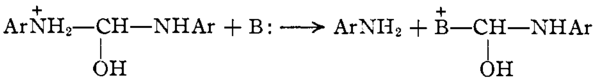
step. It is also significant that the two *o*-substituted diarylformamidines yielded ΔS^* values similar to those of the *m*- and *p*-substituted compounds. *o*-Substituents do not sterically hinder the reaction, indicating that the central carbon atom of the amidine group is far enough from the aromatic rings for hindrance by *o*-substituents to be negligible.

The rate of hydrolysis of N,N'-di-*m*-chlorophenylformamidine was found to increase with increasing dioxane content of the reaction medium, up to 60 or 70% dioxane. This acceleration in rate with diminishing solvent polarity is predicted by the proposed mechanism, according to which charge is dispersed on going from reactants to transition state (ref. 1a, p. 349). The decrease in rate above about 60% dioxane probably is due simply to the reduced concentration of water.

Kinetic studies in buffer solutions show that hydrolysis of diarylformamidinium ions is general base-catalyzed. The mechanism of the general base catalysis probably is similar to that proposed for the reaction in mineral acid solutions, with the buffer base replacing water in either the addition step or the bimolecular displacement step. In either case a highly reactive intermediate would be formed which on hydrolysis would yield the observed products. The fact that aniline catalyzes the hydrolysis of N,N'-diphenylformamidine is an argument against the buffer base participating in the displacement step



$$Ar\overset{+}{N}H_2\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}NHAr + B\text{:} \longrightarrow ArNH_2 + \overset{+}{B}\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}NHAr$$

since in this case a displacement of aniline by aniline would result in no net change, and hence no catalysis. The observed catalysis is thus evidence for the formation of the conjugate acid of trianilinomethane as an intermediate in the reaction. However, the evidence is not conclusive; the general catalysis is small, and the rate change may be due to decreasing the polarity of the solvent by replacing water with aniline.

It seems likely that the catalysis by aniline is real. The highest aniline concentrations used correspond to about 1.6% by weight of aniline. It can be estimated that increasing the dioxane concentration of the reaction medium by 1.6% would increase the reaction rate by a factor of 1.11, which is only half the increase observed in aniline solutions. Since aniline has a higher dielectric constant than dioxane (ref. 7, p. 1222), the medium effect may actually be smaller than this.

The mechanism proposed for acid hydrolysis of diarylformamidines is similar to the $A_{Ac}2$ mechanism of ester hydrolysis. It is probably also similar to the mechanism of acid hydrolysis of amides[1] and imidic esters. According to Edwards and Meacock,[14] the rates of hydrolysis of benzamide and methyl benzimidate are described by the equation

$$k_1 = C{\cdot}c_{BH^+}c_{H_3O^+}/h_0 \qquad (5)$$

where C is a constant and c_{BH^+} is the concentration of the conjugate acid of the amide or imidic ester. They do not give numerical rate data, but inspection of their graphs indicates that their results may be more closely described by equation 3 than by equation 5, in which case the mechanisms of the hydrolysis reactions may be strictly analogous to that proposed for diarylformamidine hydrolysis.

Acknowledgment.—The author wishes to express his thanks to Mr. Carl P. Ruiz and Mr. James R. Keefe for their capable assistance in performing many of the experiments, and to Research Corporation for a grant, without which this work would not have been possible.

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[14] J. T. Edwards and S. C. R. Meacock, *J. Chem. Soc.*, 2000, 2009 (1957).

GOLETA, CALIFORNIA

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Thermochromism of Two Disulfides

BY ROBERT EARL DAVIS[1] AND CHARLES PERRIN[2]

RECEIVED APRIL 13, 1959

The thermochromism of 2,2'-dibenzothiazolyl disulfide and of tetramethylthiuram disulfide has been examined in homogeneous solution in the temperature range of 25 to 100°. Beer's law is obeyed by both compounds at 25 and at 100°, thus indicating that no reversible dissociation has taken place. The thermochromism is attributed to thermal broadening of the absorption band caused by increasing population of the higher vibrational states of the ground state. Radical dissociation of the disulfides has been shown to play no part. The mode of radical decomposition of tetramethylthiuram disulfide has been discussed. Thermodynamic and quantum mechanical criteria have been used to clarify reactions involving elemental sulfurs.

Introduction

Many aryl disulfides, thiocarbonyl compounds and various other sulfur compounds are weakly thermochromic, becoming yellow or deepening in color on heating. In many cases the change is reversible and the original compound is obtained on cooling. Considerable polemic discussion[3-6] has been generated concerning whether or not a *re-*

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[1] Public Health Service predoctoral fellow of the National Cancer Institute, 1957-1958. Department of Chemistry, Purdue University, Lafayette, Ind.

[2] Submitted as an undergraduate project in physical optics to the Department of Physics of Harvard University by C.P.; presented at the 135th Meeting of the American Chemical Society, Boston, Mass., 1959.

[3] H. Z. Lecher, *Science*, **120**, 220 (1954).

[4] H. P. Koch, *J. Chem. Soc.*, 401 (1949).

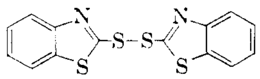
[5] A. Mustafa and M. Kamel, *Science*, **118**, 411 (1953).

[6] J. C. D. Brand and J. R. Davidson, *J. Chem. Soc.*, 15 (1956).

versible dissociation is responsible for the color change. Reported failures[7–8] of Beer's law at high temperatures have shown to be incorrect in some cases and Beer's law is obeyed for diphenyl disulfide,[3] 2,2′-dibenzothiazolyl disulfide[6] and di-*l*-thionaphthoyl disulfide[6] in solution. The color has been attributed to thermal broadening of the absorption band.[6]

Both 2,2′-dibenzothiazolyl disulfide I (MBTS) and tetramethylthiuram disulfide II (TMTD)[9] become yellow on heating.[4,6] Both are important as accelerators for vulcanizing rubber, and it has been postulated that free radicals are important in this process.[10] However, a survey of the existent literature on sulfur vulcanization does not exclude considerations of ionic type reactions. Indeed, some ionic reactions are required to give a reasonable mechanistic interpretation to a few of the known processes.

The present investigation has centered on the thermochromism of I and II and the decomposition of these materials in solution. α,α-Diphenyl-β-picrylhydrazyl, DPPH, an intensely colored, stable free radical, has been used to estimate the rate of production of radicals during the decompositions.



I

$(CH_3)_2N\overset{S}{\overset{\|}{C}}SS\overset{S}{\overset{\|}{C}}N(CH_3)_2$

II

Experimental

Materials.—Both disulfides were obtained as gifts from the B. F. Goodrich Co. and were purified by recommended methods[11] with the added precautions that the solutions were never heated above 45° and always kept in total darkness. The crystals were then dried in vacuum and stored in sealed tubes in total darkness.

cis-Decalin (Eastman Kodak Co.) was washed with dilute sulfuric acid, dried, distilled and then passed through long columns of active silica gel. Toluene was purified by washing with sulfuric acid, dried over sodium, distilled and then refluxed and distilled from diphenylpicrylhydrazyl.

Spectra.—The ultraviolet spectra were measured on a Beckman DU quartz spectrophotometer; both the wave length and the optical density scales were calibrated (Beckman manual). Matched silica cells with glass stoppers and cells which could be degassed and sealed off under vacuum were used. The cell compartment thermostat has been previously described.[12] The brass cell holders were carefully machined to ensure good thermal contact with the absorption cells. The temperature could be controlled to ±0.01 at 25°, ±0.05 at 56° and ±0.1 at 100°.

Kinetics.—Diphenylpicrylhydrazyl was prepared by the lead dioxide oxidation of the hydrazine (Eastman Kodak Co.). Aliquots of the disulfide (10^{-4} to 10^{-2} M) and DPPH solutions (1 to 5 × 10^{-5} M) were mixed and then introduced into the cell. The solution was then degassed well and sealed off in vacuum. The cells were heated in baths to the desired temperature and then placed in the thermostated cell holder at the same temperature. The optical density at 560 mμ was followed as a function of time. Assuming that radical dissociation occurs in the manner

$$A \xrightarrow{k_1} 2R. \qquad (1)$$

the proper rate expression is

$$-2\,dA/dt = 2k_1A = dR/dt \qquad (2)$$

If DPPH intercepts each radical fragment R. very rapidly then

$$-d\,\text{DPPH}/dt = dR/dt = 2\,k_1A \qquad (3)$$

with

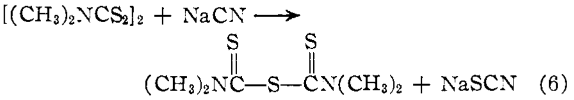
$$\text{DPPH} + R. \xrightarrow{\text{fast}} \text{non-radical products} \qquad (4)$$

Since the ratio $A/DPPH$ is in the range of from fifty to one thousand, A is constant during the time in which the color of the DPPH is fading by a zero order process. Therefore

$$k_1 = \frac{-d\,\text{DPPH}/dt}{2A} \qquad (5)$$

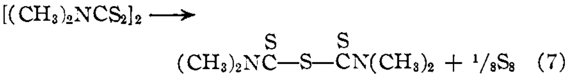
The extinction coefficients of DPPH were obtained in separated experiments. The concentration of the disulfide A was corrected for the expansion of the solvent with temperature. The values of k_1 were independent of the concentration of DPPH.

Thermochemistry.—The heat of reaction of TMTD with sodium cyanide in methanol was measured in a simple Dewar calorimeter designed by Dr. J. R. Cox, Jr. (Thesis, Harvard Univ.). From this datum and the heats of formation of sodium cyanide and sodium thiocyanate,[19] the heat of reaction (7) was calculated to be −2.4 kcal.



$$[(CH_3)_2NCS_2]_2 + NaCN \longrightarrow (CH_3)_2N\overset{S}{\overset{\|}{C}}\text{—}S\text{—}\overset{S}{\overset{\|}{C}}N(CH_3)_2 + NaSCN \qquad (6)$$

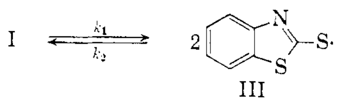
$$\Delta H = -19.8 \pm 0.4 \text{ kcal./mole}$$



$$[(CH_3)_2NCS_2]_2 \longrightarrow (CH_3)_2N\overset{S}{C}\text{—}S\text{—}\overset{S}{C}N(CH_3)_2 + {}^1/_8S_8 \qquad (7)$$

Results

MBTS.—The ultraviolet spectrum of MBTS is characterized by a gentle maximum at 273 mμ (E 21,500) and gentle inflections tailing toward longer wave lengths (Fig. 1). Superimposed upon Fig. 1 is the curve of the difference spectrum, $\Delta E = E_{100} - E_{25}$, in decalin. The maximum increase in E is observed near 300 mμ, ΔE being 1800. Beer's law is obeyed in anisole at 100° in the range[6] of 365 to 380 mμ. In decalin, Beer's law is obeyed at 100° from 230 to 400 mμ (Table I). However, there is a very slow change in the spectrum (less than 1% per hour) with time at this temperature indicating some decomposition. Magnetic measurements[13] on solutions of MBTS in toluene at 100 to 150° have indicated the *possibility* of radical dssociation with an equilibrium



III

constant $K = 6.07 \times 10^{-5}$ at 100° and $K = 5.93 \times 10^{-3}$ at 150°.

Radical dissociation of I is inferred by the use of the intensely colored free radical, α,α-diphenyl-β-picrylhydrazyl, DPPH. If DPPH reacts rapidly[14]

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[7] A. Schönberg, E. Rupp and W. Gumlich, *Ber.*, **66**, 1932 (1933).

[8] Bergem, "Contributions to the Theory of Vulcanization," A/S Askim Gummivarefabrik, Norway, 1948, pp. 136–137; *cf.* ref. 6, p. 20.

[9] The abbreviations used for these compounds are those most widely used in the literature of vulcanization.

[10] C. Walling, "Free Radicals in Solutions," John Wiley and Sons, Inc., New York, 1957, pp. 335–341.

[11] T. E. Ferington and A. V. Tobolsky, THIS JOURNAL, **77**, 4510 (1955).

[12] P. D. Bartlett and R. E. Davis, *ibid.*, **80**, 2513 (1958).

[13] H. G. Cutforth and P. W. Selwood, *ibid.*, **70**, 278 (1948).

[14] Caution must be used in considering DPPH as an *accurate* radical counter. In some cases the hydrazyl is only 60–70% efficient in capturing all the radicals produced in the system; J. C. Bevington, *Nature*, **174**, 477 (1955); *Trans. Faraday Soc.*, **51**, 1392 (1955); G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955); J. P. van Hook and A. V. Tobolsky, *ibid.*, **80**, 779 (1958). In some cases the efficiency of DPPH is only 30%, C. Rüchardt, unpublished data.

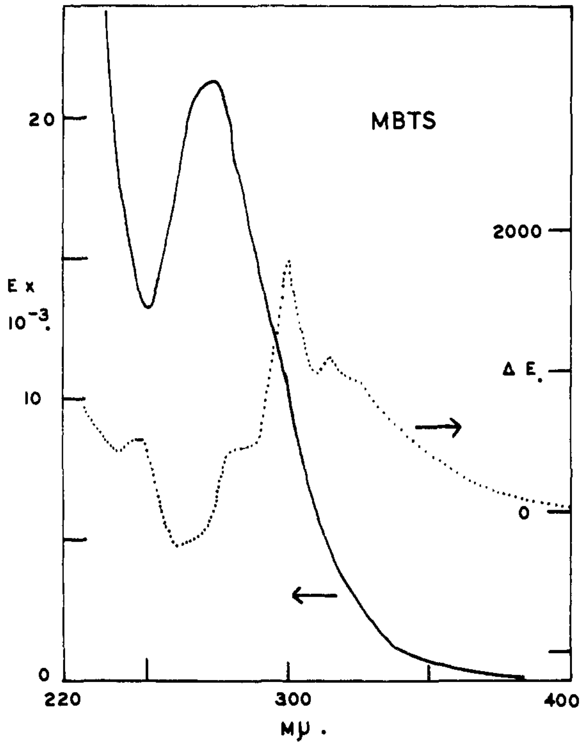


Fig. 1.—Ultraviolet spectrum of MBTS in decalin at 25.0°; right ordinate, difference spectrum: E at 100° minus E at 25°.

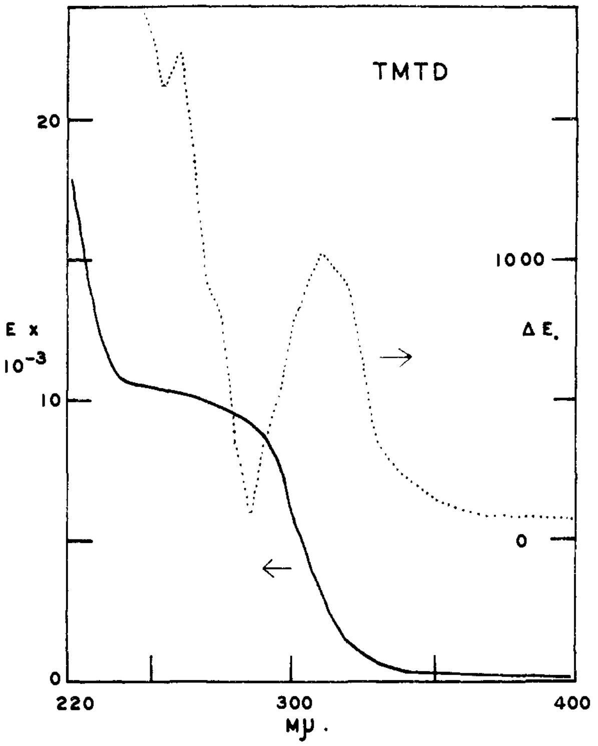


Fig. 2.—Ultraviolet spectrum of TMTD in decalin at 25.0°; right ordinate, difference spectrum: E at 100° minus E at 25°.

with each sulfenyl radical III formed, then the rate of disappearance of DPPH divided by twice the concentration of I is equal to k_1, the estimated rate of dissociation. The equilibrium value at 100° of reaction 6 in toluene[6] can be used to estimate the rate of recoupling of the radicals III. The second-order rate constant, k_2, is calculated to be 1.3 l.m.$^{-1}$ sec.$^{-1}$. The equilibrium value as obtained by magnetic measurements and therefore the value of k_2 must be regarded with some reservations.[15]

Radical III has several possible forms which would therefore increase its stability and reduce its reactivity. Radical III can abstract hydrogen from the solvent forming the thiol. Presumably, the equilibrium of reaction 6 would then not be established. It has been reported that MBTS is only slightly effective thermally in polymerizing styrene.[16] Radical III must be more stable than many other types of free radicals.

TMTD.—The ultraviolet spectrum of TMTD at 25° and the difference spectrum are shown in Fig. 2. The instability of TMTD has been well recognized.[4,6,8,10,17,18] The ultraviolet spectrum has been discussed by Koch.[4] A claim has been made the compound does not obey Beer's law at room temperature.[8] Upon reinvestigation[6] using ethylene bromide as solvent, it was reported that Beer's law was obeyed at 25° near 400 mμ but that the solutions were unstable. The spectrum of the hot solution was not investigated.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF MBTS IN DECALIN AT 100°

λ, mμ	400	350	300	275	250	230
Concn. × 10^4 M				E		
70.1	56.1					
15.8	55.9	980				
1.59		986	12000	21500	13700	35400
0.174			12000	21200	13900	35100

In pure decalin it has been found that Beer's law is obeyed by TMTD at 25° and also at 100° in the range 230 to 380 mμ (Table III). In total darkness there was only a slow change in the spectrum with time at 100°. The spectrum changed rapidly if the solutions were irradiated. Extreme care and cleanliness were required to obtained consistent and reproducible results. The results of the addition of DPPH has been recorded in Table II.

Radical Decomposition of TMTD.—Radicals have been postulated and inferred during the thermal decomposition of TMTD.[9,10,17,18] TMTD is only slightly less effective than benzoyl peroxide at any given temperature in polymerizing vinyl compounds.[16,18] A rather detailed discussion has been given concerning the initial cleavage (or cleavages) and the production of the various products of the decomposition.[18]

(15) We have been unable to detect radicals from either I or II using electron spin resonance equipment of low sensitivity. Work is in progress on an ESR with very high sensitivity (joint project with Edel Wasserman, Bell Telephone Laboratories, Murray Hill, N. J.).

(16) T. Ostu, *J. Polymer Sci.*, **21**, 559 (1956).

(17) D. Craig, "Rubbers Reviews for 1956," *Rubber Chem. Tech.*, **30**, 1291 (1957).

(18) T. Ferington and A. V. Tobolsky, THIS JOURNAL, **80**, 3215 (1958).

TABLE II

RATES OF DISSOCIATION

Compound	Solvent	k_1, sec.$^{-1}$ 100°	k_1, sec.$^{-1}$ 56°
MBTS	Decalin	4.6×10^{-5}	...
MBTS	Toluene[a]	8.3×10^{-5}	7.0×10^{-7}
TMTD	Decalin	1.2×10^{-6}	...
TMTD	Toluene[b]	5.5×10^{-6}	9.2×10^{-8}

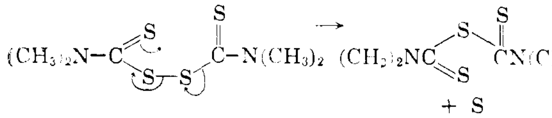
[a] E_a of MBTS 26 kcal./mole. [b] E_a of TMTD 22 kcal./mole. A value of 21.5 kcal./mole was obtained in the exchange reaction of TMTD with radiosulfur in naphthalene at 150° (G.A. Blokh, *Rubber Chem. and Tech.*, **31**, 1036 (1958)).

TABLE III

MOLAR EXTINCTION COEFFICIENTS OF TMTD IN DECALIN AT 100°

λ, mμ	380	350	300	275	250	230
Concn. × 10^4 *M*				*E*		
9.55	156	318				
3.70	158	321	6900			
1.05		317	6790	10400	11800	16300
0.336			6810	10600	12200	16700
0.102			6830	10300	12000	16400

Elemental surfur is also a product of the decomposition of II. Koch[4] suggested a one-step mechanism to produce monoatomic sulfur and the thiuram monosulfide directly. However, such a mechanism producing atomic sulfur ignores the molecularity of sulfur and is very unfavorable on thermodynamic considerations. The ΔH of reaction 7 producing $^1/_8\,S_8$ (rhombic) has been estimated to be -2.4 kcal./mole. The activation for this single step is not known so we can only use the value of the E obtained from the over-all decomposition, $E_a = 22$ kcal./mole (Table II). The ΔHf_0 for the process $^1/_8\,S_8(\text{rhombic}) \rightarrow S\,(\text{gas})$ at 25° is $+\,53.25$ kcal./mole.[19] Furthermore, the ground state of atomic sulfur with a configuration of $(3s)^2(3p)^4$ is $^3P_2$, thus changes in spin multiplicity must be considered. The lowest singlet states still of configuration $(3s)^2(3p)^4$ are $^1D_2$ at a level of 9239.0 cm.$^{-1}$ (26.4 kcal.) and $^1S_0$ at a level of 22181.4 cm.$^{-1}$ (63.4 kcal.) above the ground state.[20] The energy profile of reaction 7 has been constructed from the data obtained from thermochemical measurements and atomic spectroscopy (Fig. 3). Spin restricted transitions are listed as $\Delta S \neq 0$. The spin change T→S is 1.



(9)

Such considerations warrant the exclusion of atomic sulfur in this reaction. It is true that equations are more easily balanced and of simpler form with "atomic sulfur," but the results of kinetic studies[12,21] are *not* interpretable on the simple formula, S. Because atomic sulfur is a high energy species and an electronic triplet, its production from a complex molecule in a singlet state would be slow. Transitions with changes in spin multiplicity are 10^{-5} to 10^{-9} less likely than a transition which has no spin restriction.

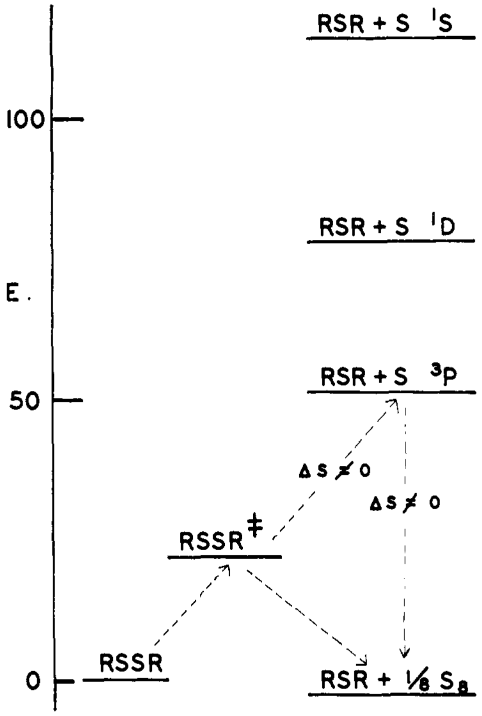
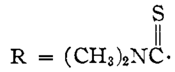


Fig. 3.—Energy profile for the decomposition of TMTD to the monosulfide and elemental sulfurs. Energy, E in kcal./mole, of RSSR is arbitrarily set at zero. RSSR* represents the activated complex. The energies of the products have been calculated on excitation of only the sulfur.

As a tentative postulate the production of S_8 from the decomposition of TMTD might arise from stepwise displacements with the radical formed by asymmetric cleavage.[18] Thus

$$RS_2R \longrightarrow R\cdot + RS_2\cdot$$
$$2RS_2\cdot \longrightarrow RS_2{-}S_2R \longrightarrow R\cdot + RS_4\cdot$$
$$RS_4\cdot + RS_2\cdot \longrightarrow R\cdot + RS_6\cdot$$
$$RS_6\cdot + RS_2\cdot \longrightarrow R\cdot + RS_8\cdot$$
$$RS_8\cdot \longrightarrow R\cdot + S_8$$

where



$$R = (CH_3)_2N\overset{\overset{\displaystyle S}{\|}}{C}\cdot$$

Discussion

If radicals have been demonstrated in these solutions both by physical and chemical methods, should we not assume that the color change is due to these radicals? Several arguments against this interpretation of the thermochromism can be given. The first and most important is the accurate conformance to Beer's law over a wide range of concentration, indicative that dissociation–association equilibria are *not* responsible for the observed spectral change.

The second argument is based upon the kinetic investigation of the decompositions which allows the calculation of the maximum amount of radicals present. In a typical experiment a 10^{-4} molar

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(19) "Selected Values of Chemical Thermodynamic Properties," Circ. 500, U. S. Natl. Bur. of Standards, 1952.

(20) "Atomic Energy Levels," Circ. 467, Natl. Bur. of Standards, Vol. I, 1949, p. 181.

(21) R. E. Davis, THIS JOURNAL, **80**, 3565 (1958).

disulfide solution is heated to 100° and the spectrum recorded within 10 minutes. Using the rate constants from Table II and a time of 600 seconds for reaction 8, the maximum concentration of radicals III from MBTS is 6×10^{-7} molar. If radical III is responsible for the increase in optical density (Fig. 1), the extinction coefficient of the radical must be at least 3×10^5 at 300 mμ. Such a value is unusually high and would require a very narrow absorption band with an oscillator strength or effective f_i number of one (fully allowed transition).[22] Such an interpretation cannot explain the time independence of the absorption values as more radicals are being produced and equilibrium established. Besides, the extinction value of radical III must be tremendous over the entire spectral range of 230 to 400 mμ.

For dissociation of TMTD the maximum amount of radicals produced by the time of measurements would be 1.4×10^{-7} molar. Once again the extinction coefficients are calculated to be abnormally high over the entire spectral range. It would be predicted that as more radicals are produced the spectrum would continue to change. However, the spectrum is nearly time independent at 100° with a change of less than 1% per hour.

The change in spectrum with increasing temperature must then be a ground state phenomenon, a property of the molecule itself rather than its dissociation products. This can be best described as thermal broadening of the absorption band. As a consequence of the Franck–Condon principle, a change in distribution of molecules over the various vibrational levels of the ground state leads to flattening and broadening of the absorption bands with rise in temperature. At low temperatures the vibrational quantum numbers of the absorbing molecules will be preponderally zero. As the temperature is raised, the absorbing molecules are raised into higher vibrational quantum states in accordance with the Boltzmann exponential distribution law. The most probable electronic transitions for these molecules would then involve different changes of the vibrational quantum numbers from those of the molecules in the lowest level. The superposition of all these transitions must result in broadening and flattening of the absorption curve. Both compounds I and II have heavy atoms and skeletal vibrations of low frequency. Therefore, the vibrational spacings of the ground states are quite close together. Compounds I and II have rather strong absorption bands tailing well toward the visible. The extra thermal perturbation extends this tail just enough such that the solution becomes perceptionally yellow.

The authors wish to thank Prof. P. D. Bartlett for helpful encouragement. We are indebted to Mr. R. Wall and T. Kaiser for their thermochemical measurements.

CAMBRIDGE, MASS.

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(22) The absorption bands of most organic compounds in solution have half-widths of the order of 5000 cm.$^{-1}$. Since oscillator strengths of greater than unity are very unusual, $E_{\max}$ values are generally not greater than 5×10^4.

[CONTRIBUTION FROM THE ORGANIC CHEMICAL RESEARCH LABORATORIES, LEPETIT S.P.A. MILANO]

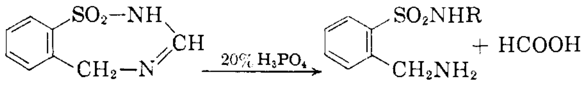
Synthesis of a New Heterocyclic Ring—2,5-Dihydro-1,2,4-benzothiadiazepine 1,1-Dioxide and its Intermediates

BY GIORGIO CIGNARELLA AND UBERTO TEOTINO

RECEIVED JUNE 30, 1959

A new heterocyclic derivative, 2,5-dihydro-1,2,4-benzothiadiazepine 1,1-dioxide (I), has been synthesized by the condensation of *o*-aminomethylbenzenesulfonamide (IIa) with ethyl orthoformate. The starting material IIa was obtained by chlorine oxidation of dithiosalicylamide (III) to *o*-cyanobenzenesulfonic acid (IV), and conversion to IV to the acid chloride V which was converted to the amide VIa. Upon catalytic reduction with palladium, VIa afforded the desired IIa. Two N′-substituted derivatives of IIa were also prepared.

In a previous paper[1] we described the synthesis of a new seven-membered heterocyclic compound, 1,3 - dihydro - 2,3,5 - benzothiadiazepine 2,2-dioxide, by the condensation of *o*-aminobenzylsulfonamide with ethyl orthoformate. We now report the preparation of a new isomeric benzothiadiazepine dioxide. The condensation of ethyl orthoformate with *o*-aminomethylbenzenesulfonamide (IIa) gave a compound, $C_8H_8N_2O_2S$ (I), which upon hydrolysis with phosphoric acid yielded *o*-aminomethylbenzenesulfonamide (IIa) and formic acid. The infrared spectrum of I was very similar to that reported for 1,3-dihydro-2,3,5-benzothiadiazepine 2,2-dioxide.[1] On the basis of these findings, the structure 2,5-dihydro-1,2,4-benzothiadiazepine 1,1-dioxide was assigned to I as shown.



I

IIa, R = H

When the N^1-substituted sulfonamides IIb and IIc (b, R = CH_3; c, R = C_6H_5) were condensed with ethyl orthoformate no product could be isolated. In our previous work,[1] however, the N^1-substituted *o*-aminobenzylsulfonamides yielded not the desired benzothiadiazepines but N,N′-disubstituted formamidines; yields were about 50%.

A few *o*-aminomethylbenzenesulfonamides II have been reported. Only the unsubstituted derivative IIa was isolated by Angyal and Foukin[2] in 9% yield as a by-product of the synthesis of the isomeric homosulfanylamide by chlorosulfonation of N-benzylacetamide followed by treatment with

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(1) U. M. Teotino and G. Cignarella, THIS JOURNAL, **81**, 4935 (1959).

(2) S. J. Angyal and S. R. Foukin, *Australian J. Sci. Research*, **3A**, 461 (1950).