Two points in favor of the dehydration concept should be stated: (1) the chloro complex exhibits an unusual stability at high acid concentrations. Such behavior is to be expected from a partial dehydration of the central atom, which can be considered as a diminished competition of water molecules in the formation of iron(III) complexes. Conversely, formation of perchlorate complexes implies a competition between perchlorate and chloride ions in attaching themselves to the central atom, and it is difficult to see why $K_1$ should rise so steeply with acidity. (2) A very low solubility of iron(III) perchlorate in 70% perchloric acid was observed. Addition of water greatly enhanced the solubility. The extensive formation of complex ions of the formula $FeClO_4^{++}$ can hardly be reconciled with this observation, while depletion of the hydration sphere of ferric ion would explain the reduced solubility.

BATON ROUGE, LOUISIANA

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# The Deuterium Isotope Effect for a Oxidation–Reduction Reaction between Aquo Ions

BY A. ZWICKEL AND HENRY TAUBE

The effect of substituting $D_2O$ for $H_2O$ on the rate of the reaction of $Cr^{++}$ with $(NH_3)_5CoOH_2^{+++}$ has been investigated. The specific rate of the reaction of $Cr^{++}$ with $(NH_3)_5CoOH_2^{+++}$ decreases by a factor of 3.8, and of $Cr^{++}$ with $(NH_3)_5$-$CoOH^{++}$ by a factor of 2.6, on making this change in solvent. The second reaction is known to proceed by transfer of oxygen from Co(III) to Cr(II), and the first probably also proceeds by the same mechanism. The decrease in rate is taken to indicate that the O–H bonds in the bridging group are stretched in the activated complex; it is evident that the rate decrease does not necessarily imply transfer of hydrogen from reducing agent to oxidizing agent. The kinetics of the reaction of $Cr^{++}$ with $(NH_3)_5CoOH_2^{++}$ have been reinvestigated, and the data reported previously have been revised in some respects.

It has been suggested[1] that electron transfer between two ions such as $Fe^{++}$aq. and $Fe^{+++}$aq. takes place through the agency of a hydrogen atom (or proton and electron) which moves from the coördination sphere of the reducing agent to that of the oxidizing agent. No proof of this kind of mechanism has been advanced, but support for it has been found by its advocates[2,3] in the circumstance that the energetics of activation for a diversity of oxidation–reduction reactions in water are so closely similar. The observation made by Hudis and Dodson[4] that the rate of electron transfer between $Fe^{++}$aq. and $Fe^{+++}$aq. decreases (by approximately a factor of 2) when the reaction medium is $D_2O$ rather than $H_2O$ has also been taken[4,5] as evidence in support of the H atom transfer mechanism.

The significance which has been attached to the twofold decrease in rate on $H_2O$–$D_2O$ substitution is surprising when it is considered that the method has not been calibrated by studying the effect for a reaction of this class of known mechanism. In this paper we report the results of experiments designed to learn the magnitude of this isotope effect for the reaction of two aquo ions which, at least by one path, react by a known mechanism which does not involve hydrogen atom transfer. Experiments have been described earlier[6] on the $H_2O$–$D_2O$ effect for the reaction

$$(NH_3)_5CrCl^{++} + Cr^{++} \longrightarrow \qquad (1)$$
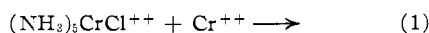
A decrease in rate by about 30% is observed when

(1) R. W. Dodson and N. Davidson, *J. Phys. Chem.*, **56**, 866 (1952).

(2) J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953).

(3) W. L. Reynolds and R. W. Lumry, *J. Chem. Phys.*, **23**, 2460 (1955).

(4) J. Hudis and R. W. Dodson, THIS JOURNAL, **78**, 911 (1956).

(5) G. S. Laurence, *Trans. Faraday Soc.*, **53**, 1316 (1957).

(6) A. E. Ogard and H. Taube, THIS JOURNAL, **80**, 1084 (1958).

$D_2O$ rather than $H_2O$ is the reaction medium. This reaction provides only a partial calibration of the effects to be expected for the $H_2O$–$D_2O$ solvent change; for complete calibration of the $H_2O$–$D_2O$ effect to be expected for a bridged activated complex, the bridging group should be $OH^-$ or $H_2O$. Accordingly we have studied the effect of the $H_2O$–$D_2O$ solvent substitution on the reaction

$$(NH_3)_5CoOH_2^{+++} + Cr^{++} \longrightarrow \qquad (2)$$
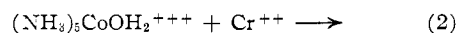
This reaction takes place by the two types of paths commonly observed for oxidation–reduction reactions of aquo ions.

$$\text{Rate} = k_1(Cr^{++})(ROH_2^{+++}) + k_2' \frac{(Cr^{++})(ROH_2^{+++})}{(H^+)}$$

|  |  |  |
|---|---|---|
| Path I | Path II | (3) |

Oxygen atom transfer by path II, which can be taken as involving the reaction of $ROH^{++}$ with $Cr^{++}$, is quantitative, and at least some transfer by path I is indicated.[7] Thus the system affords the opportunity of testing the effect of replacing $OH^-$ as bridging group by $OD^-$, and the comparison of this result with that of Hudis and Dodson[4] for the $FeOH^{++}$–$Fe^{++}$ reaction is of direct interest.

## Methods

The rate of reaction was followed spectrophotometrically, in preference to using the titration procedure adopted for the earlier work. The spectrophotometric procedure is preferred not only because of its greater convenience, but because complications in the titration procedure can arise. Apparently the $Fe^{++}$ formed when the reaction mixture is quenched by $Fe^{+++}$ can under certain conditions react with the residual $(NH_3)_5CoOH_2^{+++}$.

The solution of $Cr^{++}$ and the compound $(NH_3)_5CoOH_2^{+++}$ were prepared using procedures in general similar to the earlier ones.

Throughout this paper, the following symbols are used R represents $Co(NH_3)_5$; time, $t$, is expressed in minutes

(7) R. K. Murmann, H. Taube and F. A. Posey, *ibid.*, **79**, 262 (1957).

optical density $D = \log I_0/I = \alpha Cd$. Concentration $C$ is in moles/liter, and $d$ for all experiments was 10 cm.

The rate data were analyzed applying the equation

$$\frac{-d(ROH_2^{+++})}{dt} = k(Cr^{+++})(ROH_2^{+++}) \quad (4)$$

In all experiments, $(H^+)$ was in considerable excess and remained substantially constant as the oxidation–reduction reaction took place. The course of the reaction for any mixture can be described by the equation

$$\ln \frac{(ROH_2^{+++}) - \Delta}{(ROH_2^{+++})} + \ln \frac{(ROH_2^{+++})}{(ROH_2^{+++})_0 - \Delta} = -kt\Delta \quad (5)$$

where $\Delta = (ROH_2^{+++})_0 - (Cr^{++})_0$. To convert this equation to a form which can be tested directly experimentally, the concentrations must be expressed in terms of the optical densities. The wave length was chosen so that under the concentration conditions of the experiments only $ROH_2^{+++}$ contributes to the optical density. At 345 m$\mu$, the extinction of $Cr^{++}$ can certainly be neglected, and $\alpha$ for $Cr^{+++}$ is *ca.* 2% of that for $(NH_3)_5CoOH_2^{+++}$. The equation which was used is

$$\frac{-kD\infty t}{10\alpha_{ROH_2^{+++}}} = \ln \frac{(D - D\infty)}{D} + \ln \frac{D_0}{(D_0 - D\infty)} \quad (6)$$

where the values of $D$ and $D_0$ are as read, and $D$ has been corrected for the contribution of $Cr^{+++}$ aq. to the optical density, which amounts in the usual case to 3% of the total. The specific rates thus calculated are not more seriously in error than by 1% or so because of effects arising out of the treatment of the data. The values of $k$ are calculated simply from the slope of a plot of $\ln[(D - D\infty)/D]$ *vs.* *t*.

## Results

The results which were obtained are summarized in Table I.

Table I

VARIATION OF THE RATE OF REACTION OF $ROH_2^{+++}$ AND $Cr^{++}$ WITH TEMPERATURE, ACIDITY AND ISOTOPIC COMPOSITION OF SOLVENT

($\mu = 1.20$ using $NaClO_4/HClO_4$)

| Solvent | Temp., °C. | $(H^+)$ | $k$ |
|---|---|---|---|
| H₂O | 10 | 1.16 | 53.4 |
| | | 0.928 | 68.3 |
| | | .696 | 81.1 |
| | | .464 | 110 |
| | | .232 | 190 |
| H₂O | 20 | 1.16 | 112 |
| | | 0.464 | 235 |
| | | .348 | 301 |
| D₂O, 96.5% | 10 | .232 | 53.3 |
| 95.7 | | .348 | 35.9 |
| 92.4 | 20 | .928 | 33.8 |
| 91.8 | | .464 | 58.6 |
| 92.9 | | .232 | 112 |
| 96.5 | | .232 | 118ᵃ |

ᵃ $(ND_3)_5CoOD_2(ClO_4)_3$ in place of $(NH_3)_5CoOD_2(ClO_4)_3$.

In Fig. 1, the values of $k$ are shown plotted against $1/(H^+)$. The data for D₂O have been corrected to 100% D₂O, using a linear extrapolation. The data in H₂O at both temperatures, and for D₂O at 20°, define straight lines reasonably well and thus conform to equation 1. The two points for D₂O at 10° are insufficient to fix the slope, and the line has been drawn in using these two points and for the intercept at $1/(D^+) = 0$, a value calculated from the intercept at 20° using the temperature coefficient of path I determined in H₂O. This assumption can hardly be enough wrong to affect the slope as much as experimental errors do.
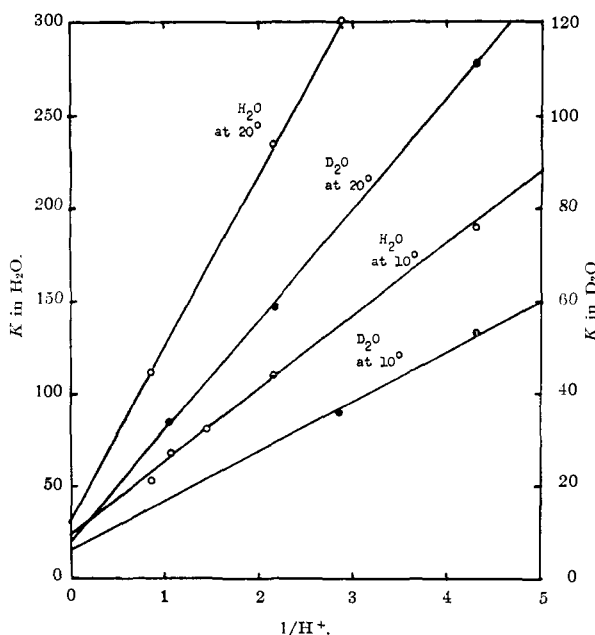


Fig. 1.—Specific rates as a function of acidity in D₂O and in H₂O.

Table II summarizes the values of the specific rates $k_1$ and $k_2'$ which are determined by the data shown in Fig. 1.

Table II

THE SPECIFIC RATES FOR PATHS I AND II

| Solvent | Temp., °C. | $k_1$ | $k_2'$ |
|---|---|---|---|
| H₂O | 10 | 24.6 | 38.6 |
| | 20 | 30.2 | 94.0 |
| D₂O | 10 | (6.5) | 10.7 |
| | 20 | 8.0 | 24.3 |

## Discussion

The new value for the specific rate $k_2'$ agrees satisfactorily with that measured earlier[7] (39 $M^{-1}$ min.⁻¹ at 10° compared to 43), but the values for $k_1$ differ significantly (25 $M^{-1}$ min.⁻¹ by Zwickel and Taube compared to 33 reported by Murmann, Taube and Posey). The reason for the difference is not known with certainty. The earlier results are internally consistent and appear to be of good quality. The recent data equally are internally consistent and of good quality but, additionally, are more extensive and provide a more rigorous test of accidental variability of rates. It is likely that the difference is caused by accidental catalysis. Such influences were admitted in the earlier work; at the beginning of the present work also, erratic rates were observed, some being higher by a factor of 3 than those we later came to regard as normal for the conditions in question. We were able to eliminate the factor causing this variability without discovering its nature. A break in the plastic coating of the magnetic stirrer allowed material to be leached out, which caused the large accelerations. However, addition of small amounts of Fe, V or Ni salts caused only minor changes in rate. The catalyst, whatever its nature, is not consumed in the reaction, either by association with $Cr^{++}$ or by reduction, and the reaction for any

mixture remains first order in $(Cr^{++})$ and $(R-OH_2^{+++})$. Observations made more recently show that the catalytic substance need not act by engaging in a oxidation–reduction process but may function simply by associating with $Cr^{++}$. Enormous effects on the reactivity of $Cr^{++}$ can be produced by small concentrations of appropriate ligands.

In preparing the present report, no data were rejected after the difficulty with the stirrer was eliminated. The results reported were obtained using different batches of redistilled water, of $ROH_2(ClO_4)_3$ and of $Cr^{++}$. For reasons already mentioned, and the additional one that the rates now reported are lower than those reported previously, we regard the present data as more nearly describing the intrinsic rate properties of the $ROH_2^{+++}-Cr^{++}$ reaction.

The most striking observation we report concerns the large effect on the rate which is produced by changing from $H_2O$ to $D_2O$ as solvent, the decrease in $k_1$ being a factor of 3.8 and $k_2'$ being 3.9. The observation that the rates for $Co(NH_3)_5-OD_2^{+++}$ and $Co(ND_3)_5OD_2^{+++}$ are almost identical shows that the rates are not much affected by the isotopic substitution in groups in Co(III) not involved in bridging. By analogy, the effect of replacing the non-bridging $H_2O$ on $Cr^{++}$ by $D_2O$ can be expected to be small; this conclusion receives direct support from the observation[6] that the rates for the reaction $(NH_3)_5CrCl^{++} + Cr^{++}$ is only 30% less in $D_2O$ than it is in $H_2O$. Thus the bulk of the large effect is expended in the bridging group.

The observed change in $k_2'$ must be factored into the part contributed by the $H_2O-D_2O$ isotope effect in the equilibrium

$$ROH_2^{+++} \longrightarrow ROH^{++} + H^+, K_D \qquad (7)$$
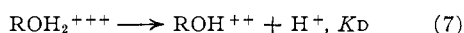
and that contributed as a true kinetic effect in the process

$$ROH^{++} + Cr^{++} \longrightarrow \qquad (8)$$
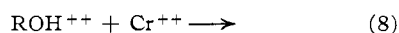
The change from $H_2O$ to $D_2O$ as solvent causes $K_D$ to decrease by a factor of 1.5,[8] and this leaves a factor of 2.6 as the H–D isotope effect in reaction 8. The source of such a large isotope effect is a matter of some interest. We ascribe it to the necessity for stretching the O–H bond in the activated complex when $OH^-$ acts as a bridging group. This may be partly a general effect arising out of the accumulation of so much positive charge adjacent to $O^-$, but it may in large part be a quite specific effect. The activated complex may in fact have a linear arrangement of the Co–O–Cr atoms. Such an arrangement provides for efficient overlap of $d_{z^2}$ metal orbitals with a $p^\sigma$ orbital of oxygen, and such an arrangement, if stabilized by $p\pi$ interactions of oxygen with the metal ions, should presumably require that the proton be substantially removed from the oxygen.

The large solvent isotope effect on $k_1$ is consistent with the view that the mechanism by path I is similar to that by path II but by no means provides additional support for this as a conclusion. The

(8) D. J. Bearcroft, D. Sebera, A. Zwickel and H. Taube, to be published.

mechanism of the reaction by the aquo ion path is an open question; the evidence for atom transfer adduced in an earlier paper is weakened by the present results which show that the contribution to the total reaction by the aquo ion path is less than was assumed in the calculations.

We incline to the view that the $Fe^{++}-Fe^{+++}$ reaction also proceeds by a bridged activated complex. Certainly the isotopic effect observed— a factor of approximately 2 by each of the paths[4]— is no proof of H atom transfer. We ascribe the weaker effect in the $Fe^{++}-Fe^{+++}$ reaction, compared to the $Co(III)-Cr^{++}$ reaction, to the greater capacity that $Fe^{+++}$ has for polarizing the OH group. (This is evidenced by the greater acidity of $Fe^{+++}$ aq. compared to $(NH_3)_5CoOH_2^{+++}$.) Whatever quality of the $Fe^{+++}$ is responsible for this, it renders dissociation of $H^+$ easier, probably also in the activated complex, and perhaps also accounts for the lower sensitivity of the $Fe^{+++}-Fe^{++}$ and $Fe^{+++}-Cr^{++}$ reactions as compared to the $(NH_3)_5CoOH_2^{+++}-Cr^{++}$ reaction to the substitution of $OH^-$ for $H_2O$. On the basis of this correlation, the $Cr^{++}-Cr^{+++}$ reaction should be intermediate in sensitivity to the $H_2O-D_2O$ substitution.

Table III shows a summary of the energetics of the two paths for the reaction of $ROH_2^{+++}$ with $Cr^{++}$.

TABLE III

HEATS AND ENTROPIES OF ACTIVATION FOR THE REACTION OF $(NH_3)_5CoOH_2^{+++}$ WITH $Cr^{++}$

| | Specific rate at 20°, l. mole$^{-1}$ min.$^{-1}$ | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ |
|---|---|---|---|
| Path 1 | 30.2 | 2.9 | -52 |
| Path 2 | $1.0 \times 10^{8a}$ | 4.6$^b$ | -18 |

$^a$ Calculated using $K_D = 9.3 \times 10^{-7}$ at $\mu = 1$ and 20°.[8]
$^b$ Calculated using for $\Delta H_D$ the value 9.5 kcal.[8]

The activation energies for the reactions are surprisingly small, but the small values are not without precedent. Keenan[9] reports for the activation energy of the reaction of $PuOH^{+++}$ with $Pu^{+++}$, 2.8 kcal mole$^{-1}$. The energies of activation for substitution in the aquo ion partner probably exceed this value, and an argument for the existence of a binuclear structure, not merely as an activated complex but also as an intermediate, can be developed on this comparison.[10] The enthalpy of formation of this intermediate is even lower than the enthalpy of activation (presumably activation of the intermediate is required to complete the electron transfer), so that in the $Cr^{++}-ROH_2^{+++}$ system and in the $Pu^{+++}-PuOH^{+++}$ system such intermediates may almost be detectable. It should be noted that the entropy term for the formation of the intermediate is probably unfavorable, so to have a favorable value of $\Delta F$, $\Delta H$ would need to be somewhat negative.

The data in $D_2O$ are too incomplete to provide a satisfactory comparison of $\Delta H$ and $\Delta S$ for the reactions in the two solvents studied. $k_2'$ changes over the 10° interval studied by a factor of 2.2 in $D_2O$ (treating the data as described under results)

(9) T. R. Keenan, J. Phys. Chem., 78, 2339 (1956).
(10) H. Taube and H. Myers, THIS JOURNAL, 76, 2103 (1954).

compared to 2.4 in H$_2$O. 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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# The Dissociation Constants of the Diiodides of Thiacyclobutane, Thiacyclopentane and Thiacyclohexane in Carbon Tetrachloride Solution[1]

BY J. D. MCCULLOUGH AND DENISE MULVEY

The dissociation constants of the diiodides of thiacyclobutane (Tcb, C$_3$H$_6$S), thiacyclopentane (Tcp, C$_4$H$_8$S) and thiacyclohexane (Tch, C$_5$H$_{10}$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
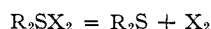
$$R_2SX_2 = R_2S + X_2$$

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$_3$H$_6$S, 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$_4$H$_8$S, 3 ml., internal breakoff-tip ampoule, dried, sealed *in vacuo*, purity 99.987 mole; thiacyclohexane, C$_5$H$_{10}$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

### TABLE I
### ABSORBANCE DATA FOR THIACYCLOBUTANE (Tcb) DIIODIDE

| Composition (formality × 10$^3$) | Cell length, cm. | λ | Av. absorbance 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 |

the solutions, the averaged observed absorbances and the final corrected absorbances for the measurements on thiacyclobutane. The data for the other compounds are similar.

## 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$_3$)$_2$SI$_2$, 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$_3$)$_2$SI$_2$ given in the above reference.

(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).