product. The intense absorption around 7 μ has not been explained but may be due to an amorphous phase, because the diffraction patterns of the crystal and powder parts of this product show only a slight difference. There is no sign of a band in this region from the crystalline Ca_2AsO_4Cl or of an analogous band in Ca_2VO_4Cl.

The infrared spectra of these two phases clearly show that the band around 12 μ is split much more for the vanadate than for the arsenate, although the spectrum of the vanadate is not as clearly resolved. A comparison of the vanadate with the phosphate and chromate shows its splitting to be between that of the other two while the arsenate has the smallest splitting of the four.

Conclusion

It is concluded from the X-ray, infrared, and density data that the vanadate and the arsenate have the formulas attributed to them and that each has the spodiosite structure. The probable reactions of formation for these two species are

$$3CaCO_3 + V_2O_5 + CaCl_2 \longrightarrow 2Ca_2VO_4Cl + 3CO_2 \quad (1)$$

$$3CaCO_3 + As_2O_3 + CaCl_2 \xrightarrow{O_2} 2Ca_2AsO_4Cl + 3CO_2 \quad (2)$$

Since the amount of splitting of the asymmetric stretch bands in the infrared spectrum is known to increase with increasing distortion of the oxygen tetrahedron and the amount of splitting is observed to be in the order AsO_4^{3-}, PO_4^{3-}, VO_4^{3-}, CrO_4^{3-}, with the CrO_4^{3-} splitting being over 50% more than that of the others, it appears that the extra distortion in the CrO_4^{3-} ion is attributable to electronic effects, as discussed by Banks, Greenblatt, and McGarvey.[2] They proposed that the ordering of the single d electron into the d_{z^2} orbital, as shown by esr data, is responsible for the extra distortion above that introduced by the packing of the tetrahedra in the spodiosite structure. The differences in distortion of the other three species appear to be small and cannot be correlated with any obvious differences in the properties of the central atoms.

Contribution from the Department of Chemistry
Stanford University, Stanford, California 94305

The Reaction between Chromate and Thiosulfate. I. The Chromatothiosulfate Intermediate

By I. Baldea and G. Niac[1]

Received August 14, 1967

Oxidations by chromate ion often occur through formation in the first step of intermediates arising by elimination of water molecules. Such intermediates were proposed for the oxidation of alcohols by Leo and Westheimer[2a] and for the oxidation of arsenite by Mason and Kowalak.[2b] Similar intermediates could reasonably be expected in the chromate oxidation of thiosulfate, but until now no data were available on the kinetics of this reaction and the nature of the intermediates. It was the goal of the present work to search for evidence of the formation of an intermediate using spectrophotometric means.

Since the redox reaction under consideration has a half-time of 10–50 sec under the acidic conditions used, kinetic records of the absorbance were made during the reaction, and values extrapolated to zero time were used to determine the molar absorptivity of the intermediate and the equilibrium constant for its formation. A flow device was used to record the absorption spectrum of the intermediate at steady state.

Experimental Section

Chemicals.—Merck Analytical grade chemicals were used without further purification. The $NaClO_4$ was prepared by neutralization of $HClO_4$ with NaOH of known concentration. The equivalence point was established by means of a glass-electrode pH meter. The solutions were made using twice distilled water (over $KMnO_4$). Air was eliminated by bubbling natural methane gas from which traces of O_2 were removed by an alkaline pyrogallol solution and mercaptans were removed by adsorption on active carbon.

Kinetic Runs.—These were performed by a syringe technique, introducing 1 ml of the Cr(VI) solution into a photometer cell of 10-mm path length containing 4 ml of the thiosulfate solution. Both solutions were prepared from stock solutions of $Na_2S_2O_3$, $K_2Cr_2O_7$, $HClO_4$, and $NaClO_4$. The needed amount of $HClO_4$ was added to the Cr(VI) solution, while the $NaClO_4$ was added to the thiosulfate solution.

The mixing time was found to be less than 0.4 sec, determined by mixing under the same conditions a methylene blue solution with water and recording the process photometrically using a photomultiplier and an oscilloscope.

The reaction itself was followed by means of a spectrophotometric device composed of a VSU 1 spectrophotometer (manufactured by Zeiss-Jena), provided with a hydrogen lamp, a photocell, and a Wulff string electrometer, the image of which was projected on the inlet slit of a photographic recorder. This device was able to record a transmitted light intensity *vs.* time curve. The spectral slit width was 1 mμ. The photometric cell was surrounded by a temperature jacket with tube connections to a thermostat. The photographic records were enlarged and then used to calculate the absorbance at zero time, *i.e.*, at the time of mixing.

Continuous-Flow Technique.—This technique was used to record the absorption spectra at reaction times close to zero. The records were made with a Beckman Model DB spectrophotometer, adapting to the 1-cm cell a mixing chamber, shown in Figure 1, following the design of Dixon's cell used for electron spin resonance studies.[3] The two reagent solutions flowed from two 10-l. flasks through the mixing chamber into the photometer cell. A thermometer placed in the exit tube of the photometer cell served to indicate the reaction temperature. The time elapsed between the mixing of solutions and their crossing the light beam was about 0.5 sec.

The over-all flow velocity was determined for the flow of 200 ml of solution, and the mixing ratio for the two solutions was determined by titration of the excess of one of the reactants after the reaction was terminated. The flow velocity was between 2

---

[1] Visiting Scholar at Stanford University, 1966–1967, from the University of Cluj, Cluj, Rumania, during which time this paper was prepared.

(2) (a) A. Leo and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4383 (1952); (b) I. G. Mason and A. D. Kowalak, *Inorg. Chem.*, **3**, 1248 (1964).

(3) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

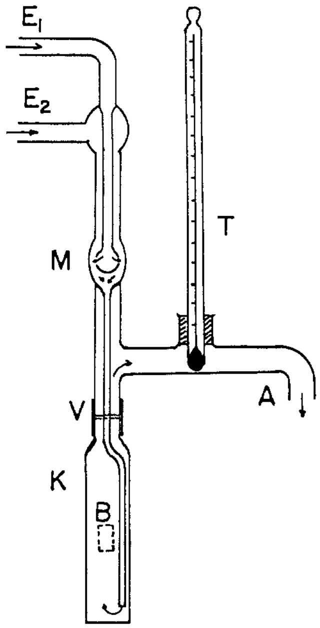

Figure 1.—Photometer cell with mixing chamber: E_1 and E_2, inlets; M, mixing chamber; K, photometer cell; V, plastic tubing; B, position of the spectrophotometer light beam; T, thermometer; A, outlet.

and 5 ml/sec, and the ratio of the two solutions was kept close to 1.

Results

Combination Ratio.—The shape of the kinetic records showed the fast formation of an intermediate, presenting a shorter half-time than the mixing time, followed by a slower decay, with half-times of 30 sec.

Zero-time absorption at 400 and 420 mμ obtained by extrapolation was determined for different Cr(VI):$Na_2S_2O_3$ ratios in isomolar and nonisomolar mixtures. All curves show a maximum absorbance difference for the Cr(VI):$S_2O_3^2$ 1:1 ratio. One of these curves is shown in Figure 2. Ionic strength and acidity were kept constant at 0.11 and 1×10^{-2} *M*, respectively. Temperature was kept constant at 20.0 ± 0.1°.

Molar Absorptivity ε.—The kinetic runs done under conditions mentioned in Table I make possible calculation of the molar absorptivity and the formation constant of the intermediate.

In mixtures with a higher concentration of thiosulfate than 6.0×10^{-3} *M*, the concentration of Cr(VI) having been maintained constant at 4×10^{-4} *M*, no further increase of the absorbance was registered as the concentration of $S_2O_3^{2-}$ was raised. The absorbance value thus found was used to calculate a first approximation of ε. Using this value of ε the data in Table I at lower $(S_2O_3^{2-})$ led to a first approximation of the formation constant. Corrected values were obtained in second and third approximations, which led to the same values for the formation constant *K* and the molar absorptivity within the limits of experimental errors.

The rapid equilibrium

$$HS_2O_3^- \rightleftharpoons S_2O_3^{2-} + H^+ \qquad K_2$$

was taken into account. The dissociation constant K_2 of the thiosulfuric acid was calculated for the ionic strength 0.11 by means of the Davies formula and the experimental data of Page,[4] given for 25°. To obtain the constant at 20° a dissociation heat of −2 kcal/mol was assumed by analogy with the dissociation of HSO_4^- and H_3PO_4. At 20° and ionic strength 0.11 a value of $K_2 = 6.0 \times 10^{-2}$ was found. (The influence of the ionic strength close to the value 0.11 and of the temperature is not too important.)

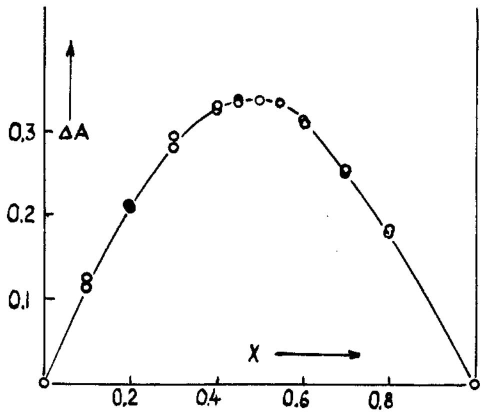

Figure 2.—Plot of the absorbance difference ΔA *vs.* chromate fraction X. Total concentration, (thiosulfate) + (chromate) = 2×10^{-3} *M;* wavelength, 420 mμ. Path length of the cell, 10 mm.

TABLE I

MOLAR ABSORPTIVITY ϵ_{420} AND FORMATION CONSTANT *K* OF $CrO_3 \cdot S_2O_3^{2-}$ AT 20.0°, IONIC STRENGTH $\mu = 0.11$, AND $(H^+) = 10^{-2}$ *M*

10^4 $(S_2O_3Na_2)_a$, *M*	10^4 $(KHCrO_4)_a$, *M*	Absorbance	ϵ_{420}, cm^{-1} M^{-1}	10^4 $(CrS_2O_6^{2-})$, *M*	$10^{-4}K$
16	4	0.325	998	2.91	1.28 ± 0.38
12	8	0.552	1028	4.60	1.15 ± 0.14
11	9	0.613	1050	5.00	1.31 ± 0.15
10	10	0.621	1030	4.90	1.24 ± 0.14
9	11	0.653	1034	5.00	1.31 ± 0.17
30	4	0.362	1031	3.37	1.27 ± 0.49
60	4	0.397	1033	3.80	...
90	4	0.401	1040	3.90	...

The dissociation of $HCrO_4^-$ is not significant under our working conditions,[5] and the formation of the dichromate ion is so small that it could be neglected.

The only reasonable formula for the intermediate seems to be $CrO_3 \cdot S_2O_3^{2-}$, leaving open the problem of protonation and the nature of the bridging atom. The stability constant given in Table I is calculated as

$$K = \frac{(CrO_3 \cdot S_2O_3^{2-})}{(HCrO_4^-)(HS_2O_3^-)} = \frac{(CrO_3 \cdot S_2O_3^{2-})[K_2 + (H^+)]}{[(HCrO_4^-)_a - (CrS_2O_6^{2-})][(S_2O_3^{2-})_a - (CrS_2O_6^{2-})](H^+)}$$

(where the subscript a indicates analytical concentrations), according to the reaction

$$HCrO_4^- + HS_2O_3^- \rightleftharpoons CrO_3 \cdot S_2O_3^{2-} + H_2O \qquad K$$

The concentration of the intermediate was calculated from the measured absorbance at zero time, *A*

$$A = \epsilon(CrS_2O_6^{2-}) + \epsilon_{HCrO_4^-}[(HCrO_4^-)_a - (CrS_2O_6^{2-})]$$

---

(4) F. M. Page, *J. Chem. Soc.*, 1719 (1953).

(5) J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953).

with $\epsilon_{HCrO_4^-} = 228$ at 420 mμ. The error limits of the constant were derived from the individual measurements by means of propagations of error calculations, taking into account the standard deviations of volume, time, and absorbance measurements. As the best value $K = (1.24 \pm 0.14) \times 10^4$ (for equal concentrations of the reactants) can be taken. At 420 mμ the molar absorptivity is 1040 ± 40 cm^{-1} M^{-1}.

Absorption Spectrum.—The spectrum recorded using the flow device is a superposition of the spectra of the different ionic species existing in solution. After correction for $HCrO_4-$ the absorption spectrum given in Figure 3 was found for the intermediate. The reaction is faster in an excess of thiosulfate, and it shows an induction period with chromate in excess. The measurements were, therefore, carried out in a slight excess of chromate, in order to avoid an appreciable decay of the chromatothiosulfate during the flow from the mixing chamber to the light path in the cell. The calculations were made for the time of mixing. The absorption curve shows a maximum at 390 mμ with ϵ_{max} 1400 cm^{-1} M^{-1}. This value was found also in a high excess of $HS_2O_3^-$.

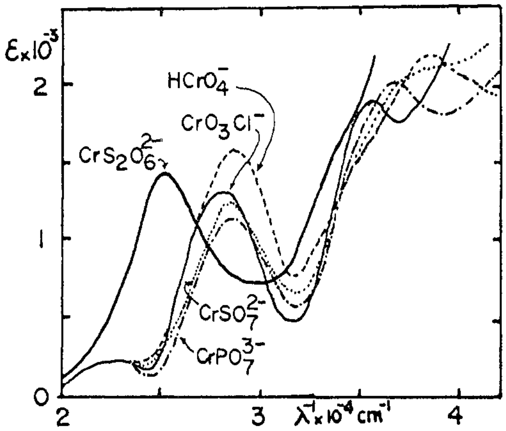

Figure 3.—Absorption spectra of some Cr(VI) compounds.

Absorption curves for $HCrO_4^-$, CrO_3Cl^-, $CrSO_7^{2-}$, and $CrPO_7^{3-}$ as determined by us are included in Figure 3. In every case they are in good agreement with published spectra for these species.[6-9]

Discussion

The band at 390 mμ can be ascribed to a charge-transfer transition, as can the 350 mμ band for $HCrO_4^-$.[10] A number of other species having a Cr–O–R group (*e.g.*, where R is PO_3, SO_3, or $COCH_3$[11]) also have an absorption maximum near 350 mμ. The chlorochromate ion[7,8] has a maximum slightly shifted toward longer wavelengths.

The nature of the R group apparently does not affect the position of the charge-transfer band, but the exchange of the oxygen atom with a chlorine atom of low electronegativity shifts the absorption band to lower frequencies. The even more pronounced shift in the case of the chromatothiosulfate is consistent with the assumption that the sulfur atom acts as a bridge rather than an oxygen atom, and therefore the probable formula of the intermediate is $^-O_3CrSSO_3^-$. The formation of this ion can be assumed to take place by the displacement of OH^- in the $HCrO_4^-$ ion by the sulfur of the $HS_2O_3^-$ ligand.

Acknowledgment.—The authors wish to express their appreciation to Professor Henry Taube of the Department of Chemistry, Stanford University, Stanford, Calif., for helpful discussions.

---

(6) G. P. Haight, D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, **3**, 1777 (1964).

(7) F. Holloway, *J. Am. Chem. Soc.*, **74**, 224 (1952).

(8) O. Lukkari, *Suomen Kemistilehti*, **35B** (5–6), 91 (1962); **38B** (5–6), 121 (1965).

(9) M. Cohen and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4387 (1952).

(10) A. Carrington and M. C. R. Symons, *J. Chem. Soc.*, 889 (1960).

(11) U. Kläning and M. C. R. Symons, *ibid.*, 3204 (1961).

Contribution from the Department of Chemistry,
The University of Texas, Austin, Texas 78712

The Reaction of Borazines with Sodium Biphenylide

By R. D. Compton and J. J. Lagowski

Received September 28, 1967

The formation of alkali metal derivatives of the borazines, *e.g.*, $LiN_3(CH_3)_2B_3(CH_3)_3$, was first reported by Wagner and Bradford.[1] However, attempts to methylate B-methyl- and B-phenylborazines at the nitrogen positions with alkali metal–ammonia solutions or with alkali metal amides led to addition products rather than to the expected alkali metal derivatives.[2] The alkali metals react with solutions of aromatic hydrocarbons such as biphenyl in tetrahydrofuran and other ethers to form solutions of radical anions (eq 1) which can also be used as metalating

$$C_6H_5C_6H_5 + Na \longrightarrow C_6H_5C_6H_5\cdot^- + Na^+ \qquad (1)$$

agents.[3] Thus, it might reasonably be expected that these solutions could be used to prepare alkali metal borazine derivatives.

Experimental Section

Blue-green solutions of sodium biphenylide in anhydrous tetrahydrofuran or ethylene glycol dimethyl ether were prepared according to the procedure of Scott, Walker, and Hansley;[4] aliquots of these solutions were hydrolyzed and titrated with standard acid before use.

B-Trimethylborazine and B-trimethyl-N-methylborazine were prepared from the copyrolysis of $(CH_3)_3BNH_3$ and $(CH_3)_3BNH_2$-CH_3 and were isolated by conventional methods.[1] B-Triphenylborazine was obtained by the reaction of phenylmagnesium bromide with B-trichloroborazine.[5] Pentacarbonylmanganese

---

(1) R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, **1**, 93 (1962).

(2) R. D. Compton, H. Köhl, and J. J. Lagowski, *ibid.*, **6**, 2265 (1967).

(3) E. DeBoer, *Advan. Organometal. Chem.*, **2**, 115 (1964).

(4) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

(5) W. D. English and A. L. McClosky, U. S. Patent 3,000,937 (1959); *Chem. Abstr.*, **56**, 1479*h* (1962).