

Each uranium atom is surrounded by eight fluorines, with $U-F = 2.29 \text{ \AA}$. and $F-F = 2.63$ and $2.67 \text{ \AA}$. Each sodium atom is also surrounded by eight fluorines with $Na-F = 2.37 \text{ \AA}$. and $F-F = 2.63$ and $2.97 \text{ \AA}$. The metal-metal distances are normal. All distances are more or less close to ideal values, based on $R_{U^{6+}} = 0.83$, $R_{Na} = 0.98 \text{ \AA}$., and $R_{F^-} = 1.33 \text{ \AA}$. We hope to obtain additional data in the future in order to check the validity of the model.

For this structure, all $U-F$ distances are equivalent, and all $Na-F$ distances are equivalent. There is therefore no indication of shorter or longer bonds which could lead to the identity of UF_6 or NaF configurations.

Discussion

The preparation of pure Na_2UF_8 substantiates the results of the F^{18} -exchange studies⁸ and recent results on solid-gas reactions⁹ that the compound originally described as Na_3UF_9 is in fact Na_2UF_8 . Earlier erroneous

identifications⁴⁻⁷ were due to the incomplete reaction obtained between gaseous UF_6 and solid NaF . These problems have been overcome however by the use of more finely divided NaF obtained by decomposition of sodium bifluoride.⁹ In our experiments these difficulties were obviated by dispersing NaF in an inert liquid, C_7F_{16} . The refluxing of C_7F_{16} carries away the heat of the reaction and retains NaF in a finely divided state. Analogous results were obtained with KF .

In addition, we have obtained two new compounds of the type MUF_7 ($M = Na, K$) analogous to the previously reported $CsUF_7$ ¹⁰ and NH_4UF_7 .^{10,11}

Exchange data with F^{18} did not show evidence of compound formation with KF .⁸ Our results do not agree with this. The exchange work was done with readily available reagent grade KF . Our experience with such KF has shown that this material is completely unreactive toward UF_6 . Only the very finely divided KF prepared by decomposition of KHF_2 has been found to react with UF_6 .

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Nucleophilic Displacement in the Oxidation of Iodide Ion by Dimethyl Sulfoxide¹

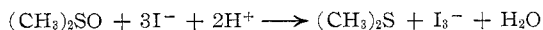
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The rates of oxidation of iodide ion in acidic solution have been studied at 25.00° in various dimethyl sulfoxide-water solvent mixtures: $(CH_3)_2SO + 3I^- + 2H^+ \rightarrow (CH_3)_2S + I_3^- + H_2O$. Second-order hydrogen ion and first-order iodide ion dependence was observed in each solvent employed. The value of the third-order rate constant increases rapidly with decreasing water content. Nucleophilic catalysis by added bromide or chloride occurs, with an observed order of reactivity: chloride > bromide > iodide. The dependence of the relative reactivity of these nucleophiles on the water content of the solvent has been determined. The results indicate halide ions to be very reactive in a dipolar aprotic solvent; the effectiveness of chloride is increased by a factor of 3700 on going from 75.00% to 98.50% dimethyl sulfoxide.

Introduction

Dimethyl sulfoxide (DMSO) has several properties which make it useful as a solvent for inorganic reactions. Important among them are high dielectric constant and ability to dissolve fairly high concentrations of many inorganic solutes.² DMSO is a typical dipolar aprotic solvent, which lacks any capacity for hydrogen bonding to solute species. It is reasonable to expect that this marked contrast with solvent water would have an important effect on reaction rates and mechanisms. To learn more about this effect we have studied the rate of reaction of DMSO with iodide ion in acidic DMSO-water solvent mixtures.



A kinetic analysis of this reaction in DMSO-water solvents has not been reported; however, Landini, *et al.*,³ have investigated the reduction of sulfoxides by hydriodic acid in acetic acid.

Experimental Section

Solvent.—Crown-Zellerbach commercial grade DMSO was distilled twice at 72° (10 mm.), the center 60% in each distillation being retained for use. A Karl Fischer titration of the freshly distilled DMSO indicated the presence of 0.03% water. Solvent mixtures were prepared on a weight basis by slow addition of redistilled water to a partially frozen sample of DMSO. Both DMSO and water were initially swept with prepurified nitrogen and all subsequent operations were performed under an atmosphere of nitrogen. The solvent mixtures were used immediately after preparation.

For each of the kinetic runs, a stock solution of perchloric acid in DMSO-water was prepared by slow addition of 35% aqueous perchloric acid to the solvent, cooled in an ice bath.

(1) Presented to the Division of Inorganic Chemistry at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

(2) H. L. Schläfer and W. Schafermicht, *Angew. Chem.*, **72**, 618 (1960).

(3) D. Landini, F. Montanari, H. Hogeveen, and G. Maccagnani, *Tetrahedron Letters*, **38**, 2691 (1964).

Allowing for water introduced from the aqueous perchloric acid (and for residual water in the DMSO) the composition of the mixture can be specified to ± 0.05 wt. %. Aliquots of the acid stock solution were diluted fourfold in water and titrated with carbonate-free sodium hydroxide.

Reagent grade perchloric acid was diluted from 72% to 35% before use. The various potassium salts, iodide, bromide, chloride, thiocyanate, and perchlorate, were all reagent grade and dried at 125° before use.

Kinetic Measurements.—The initial rates of triiodide formation were obtained by following the absorbance at 365 m μ , using a Beckman DU spectrophotometer. An aliquot of perchloric acid solution was added to a solution of the other reactants and a 4-ml. quantity of this solution was quickly transferred to a 1-cm. glass-stoppered silica cell. The cells were mounted in a cell holder, thermostated to $25.00 \pm 0.05^\circ$.

The influence of ionic strength was determined in 85.00% DMSO by adding potassium perchlorate. No significant variation in the rate was found, either as a function of ionic strength or of total perchlorate ion present. However, the ionic strength was maintained within any given series of runs to eliminate any possible medium effects (typical values, 0.14–0.18). Saturation of a reacting solution with oxygen caused a 10% increase in rate, which may be due to the oxidation of iodide ion by oxygen. Since the reaction is mildly sensitive to the presence of oxygen, all runs reported were carried out under nitrogen.

The stoichiometry was checked by titrimetric analysis with 0.1 *N* sodium thiosulfate, followed by 0.1 *N* sodium hydroxide. A separate portion of the reacting solution was diluted with water, neutralized with thiosulfate and base, and extracted once with chromatography cyclohexane. A gas chromatogram of this extract was obtained at 35° on a diisodecyl phthalate column.

Beer's Law.—Triiodide ion is the only species with an appreciable absorbance at 365 m μ . Plots of absorbance *vs.* triiodide concentration at 365 m μ were linear, but a slightly negative absorbance intercept was observed in cases where the DMSO was not highly purified. The molar absorption coefficient in 85.00% DMSO is 25,800 (l. mole⁻¹ cm.⁻¹) at 365 m μ . Since values in 75.00% and 98.50% DMSO were the same, within 1%, 25,800 was used in obtaining all the numerical results reported. The equilibrium constant for the reaction $I_2 + I^- \rightleftharpoons I_3^-$ has not been determined in DMSO–water mixtures. Complete conversion of iodine to triiodide was assumed, however, since the molar absorption coefficient observed was independent of the iodide ion concentration in the region of 0.03 to 0.18 *M* iodide. The presence of added chloride, bromide, or thiocyanate in large concentrations affected the triiodide absorption, presumably through the diversion of I_3^- to species of the type I_3X^- .⁴ To minimize this effect, iodide was kept in excess over the other anions in the catalytic runs.

Results

(A) Uncatalyzed Reaction.—The system was first studied under conditions where iodide was the only reactive anion present.

Stoichiometry.—Based on hydrogen ion consumed and total iodide produced, the stoichiometry of the reaction checked to within 1%, at least up to one half-life. A gas chromatographic analysis of the products showed a single volatile component to be present, with a retention time corresponding to that of pure dimethyl sulfide.

Rate Law.—The basic kinetic characterization was carried out in 85.00% DMSO as the solvent; these results will be considered first. Initial rates of appearance of triiodide were obtained during the first 90 min., corresponding to approximately 0.1% reaction. Plots

of triiodide absorbance *vs.* time displayed a high degree of linearity. The slopes of these plots were taken as the initial rates, R_0 , with an uncertainty of $\pm 1\%$. Addition of small amounts of iodine or dimethyl sulfide to the reacting solutions had no significant effect on the slopes. Initial rates were obtained as a function of initial iodide ion and hydrogen ion concentrations. The data are summarized in Table I.

TABLE I
VALUES OF THE THIRD-ORDER RATE CONSTANT AT 25.00° FOR THE REACTION OF DMSO WITH IODIDE ION

$10^3[I^-]$, <i>M</i>	$10^3[H^+]$, <i>M</i>	10^5k_I , <i>M</i> ⁻² sec. ⁻¹	$10^3[I^-]$, <i>M</i>	$10^3[H^+]$, <i>M</i>	10^5k_I , <i>M</i> ⁻² sec. ⁻¹
85.00% (0.566) DMSO ^a			75.00% (0.409) DMSO		
3.00	5.99	1.45	4.00	15.27	0.52
6.00	5.99	1.46	6.01	15.27	0.56
9.00	5.99	1.45	10.0	15.27	0.57
12.0	5.99	1.43	6.01	10.17	0.54
18.0	5.99	1.43	6.01	20.34	0.58
			92.50% (0.740) DMSO		
1.00	10.3	1.35	4.00	3.71	6.0
2.00	10.3	1.36	6.00	3.71	6.0
3.00	10.3	1.35	10.0	3.71	6.0
4.00	10.3	1.40	6.00	2.48	5.9
6.00	10.3	1.39	6.00	4.95	6.1
			98.50% (0.938) DMSO		
6.00	3.66	1.34	2.80	2.38	32.1
6.00	5.49	1.43	4.20	2.38	31.7
6.00	7.32	1.42	7.00	2.38	32.1
6.00	9.15	1.45	4.20	1.59	30.8
6.00	11.0	1.45	4.20	3.18	32.2

^a Weight % and (mole fraction) DMSO in the solvent, omitting solutes present.

The data conform quite accurately to the rate law

$$\frac{d[I_3^-]}{dt} = k_I [H^+]^2 [I^-]$$

Values of the third-order rate constant, k_I , are included for each run in Table I. The average value at 25.00° in 85.00% DMSO is $1.41 \times 10^{-5} M^{-2} \text{ sec.}^{-1}$, with an uncertainty of $\pm 3\%$. Even though the concentration of potassium ion was as high as 0.2 *M*, there was no indication of ion pairing.

The determinations were extended to solvent mixtures of different composition. By systematically varying the iodide and hydrogen ion concentrations as described above, the third-order rate law was verified from 75.00% to 98.50% DMSO. The data are shown in Table I. The third-order rate constant is greatly increased by increasing the DMSO content, the reaction being 56 times faster in 98.50% than in 75.00% DMSO. The measurements were extended down to 62.50% DMSO, but in this solvent there appeared a tendency for deviation from strictly third-order kinetics; these results have not been included.

(B) Catalyzed Reaction.—The reaction is accelerated by the addition of potassium chloride or potassium bromide to the solution. The over-all stoichiometry is maintained. Since iodide ion is the strongest reducing agent present, iodine is the observed product in both the catalyzed and uncatalyzed reactions. Experiments carried out at constant concentrations of

(4) D. Meyerstein and A. Treinin, *Trans. Faraday Soc.*, **59**, 1114 (1963).

TABLE II
INITIAL RATES AND VALUES OF THE CATALYTIC RATE CONSTANT
AT 25.00° FOR THE CHLORIDE-CATALYZED REACTION

% DMSO	$10^2[I^-]$, M	$10^2[H^+]$, M	$10^3[Cl^-]$, M	10^2R_0 , M sec. ⁻¹	10^3k_{Cl} , M ⁻² sec. ⁻¹
75.00	8.99	8.55	6.06	4.33	1.60
(0.409) ^a	8.99	8.55	18.2	5.66	1.54
	8.99	8.55	30.2	6.94	1.49
85.00	9.00	3.64	4.00	2.66	18.5
(0.566) ^a	9.00	3.64	8.00	3.54	17.4
	9.00	3.64	12.0	4.32	16.5
	9.00	3.64	16.0	5.20	16.6
	9.00	3.64	20.0	6.02	16.3
92.50	4.88	2.58	0.515	2.90	280.
(0.740) ^a	4.88	2.58	1.030	3.80	270.
	4.88	2.58	1.545	4.60	260.
	4.88	2.58	2.06	5.44	250.
	4.88	2.58	2.58	6.27	250.
98.50	2.71	1.99	0.320	9.81	5100.
(0.938) ^a	2.71	1.99	0.480	13.22	5200.
	2.71	1.99	0.640	16.52	5200.

^a Mole fraction DMSO in the solvent.

TABLE III
INITIAL RATES AND VALUES OF THE CATALYTIC RATE CONSTANT
AT 25.00° FOR THE BROMIDE-CATALYZED REACTION

% DMSO	$10^2[I^-]$, M	$10^2[H^+]$, M	$10^3[Br^-]$, M	10^2R_0 , M sec. ⁻¹	10^3k_{Br} , M ⁻² sec. ⁻¹
75.00	8.99	8.55	8.00	4.02	0.70
(0.409) ^a	8.99	8.55	24.0	4.67	0.60
	8.99	8.55	40.0	5.35	0.59
85.00	5.99	5.51	5.00	3.18	4.1
(0.566) ^a	5.99	5.51	10.0	3.59	3.4
	5.99	5.51	15.0	4.12	3.4
	5.99	5.51	20.0	4.63	3.4
	5.99	5.51	25.0	5.14	3.4
92.50	4.52	3.204	2.97	3.94	38.
(0.740) ^a	4.52	3.204	8.92	5.72	32.
	4.52	3.204	14.86	7.39	30
98.50	2.99	1.610	0.815	3.27	380.
(0.938) ^a	2.99	1.610	2.44	4.47	320.
	2.99	1.610	4.08	5.81	320.

^a Mole fraction DMSO in the solvent.

hydrogen ion and iodide ion showed that the initial rates were linearly dependent on the concentration of added chloride or bromide ion. This suggests a catalytic rate law of the form

$$\frac{d[I_3^-]}{dt} = k_I[H^+]^2[I^-] + k_N[H^+]^2[N]$$

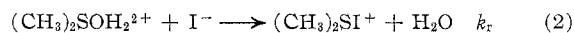
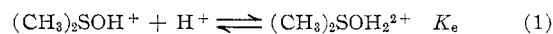
in which N represents the added nucleophile, chloride or bromide. Values of the third-order catalytic constant, k_N , calculated using k_I values determined in the same solvent, are summarized in Tables II and III. In addition to the halides, thiourea and thiocyanate were tested for catalytic activity. The rate was completely unaffected by added potassium thiocyanate, both in 85.00% and 98.50% DMSO. Third-order constants for catalysis by thiourea are presented in Table IV. The second-order hydrogen ion dependence in the catalytic term of the rate law was checked by varying the hydrogen ion concentration in the presence of both iodide and chloride ions. A plot of R_0 vs. $[H^+]^2$ was linear for an experiment with initial concentrations such that 75% of the triiodide was produced *via* the catalytic path.

TABLE IV
INITIAL RATES AND VALUES OF THE CATALYTIC RATE CONSTANT
AT 25.00° FOR THE THIOUREA-CATALYZED REACTION
IN 85.00% DMSO

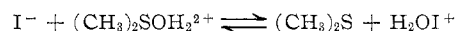
$10^2[I^-]$, M	$10^2[H^+]$, M	$10^3[TU]$, M	10^2R_0 , M sec. ⁻¹	10^3k_{TU} , M ⁻² sec. ⁻¹
9.00	3.61	3.50	2.91	27.6
9.00	3.61	6.99	3.91	24.8
9.00	3.61	10.5	4.83	23.3
9.00	3.61	14.0	5.72	22.4
9.00	3.61	17.5	6.57	21.6

Discussion

Mechanism.—The kinetic results lead to a mechanism involving nucleophilic attack on the sulfur-oxygen bond in a molecule of dimethyl sulfoxide. Since the oxidizing agent is the solvent species itself, no kinetic evidence is available to show that dimethyl sulfoxide is a specific part of the activated complex. However, in solvent acetic acid, a first-order dependence on sulfoxide concentration has been observed by Landini, *et al.*³ Also, a first-order dependence has been reported by Allenmark⁵ for the related alkylsulfinyl-carboxylic acid oxidation of iodide in aqueous perchloric acid. Assuming similar behavior in DMSO-water, we propose the mechanism shown in eq. 1-4. If (2) is considered the slow step, preceded by a rapid and reversible formation of $(CH_3)_2SOH_2^{2+}$, the proposed mechanism is consistent with the rate law for the un-



catalyzed reaction. There is no kinetic evidence bearing on the validity of (3) or (4), which we have introduced to indicate a reasonable path leading to final products. $(CH_3)_2SOH^+$ is represented as a reactant, because it is likely that a large fraction of the protons reside on sulfoxide molecules, especially as the water content decreases.⁶ Though this mechanism for the uncatalyzed reaction is a reasonable one, it is not the only one that should be considered. The attack of iodide could occur at oxygen, as well as at sulfur, so that the rate-determining step would become

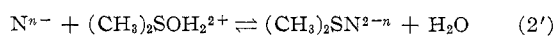


The essential feature of the mechanism proposed is the iodide ion displacement of a leaving group (the water molecule) from the positive sulfur center. This nucleophilic cleavage of the sulfur-oxygen bond suggests that the reaction should be catalyzed by other nucleophiles. The experimental results show that such catalysis does occur with chloride ion, bromide ion, and probably thiourea. Since the catalytic pathway, which occurs simultaneously with the direct iodide step, also involves a second-order hydrogen ion dependence, the substrate is presumed to be $(CH_3)_2SOH_2^{2+}$ in both

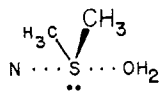
(5) S. Allenmark, *Acta Chem. Scand.*, **19**, 1 (1965).

(6) J. R. Holmes, D. Kivelson, and W. C. Drinkard, *J. Am. Chem. Soc.*, **84**, 4677 (1962).

cases. Reaction 2 can be generalized to nucleophiles N



attacking the substrate, leading to an activated complex that can be visualized as



An intermediate of the composition $(CH_3)_2SN^+$ is involved when N is I^- , Br^- , or Cl^- . The existence of these halodimethylsulfonium ions has been mentioned in the literature on several occasions, and some experimental justification for them has been offered recently.⁷ The ultimate product of the reaction will be iodine, whenever iodide is present, regardless of the intermediate forms of the oxidizing species.

The range of nucleophiles which can be employed as catalysts is rather limited. Bases or easily oxidizable species are ruled out. The nonlinear behavior of thiourea is probably due to a subsequent reaction between thiourea and iodine.⁸ Perchlorate ion has no observable catalytic effect. The possibility of nucleophilic attack by solvent water, leading to oxygen exchange, is unlikely since it has been observed that such exchange does not occur with diphenyl sulfoxide in 97% sulfuric acid.⁹

Examples of nucleophilic displacements at sulfur in substrates similar to $(CH_3)_2SOH_2^{2+}$ have been reported recently. $(CH_3)_2S-SCH_3^+$ is attacked by iodide and water¹⁰ and $(CH_3)_2S-OCH_3^+$ is subject to attack by water or alkoxide ion.¹¹ It seems likely that halide ion catalysis should occur in these substrates and, in general, at sulfur centers subject to nucleophilic attack.

Solvent Effect.—Although the rate law remains unchanged throughout the solvent range studied, the third-order rate constants are very sensitive to the composition of the solvent. As shown in Figure 1, the rate constants for iodide, bromide, and chloride increase rapidly as the water content decreases. Since these observed constants are composed of both an equilibrium constant K_e and a bimolecular constant k_r , any explanation of this increase must take into account the simultaneous effect of solvent change on each of the constants. Significant in our results is the fact that not only is the order of reactivity in any given solvent $Cl^- > Br^- > I^-$, but also the *increase in reactivity*, on going to lower water content, is $Cl^- > Br^- > I^-$. Since changes in the solvent will influence K_e in the same way for each nucleophile, the observed

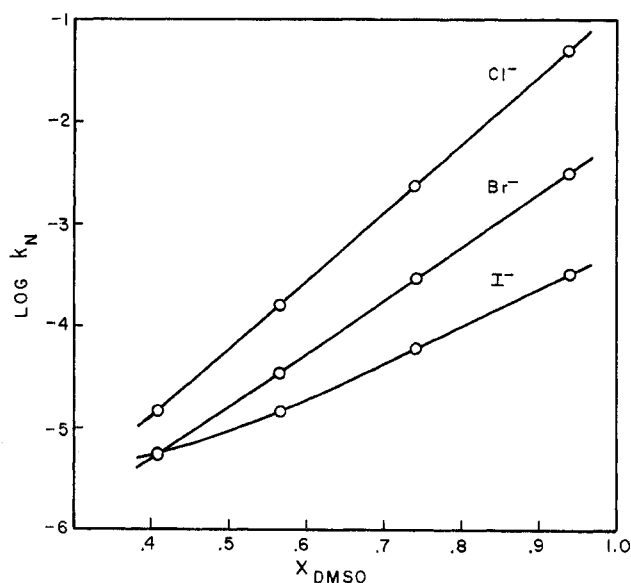


Figure 1.—Log of the third-order rate constant for chloride, bromide, and iodide vs. mole fraction of DMSO in the solvent. Each k_N value was obtained from the slope of a plot of $R_0/[H^+]_0^2[I^-]_0$ vs. $[N]_0/[I^-]_0$.

order of reactivity is a function of k_r and therefore dependent upon the specific nature of each nucleophile. Thus, the order of decreasing nucleophilicity in the solvent mixtures studied is $Cl^- > Br^- > I^-$.

The above order is just the reverse of that usually observed for nucleophilic displacements occurring in protic solvents.^{12,13} This reversal of nucleophilic reactivity on going from protic to aprotic solvents has been noted by others.¹⁴⁻¹⁶ Parker has discussed the factors which determine the characteristics of ions in dipolar aprotic solvents.¹⁴ It is predicted that chloride and bromide, which are more dependent upon hydrogen bond stabilization than is iodide, should increase in reactivity as the water content of the solvent decreases. Over the range of solvent composition involved in this study, there is a significant change in the availability of hydrogen bonds, since the ratio moles of DMSO/moles of water increases from 0.69 in 75.00% to 15.1 in 98.50% DMSO. Our observation that chloride is most sensitive and iodide least sensitive to decreasing water content lends support to the current theory of ion-solvent interactions in dipolar aprotic solvents.

It should be true that as the water content increases, there will be a tendency for the reactivity of chloride and bromide to decrease below that of iodide, thus going over to the usual order in protic solvents, $I^- > Br^- > Cl^-$. The data at 0.409 mole fraction DMSO, Figure 1, indicate that such an inversion in reactivity is likely. Qualitative results at 0.277 mole fraction DMSO show chloride ion to be less reactive than iodide.

(7) H. Böhme and E. Boll, *Z. anorg. allgem. Chem.*, **290**, 17 (1957).

(8) Thiourea rapidly decolorizes iodine solutions in DMSO under conditions similar to those in the reacting solutions, except for the omission of perchloric acid. Also, see R. P. Lang, *J. Am. Chem. Soc.*, **84**, 1185 (1962).

(9) S. Oae, T. Kitao, and Y. Kitaoka, *Bull. Chem. Soc. Japan*, **38**, 543 (1965).

(10) G. K. Helmkamp, H. N. Cassey, B. A. Olsen, and D. J. Pettitt, *J. Org. Chem.*, **30**, 933 (1965).

(11) (a) C. R. Johnson and W. G. Phillips, *Tetrahedron Letters*, **25**, 2101 (1965); (b) N. J. Leonard and C. R. Johnson, *J. Am. Chem. Soc.*, **84**, 3701 (1962).

(12) J. F. Bunnett, "Nucleophilic Reactivity," in H. Eyring, C. J. Christensen, and H. S. Johnston, Eds., *Annual Review of Physical Chemistry*, Vol. 13, Annual Reviews Inc., Palo Alto, Calif., 1963, p. 271.

(13) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, Chapter 4.

(14) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).

(15) A. J. Parker, *J. Chem. Soc.*, 1328 (1961).

(16) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, **9**, 24 (1960).

Recently, Edwards and Pearson¹⁷ have discussed important factors which contribute to nucleophilicity. Basicity and polarizability of the nucleophile play an important role. In the $(\text{CH}_3)_2\text{SOH}_2^{2+}$ substrate, nucleophilic attack at either sulfur or oxygen should be correlated by a combination of basicity and polarizability in the nucleophile, because each center bears a positive charge and possesses an unshared pair of electrons. Since polarizability increases and basicity decreases in the series Cl^- , Br^- , I^- , the two factors cannot be separated unambiguously in this system. It is likely that the solvent-solute interactions control the

nucleophilicities observed. For example, thiocyanate ion, which is more basic and more polarizable than the halide ions, should be an effective nucleophile. The lack of reactivity of thiocyanate must be due to its considerable stability in both protic and aprotic solvents. Thus, the nature of the solvent is critical in understanding reactivity in the system investigated in this paper and, in general, should be taken into account whenever comparisons of nucleophilicity are made among solvents of different types.

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(17) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

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Substoichiometry of Tungsten Trioxide; the Crystal Systems of $\text{WO}_{3.00}$, $\text{WO}_{2.98}$, and $\text{WO}_{2.96}$ ¹

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From the results of powder and single crystal X-ray measurements together with measured densities and chemical analyses it has been demonstrated that substoichiometric tungsten trioxides possess structures which are significantly different from that of the stoichiometric trioxide. For the composition $\text{WO}_{2.98}$ the space group is $\text{P2}_1/\text{m}$ and the unit cell contains four tungsten atoms and has the dimensions $a = 7.354 \pm 0.005 \text{ \AA}$, $b = 7.569 \pm 0.005 \text{ \AA}$, $c = 3.854 \pm 0.005 \text{ \AA}$, and $\beta = 90.6^\circ$. The tungsten subcell is of the same type but slightly larger than that of the stoichiometric oxide. The results for the composition $\text{WO}_{2.96}(\alpha)$ indicate the space group $\text{P2}/c$ and a unit cell containing the formula $\text{W}_{50}\text{O}_{148}$ and having the cell constants $a = 11.90 \pm 0.02 \text{ \AA}$, $b = 3.826 \pm 0.012 \text{ \AA}$, $c = 59.64 \pm 0.06 \text{ \AA}$, and $\beta = 98.4^\circ$. The proposed structure is uniquely solved for the x and z coordinates but not for the y coordinates, which appear to be located in a number of planes staggered about $y = 1/2$. Each unit cell contains two hexagonally-shaped ordered defects that are bisected by recurrent dislocation planes. A higher temperature polymorph, $\text{WO}_{2.96}(\beta)$, with a unit cell tentatively containing the formula $\text{W}_{25}\text{O}_{74}$ becomes stable at approximately 1250° .

Introduction

The basic chemical and physical properties of binary compounds of the group VI transition metals Cr, Mo, and W are generally complex. In recent years, a number of investigations dealing with the crystallographic and thermodynamic behavior, particularly of Mo and W oxides, have elucidated the complex chemical bonding that occurs both in the solid and vapor phases. Furthermore, in the case of a number of transition metal oxides, carbides, sulfides, and phosphides, gross deviations from ideal stoichiometry are readily obtained and must be acknowledged in physicochemical descriptions of these systems. In a recent thermodynamic investigation of the tungsten-oxygen system² it was observed at temperatures of 1300 – 1550°K . that tungsten trioxide becomes substoichiometric and evaporates congruently at a composition near $\text{WO}_{2.96}$ under the influence of the particular vacuum conditions (10^{-6} – 10^{-7} mm. pressure) employed.

The X-ray diffraction patterns of powders of this material at room temperature are significantly different from those of the stoichiometric trioxide and cannot be explained on the basis of only an oxygen-deficient trioxide structure. Actually, the existence of a substoichiometric region of WO_3 was first suggested by Glemser and Sauer,³ who reported that the basic structure of the WO_3 phase extends to the composition $\text{WO}_{2.96}$. However, Hägg and Magneli⁴ refer to a paper given by Westgren⁵ in which is proposed the existence of a new oxide phase corresponding to approximately $\text{WO}_{2.97}$. Gado⁶ has recently reported the existence of a phase between $\text{W}_{20}\text{O}_{58}$ and WO_3 . The structure at room temperature of the unit cell of the stoichiometric trioxide as reported by Andersson⁷ and by previous investigators contains four WO_3 units and has the space group $\text{P2}_1/a$; however, the direct observations by

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) R. J. Ackermann and E. G. Rauh, *J. Phys. Chem.*, **67**, 2596 (1963).

(3) O. Glemser and H. Sauer, *Z. anorg. Chem.*, **252**, 144 (1943).

(4) G. Hägg and A. Magneli, *Arkiv Kemi, Mineral. Geol.*, **19A**, No. 2 (1944).

(5) A. Westgren, *Nord. Naturforskmötet Helsingfors*, **89** (1936).

(6) P. Gado, *Acta Cryst.*, **16**, Part 13, A182 (1963).

(7) G. Andersson, *Acta Chem. Scand.*, **7**, 154 (1953).