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Supplementary Material Available: Tables of nitrate (Table T1) and bound MeCN (Table T2) vibrations in solutions of $Ln(NO_3)_3$ in acetonitrile and figures showing calibration curves for DMSO in acetonitrile (Figure F1) and absorbances of bound and free DMSO in solutions of $Ln(NO_3)_3$ in acetonitrile (Figure F2) (8 pages). Ordering information is given on any current masthead page.

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AM1 Parameters for Sulfur

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AM1 has been parametrized for sulfur. Calculations are reported for a wide range of sulfur-containing molecules. The calculated heats of formation and other properties of organosulfur molecules are much superior to those from MNDO and superior overall to those from PM3. AM1 calculations for several reactions agree well with experimental values. The results for compounds of sulfur in its higher valence states are also satisfactory, except for SF_4, where the error is probably due to the neglect of d AOs.

Introduction

Organosulfur chemistry has developed very rapidly in recent years[1] and now plays an integral role in organic chemistry. New types of structures found recently[2] in organosulfur compounds have enlarged our general knowledge of bonding and the electronic distributions in molecules. Many new reactions of compounds containing sulfur are now widely used in organic synthesis,[3] and many new types of biologically important organosulfur compounds have been discovered.[4]

The need for an effective theoretical treatment of organosulfur compounds is therefore clear. Use of ab initio procedures is restricted in this connection, as in many others,[5] by the computing time they need. Computational studies of chemical problems by adequate ab initio methods are frequently impracticable. These comments apply with special force to studies of chemical reactions, which require not only extensive exploration of potential surfaces but also the use of relatively high-level ab initio procedures, involving the use of split-plus-polarization basis sets and allowance for electron correlation. Sulfur presents more problems than the "organic" elements in this connection because it contains more orbitals and because the formal charge on it varies greatly, becoming very large in its higher valence states (S^{IV}, S^{VI}).

Table I. Optimized AM1 Parameters for Sulfur

optimized params	AM1	MNDO	PM3
U_{ss}/eV	−56.694 056	−72.242 281	−49.895 371
U_{pp}/eV	−48.717 049	−56.973 207	−44.392 583
Z_s/au	2.366 515	2.312 962	1.891 185
Z_p/au	1.667 263	2.009 146	1.658 972
β_s/eV	−3.920 566	−10.761 610	−8.827 465
β_p/eV	−7.905 278	−10.108 433	−8.091 415
α/Å^{-1}	2.461 648	2.478 026	2.269 706
G_{ss}	11.786 329	12.880 000	8.864 667
G_{pp}	10.039 308	9.900 000	9.968 164
G_{sp}	8.663 127	11.260 000	6.785 936
G_{p2}	7.781 688	8.830 000	7.970 247
H_{sp}	2.532 137	2.260 000	4.041 836
K_1	−0.509 195		−0.399 191
K_2	−0.011 863		−0.054 899
K_3	0.012 334		
L_1	4.593 691		6.000 669
L_2	5.865 731		6.001 845
L_3	13.557 336		
M_1	0.770 665		0.962 123
M_2	1.503 313		1.579 944
M_3	2.009 173		

In organic chemistry, these difficulties have been largely solved by the development here of effective parametric ("semiempirical") procedures, in particular MNDO[6] and AM1,[7] which give results comparable[8] with those from quite good ab initio methods at less than one-thousandth of the cost. They are generally much superior to ones using minimum basis sets.[8] However, determined attempts to parametrize MNDO or AM1 for phosphorus or sulfur failed. No set of parameters could be found that gave satisfactory results for compounds containing them in all their valence states. In hindsight, this failure was due to one of the major problems met in developing semiempirical treatments such as AM1, i.e. the fact that the hypersurface representing the mean error as a function of the parameters (*parameter hypersurface*) usually has numerous minima and it is not easy to find the optimum one. While we would normally have continued the search for a better minimum, we were not unnaturally misled by the fact that split-plus-d basis sets have to be used in ab initio studies of compounds of P and S and the natural assumption that the same might be true in AM1. Recently, however, Dewar and Jie[9] succeeded in finding a better minimum on the parameter hypersurface for phosphorus, leading to a set of parameters that reproduced the properties of compounds containing it in both its valence states, and we have now likewise succeeded in finding a set of parameters that deals effectively with the even worse case of sulfur, where *three* valence states are involved. The effect of d AOs can apparently be largely compensated via the parametrization. However, as noted below, there are exceptional molecules where AM1 gives poor results and where the error can reasonably be attributed to d AOs, or changes in AOs, playing an unusually large role. A similar situation exists in the case of anions. In ab initio studies of anions, it is necessary to use a basis set containing diffuse AOs to allow for the orbital expansion due to negative charge. Yet, AM1 gives good results

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(1) Senning, A., Ed. *Sulfur in Organic and Inorganic Chemistry*; M. Dekker Inc.: New York, 1971 and 1982; Vols. 1 and 4.

(2) Kresze, G. In *Sulfur, its Significance for Chemistry, for* the *Geo-, Bio, and Cosmosphere and Technology: New Developments in The Field or Organic Sulfur Chemistry*; Muller, A., Krebs, B., Eds.; Studies in Inorganic Chemistry, Vol. 5; Elsevier Science Publishers: Amsterdam, 1984; pp 93–120.

(3) Bernardi, F.; Csizmadia, I. G.; Mangini, A. *Organic Sulfur Chemistry*; Elsevier Science Publishers: Amsterdam, 1985.

(4) Muller, A.; Krebs, B.; *Sulfur, its Significance for Chemistry, for the Geo-, Bio, and Cosmosphere and Technology*; Elsevier Science Publisher: Amsterdam, 1984; Chapter IV.

(5) See e.g.: Dewar, M. J. S. *Int. J. Quantum Chem.* **1988**, *22*, 557.

(6) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(7) Deward, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(8) (a) Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898. (b) Dewar, M. J. S.; O'Connor, B. M. *Chem. Phys. Lett.* **1987**, *138*, 141.

(9) Dewar, M. J. S.; Jie, C. *THEOCHEM* **1989**, *187*, 1–13.

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Table II. Calculated AM1 and Observed Heats of Formation and Comparison of Errors for AM1, MNDO, PM3, and SINDO1

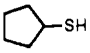
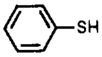
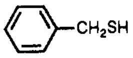
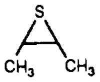
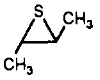
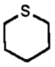
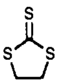
molecule	exp[a]	calcd	error			
			AM1	MNDO	PM3	SINDO1[b]
*CS_2	28.0[c]	17.5	-10.4	8.9	9.0	-19.6 (-19.5)
*CH_3SH	-5.5[c,d]	-4.4	1.1	-1.8	-0.1	5.0 (2.4)
*CH_3CH_2SH	-11.1[c,d]	-10.6	0.5	-2.6	2.3	5.3 (1.1)
$CH_3(CH_2)_2SH$	-16.2[c]	-16.7	-0.5	-1.6	2.1	7.0
$CH_3(CH_2)_3SH$	-21.1[c]	-23.5	-2.4	-1.1	1.6	9.0
$((CH_3)_2CH)SH$	-18.2[c]	-15.6	2.6	2.0	4.8	21.2
$HS(CH_2)_2SH$	-2.2[e]	-3.8	-1.6	-4.2	7.0	5.8
$HS(CH_2)_3SH$	-7.0[e]	-9.5	-2.5	-3.7	3.9	
	-11.4[e]	-20.3	-8.9	-10.6	-2.5	
	-22.9[e]	-29.8	-6.9	-2.8	2.4	
	26.9[c]	25.7	-1.2	-3.5	0.8	
	22.0[c]	22.4	0.4	-1.7	3.0	
$(CH_3)_2S$	-9.0[c]	-9.3	-0.3	-8.1	-2.0	12.6 (8.7)
*$CH_3SCH_2CH_3$	-14.2[c]	-15.6	-1.4	-8.8	0.1	
$CH_3S(CH_2)_2CH_3$	-19.6[c]	-21.6	-2.0	-7.8	1.1	
*CH_3SSCH_3	-5.8[c]	-4.2	1.6	-9.0	1.0	14.7 (10.8)
$CH_3CH_2SSCH_3CH_2$	-17.8[c]	-16.7	1.1	-9.0	6.8	
CH_3SSSCH_3	-3.0[c]	-4.0	-1.0	-9.1	-3.9	14.8
*SCO	-33.9[c]	-29.0	4.9	11.0	10.1	-2.7 (-3.5)
$(CH_3)_2SO$	-34.0[c]	-39.4	-5.2	38.2	-4.7	43.7 (38.9)
*$(CH_3CH_2)_2SO$	-49.1[c]	-51.8	-2.7	40.6	2.5	
*$(CH_3)_2SO_2$	-89.1[c]	-70.3	18.8	142.8	12.8	
*$CH_3(SO_2)CH_2CH_3$	-98.7[e]	-75.8	22.9	146.4	19.7	
$(CH_3CH_2)_2SO_2$	-103.4[c]	-81.2	22.0	143.8	22.4	
$(CH{=}CH)_2SO_2$	-36.4[c]	-25.4	11.0	138.9	12.2	
$(CH_3O)_2SO$	-115.5[c]	-139.3	-23.8	50.4	-14.5	
*$(CH_3O)_3SO$	-164.1	-174.7	-10.6	158.6	-8.0	
$((CH_3CH_2)_2N)_2S_2$	-16.8[f]	-14.6	2.2	9.3	-17.0	
$((CH_3CH_2)_2N)_2SO$	-66.2[f]	-59.2	7.0	65.2	-2.8	
*$CH_3(CO)SH$	-42.2[c]	-39.2	3.0	3.7	5.0	
SCH_2	25.0[c]	29.9	4.9	2.8	2.2	6.4 (7.0)
HNCS	31.0[c]	27.4	-3.6	12.7	8.5	-4.4
*CH_3NCS	31.0[c]	27.6	-3.4	6.1	-2.7	-1.2 (-7.6)
CH_3SCN	38.3[c]	22.1	-16.2	-14.9	-2.2	6.3
CH_3SSH	-0.9[d]	1.9	2.8	-3.3	2.7	
$S_2(CN)_2$	83.6	64.1	-19.5	-12.6	-5.1	8.9
CH_3SCH_2SH	0.1[d]	-3.3	-3.4	-10.4	-1.1	
$NH_2(CS)NH_2$	-6.0	9.9	15.9	15.4	29.9	
*S_4	35.0[c]	41.6	6.6	10.8	20.2	-9.1
*S_8	24.0[c]	15.3	-7.8	-1.1	-5.8	1.6 (-0.7)
	19.6[c]	30.7	11.1	-0.7	9.2	-14.6 (-17.6)
	2.7[e]	17.8	15.1	2.1	13.2	
	0.9[e]	16.8	15.9	3.1	14.3	
* 	14.5	7.2	-7.3	-19.6	-7.1	4.6
* 	8.1[c]	-15.7	-7.6	-16.0	-2.3	14.6
	-15.2[c]	-23.9	-8.7	-12.8	-0.5	
* 	27.5[c]	27.4	-0.1	-1.0	3.2	24.6
	20.9[c]	12.7	-8.2	-16.6	-6.1	
	21.8[h]	10.2	-11.6	-18.0	-8.4	
	22.4[c]	20.6	-1.8	-11.0	17.7	-3.9

Table II (Continued)

			error			
molecule	exp[a]	calcd	AM1	MNDO	PM3	SINDO1[b]
*H_2S	−4.9[i]	1.2	6.1	8.7	4.0	2.4 (1.7)
*H_2S_2	3.7[j]	8.6	4.9	2.8	4.9	1.3
H_2S_3	7.3[j]	7.8	0.5	1.1	19.1	0.3
H_2S_4	10.6[j]	3.1	−7.5	0.0	−10.9	0.1
*H_2S_5	13.8[j]	5.3	−8.5	−0.6	−11.9	0.1
*SO_2	−70.9[d]	−47.0	23.9	75.4	20.2	−8.2 (−8.8)
*SO_3	−94.6[k]	−97.2	−3.4	153.1	−10.2	20.3 (18.9)
*H_2SO_4	−175.6[d]	−186.3	−10.7	162.5	−5.8	−7.8 (−10.0)
*SF_2	−72.4	−102.1	−29.7	19.5	−19.5	−17.2 (−19.2)
SF4	−186.3[d]	−213.1	−26.8	144.5	−5.8	4.1 (−1.3)
SF_6	−291.4[d]	−330.7	−39.3	320.7	−13.2	19.2 (16.2)
*SOF_2	−135.0[k]	−156.2	−21.2	89.3	−3.2	−1.9 (−7.9)
SO_2F_2	−181.3[j]	−195.8	−14.5	203.3	−3.0	28.1 (26.1)
*SCl_2	−5.4[k]	−26.4	−20.8	−18.4	−5.5	0.1
*S_2Cl_2	−4.0[d]	−24.6	−20.6	−16.8	−3.7	−1.2 (−1.0)
$SOCl_2$	−50.8[g]	−64.3	−13.5	28.6	3.2	20.2 (19.5)
SO_2Cl_2	−84.8[g]	−69.3	15.5	129.2	22.5	37.9 (36.4)
SBr_2	−3.0[g]	−2.1	0.9	2.8	−27.9	
S_2Br_2	7.4[g]	−4.4	−11.8	−5.8	−14.4	

[a] Unless otherwise referenced, the experimental values are from: Pdley, J. B.; Rylance, G. Sussex N. P. L. *Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex, Brighton, U. K., 1977. [b] Jug, K.; Iffert, R. *J. Comput. Chem.* **1987**, *8*, 1004. Values listed in the table are errors for heats of formation at 298 K, those for heats of formation at 0 K being given in parentheses. [c] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levins, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. [d] Grabowski, J. J.; Zhang, L. *J. Am. Soc. Chem.* **1989**, *111*, 1193. [e] Mackle, H.; O'Hare, P. A. G. *Tetrahedron* **1963**, *19*, 961. [f] Claydon, A. P.; Mortimer, C. T. *J. Chem. Soc.* **1962**, 3212. Sunner, S. *Acta Chem. Scand.* **1955**, *9*, 847. [g] Barin, I.; Knacke, O.; Kubaschewski, O. *Thermochemical Properties of Inorganic Substances*; Springer-Verlag: Berlin, 1977. [h] Guthrie, G. B.; Scott, D. W., Jr.; G. *J. Am. Chem. Soc.* **1954**, *76*, 1488. [i] Benson, S. W. *Chem. Rev.* **1978**, *78*, 23. [j] *NBS Tables of Chemical Thermodynamic Properties*. [k] *JANAF Thermochemical Tables*, 3rd Ed.; Dow Chemical: Midland, MI, 1985.

Table III. Comparisons of Mean Errors in Various Properties, Given by AM1, MNDO, and PM3

		mean unsigned error (std dev)			
property	no. of molecules	AM1	MNDO	PM3	SINDO1
heats of formn/kcal/mol	41[a]	9.50 (13.24)	38.57 (78.2)	7.35 (9.51)	10.54 (14.62)
	50 (org)	7.04 (9.61)	24.72 (49.07)	6.97 (9.60)	
	69 (total)	9.16 (12.47)	37.96 (73.99)	8.08 (10.75)	
ionization potential/eV	33[b]	0.51 (0.67)	0.69 (0.78)	0.40 (0.57)	0.54 (0.68)
	27 (org)	0.35 (0.42)	0.61 (0.67)	0.31 (0.40)	
	40 (total)	0.47 (0.63)	0.69 (0.77)	0.41 (0.56)	
dipole moment D	17[c]	0.42 (0.80)	0.41 (0.67)	0.46 (0.66)	0.41 (0.64)
	12 (org)	0.21 (0.41)	0.26 (0.40)	0.35 (0.41)	
	19 (total)	0.52 (0.97)	0.49 (0.79)	0.49 (0.68)	

[a] 20 molecules are organic sulfur compounds and 21 molecules are inorganic sulfur compounds which are available for AM1, MNDO, PM3, and SINDO1. [b] 21 molecules are organic sulfur compounds and 12 molecules are inorganic sulfur compounds which are available for AM1, MNDO, PM3, and SINDO1. [c] 11 molecules are organic sulfur compounds and 6 molecules are inorganic sulfur compounds which are available for AM1, MNDO, PM3, and SINDO1.

for the large majority of anions, using the usual parameters. Errors occur only in the case of anions where almost a whole unit of negative charge is concentrated on a single atom.[10]

Stewart has recently described[11] a new version (PM3) of AM1, which he claims to represent a significant improvement and which includes parameters for sulfur. Jug[12] has also extended his SINDO1 semiempirical method to sulfur. The results from both procedures are compared with those for AM1 below.

Procedure

The AM1 parameters for sulfur were determined by minimizing the errors in the values calculated for various properties of a selected set (basis set) of molecules, with the use of standard AM1 parameters[13] for other elements and a recently described optimization procedure.[14] This involves minimizing an error function (SSQ), defined as a sum of the squares of the differences between the individual calculated and experimental values, suitably weighted for different properties. The choice of molecules in the basis set and the values of the weighting factors for different molecular properties are found by trial and error, on the basis of the chemical acceptability of results obtained by using the corresponding parameters. These tests are carried out for a number of additional molecules as well as those in the basis set. The AM1 calculations were carried out by using the AMPAC program.[15]

The minimization of SSQ is effected by a derivative optimization method, based on the Davidon–Fletcher–Powell (DFP) algorithm.[16] The minimization in itself presents no problems. However, the parameter

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(10) See: Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 8075.

(11) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) *Ibid.* **1989**, *10*, 221.

(12) Jug, K.; Iffert, R. *J. Comput. Chem.* **1987**, *8*, 1004.

(13) (a) C, H, N, O.: ref 8. (b) Halogens: Dewar, M. J. S.; Zoebisch, E. G. *THEOCHEM* **1988**, *180*, 1–21.

(14) (a) Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6771. (b) Dewar, M. J. S.; Grady, G. L.; Kuhn, D. R.; Merz, K. M., Jr. *Ibid.* **1984**, *106*, 6773.

(15) Available from: QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47405 (Program No. 506). The calculations reported here were carried out by using a new version (AMPAC 2.1) which has just been submitted to QCPE.

(16) (a) Davidon, W. C. *Comput. J.* **1968**, *10*, 406. (b) Fletcher, R.; Powell, M. J. D. *Ibid.* **1963**, *6*, 163.

Table IV. Calculated and Observed Ionization Potentials (eV) and Dipole moment (D) and Comparison of errors for AM1, MNDO, PM3, and SINDO1

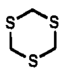
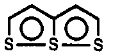
	ionization potential					dipole moment				
		error					error			
	exp[a]	AM1	MNDO[b]	PM3	SINDO1	exp	AM1	MNDO	PM3	SINDO1[c]
CS	11.33	-0.91	-0.24	-0.73	0.27					
*CS2	10.07	-0.69	-0.41	-0.24	-1.03	0.00	0.00	0.00	0.00	0.00
*CH_3SH	9.44	-0.51	0.33	-0.23	0.25	1.52	0.24	0.01	0.43	0.05
*CH_3CH_2SH	9.29	-0.38	0.44	-0.10	0.42	1.52	0.27	0.01	0.46	0.11
$CH_3(CH_2)_2SH$	9.20	-0.33	0.53	-0.01	0.52	1.90	-0.01	-0.41	0.02	-0.26
$CH_3(CH_2)_3SH$	9.14	-0.25	0.59	0.05	0.58					
$((CH_3)_2CH)SH$	9.14	-0.23	0.57	0.08	0.46					
*$CH_3(CO)SH$	10.00	0.02	0.52	0.05						
PhSH	8.30	0.13	0.53	0.48						
$HS(CH_2)_2SH$	9.00[b]	0.03	0.82	0.32	0.77					
$(CH_3)_2S$	8.69	-0.21	0.89	0.17	0.43	1.55	0.02	0.02	0.41	0.00
*CH_3SSCH_3	8.71	0.36	1.07	0.69	0.27	1.98	0.19	-0.09	0.59	-0.14
$S_2(CN)_2$	10.50	-0.12	0.74	0.06	-0.57	1.98	-0.02	-0.34	0.02	0.73
SC_2H_4	9.05	-0.18	0.61	0.18	0.11					
*SC_3H_6	8.69	-0.13	0.84	0.26	0.64					
*SC_4H_8	8.47	-0.12	0.98	0.32	0.76					
SC_4H_4	8.87	0.35	0.64	0.67	0.10	0.53	-0.19	0.01	0.40	0.15
S_3C_5	8.11[b]	0.49	1.00	0.64						
HNCS	9.94	-0.47	-0.23	-0.56	-0.67					
*CH_3NCS	9.25	-0.12	0.21	-0.08	-0.46	4.03	-1.34	1.00	-0.64	-1.87
CH_3SCN	9.96	-0.73	0.33	-0.28	-0.46					
CH_3CHS	8.98	-0.34	0.89	0.08						
SCH_2	9.34	-0.67	0.12	-0.28	-0.24	1.65	0.19	0.20	0.42	0.13
$S{=}C{=}CH_2$	8.77	-0.38	0.46	0.04	-0.36					
*SCO	11.17	-0.40	-0.66	-0.46		0.71	-0.03	-0.31	-0.33	
*$SO(CH_3)_2$	9.01	0.52	0.79	0.34	-0.07	3.96	-0.01	0.67	0.53	-1.07
$C_3H_4S_3$	8.40	0.45	1.05	0.85						
SH	10.37	0.05	0.81	-0.58	-0.07					
*SH_2	10.45	-0.96	-0.46	-0.82	0.14	0.79	0.89	0.51	-0.80	0.66
*S_2H_2	9.30	0.31	0.92	0.56	0.25					
*SF_2	10.08	-1.09	0.66	-0.27	0.22	1.05	0.28	0.88	-0.06	0.21
SF_6	15.33	0.83	1.05	1.06	0.69					
*S_2F_2	10.62	-0.76	0.53	-0.15	-0.42	1.45	-0.83	0.09	-0.76	-0.01
SSF_2	10.41	-0.23	-0.25	-0.42		1.03	2.65	2.03	1.16	
*SCl_2	9.45	-0.10	1.25	0.24	0.34	0.36	-0.33	0.61	0.23	0.77
$SOCl_2$	10.96	0.23	1.38	-0.31	-0.62					
SO_2Cl_2	12.05	1.35	1.44	-1.50	-0.94					
*SO_2	12.32	-1.83	-0.46	-1.76	-1.86	1.61	2.68	2.12	2.02	-0.79
*SO_3	12.80	1.46	0.36	0.21	-1.09					
*S_8	9.04	0.26	1.51	0.05	-1.71	0.00	0.00	0.00	0.00	0.00

[a] Lias S. G.; Bartmess J. E.; Liebman J. F.; Holmes J. L.; Levins R. D.; Mallard W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. [b] Dewar, M. J. S.; McKee, M. L. *J. Comput. Chem.* **1983**, *4*, 84. [c] Jug, K.; Iffert, R. *J. Comput. Chem.* **1987**, *8*, 1004.

Table V. Comparison of Higher Ionization Potential[a] Given by Various Methods

molecule	point group	assgnt	exp	AM1	MNDO[b]	ab initio	molecule	point group	assgnt	exp	AM1	MNDO[b]	ab initio
SH_2	C_{2v}	b_1	10.50[c]	9.49	10.65	10.35[d]	S_2N_2	D_{2h}	b_{2g}	10.52[n]	9.81	10.81	10.41[o]
		a_1	13.50	12.23	13.88	13.45			b_{3g}	10.86	10.87	11.48	10.80
		b_2	15.30	15.41	15.73	16.07			b_{3u}	11.05	11.02	11.94	12.29
		a_2	27.00	29.71	23.01	26.63			b_{2u}	12.30	11.98	14.01	13.39
CH_3SH	C_s	a″	9.44[e]	8.93	10.33	9.57[d]			a_g	14.40	13.84	15.48	14.40
		a′	12.08	11.51	12.87	12.49			b_{1u}		16.32	16.05	16.77
		a′	13.67	13.50	14.02	14.43			b_{1g}		18.20	18.46	
		a″	15.00	14.62	14.94				a_g		20.33	21.17	
		a′	15.63	15.50	16.01	16.01	CS_2	$D_{\infty h}$	π_g	10.07[p]	9.38	10.59	9.68[q]
CH_3SCH_3	C_{2v}	b_1	8.68[f]	8.48	10.07	9.03[f]			π_a	12.69	12.78	14.38	12.84
		a_1	11.35	11.03	12.20	11.30			$\Sigma^+{}_u$	14.47	13.92	15.36	14.18
		b_2	12.75	12.65	13.32	13.29			$\Sigma^+{}_g$	16.18	14.91	18.83	16.06
		a_2	14.25	13.73	14.34	15.49	COS	$C_{\infty h}$	$^2\pi$	11.18[r]	10.77	10.51	10.83[q]
		b_2	14.90	14.80	15.26	15.63			$^2\pi$	15.52	13.73	14.95	15.69
		a_1	15.50	14.94	15.17	16.44			$^2\Sigma$	16.04	17.09	16.65	15.64
		b_1	15.50	15.11	15.32	16.44			$^2\Sigma$	17.90	19.08	19.36	17.87
$S(CN)_2$	C_{2v}	b_1	11.32[g]	9.88	11.41	10.70[h]			$^2\Sigma$	27.40	28.49	28.88	26.13
		a_1 (b_2)	13.20	12.58	13.83	10.91			$^2\Sigma$	35.80	40.54	44.93	35.80
		b_2 (a_1)	13.59	13.92	13.93	13.83	$S{=}CH_2$	C_{2v}	b_2	9.38[s]	8.67	9.98	9.44[s]
		a_2	14.22	14.50	14.27	13.77			b_1	11.76	12.31	11.82	11.25
		a_1 (b_2)	14.02	15.10	15.21	15.87			a_1	13.85	12.55	14.39	14.62
		b_2 (a_1)	15.02	15.30	15.22	17.37			b_2	15.20	15.64	15.99	17.40
		b_1	16.50	15.86	15.57	18.19			a_1	19.90	17.93	21.52	21.97
		a_1	19.70	16.88	18.41	18.24			a_1		30.43	32.06	
		b_1	23.00	22.99	22.29								
		b_1		26.09	29.10								

Table V (Continued)

molecule	point group	assgnt	exp	AM1	MNDO[b]	ab initio
SCl_2	C_{2v}	b_1	9.67[i]	9.35	11.04	10.03[i]
		b_2 (a_1)	12.19	12.14	13.33	12.75
		a_1 (b_2)	12.19	12.87	13.39	12.69
		a_2	12.45	13.29	13.73	13.41
		b_1	13.91	14.87	15.25	15.37
		a_1	14.67	14.88	16.20	15.63
		b_2	15.70	17.85	17.85	16.49
		a_1	21.00	20.71	24.78	24.34
HSSH	C_2	b	10.01[j]	9.60	10.75	9.62[k]
		a	10.28	10.03	11.12	9.46
		a	12.62	12.34	11.66	12.57
		b	14.02	13.82	15.49	14.48
		a	15.20	15.77	16.25	15.14
		b		18.70	23.01	
CH_3SSCH_3	C_2	b	9.01[l]	9.07	10.19	
		a	9.28	9.21	10.69	
		b	11.30	11.07	12.41	
		a	12.32	12.64	13.91	
		b	13.50	13.54	14.06	
		a		14.30	14.72	
		b		14.86	15.17	
		a	14.80	14.88	15.24	
		b		15.66	16.11	
		a	18.30	16.81	21.37	
		b	21.40	19.52	24.55	
FSSF	C_2	a	10.84[j]	9.98	11.71	11.93[j]
		b	11.25	11.56	11.84	12.39
		a	12.94	13.98	13.41	13.86
		b	15.11	15.58	16.38	16.91
		a	15.60	16.45	16.74	18.55
		b	(16.0)	16.94	16.74	18.73
		a	(16.5)	17.00	17.33	19.30
		b	17.26	18.65	17.49	19.35
		a	(18.0)	20.35	18.73	19.90
		b	(20.0)	21.61	23.76	24.55
ClSSCl	C_2	a	(10.1)[j]	9.98	11.45	11.02[j]
		b	(10.3)	10.09	11.45	11.30
		a	11.43	11.33	12.60	12.32
		b	12.20	13.22	13.86	13.59
		a	12.52	13.67	14.35	14.05
		b	(12.60)	13.69	13.39	14.13
		a	14.07	14.91	15.83	15.88
		b	15.65	15.19	16.62	16.05
		a	(17.02)	18.13	17.95	16.72
		b	(19.3)	19.81	23.77	23.29
$HSCH_2SH$	C_2	b	9.42[m]	9.11	10.47	
		a	10.49	9.28	10.76	
		b	11.90	11.59	12.80	
		a	13.40	11.99	14.43	
$S{=}CH(CH_3)$	C_2	a′	8.98[t]	8.64	9.87	
		a″	10.87	11.40	11.41	
		a′	12.74	12.08	13.45	
$S{=}C(CH_3)_2$	C_{2v}	b_2	8.60[t]	8.59	9.78	
		b_1	10.46	10.97	11.07	
		a_1	12.40	11.95	13.24	
$S{=}C{=}CH_2$	C_{2v}	b_1	8.89[u]	8.39	9.23	8.89[u]
		b_2	11.32	11.62	11.68	11.44
		b_1	12.14	12.96	13.15	13.65
		a_1	14.55	13.64	15.19	15.92
		b_2	(15.50)	15.48	15.61	17.03
		a_1	(17.20)	16.74	19.05	19.49
SC_2H_4	C_{2v}	b_1	9.03[f]	8.87	10.17	9.36[f]
		b_2	11.37	11.89	12.46	11.51
		a_1	11.93	12.14	12.26	11.71
		a_2	13.51	13.00	13.77	14.91
		a_1	15.33	14.42	15.66	16.43
		b_1	16.58	16.71	16.62	18.50
SC_4H_4	C_{2v}	a_2	8.90[v]	9.22	9.51	9.3[w]
		b_1	9.50	9.55	9.95	9.31
		b_1	12.70	11.67	12.83	12.92
		b_2	13.30	13.16	13.79	14.23
		a_1	13.90	13.33	13.88	14.69
		b_2	14.30	13.83	14.39	15.86
		a_1	16.60	16.38	17.37	19.10
		b_2	17.60	18.40	20.69	20.41
		a_1	22.10	25.03	27.05	26.83
	C_{3v}	e	8.83[r]	8.73	10.58	
		a_1	9.27	8.99	10.53	
		e	11.22	11.38	12.65	
		e	13.07	13.32	14.08	
		a_1	14.91	15.50	15.27	
		a_2	16.06	15.64	15.92	
	C_{2v}	a_2	8.11[x]	8.60	9.11	
		b_2	8.27	9.01	9.43	
		b_1	9.58	10.31	10.62	
		b_1	10.01	10.71	11.17	
		a_2	10.64	12.06	12.43	
		b_1	11.10	12.65	13.29	
S_8	D_{4d}	a_1 (e_3)	9.23[y]	9.30	11.02	10.01[z]
		e_3 (a_2)		10.14	11.21	
		e_2 (b_2)	9.47	10.55	11.66	10.22
		e_1 (e_1)	9.83	10.78	12.14	10.99
		b_2 (a_1)	10.12	12.97	13.04	11.07
		e_1	11.35	13.57	14.60	12.71
		e_2	12.54	13.66	15.40	
		a_1	13.47	14.90	15.76	
		b_1	14.08	15.42	17.20	
		e_3		16.21	17.30	

[a] Calculated via Koopmans' theorem. [b] Dewar, M. J. S.; McKee, M. L. *J. Comput. Chem.* **1983**, *4*, 84. [c] Reference 25. [d] Reference 26. 4-31G**. [e] Reference 27. [f] Reference 28. 4-31G. [g] Reference 29. [h] Reference 30. 4-31G. [i] Reference 31. [(10s6p)/s(4,1,1,1,1,11)p(3,1,1,1)] for S and Cl. [j] Reference 32. 4-31G. [k] Reference 33. DVGF/6-31G**. [l] Reference 34. [m] Reference 35. [n] Reference 36. [o] Reference 37. S(12s9p)/N(.s5p)/MRD-CI. [p] Reference 38. [q] Reference 39. [(9s6p3d/4s2p) for C and (11s7p3d/6s4p) for S]. [r] Reference 40. [s] Reference 41. [t] Reference 42. (9s5p2d) for C, (11s7p2d) for S, and (5s,1p) for H. [u] Reference 43. (9s5p1d) for C, (11s7p1d) for S, and (5s1p) for H. [v] Reference 44. [w] Reference 45. (7s3p) for C, (10s6p1d) for S, and (4s1p) for H. [x] Reference 46. [y] Reference 47. [z] Reference 48. spd-basis (192 G) by CI.

hypersurfaces, corresponding to plots of SSQ vs the parameters, usually have numerous local minima, and the one found by minimizing SSQ depends on the choice of initial values for the parameters. It is impossible to tell whether or not a given minimum is the global minimum, and there is also no systematic way to pass from one minimum to another. Much therefore depends on the availability of effective tests, which can be provided only by results for additional molecules and/or properties that are not used in the parametrization. The development of effective procedures of this kind thus depends on chemical judgment.

The experimental values used in the present work included the heats of formation, ionization energies, and dipole moments of the basis set molecules together with 31 bond lengths, 30 bond angles, and 17 dihedral angles. It became clear at an early stage that the errors for organic and inorganic sulfur compounds were largely complementary, a reduced error for one being obtained only at the expense of an increased error for the other. Since our main concern was to provide an interpretation of organic sulfur chemistry, we increased the weighting for the organic molecules in our final parametrization.

Results and Discussion

A. Parameters. Table I shows the final set of parameters for sulfur in the standard[7] notation. MNDO[6] and PM3[11] parameters are listed for comparison to show the changes that have been made to accommodate both the low- and high-valence states of sulfur.

The large differences between the AM1 parameters and those for MNDO and PM3 indicate that they refer to different minima on the corresponding parameter hypersurfaces. Indeed, an alternative set of AM1 parameters, similar to those in the other two methods, was obtained by using the MNDO ones as the starting values in the optimization. While there are also significant differences between the MNDO and PM3 parameters, these may be due to the use of a different core repulsion function. Our values for U_{ss} and U_{pp} are much less negative than the MNDO ones, while the PM3 values are even less negative than ours. This change offsets the increase in the electron-electron and core-core repulsions in S^{IV} and S^{VI}, due to the additional bonds. The AM1 values for the resonance integral parameters, β_s and β_p, differ greatly, β_p being more than double β_s. In MNDO and PM3, β_s was slightly larger than β_p. We found this change necessary to obtain good estimates of geometries. Our values lead to greater p character in bonding interactions and hence to smaller bond angles. The one-center two-electron parameters (g_{ij} and h_{ij}) have also been revised from the Oleari values[17] used previously in MNDO.

B. Heats of Formation. Experimental and calculated (AM1) heats of formation (ΔH_f) for 69 neutral molecules are listed in Table II, together with a comparison of the errors in the values given by AM1, MNDO, PM3, and SINDO1. The other three methods clearly all represent a dramatic improvement over MNDO, the errors for compounds containing S^{IV} or S^{VI} being reduced by more than 1 order of magnitude. Problems arise in the case of SINDO1 because it was parametrized to reproduce heats of formation at 0 K whereas the other procedures were parametrized for heats of formation at 298 K. Since few experimental values are available for 0 K, both errors are listed for SINDO1, those for heats of formation at 0 K being given in parentheses. It will be seen that, overall, the differences are small.

Table III shows a statistical comparison of the AM1, MNDO, PM3, and SINDO1 results for the compounds listed in Table II. While AM1 is a little better than PM3 in the case of the low-valent organic sulfur molecules, the reverse is true for high-valent inorganic ones. Overall, there is little to choose between the two methods, so far as this set of molecules is concerned. Both are of course much superior to MNDO because of the failure of MNDO to account for the properties of hypervalent sulfur compounds. SINDO1 performs better for inorganic compounds of sulfur and less well for organic ones.

It should be noted that Stewart included[11] results for a number of sulfur-iodine molecules. Finding that AM1 performed less well for these, we checked Stewart's reference[18] to his quoted experimental values. It turned out that these were in fact derived from an unsubstantiated theoretical treatment, not from experiment. In fact, no thermochemical measurements seen to have been reported for molecules of this kind.

Note that the AM1 parameters were determined by using a basis set of the 27 molecules marked with asterisks in Table II. The results for the other 42 thus serve as an independent check. If all available data are used for determining parameters, the ability of the resulting procedure to deal with other kinds of situations remains uncertain.

The average unsigned error (7.0 kcal/mol) in the AM1 ΔH_f for the 50 organosulfur compounds is smaller than the corresponding errors for other second-row elements (aluminum, 12.4 kcal/mol;[19] silicon, 7.5 kcal/mol;[20] phosphorus, 11.0 kcal/mol[9]). The Am1 errors for organosulfur species exceeded 20 kcal/mol in only three cases, i.e. methyl ethyl sulfone ($MeSO_2Et$, 22.9 kcal/mol), diethyl sulfone (Et_2SO_2, 21.4 kcal/mol), and dimethyl sulfite ($(MeO)_2SO$, −23.8 kcal/mol).

C. Dipole Moments and Ionization Energies. Table IV compares the calculated (AM1) first ionization energies and dipole moments with experimental values, while Table III provides a statistical comparison of the AM1 results with those from MNDO, PM3, and SINDO1. The ionization energies were estimated by using Koopmans' theorem.[21] Table IV also lists errors in the values given by MNDO, PM3, and SINDO1. The mean unsigned error in the AM1 ionization energies for 27 organosulfur compounds (0.35 eV) is comparable with that (0.35 eV[8]) for compounds of the "organic" elements. The corresponding error for all 40 sulfur-containing compounds is 0.47 eV, which is less than those for compounds of other second-row elements calculated by using AM1 (Al, 0.82 eV;[19] Si, 0.59 eV;[20] P, 0.70 eV[9]). The improvement is due mainly to the use of different values of ζ and β for the s and p AOs in AM1. Similar comments apply to PM3, the errors from which are a little less than those from AM1. Again, AM1 gives a better prediction for organic sulfur compounds as compared to SINDO1 than for inorganic compounds. SINDO1, however, is better at calculating properties of inorganic compounds.

Table VI. Calculations for Cations and Anions

	heat of formn/kcal/mol			
molecule	obsd[a]	AM1 error	MNDO error	PM3 error
HS^+	272.4	51.1	26.2	48.5
H_3S^+	190.0	−8.1	22.2	−14.4
$HSCH_2^+$	206.0	−5.7	10.5	8.7
$CH_3SH_2^+$	173.0	−4.7	24.7	−6.0
$HS(CH_3)_2^+$	156.0	0.0	28.0	−7.6
CH_3S^+	215.0	−14.7	48.3	65.1
PhS^+	254.0	1.4	−5.1	17.1
av unsigned error		12.2	23.6	23.9
CH_3S^-	−14.3	−2.6	−0.6	0.5
$CH_3CH_2S^-$	−21.5	−2.1	1.4	−5.0
CH_3SS^-	−23.5[b]	−1.2	0.7	−9.7
$CH_3SCH_2S^-$	−15.7[c]	−12.9	−12.3	−16.6
H_2CS^-	13.4	−10.4	−5.6	−14.0
av unsigned error		5.8	4.1	9.2

[a] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levins, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. [b] Baer, T. Report No. DOE/ER/10641-1; Order No. DE83013717; 18 pp. Available NTIS from: *Energy Res. Abstr.* **1983**, *8* (18); Abstr. No. 44350. [c] (1) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23. (2) Benson, S. W. *Thermodynamical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

The mean unsigned error (0.21 D) in the dipole moments for 12 organosulfur compounds is not only less than those for Al (0.63 D[19]), Si (0.35 D[20]), and P (0.77 D[9]) but similar to that (0.21 D[7]) obtained for compounds of the "organicσqt elements by using AM1. The corresponding error (0.52 D) for all 19 sulfur-containing compounds is also less than the corresponding error for P (0.72 D[9]). In this case, AM1 is again better than PM3 and SINDO1 for the organic compounds while the others are better for the inorganic ones.

Large errors are seen only in the case of SO_2 (2.68 D) and SSF_2 (2.65 D). These are presumably due to the neglect of d AOs. While inclusion of d AOs has no major effect on the ab initio energies of sulfur compounds, it greatly reduces the polarity of molecules containing sulfur in its higher valence states. A comparable error (2.02 D) appears in the PM3 value for SO_2, presumably for the same reason.[23]

Table V compares the calculated and observed orbital energies for some sulfur-containing molecules with vertical ionization energies derived from photoelectron spectroscopy (PES) and with ab initio orbital energies. AM1 seems to perform well in this connection, reproducing all the higher vertical ionization energies

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Table VII. Calculations for Thiosulfonium Ions

	heat of formn error/kcal/mol											
		ΔH_f(M)			$\Delta H_f(MH^+)$			$\Delta H_f(MCH_3^+)$			$\Delta H_f(MSCH_3^+)$	
M	exp[a]	AM1	PM3	exp[a]	AM1	PM3	exp[a]	AM1	PM3	exp[b]	AM1	PM3
H_2S	-4.9	6.1	4.0	190	-8.1	-14.4	173	-4.7	-6.0			
CH_3SH	-5.4	1.1	-0.1	173	-4.7	-6.0	156	-0.0	-7.6	164	-6.0	5.9
CH_3SCH_3	-8.9	-0.4	-2.1	156	-0.0	-7.6	138[b]	6.0	119	145	15.0	21.9
CH_3SSCH_3	-5.8	1.6	1.0	164[b]	-6.0	5.9	145[b]	15.0	21.9	150	19.6	23.3

[a] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levins, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. [b] Kim, J. K.; Bonicamp, J.; Caserio, C. *J. Org. Chem.* **1981**, *46*, 4230–4236.

Table VIII. Calculations for Radical Cations[a]

	heat of formn/kcal/mol			
molecule	obsd[b]	AM1 error	MNDO error	PM3 error
$H_2S^{\bullet+}$	236.0	-18.0	9.7	-3.4
$CH_3SH^{\bullet+}$	212.3	-13.6	13.7	-7.9
$S(CH_3)_2^{\bullet+}$	191.0	-11.0	17.0	-1.6
$CS_2^{\bullet+}$	260.0	-30.2	11.0	2.3
$SCO^{\bullet+}$	224.0	-9.4	-12.8	-6.8
$SC_4H_4^{\bullet+}$	232.0	-0.1	6.5	13.8
av unsigned error	13.7	11.8	6.0	

[a] Calculated using the half-electron approximation. [b] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levins, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

apparently in the correct order and in reasonably good agreement with experimental values. The numberical results seem clearly superior to those given by MNDO and somewhat better than the ab initio values cited. Comparisons of this kind, however, are somewhat dubious because there the experimental ionization energies cannot usually be assigned on the basis of experiment alone. As Heilbronner has emphasized,[22] lining up the experimental and theoretical values is essentially meaningless in this connection, comparable correlations being given by sets of random numbers.

D. Ions and Radicals. Table VI shows the ΔH_f calculated by AM1 for some sulfur-containing cations and anions for which experimental data are available. The AM1 results are generally satisfactory, the results for anions being better than those for cations and the errors for both being much less than those given by MNDO or PM3. The very large AM1 error (51.1 kcal/mol) for HS^+ can be attributed to the use of a minimum basis set in AM1.[10]

Table VII compares the calculated (AM1) and observed ΔH_f for a number of sulfonium and thiosulfonium ions. The average error is less than 10 kcal/mol, which suggests that AM1 may prove useful in interpreting the behavior of such species.

Table VIII compares with experimental values the ΔH_f calculated by AM1 and MNDO for some sulfur-containing radical cations. The calculations were carried out by using the "half-electron" approximation[24] with 3 × 3 CI, the default procedure for open shell systems in AMPAC.[15] The average error for PM3 is less than that for AM1. Again, AM1 gives a better prediction for organic sulfur compounds as compared to MNDO. The large error for CS_2^+ can be presumably attributed to the neglect of d AOs.

E. Molecular Geometries. Table IX shows the geometries calculated by AM1 for 53 organic and 18 inorganic sulfur compounds for which experimental geometries are available. The experimental values are shown in parentheses. Table X compares the AM1 geometries for some organosulfur compounds with experimental values and with values calculated by the 6-31G* ab initio model, with and without allowance for electron correlation by third-order Moller–Plesset perturbation theory. While the ab initio values are clearly better, particularly at the MP2 level, the AM1 results are good enough for most purposes and they can of course be obtained at far less cost.

Table XI shows a statistical comparison of the mean errors in the AM1 bond lengths and bond angles for sulfur-containing compounds with the corresponding errors for MNDO and PM3. The AM1 and PM3 errors are less than those for MNDO. Since the AM1 values for the bond lengths are systematically too small, better estimates can be obtained by applying appropriate empirical corrections.

The only large error in the AM1 result is the incorrect prediction that SF_4 is tetrahedral, due undoubtedly to the neglect of d AOs in AM1. While PM3 seems at first sight to do better, predicting a geometry of the correct general shape, it gives much too small a value for the $F_{ax}SF_{ax}$ angle (140° vs 173.1° (obsd)). This difference between AM1 and PM3 reflects the difference between the corresponding ratios of the resonance integral parameters (β_s/β_p); see Table I and the discussion concerning it above.

Table XII shows the results of AM1 and MNDO calculations for some "nonclassical" molecules whose structures have been determined by electron diffraction and X-ray crystallography. While AM1 gives better estimates of the bond lengths, both models reproduce the essential geometries of these unusual molecules in a satisfactory manner.

Conclusions

The results reported here suggest that AM1 can, when properly parametrized, reproduce the properties of compounds of sulfur

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Table IX. Calculated and Observed Geometrical Parameters

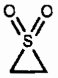
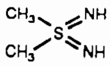
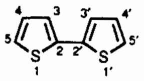
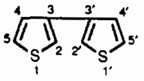
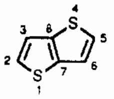
molecular	point group	geometries calcd (obsd)	ref[a]
*SH_2	C_{2v}	SH 1.323 (1.335), HSH 95.5 (92.2)	
*CH_3SH	C_s	SC 1.754 (1.819), SH 1.322 (1.335), CSH 99.6 (96.5)	*f*
*CH_3CH_2SH	C_s	SC 1.774 (1.820), SH 1.318, CSH 99.3	*f*
$(CH_3)_2CH_2SH$	C_s	SC 1.773, SH 1.321, CSH 99.1	
$CH_3(CH_2)_2SH$	C_s	SC 1.775, SH 1.320, CSH 99.1	
$CH_3(CH_2)_3SH$	C_s	SC 1.774, SH 1.309, CSH 99.0	
*CH_3COSH	C_s	SC 1.726, SH 1.323, CSH 101.6, HSCO 180.0	
CH_3CSH	C_s	CC 1.476 (1.506), CS 1.526 (1.610), CH 1.110 (0.098), CCS 1.27.1 (125.3)	
*HNCS	C_s	SC 1.473 (1.560), SCN 170.7, SCNH 180.0	*f*
PhSH	C_s	SC 1.696, SH 1.322, CSH 100.0, HSCC 0.0	*f*
$HSCH_2C'H_2S'H$	C_s	SC 1.775 (1.819), SH 1.322, S′H 1.326, CSH 99.4, CS′H 99.7, SCC 107.7, S′CC 114.4, SCCS′ 115.6	
*$CH_3SC'H_2CH_3$	C_s	SC 1.752 (1.806), SC′ 1.776 (1.818), CSC′ 101.9 (97.1), SC′C3 108.1 (11.4.0), CSC′C3 180.0	
$CH_3SC'HCH_2$	C_s	C′C 1.332 (1.341), CS 1.689 (1.747), SC′ 1.752 (1.794), CC′S 122.8 (127.5), CSC′ 102.7 (102.5)	*b,c*
$CH_3SC'HC{=}CH_2$	C_s	SC 1.749 (1.800), SC′ 1.678 (1.745), CSC′ 106.3 (98.1), SC′C 129.6 (125.4)	
$S(CH_3)_2$	C_{2v}	SC 1.750 (1.802), CSC 102.9 (99.91)	*f*
$S(CN)_2$	C_{2v}	SC 11.618 (1.701), CN 1.169 (1.163), CSC 103.1 (98.3), SCN 176.5 (175.0)	*f*
*S_2H_2	C_2	SS 2.107 (2.055), SH 1.325 (1.327), HSS 98.8 (91.3), HSSH 99.5 (90.6)	*e, f*
*CH_3SSCH_3	C_2	SS 2.107 (2.022), SC 1.752 (1.802), CSS 106.1 (104.1), CSSC 93.5 (84.7)	*f*
*$S_2(CN)_2$	C_2	SS 2.130, SC 1.608, CSS 105.2, SCN 176.9, CSSC 89.9, NCSS 173.8	
CH_3SSSCH_3	C_2	SS 1.955 (2.042), SC 1.756 (1.780), SSS 123.0 (104.0), CSS 109.7 (104.0), CSSS 104.8	
HSSSH	C_2	SS 1.949, SH 1.329, SSS 126.0, SSH 105.2, SSSH 85.4	*d*
HSSSSH	C_2	S_1S_2 1.952, S_2S_3 1.747, SH 1.325, SSS 141.7, SSH 105.2, SSSS 178.7, SSSH 0.1	*d*
HSSSSSH	C_2	S_1S_2 2.090, S_2S_3 1.953, SSS 111.3, SSH 99.3	
*SC_2H_4	C_2	SC 1.791 (1.815), CSC 49.1 (48.5), SCH 117.9, HCCS 110.6	*f*
*SC_3H_6	C_2	SC 1.809 (1.847), CSC 79.1 (76.8), SCH 113.0, CCSC 0.0 (26.2), HCSC 117.0	
SC_4H_8	C_2	SC 1.769 (1.839), CSC 96.7 (93.4), SCH 121.7, CCS 109.8 (106.1), CSCC 0.0, HCSC 121.0	
*SC_4H_4	C_{2v}	SC 1.674 (1.714), CSC 93.8 (92.2), SCH 122.7, CCS 111.5, CSCC 0.0, HCSC 180.0, C=C 1.377 (1.369), CC 1.432 1.423)	*f*
*CS_2	$D_{\infty h}$	SC 1.459 (1.553), CSC 180.0	*f*
$S{=}CH_2$	C_{2v}	SC 1.511 (1.611), CH 1.106 (1.096), HCH 109.3 (116.2)	*f*
$S{=}C{=}CH_2$	C_{2v}	SC 1.440 (1.554), CC 1.311 (1.314), CH 1.098 (1.090), HCH 115.1 (120.3)	
$S{=}CH(NH_2)$	C_2	SC 1.571 (1.626), CN 1.351 (1.358), NH 0.991 (0.990), CH 1.116 (1.120), SCN 127.5 (125.3), SCH 120.6 (127.0)	*f*
$S{=}C(NH_2)$	C_{2v}	SC 1.63 (1.72), CN 1.38 (1.34), NH 0.99 (0.85), SCN 120.5 (120.5), NCN 119.1 (119.0)	*g*
*$SC(CH_3)_2$	C_{2v}	SC 1.538, CCS 123.6, CCSC 180.0, HCCS 2.3	
SCF_2	C_{2v}	SC 1.560 (1.589), CF 1.346 (1.317), FCF 102.4 (107.1)	
$SCCl_2$	C_{2v}	SC 1.521 (1.602), CCl 1.713 (1.728), ClCCl 110.7 (111.2)	
$SCBr_2$	C_{2v}	SC 1.505 (1.597), CBr 1.890 (1.894), BrCBr 109.2 (111.6)	
SCFCl	C_s	SC 1.545 (1.593), CF 1.350 (1.339), CCl 1.739 (1.718), FCCl 111.1 (127.3)	
*CH_3SCN	C_s	SC 1.472, SCN 170.5, SCNC 180.0	
*SCO	$C_{\infty v}$	SC 1.458 (1.560), SCO 180.00, CO 1.201 (1.157)	*f*
*$(CH_3)_2SO$	C_s	SO 1.491 (1.485), SC 1.740 (1.799), CSO 105.7 (106.7), CSC 99.7 (96.6), SCH 110.8 (108.3), CSOC 103.4	*f*
	C_{2v}	SO 1.478 (1.483), CC 1.489 (1.504), CSC 49.8 (48.8), CD 1.769 (1.731), OSC 110.2 (110.0)	*f*
*$(CH_3)_2SO_2$	C_{2v}	SO 1.400 (1.431), SC 1.690 (1.771), CSC 99.5 (103.3), CSO 110.0, OSO 117.6 (117.9), OSOC 125.7	
	C_{2v}	SO 1.381 (1.439), CC 1.512 (1.590), OSO 118.5 (121.4), CS 1.674 (1.731), CSC 53.754.7 (53.7)	
*$CH_3SO_2C_2H_5$	C_s	SO 1.400, SC 1.700, CSC 100.1, CSO 109.4, OSO 117.3, CCS 113.8, OSOC 116.2, CCSC 78.1	
*$(CH_3CH_2O)SO_2$	C_2	SO 1.398, SC 1.732, CSC 95.8, CSO 110.4, OSO 117.4, CCS 107.7, CCSC 0.0	
$(CH_3O)_2SO$	C_2	S=O 1.432, SO 1.687, O=SO 101.5, OSO 98.5, COS 121.4, COSO 23.9, OSOO 101.2	
$(CH_3O)_2SO_2$	C_2	S=O 1.348 (1.419), SO 1.640, O=S=O 126.8, OSO 97.4, COS 122.9	
	C_{2v}	SN 1.656 (1.631), NC 1.318 (1.328), CC 1.477 (1.418), CH 1.096 (1.079), NSN 99.0 (99.5), CNS 107.2 (106.4), CCN 113.1 (112.2), CCH 123.9 (126.2)	*f*
	C_{2v}	CS 1.710 (1.405), CN 1.346 (1.302), NN 1.310 (1.371), CH 1.092 (1.079), CSC 87.5 (86.4), SCN 113.2 (114.6), CNN 113.1 (112.1), SCH 125.1 (121.9), NCH 121.7 (124.0)	*f*
	C_{2v}	SN 1.351 (1.533), SC 1.758 (1.791), NH 0.955 (1.022), CH 1.114 (1.085), NSN 123.9 (135.0), CSC 94.4 (101.2), NSC 108.6 (104.1), SNH 111.7 (114.1), HCH 107.3 (108.2)	
	C_{2v}	S_1C_2 1.668 (1.717), C_2C_3 1.378 (1.357), C_3C_4 1.428 (1.433), C_4C_5 1.386 (1.357), C_5S_1 1.690 (1.717), $C_2C_{2'}$ 1.425 (1.480)	*h*
	C_{2v}	S_1C_2 1.67 (1.71), C_2C_3 1.37 (1.36), C_3C_4 1.44 (1.43), C_4C_5 1.389 (1.38), C_5S_1 1.67 (1.67), $C_3C_{3'}$ 1.44 (1.48)	*h*
	C_s	S_1C_2 1.68 (1.72), S_1C_7 1.66 (1.74), C_2C_3 1.37 (1.36), C_3C_8 1.43 (1.41), C_7C_8 1.43 (1.36)	*h*

Table IX (Continued)

molecular	point group	geometries calcd (obsd)	ref[a]
*SF_2	C_2	SF 1.556 (1.589), FSF 99.0 (98.2)	f
SF_4	C_{2v}	SF_{eq} 1.552 (1.545), SF_{ax} 1.554 (1.646), $F_{ax}SF_{ax}$ 109.6 (173.1), $F_{eq}SF_{eq}$ 109.4 (101.6), FSFF 120.0	f
SF_6	O_H	SF 1.540 (1.561), FSF 90.0, FSFF 90.0	
*S_2F_2	C_2	SS 2.131 (1.888), SF 1.564 (1.635), SSF 109.0 (108.3), FSSF 89.1 (87.9)	f
SSF_2	C_{2v}	SS 1.832 (1.860), SF 1.551 (1.598, SSF 119.9 (107.5), FSF 93.6 (92.5)	f
*SCl_2	C_{2v}	SCl 1.958 (2.014), ClSCl 106.3 (102.7)	
*S_2Cl_2	C_2	SS 1.928 (2.050), SCl 1.959 (1.990), SSCl 116.2 (104.5), ClSSCl 94.0 (84.8)	
*$SClF_5$	C_{4v}	SF 1.537, SCl 2.313 (2.030), FSCl 90.5, FSClF 90.5	
*SOF_2	C_{2v}	SO 1.434 (1.413), SF 1.548 (1.585), OSF 102.7 (106.2), FSF 96.6 (92.3), OSFF 180.0	f
SO_2F_2	C_2	SO 1.359 (1.405), SF 1.515 (1.530), OSO 124.9 (124.0), FSF 97.3 (96.1)	f
*$SOCl_2$	C_{2v}	SO 1.421 (1.435), SCl 1.956 (2.070), OSCl 113.1 (108.0), OSClCl 180.0, CLSCL 133.9 (97.2)	
*$SOBr_2$	C_{2v}	SO 1.465 (1.449), SBr 2.207 (2.2255), OSBr 111.1 (107.6), BrSBr 103.9 (98.2), OSBrBr 180.0	
*SO_2	C_{2v}	SO 1.429 (1.431), OSO 107.9 (119.3)	f
*SO_3	D_{3h}	SO 1.350 (1.420), OSO 120.0 (120.0), OSOO 180.0	f
*H_2SO_4	C_{2v}	S=O 1.358 (1.422), SO 1.622 (1.574), O=S=O 128.3 (123.3), OSO 96.9 (101.3), HOS 121.2 (108.5)	
*S_4	C_2	S_1S_2 1.983, S_2S_3 1.952, SSS 60.2, SSSS 70.8	
*S_6	D_{3d}	SS 2.080 (2.057), SSS 102.8 (102.6), SSSS 74.3 (73.8)	
*S_8	D_{4d}	SS 2.060 (2.046), SSS 111.5 (108), SSSS 94.2 (98.5)	

[a] Except where otherwise referenced, values from: Dewar, M. J. S.; McKee, M. L. *J. Comput. Chem.* **1983**, *4*, 84. [b] Samdal, S.; Seip, H. M. *J. Mol. Struct.* **1975**, *28*, 193; *Acta Chem. Scand.* **1971**, *25*, 1903. [c] Almond, V.; Charles, S. W.; Macdonald, J. N.; Owen, N. L. *J. Chem. Soc., Chem. Commun.* **1977**, 483. [d] Risto, L.; Pakkanen, T. A.; Steudel, R. *J. Am. Chem. Soc.* **1987**, *109*, 710. [e] Kohata, K.; Fukuyama, T.; Kuchitsu, K. *J. Phys. Chem.* **1982**, *86*, 602. [f] Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; etc. *J. Phys. Chem. Ref. Data* **1979**, *8*, 3. [g] Orita, Y.; Ando, A.; Abe, H. *Theoret. Chim. Acta* **1979**, *54*, 73. [h] Dewar, M. J. S.; Trinajstic, N. *J. Am. Chem. Soc.* **1970**, *92*, 1453.

Table X. Geometrical Comparison for Organosulfur Compounds

molecule	type	exp[a]	AM1	MNDO	STO-3G[a]	3-21G[a]	3-21G*[a]	6-31G*[a]	MP3/DZP[b]
S_2H_2	SS	2.055	2.107	1.924	2.065	2.264	2.057	2.064	2.095
	SH	1.327	1.325	1.304	1.334	1.352	1.327	1.327	1.350
	SSH	91.3	98.8	102.5	96.9	96.7	99.0	99.1	98.13
	HSSH	90.6	99.5	99.2	92.6	93.7	89.9	87.9	91.18
CH_3SH	CS	1.819	1.754	1.718	1.798	1.895	1.823	1.817	
	CH_{tr}	1.091	1.115	1.107	1.085	1.078	1.081	1.082	
	SH	1.336	1.321	1.302	1.331	1.352	1.327	1.327	
	HCH	109.8	108.8	108.0	108.1	111.4	110.1	109.9	
	CSH	96.5	99.6	102.3	95.4	97.9	97.5	97.9	
SCH_2	CS	1.611	1.511	1.537	1.574	1.638	1.594	1.597	
	CH	1.093	1.106	1.093	1.090	1.073	1.076	1.078	
	HCH	116.9	109.3	111.9	112.0	116.5	115.3	115.5	

[a] Hehre, W. J.; Radom, L.; Scheleyer, P. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John-Wiley: New York, 1986. [b] Marsden C. J.; Smith B. J. *J. Phys. Chem.* **1988**, *92*, 347.

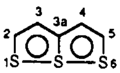
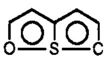
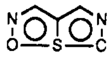
Table XI. Mean Errors in Bond Lengths and Bond Angles for Sulfur Compounds

		av error		
type	mol no.	AM1	MNDO	PM3
		Bond Length (Å)		
C—S	14	0.056	0.070	0.021
S—S	9	0.080	0.100	0.059
S—H	3	0.009	0.030	0.018
S—O	1	0.048	0.055	0.118
S—F	8	0.040	0.048	0.033
S—Cl	4	0.099	0.059	0.061
S—Br	1	0.048	0.120	0.067
S=C	6	0.093	0.057	0.065
S=O	10	0.036	0.067	0.051
		Bond Angle (deg)		
	44	4.8	4.9	4.9

in all three of its valence states with reasonable success, even though d AOs are not included in AM1. The omission seems to cause problems only in a few specific cases, e.g. the incorrect geometry predicted for SF_4. While further tests are needed, it seems likely that our AM1 parameters will prove generally useful in the study of sulfur chemistry, particularly in biological connections.

Stewart[11] has claimed that his reparametrized version (PM3) of AM1 represents a significant improvement, particularly for compounds containing second-row elements (Al, P, S). His quoted "AM1" results were, however, obtained by using MNDO parameters in AM1, a wholly unacceptable procedure, and by including comparisons with experimental values for molecules for

Table XII. Geometries of Thiapentalene Derivatives[a]

molecule	bond	ED	X-ray	AM1	MNDO
	S-S	2.360		2.190	2.095
	S_{6a}-C_{3a}	1.736		1.658	1.686
	S_1-C_1	1.688		1.644	1.626
	C_2-C_3	1.392	1.354	1.390	1.393
	C_3-C_{3a}	1.421	1.409	1.414	1.422
	C_3-C_{3a}-C_4	121.6	123.0	125.9	127.9
	S-S-S			173.1	172.6
	S-O	1.865		1.847	1.813
	S-C	1.752		1.680	1.715
	C-O	1.310		1.317	1.294
	C_2-C_3	1.375		1.395	1.417
	C_3-C_{3a}	1.397		1.407	1.409
	C-O	1.827	1.852	1.874	1.810
	S-C	1.696	1.683	1.665	1.694
	N-O	1.325	1.350	1.248	1.236
	N-C	1.329	1.309	1.355	1.370
	C-C	1.411	1.407	1.423	1.419

[a] Compound 1: Faegri, K., Jr. *J. Mol. Struct.* **1977**, *41*, 271. Compound 2: (1) Faegri, K., Jr. *J. Mol. Struct.* **1977**, *41*, 271. (2) Hagen, K.; Sathre, L. J.; Pedersen, C. T.; Pedersen, T. *Acta Chem. Scand.* **1988**, *42*, 71. Compound 3: Hagen, K.; Sathre, L. J.; Pedersen, C. T.; Pedersen, T. *Acta Chem. Scand.* **1988**, *42*, 71.

which thermochemical data were not in fact available. Now that genuine AM1 parameters are available for sulfur, the AM1 and PM3 results for sulfur compounds are seen to be comparable. We have always avoided changes in our procedures unless and until they lead to major improvements. As a result, there is only one version of each, ensuring that results obtained in different laboratories are comparable. This unfortunately is not true in the ab initio area because the use of different basis sets usually precludes such comparisons.

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Notes

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Electron Transfer. 105. Redox Reactions of Nitrosonium-Bound Chromium(I), $Cr^I(NO^+)$[1]

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Ligation by the nitrosonium ion, NO^+, can stabilize the low oxidation states of a number of transition metals.[2] The prototype example is the "brown ring" cation $(FeNO)^{2+}$, which has been shown[3] to be a NO^+ complex of Fe(I) rather than a NO complex of Fe(II). Similarly, complexes appearing to be NO^+ derivatives of V(−I) and Mo(II) have been described.[4]

The unusual oxidation state, chromium(I), has become accessible through nitrosonium coordination. The cyano complex, $[Cr^I(NO^+)(CN)_5]^{3-}$, was reported in 1959 by Griffith,[4] the aqua complex, $[Cr^I(NO^+)(H_2O)_5]^{2+}$, was characterized by Ardon in 1962,[5] and a related $Cr^I(NO^+)$ chelate, formed from the bidentate anion of 2-ethyl-2-hydroxybutanoic acid, was prepared by Rajasekar in 1983.[6] A greatly improved synthesis of the pentaaquo cation was described by Armor in 1973.[7] Each of these complexes exhibits a magnetic moment and spectral features characteristic of a low-spin $(t_{2g})^5$ derivative.[6,8] Solutions of such complexes survive for several hours at ambient temperatures, and with care, crystalline derivatives may be isolated.[5] Yet, aside from a detailed study of the reaction of $[Cr(NO)(H_2O)_5]^{2+}$ with Cr^{2+} by Armor,[7] little is known concerning the chemistry of $Cr^I(NO^+)$ species. Although the $[Cr(NO)(H_2O)_5]^{2+}$ cation has two sites where redox reactions may, in principle, occur, we find that it is quite resistant to all but the most powerful oxidants and reductants. The present study deals with reactions of this complex with the oxidants BrO_3^- ($E° = 1.52$ V) and IO_4^- (1.7 V) and with the reductant U^{3+} (−0.61 V).[9]

Experimental Section

Materials. Sodium bromate (Sargent) and sodium periodate (Alfa) were used as received. Sodium perchlorate solutions (for use in kinetic experiments) were prepared by careful neutralization of $NaHCO_3$.

Table I. Stoichiometries of the Reactions of $[Cr(NO)(H_2O)_5]^{2+}$ with Inorganic Redox Reagents (0.5 M $HClO_4$)

A. Reactions with IO_2^- (450 nm)

$10^3 \times [Cr(NO)^{2+}]$	$10^3 \times [IO_4^-]$	$10^3 \times \Delta[Cr(NO)^{2+}]$	$\Delta[Cr(NO)^{2+}]/\Delta[IO_4^-]$
1.50	0.50	0.40	0.80
1.50	1.00	0.90	0.90
1.50	1.25	1.23	0.98
1.50	1.50	1.43	0.95

B. Reactions with BrO_3^- (325 nm)

$10^3 \times [Cr(NO)^{2+}]$	$10^3 \times [BrO_3^-]$	$10^3 \times \Delta[Cr(NO)^{2+}]$	$\Delta[Cr(NO)^{2+}]/\Delta[BrO_3^-]$
10.5	4.0	5.9	1.46
10.5	7.0	9.8	1.39

C. Reactions with U(III) (450 nm)

$10^3 \times [Cr(NO)^{2+}]$	$10^3 \times [U(III)]$	$10^3 \times \Delta[Cr(NO)^{2+}]$	$\Delta[Cr(NO)^{2+}]/\Delta[U(III)]$
6.40	4.17	1.77	0.42
5.60	6.77	4.14	0.61
6.50	7.22	3.59	0.49
3.80	3.65	1.72	0.47

Table II. Variation, with Acidity, of the Spectrum of $[Cr(NO)(H_2O)_5]^{2+}$ (25 °C)[a]

$10^6[H^+]$, M	R_{obsd}[b]	R_{calcd}[c]	$10^6[H^+]$, M	R_{obsd}[b]	R_{calcd}[c]
316	1.45	1.41	6.2	0.88	0.85
72	1.25	1.30	3.9	0.86	0.78
17.3	0.96	1.06	2.5	0.83	0.73
10.9	0.93	0.96	0.04	0.61	0.61

[a] $[H^+]$ was adjusted by addition of $HOAc/OAc^-$ buffer or tris(hydroxymethyl)aminomethane (Tris). [b] Observed ratio of absorbances at 448 and 380 nm. [c] Absorbance ration (448/380 nm) calculated by using eq 1, with R_B taken as 0.61, R_{BH} as 1.45, and K_A as 1.49×10^{-5} M.

Uranium(III) solutions were prepared by dissolving dry U_3O_8 in warm dilute $HClO_4$ and then reducing with Zn(Hg) under N_2 until the spectrum of the resulting olive green solution remained invariant.[10]

Solutions of $[Cr(NO)(H_2O)_5]^{2+}$ were prepared[5] by reducing 0.6 M $Cr(ClO_4)_3$ (Alfa) in 1 M $HClO_4$ with zinc amalgam under N_2 and then adding the resulting $Cr(ClO_4)_2$ solution (6 mL) dropwise to 150 mL of water, which was stirred and continuously saturated with NO.[11] The NO flow was then switched to N_2 to expel the excess NO, and the solution was absorbed onto a column of Dowex 50W-X8 (H^+ form). The desired complex was eluted with 0.5 M $HClO_4$. Solutions were standardized spectrophotometrically ($\epsilon_{449}^{max} = 120$ M^{-1} cm^{-1}).[5]

Stoichiometric Studies. The stoichiometries of the reactions of $Cr(NO)^{2+}$ with IO_4^- and BrO_3^- were determined in 0.5 M $HClO_4$ by adding known deficiencies of the oxidants to an excess of the chromium complex, waiting until completion of the reaction, and then estimating the decreases in absorbance due to $Cr(NO)^{2+}$. Measurements were made at 450 nm for the I(VII) reactions and 325 nm for Br(V). The resulting changes were compared with those occurring on treatment with excess oxidant. The stoichiometry of the reaction with U(III) was determined

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(2) Reviews: (a) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53. (b) Bottomley, F. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1989; Vol. 2, p 115. (c) Mingos, D. M. P.; Sherman, D. J. *Adv. Inorg. Chem.* **1989**, *34*, 293.

(3) Griffith, W. P.; Lewis, J.; Wilkinson, G. *J. Chem. Soc.* **1958**, 3493.

(4) Griffith, W. P.; Lewis, J.; Wilkinson, G. *J. Chem. Soc.* **1959**, *872*, 1632.

(5) Ardon, M.; Herman, J. I. *J. Chem. Soc.* **1692**, 507.

(6) Rajasekar, N.; Subramaniam, R.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 971.

(7) Armor, J. N.; Buchbinder, M. *Inorg. Chem.* **1973**, *12*, 1086.

(8) Griffith, W. P. *J. Chem. Soc.* **1963**, 3286.

(9) Latimer, W. M., *Oxidation Potentials*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; Chapters 5 and 21. The potentials listed refer to the conversions $2BrO_3^- \rightarrow Br_2$, $H_5IO_6 \rightarrow HIO_3$, and $U^{4+} \rightarrow U^{3+}$, each in 1 M H^+. Complications in the I(VII) system due to the equilibrium between IO_4^- and its hydrated form $H_4IO_6^-$ appear to play no part in this study.

(10) Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 330.

(11) Blanchard, A. A. *Inorg. Synth.* **1946**, *2*, 126.

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