compared to 2.4 in H_2O. The comparison serves only to indicate that no great disparity is observed and indicates that the data for the two solvents are reasonably consistent.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Dissociation Constants of the Diiodides of Thiacyclobutane, Thiacyclopentane and Thiacyclohexane in Carbon Tetrachloride Solution[1]

BY J. D. MCCULLOUGH AND DENISE MULVEY

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The dissociation constants of the diiodides of thiacyclobutane (Tcb, C_3H_6S), thiacyclopentane (Tcp, C_4H_8S) and thiacyclohexane (Tch, $C_5H_{10}S$) have been determined spectrophotometrically in carbon tetrachloride solution at 25°. The values of K(moles/liter) were found to be: $TcbI_2$, 1.15×10^{-2}; $TcpI_2$, 5.40×10^{-3} and $TchI_2$, 9.07×10^{-3}. Iodine was found to induce polymerization of Tcb in carbon tetrachloride solution.

This study is an extension of previous investigations[2,3] in these laboratories on the dissociation constants of compounds of the type $R_2(S,Se)X_2$ where R is CH_3 or an aryl group and X is iodine or bromine. The dissociations are of the type

$$R_2SX_2 = R_2S + X_2$$

and the dissociation constant has the form

$$K = (R_2S)(X_2)/(R_2SX_2)$$

Experimental

Materials.—The three cyclic sulfides used in this work were supplied through the American Petroleum Institute Research Project 48A, Bartlesville, Oklahoma. The following information was supplied with the samples: **thiacyclobutane**, C_3H_6S, 7 ml., internal breakoff-tip ampoule, dried with $Mg(ClO_4)_2$ sealed *in vacuo*, purity 99.888 mole % as determined by the calorimetric method; **thiacyclopentane**, C_4H_8S, 3 ml., internal breakoff-tip ampoule, dried, sealed *in vacuo*, purity 99.987 mole; **thiacyclohexane**, $C_5H_{10}S$, 2 ml. sealed ampoule, Laramie TC-50-328. Furnished by the British Petroleum Company, Ltd., purity not known but probably 99+%.

The thiacyclopentane (Tcp) was distilled *in vacuo* into four small ampoules sealed on to a side-arm of the original ampoule. The same procedure was attempted with thiacyclobutane (Tcb) but a leak in the system prevented this. The sample was accordingly poured into smaller ampoules and sealed off. Most of the data were obtained by use of these samples but for the final set, a bulb-to-bulb distillation *in vacuo* was performed. The thiacyclohexane (Tch) was used without further purification.

Iodine (J. T. Baker Reagent) was resublimed and stock solutions in dry carbon tetrachloride were prepared.

Carbon tetrachloride (J. T. Baker Reagent) was dried, distilled through a vacuum jacketed bubble plate column (30 bubble plates) and stored so as to exclude moisture. The initial 10% and final 10% of the distillate were rejected.

Spectrophotometric Measurements.—All spectra were measured on a Cary recording spectrophotometer, Model 11PMS, equipped with thermostatic enclosure for the absorption cells. Measurements were made as soon as possible after preparation of the solutions. Matched sets of absorption cells having lengths of 1.000, 9.998 and 25.025 mm. were employed. For each sulfide, some eight to ten solutions were prepared covering a wide range of ratios of sulfide to iodine. Several recordings were made of each sample and the results averaged.

Method of Calculation.—The method of calculation was essentially that described by Keefer and Andrews[4] which permits more accurate correlation of data than the methods used in the previous work.[3] This is especially important with the more highly dissociated sulfide diiodides. The equilibrium constant was determined for each compound by successive approximations. In order to correct the observed absorbances for absorption due to free iodine, it was at first assumed that all of the iodine was free. This permits the calculation of an approximate equilibrium constant. By use of this tentative constant, the amount of iodine combined with the sulfide is calculated and a more accurate value of the concentration of uncombined I_2 obtained. Three cycles for each compound were sufficient to assure the best value permitted by the data. A least-squares line was computed in the last cycle for each compound at each of four wave lengths. The reciprocal of the intercept of this line on the y-axis gives the molar absorbancy of the compound at that wave length and the slope of the line yields the equilibrium constant. Table I shows the compositions of the solutions, the averaged observed absorbances and the final corrected absorbances for the measurements on thiacyclobutane. The data for the other compounds are similar.

TABLE I

ABSORBANCE DATA FOR THIACYCLOBUTANE (Tcb) DIIODIDE

Composition (formality × 10^3)	Cell length, cm.		Av. absorbance			
		λ	420	430	440	450
Tcb 1.443	1	Obsd.	0.290	0.356	0.424	0.507
I_2 1.590		Cor.	.257	.288	.296	.280
Tcb 1.164	2.5	Obsd.	.506	.635	.772	.945
I_2 1.282		Cor.	.438	.497	.511	.481
Tcb 2.060	1	Obsd.	.494	.598	.687	.781
I_2 2.097		Cor.	.452	.512	.525	.493
Tcb 0.825	2.5	Obsd.	.261	.337	.424	.548
I_2 0.840		Cor.	.215	.244	.249	.236
Tcb 2.836	1	Obsd.	.200	.238	.263	.280
I_2 0.599		Cor.	.189	.215	.220	.203
Tcb 2.294	2.5	Obsd.	.351	.418	.471	.515
I_2 0.484		Cor.	.327	.370	.380	.353
Tcb 2.151	1	Obsd.	.274	.329	.373	.418
I_2 1.048		Cor.	.253	.287	.293	.276
Tcb 1.604	2.5	Obsd.	.409	.500	.583	.677
I_2 0.782		Cor.	.369	.418	.429	.403

Results and Discussion

Spectral data and dissociation constants for the cyclic sulfide diiodides are given in Table II. These equilibrium constants may be compared with that for the dissociation of $(CH_3)_2SI_2$, which has the value 14.0×10^{-3} at 25°.[3] The absorption curves for the cyclic sulfide diiodides are similar to that for $(CH_3)_2SI_2$ given in the above reference.

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(1) This research was sponsored by the National Science Foundation under Research Grant NSF-G2354.

(2) J. D. McCullough and B. A. Eckerson, THIS JOURNAL, **73**, 2954 (1951).

(3) N. W. Tideswell and J. D. McCullough, *ibid.*, **79**, 1031 (1957).

(4) R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 1891 (1952).

TABLE II

SPECTRAL DATA AND DISSOCIATION CONSTANTS FOR CYCLIC SULFIDE DIIODIDES

	Thiacyclobutane		Thiacyclopentane		Thiacyclohexane	
λ (mμ)	ϵ	$K \times 10^3$	ϵ	$K \times 10^3$	ϵ	$K \times 10^3$
420	1690	12.0	2310	5.46	2570	8.85
430	1855	11.6	2500	5.30	2810	9.30
440	1920	11.7	2460	5.41	2620	8.98
450	1680	10.7	2130	5.38	2330	9.16
Av. K	11.5 ± 0.5		5.39 ± 0.06		9.07 ± 0.17	
λ_{max} (mμ)	437		431		431	

The iodine absorptivities are also taken from that work.

Too little is known at the present time about dissociation constants of compounds of the type R_2SI_2 to discuss the results in terms of either structure or $\lambda_{max.}$ values. It is interesting to note that, although the constants are all comparable to that for dimethyl sulfide diiodide, there is no systematic relationship among the cyclic sulfide diiodides with respect to ring size. The accuracy of the present determination is, without doubt, high enough to state that the order of stability of the diiodides is definitely thiacyclopentane > thiacylohexane > thiacyclobutane > dimethyl sulfide.

The position of the four-membered ring compound (Tcb) in this series is at variance with the results of Tamres and Hudson[5a,b] on the stabilities of cyclic ether–iodine complexes in *n*-heptane solution.

The order of the stabilities of the ether–iodine complexes was found to be trimethylene oxide > tetrahydrofuran > tetrahydropyran. As a check on the dissociation constant of the Tcb–I_2 compound, a sample of Tcb was redistilled *in vacuo* in an all-glass system to minimize the possibility of Tcb polymer or other impurities being present. A new series of solutions was prepared and measured and the results were in excellent agreement with the previous findings for Tcb–I_2.

Polymerization of Thiacyclobutane.—In the preliminary work on the Tcb-I_2 compound it was found that the more concentrated solutions (*i.e.*, those with formalities of Tcb and I_2 both above 3×10^{-3} F) deposited a brown material on the container walls. This material was insoluble in the common organic solvents but was bleached white by aqueous sodium metabisulfite, probably by removal of iodine. The white residue was also insoluble in acetone, ether, alcohol, etc. Solutions with the compositions in Table I show no deposits, even after several weeks. However, there is a slow decrease in the absorbances with time over the range 400–550 mμ. For this reason, all data used in the final computations were obtained within a few hours after mixing the solutions. No deposits were evident in any of the Tcp and Tch solutions. Further studies of the Tcb polymer are in progress.

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LOS ANGELES, CALIF.

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[5] (a) M. Tamres and M. Hudson (to be published). (b) Sister Mary Brandon Hudson, Ph.D. thesis, University of Michigan, June 1957.

[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

Metastability in Niobate Systems

BY ARNOLD REISMAN, FREDERIC HOLTZBERG AND MELVIN BERKENBLIT

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Experiments are described which together with previous information[2] elaborate on one of the metastable equilibria in the interaction K_2O–Nb_2O_5. Quenched samples having an initial composition of 49.9 mole % K_2O were found to consist of fibrous insoluble and non-descript soluble fractions. The fibrous phase was found to contain 76.55 ± 0.15 weight % Nb_2O_5 corresponding to approximately $6K_2O \cdot 7Nb_2O_5$. On the basis of DTA and X-ray analysis, the recrystallized water-soluble fraction appeared to be identical to the $7 \cdot 6 \cdot 27H_2O$ compound reported in the early literature. It is believed that the metastable system 6:7–7:6 exists at the expense of the 2:3–1:1 and 1:1–3:1 fields and that such behavior in intermediate composition ranges is directly related to deviations from model behavior and shows a possible extension of the ternary aqueous, into the anhydrous system.

Introduction

In studying "equilibrium" interactions of the type M_2O–$M_2'O_5$, two problems have been encountered with disturbing regularity. The first involves metastable field formation, and the second relates to the dissimilarity between the aqueous and anhydrous systems. In a recent paper,[1] model relationships among several niobate systems have been qualitatively explained on the basis of the relative structural stability of the end members. Subsequent re-evaluation of certain data pertaining to intermediate composition metastability in the system K_2O–Nb_2O_5[2] indicated that the problem was directly related to the model system hypothesis and that a possible correlation existed between the aqueous and anhydrous systems *via* this metastability.

Discussion of Experimental Results

Because the experiments are best described in context, a separate Experimental section has been omitted. The techniques of measurement re-

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[1] A. Reisman and F. Holtzberg, THIS JOURNAL, **80**, 6503 (1958).

[2] A. Reisman and F. Holtzberg, *ibid.*, **77**, 2115 (1955).