHBT

Reactants	pH at 20°C [a]	Temperature (°C)	Time (h)	Mass Increase	% Exchange
BT/D_2O [b]	7	150	24	<0.05	<1
BT/$RuCl_3$	1.48	150	24	<0.05	<1
BT/DCl	1.47	150	24	<0.05	<1
BT/$RuCl_3$	1.48	200	24	1.74	29.0
BT/DCl	1.47	200	24	1.86	31.0
BT/D_2O	7	260	0.5	0.20	3.33
BT/$RuCl_3$	1.48	260	0.5	3.34	55.7
BT/DCl	1.47	260	0.5	3.56	59.3
BT/D_2O	7	260	24	0.37	6.00
BT/$RuCl_3$	1.48	260	24	5.58	93.0
BT/DCl	1.47	260	24	5.51	92.0
BT/$FeCl_3$	2.14	250	24	5.61	93.6
BT/DCl	2.13	250	24	5.49	91.5
BT/$CrCl_3$	2.97	250	24	5.61	93.4
BT/DCl	2.97	250	24	3.57	59.4
BT/$FeCl_3$	2.14	250	0.5	3.19	53.2
BT/DCl	2.13	250	0.5	2.17	36.1
BT/$CrCl_3$	2.97	250	0.5	1.98	33.0
BT/DCl	2.97	250	0.5	0.67	11.2
DHBT/D_2O	7	260	24	0.40	5.00
DHBT/$RuCl_3$	1.48	260	24	3.68	46.0
DHBT/DCl	1.47	260	24	3.75	46.9
BT+PhEt/$RuCl_3$	1.48	250	0.75	0.20 (PhEt)	2.6
				1.38 (BT)	23.1
BT+PhEt/DCl	1.47	250	0.75	0.13 (PhEt)	1.3
				1.11 (BT)	18.5

[a] Determined for aqueous reactant prior to addition to organosulfur compound.

[b] Groups of experiments were conducted in the same autoclave.

the following formula and the amount of D-incorporation was taken as the difference between the values obtained for the reactants and products.

$$\text{Average Mol. Wt} = \frac{\sum \text{(mass of peak) (intensity of peak)}}{\sum \text{(intensity of peak)}}$$

In experiments which yielded partially deuterated products, the position of D-incorporation was determined by ^1H and ^{13}C NMR spectroscopy of products from which as much pentane as possible had been removed (bearing in mind the volatility of some products). These spectra were obtained in $CDCl_3$ solution on a Bruker ACE-200 spectrometer using solvent resonances as internal references.

Competitive Experiments. Competitive experiments with BT/ethylbenzene and *p*-toluenethiol/toluene were conducted to assess the reactivity of the sulfur compounds. These experiments were performed by placing an equimolar mixture of the substrates in the same tube along with the desired D_2O solution in quantities to achieve a theoretical maximum possible D-exchange of 96% for each substrate.

Large Scale Reaction of BT and Preparation of Ethylbenzene-d_{10}. BT (10 g, 74.5 mmol), $RuCl_3$ (0.1 g, 0.48 mmol) and D_2O (50 g, 2.5 mol) were placed in a cap enclosure autoclave and the autoclave was heated for 17 h at 260°C. After cooling, the reaction mixture was extracted into pentane (100 mL) and the extracts were dried ($MgSO_4$) and were evaporated. The BT product was purified by sublimation

TABLE II

H-D Exchange in aromatic thiols and methyl phenyl sulfide

Reactants	pH at 20°C [a]	Temperature (°C)	Time (h)	Mass Increase	% Exchange [c]	% Diaryl Sulfide Formation [d]
PhSH/D_2O[b]	7	260	48	2.89	57.8	1
PhSH/$RuCl_3$	1.48	260	48	3.95	79.0	20
PhSH/DCl	1.47	260	48	3.96	79.2	5
PhSH/$RuCl_3$	1.48	315	48	4.85	97.0	82
PhSH/DCl	1.47	315	48	4.74	94.8	77
PhSMe/D_2O	7	260	48	0.35	7.10	-
PhSMe/$RuCl_3$	1.48	260	48	3.86	77.2	-
PhSMe/DCl	1.47	260	48	3.83	76.6	-
PhSH/$FeCl_3$	2.14	250	48	2.98	59.5	4
PhSH/DCl	2.13	250	48	2.94	58.7	<1
PhSH/$CrCl_3$	2.97	250	48	3.43	68.5	<1
PhSH/DCl	2.97	250	48	2.88	57.5	<1
PhSH/$FeCl_3$	2.14	315	48	4.66	93.1	74
PhSH/DCl	2.13	315	48	4.51	90.3	76
PhSH/$CrCl_3$	2.97	315	48	4.70	94.1	79
PhSH/DCl	2.97	315	48	3.67	74.0	73
o-TolSH/D_2O	7	260	48	3.63	51.9	24
o-TolSH/$RuCl_3$	1.48	260	48	3.68	55.4	18
o-TolSH/DCl	1.47	260	48	3.88	55.4	17
o-TolSH/$RuCl_3$	1.48	315	48	5.83	83.3	48
o-TolSH/DCl	1.47	315	48	5.74	82.0	52
o-TolSH/$FeCl_3$	2.14	250	48	3.91	55.8	32
o-TolSH/DCl	2.13	250	48	3.98	56.9	34
o-TolSH/$CrCl_3$	2.97	250	48	4.00	57.1	40
o-TolSH/DCl	2.97	250	48	4.08	58.1	39
o-TolSH/$FeCl_3$	2.14	315	48	6.07	86.7	62
o-TolSH/DCl	2.13	315	48	5.53	79.0	64
o-TolSH/$CrCl_3$	2.97	315	48	6.16	87.9	66
o-TolSH/DCl	2.97	315	48	5.44	77.7	63
p-TolSH/D_2O	7	260	48	1.94	28.0	0
p-TolSH/$RuCl_3$	1.48	260	48	3.59	51.0	5
p-TolSH/DCl	1.47	260	48	3.02	43.0	0
p-TolSH/$RuCl_3$	1.48	315	48	6.58	94.0	34
p-TolSH/DCl	1.47	315	48	6.34	90.6	44
p-TolSH/$FeCl_3$	2.14	250	48	4.69	67.0	8
p-TolSH/DCl	2.13	250	48	4.04	57.7	7
p-TolSH/$CrCl_3$	2.97	250	48	5.00	71.4	17
p-TolSH/DCl	2.97	250	48	3.27	46.7	9
p-TolSH/$FeCl_3$	2.14	315	48	6.52	93.2	59
p-TolSH/DCl	2.13	315	48	6.53	93.3	72
p-TolSH/$CrCl_3$	2.97	315	48	6.53	93.3	43
p-TolSH/DCl	2.97	315	48	6.48	92.6	78

[a] Determined for aqueous reactant prior to addition to organosulfur compound.

[b] Groups of experiments were conducted in same autoclave.

[c] Calculation excludes -SH as -SD back-exchanged to -SH during isolation procedure.

[d] H-D exchange was ascertained to be very similar for these products.

of the residue; yield 95%. This procedure was repeated with sublimed product to increase the D-content to 98%. (Note: further enrichment can be achieved by increasing the amount of D_2O in the system or carrying out further repeats.)

A solution of BT-d_6 (7 g, prepared by the previous procedure) in pentane (50 mL) was placed in an autoclave with Nalco-477 (a commercially available Co-Mo hydrodesulfurization catalyst, 0.07 g). The system was pressurized with D_2 (5.61 MPa at 20°C) and was heated at 350°C for 3 h. Ethylbenzene (80%) was recovered by removing the catalyst by filtration and distillation of the liquid residue. No other product was observed (GC-MS, NMR) leading to the conclusion that the less than quantitative yield was due to transfer losses.

(Note: it is important to dry the catalyst thoroughly as back exchange of water absorbed on the catalyst surface lowers the D-content of the product.)

RESULTS AND DISCUSSION

H-D Exchange in BT and 2,3-DihydroBT

Experiments with BT at or below 150°C resulted in no H-D exchange (Table I). At 200°C and at higher temperatures significant H-D exchange was observed using either the Ru or reference DCl solutions but only minimal D-incorporation was observed using pure D_2O at 260°C over 0.5–24 h reaction times. No significant difference in % of H-D exchange was observed for the Ru and DCl solutions suggesting that it is the acidity of the solutions which controls the degree of exchange. Values close to the theoretical exchange limit were observed in 24 h experiments conducted at 260°C. In addition, high yields (>95%) of deuterated BT were obtained in these experiments. Comparison of the ^1H and ^{13}C NMR spectral data of partially deuterated BT samples to published data for BT[13] showed that the positional order of H-replacement was $3 \approx 2 > 5$. This is the same positional order of reaction of small electrophiles with BT.[16] Thus, the mechanism of H-D exchange with Ru solutions appears to be via simple electrophilic substitution, the deuterons being provided by hydrolysis of water molecules coordinated to the metal.[17] (Note: most transition metal species in dilute aqueous solution are considered to be hexa-aqua solvates.)

$$[M(D_2O)_6]^{3+} \rightarrow [M(D_2O)_5OH]^{2+} + D^+ \qquad M = \text{Ru, Fe or Cr} \tag{1}$$

This hydrolysis process is very well known[17] and proceeds further for most transition metal species yielding a complex mixture of oxide-hydroxy species and further deuterons. Experiments with Ru solutions yielded a black solid (not containing sulfur) with properties similar to ruthenium oxide. Consequently, the hydrolysis constitutes a method of providing the acidic conditions necessary for H-D exchange without having to use expensive D-containing reagents. As is evident from data in Table I, iron salts are equally as effective as ruthenium salts thus providing a very inexpensive way of deuterating aromatic materials.

2,3-DihydroBT (DHBT) is known to form stable complexes with second and third row transition metal species by sulfur atom-metal coordination.[14] Such complexes could affect the deuteration of the compound. Formation of an orange solid on adding DHBT to the Ru solution at 20°C confirmed that a complex was formed. However, it appears that complexation has no effect on H-D interchange since no replacement occurred at the 2- and 3-positions and exchange occurred only at the aromatic ring positions to an extent almost identical to that obtained using the control DCl/D_2O solution (Table I and NMR data). In addition, it appears that the complex did not survive the reaction conditions (260°C) as only a black precipitate of ruthenium oxides was observed after the heating period. Consequently, we conclude that either the complex has no effect on H-D exchange or it did not survive long enough to have any impact D-incorporation. It should be noted that no exchange of the 2,3-dihydro-protons would be expected under simple acidic conditions because of the aliphatic nature of these hydrogens.

Both Fe and Cr solutions promoted H-D exchange in BT and it is clear from experiments done at 250°C over 0.5 h (Table I) that the DCl control solutions were not as effective as their Fe and Cr counterparts. Although it is tempting to explain the superior D-exchange by postulating coordination of the metals to the substrate, it should be remembered that the metal solutions and respective DCl control solutions may only have the same pH at 20°C. Under reaction conditions, the hydrolysis processes represented by equation (1) may proceed further to increase the acidity of the metal solutions in comparison to the control DCl solutions. Evidence that hydrolysis did occur in Fe and Cr experiments was given by the isolation of chromium and iron oxides in all experiments with BT. Use of solutions prepared from Fe(III) and Cr(III) sulfates at 250°C over 30 min. gave results equivalent to those obtained with chloride-based solutions.

Competitive experiments with equimolar amounts of BT and ethylbenzene in D_2O (Table I) illustrate that BT undergoes H-D exchange at a faster rate than the hydrocarbon. This result is likely due to greater reactivity of BT towards electrophiles and was found in experiments using either the Ru solution or its DCl counterpart. Although the degree of D-incorporation in ethylbenzene was small, no evidence (NMR) for H-D exchange in the side-chain was found.

H-D Exchange in Benzenethiols and Methyl Phenyl Sulfide

Since per-deuterated PhSH and toluenethiols could be used to prepare per-deuterated benzene and toluene, it was of interest to examine D-incorporation in these sulfur compounds. Experiments with PhSH showed that Ru and DCl solutions promoted H-D exchange although it was necessary to heat the compound at 315°C over 48 h to achieve the theoretical extent of deuteration. In these reactions, the deuterated compound was not the only product formed, as per-deuterated diphenyl sulfide (40–70%, depending on reaction conditions) was also recovered from the reaction mixture of experiments performed at 315°C. This product is probably formed by *ipso*-attack of the benzenethiolate anion at the sulfur-substituted carbon of another molecule followed by elimination of H_2S. There is ample precedence for this mechanism[18] although formation of diphenyl sulfide could also occur by radical processes. Formation of the phenylthiolate anion by dissociation of PhSH in the aqueous conditions is expected and explains why PhSH undergoes significant deuteration when heated with D_2O alone at 260°C. As would be expected, methyl phenyl sulfide does not undergo H-D exchange with pure D_2O (Table II) but reacts at approximately the same rate as PhSH when the Ru or DCl solutions were used to provide an acidic environment.

Fe and Cr solutions also promoted H-D exchange in PhSH (Table II) and, as was the case in experiments with BT, the Cr solution was more reactive than its reference DCl solution. An interesting feature of the PhSH-Fe solution experiments was that no precipitate of iron oxide was observed at the end of the heating period. Based on literature evidence,[19] we conclude that the iron is held in solution as a thiolate complex although, because of the very small amount of iron used in these experiments, we did not attempt to isolate such a complex. Whether using Ru, Fe, Cr or the reference DCl solutions, NMR analysis of partially deuterated PhSH (from experiments conducted at 250–260°C) showed that deuterium was incorporated specifically at the *ortho-* and *para*-positions. This is further evidence that the mechanism of H-D exchange follows a standard electrophilic pathway.

Similar trends were observed when *o-* or *p*-tolSH was treated with the various D_2O solutions (Table II). Both compounds underwent some exchange with pure D_2O as a result of acidic properties of the -SH group and the Cr solution was more effective than its control DCl solution. In general, *p*-tolSH was more susceptible to reaction such that D-incorporation close to the theoretical value (96%) was achieved by heating at 315°C for 48 h. Less than 90% exchange was observed for the *ortho*-compound at the same reaction conditions. Examination of NMR spectra of products from the deuteration of *o*-tolSH at 315°C showed that it was mostly the methyl group hydrogens which had remained unexchanged. Methyl group hydrogens were more readily exchanged in all experiments using *p*-tolSH. As was the case in experiments with PhSH, deuterated diaryl sulfides were formed in addition to deuterated thiols (Table II). These by-products were formed in highest yield at 315°C representing (depending on reaction conditions) 34–78 and 48–66% of the product mixtures obtained from the reaction of *p-* and *o*-tolSH respectively when using metal catalyst/D_2O solutions.

Since hydrodesulfurization of per-deuterated *p*-tolSH using D_2 would constitute a synthesis of per-deuterated toluene, it was of interest to conduct competitive experiments with *p*-tolSH and toluene to determine if the use of the thiol offers any substantial advantage in terms of rate or improved D-incorporation into the methyl group. These experiments (Table III) showed that D-incorporation was

TABLE III

Competitive experiments with *p*-TolSH and toluene

		250°C - 36h		315°C - 30.5h	
Reactants	pH at 20°C	Mass increase [a]	% Exchange [a]	Mass Increase [a]	% Exchange [a]
DCl	1.0	4.48/4.52 [b]	63.6/56.1	-	-
DCl	1.47	4.23/4.17	60.1/51.9	6.6/6.9	93.3/85.3
DCl	2.13	3.27/2.99	46.4/37.2	6.4/6.8	91.1/84.2
DCl	2.97	1.24/2.7	38.2/15.4	6.2/6.4	88.5/79.4
$RuCl_3$	1.47	4.7/4.4	67.1/54.6	6.6/6.9	93.6/85.7
$FeCl_3$	2.13	4.1/3.6	57.8/45.2	6.5/6.8	91.7/84.1
$CrCl_3$	2.97	4.2/4.0	59.0/50.2	6.4/6.9	91.2/85.4

[a] x/y represent results for p-tolSH and toluene respectively.
[b] Theoretical maximum number of hydrogens exchanged for p-tolSH and toluene is 7 and 8 respectively. Note: S-D completely back-exchanged to S-H before MS analysis.

greater for the thiol using either DCl or metal chloride/D_2O solutions at 250 or 315°C. NMR data indicate that a greater degree of replacement of the methyl group hydrogens occurred for the thiol. Overall, we ascribe the increased reactivity of the *p*-tolSH to the dual activating effect of the thiol and methyl groups as in these competitive experiments both compounds experience the same acidic environment. The data in Table III illustrate the importance of $[D^+]$ on the degree of H-D exchange. It is tempting to couple these data with the amount of exchange obtained using metal chloride solutions at equivalent conditions and so estimate the degree of solvolysis of the metal species at high temperature. However, such an exercise would be invalidated to some extent by dissociation of the thiol, the degree of which is unknown at the reaction conditions.

Conversion of Per-Deuterated Organosulfur Compounds to Per-Deuterated Hydrocarbons

Hydrodesulfurization of organosulfur compounds is a mature technology because of the importance of removing sulfur from fossil fuels.[10] For simple organosulfur compounds, it is usually sufficient to heat the compound with H_2 gas over a Co/Mo oxide mixture supported on alumina at elevated temperatures (350–400°C). Using the per-deuterated BT prepared by the large scale synthesis described in the Experimental Section, per-deuteroethylbenzene was obtained in quantitative yield by treating the BT with D_2 gas over Nalco-477 Co/Mo catalyst at 350°C for 3 h in a standard autoclave system. Preliminary experiments showed that it was necessary to dry the catalyst very thoroughly in order to prevent reduction of D-content as a result of exchange with water absorbed on the catalyst surface. It is anticipated that per-deuterated benzene and toluene could be prepared by desulfurization of per-D PhSH and per-D *p*-TolSH using similar procedures.

CONCLUDING COMMENTS

It has been established that solutions of chlorides of Ru, Fe and Cr in D_2O readily promote H-D exchange in BT and benzenethiols. Although these metal species could coordinate to the sulfur compounds and enhance H-D exchange, it appears that formation of low pH conditions as a result hydrolysis of D_2O molecules solvated with the metal species is the major reason for the efficacy of the metal solutions. Substitution patterns obtained for partially deuterated compounds imply that D-incorporation occurs by standard electrophilic processes. Introduction of deuterium into organosulfur compounds is facilitated by the electron donor properties of the sulfur substituents. Subsequent removal of the sulfur substituent offers a convenient way of producing per-deuterated aromatic hydrocarbons.

ACKNOWLEDGEMENTS

The authors thank Alberta Sulphur Research Ltd. and The Natural Sciences and Engineering Research Council of Canada (NSERCC) for financial assistance and support of the NSERCC Industrial Research Professorship held by PDC.

REFERENCES

1. A. F. Thomas, *Deuterium labeling in organic chemistry*, Meredith Corp., New York, 1971, Chapter 3 for a general review.
2. N. H. Werstiuk and T. Kadai, *Can. J. Chem.*, **51,** 1485 (1973).
3. N. H. Werstiuk and G. Timmins, *Can. J. Chem.*, **59,** 3218 (1981).
4. N. H. Werstiuk and G. Timmins, *Can. J. Chem.*, **63,** 530 (1985).
5. N. H. Werstiuk and G. Timmins, *Can. J. Chem.*, **64,** 1072 (1986).
6. J. W. Larsen and L. W. Chang, *J. Org. Chem.*, **43,** 3602 (1978).
7. N. H. Werstiuk and T. Kadai, *Can. J. Chem.*, **52,** 2169 (1974).
8. N. H. Werstiuk and G. Timmins, *Can. J. Chem.*, **59,** 1022 (1981).
9. G. Fischer and M. Puza, *Synthesis*, 218 (1973).
10. R. J. Angelici, *Accounts of Chemical Res.*, **21,** 387 (1988) and references therein.
11. E. A. Karakhanov and A. G. Dedov, *Khim. Getero. Soed.*, 1011 (1982); *Chemical Abstracts*, **97,** 161873e.
12. E. A. Karakhanov, A. G. Dedov, A. S. Loktev, L. V. Popov, P. A. Sharbatyan and I. V. Arkhangel'skii, *Khim. Getero. Soed.*, 754 (1983); *Chemical Abstracts*, **99,** 87587n.
13. P. D. Clark, D. F. Ewing and R. M. Scrowston, *Org. Magn. Reson.*, **8,** 252 (1976).
14. P. D. Clark, C. J. Jones and M. J. Kirk, *Can. J. Chem.*, **69,** 590 (1991).
15. F. G. Bordwell and W. H. Mckellin, *J. Am. Chem. Soc.*, **73,** 2251 (1951).
16. B. Iddon and R. M. Scrowston, *Adv. Heterocycl. Chem.*, **11,** 191 (1970).
17. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th Edition, Wiley-Interscience, New York, 1980, pp. 66–67.
18. R. D. Hei, P. G. Sweeny and V. I. Stenberg, *Fuel*, **65,** 577 (1986).
19. S. D. Killops and S. A. R. Knox, *J. C. S. Dalton*, 1260 (1978).