Accurate values of the quantities in equation 2 for polar molecules have not been generally available. However in the case of steam highly accurate values of C_v^0 and of C_v[18] under pressure are available, and now also η and λ values from the correlation of the available viscosity data and the new heat conductivity data given in Table I. The value of f is given in Table VI for steam at "zero" pressure and at saturation for 300° and 84.78 atm.

TABLE VI

VALUES OF THE RATIO $\lambda/\eta C_v$ FOR STEAM

t, °C.	C_{p0} i. j.	$10^5\lambda$ i. j.	$10^5\lambda$	C_v^0 i. j.	$\lambda_0/(\eta_0 C_v^0)$	Prandl number $(\eta_0 C_p^0)/\lambda_0$
100	1.891	22.10	12.67	1.457	1.20	1.08
300	2.002	38.42	20.27	1.540	1.20	1.06
600	2.206	63.95	30.75	1.744	1.19	1.06

For t = 300°C. and p_{sat}; 84.78 atm. we have $C_v = 2.89$ i.j.; $\eta_p = 3.34 \cdot 10^{-4}$(H.S.P.); $\lambda_p = 6.00 \cdot 10^{-4}$ i.j. (K.S.), and $\lambda_p/\eta_p C_v = 0.622 = f$.

It appears from Table VI that the value of f for steam in the perfect gas state is independent of temperature within the accuracy of the elements of the ratio and very much smaller than the values derived from the Eucken relation $1/4\ (9\gamma - 5)$ which is 1.68 for C_p^0/C_v^0 or γ_0, 1.30, 1.30, 1.26, respectively, for the temperatures of the table. The assumption underlying the Eucken relation must accordingly be invalid, a situation which is recognized and discussed in Chapman and Cowling's book.[19] Hirschfelder, Bird and Spotz[3] after noting the discrepancies between theory and observation using the potential equation (1) for non-polar substances, state "This indicates that the Eucken assumption is not valid[20] and hence equation (76) must be modified so as to take into account the difficulty of transferring energy from translation to rotation and vibration." The f value in Table VI for steam indicates a very large deviation in the case of the polar molecule water relative to non-polar gases.

Summary

A series of measurements of the heat conductivity of steam to 350° and 150 atm. have been made during the past two years using a concentric cylinder device especially adapted for measurements under pressure. Comparison with data published by Timroth and Vargaftig obtained through the use of hot wire method shows the new values to be lower by amounts up to 38% (150 atm.). The low pressure (zero) values of Timroth and Vargaftig exhibit a trend to very high values with increasing temperature which is not verified in new measurements.

A correlation of the viscosity values of steam due to Timroth and to Hawkins, Solberg and Potter has been carried out. The values of the latter are believed to be the more reliable. The value of the ratio, heat conductivity, by the product, specific heat and viscosity, is 1.2 and independent of temperature between 100 and 600°. The ratio decreases with pressure increase.

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[18] F. G. Keyes, *J. Chem. Phys.*, **15**, 602 (1947); **17**, 923 (1949).

[19] Ref. 1, pp. 238 and 240 in particular.

[20] That is for non-polar substances having more than two atoms.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, AND THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

The Dipole Moments and the Interconvertibility of Diethyl Disulfide and Trisulfide[1a]

BY HARRY E. WESTLAKE, JR.,[1b] HENRY L. LAQUER[1c] AND CHARLES P. SMYTH*

Polysulfides of an order higher than two have been known for many years.[2] Likewise their interconvertibility was separately recognized by various early investigators. Holmberg[2] observed that diethyl disulfide gave higher order polysulfides in a sealed tube reaction with sulfur and ammonia. Recently, Olin[3] reported that heating disulfides with sulfur and a trace of amine gave polysulfides. The reverse reaction was observed by Twiss[4] to take place when polysulfides were destructively distilled at atmospheric pressure.

The linear structure of disulfides was indicated by the electron diffraction work of Beach and Stevenson.[5] The structure of diethyl trisulfide was investigated chemically by Baroni and Levi,[6] who claimed to isolate a linear trisulfone from the oxidation with nitric acid. We have been unable to repeat this reaction. Baroni, further, made parachor measurements to confirm the linear structure. Bezzi[7] claimed to have proved the linear structure by molecular refraction calculations. While this paper was in preparation, Dawson and Robertson[8] reported the X-ray diffrac-

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[2] Claesson, *J. prakt. Chem.*, **15**, 216 (1877); Holmberg, *Ann.*, **359**, 81 (1908); *Ber.*, **43**, 220 (1910); Thomas and Riding, *J. Chem. Soc.*, 3271 (1923); *ibid.*, 2460 (1925); Chakravarti, *ibid.*, 964 (1923).

[3] Olin, U. S. Patent 2,237,627 (1941).

[4] Twiss, THIS JOURNAL, **49**, 493 (1927).

[5] Beach and Stevenson, *ibid.*, **60**, 2872 (1938).

[6] Levi and Baroni, *Atti Accad. Lincei*, **9**, 772, 903 (1929); Baroni, *ibid.*, **11**, 905 (1930); **14**, 28 (1931).

[7] Bezzi, *Gazz. chim. ital.*, **65**, 693, 704 (1935).

[8] Dawson and Robertson, *J. Chem. Soc.*, 1256 (1948).

tion of bis-(2-iodoethyl) trisulfide, showing a linear structure, and Donohue and Schomaker[9] drew a similar conclusion from electron diffraction measurements on methyl trisulfide.

Dipole Moment Measurements.—In an attempt to throw light upon the problem of the structures of polysulfides, samples of diethyl disulfide and trisulfide were prepared and their dipole moments measured some five years ago. The results are presented here as a check upon new measurements upon four dialkyl polysulfides with which they are in excellent agreement. The new measurements will be reported in a subsequent paper, which will consider all the results in their relation to the molecular structures.

The dipole moments were calculated by means of the Debye equation from measurements of the densities and dielectric constants of dilute solutions of the substances in benzene. These constants were measured with a pycnometer and a heterodyne beat apparatus in a manner previously described.[10] The mole fractions, c_2, of the polar solute, the dielectric constants, ϵ, the densities, d, and the molar polarizations, P_2, are given in Table I. The molar refractions, R_D, calculated from densities and refractive indices in the literature, the polarizations, P_∞, obtained by averaging the values of P_2, and the dipole moments are given in Table II.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AND POLARIZATIONS, P_2, AT 25°

c_2	ϵ	d	P_2
	Diethyl disulfide		
0.000000	2.2751	0.87313	
.003562	2.2951	.87372	118.9
.007228	2.3151	.87427	117.7
.011752	2.3409	.87495	118.3
.017132	2.3715	.87579	118.3
.017462	2.3736	.87586	118.5
	Diethyl trisulfide		
0.000000	2.2745		
.002012	2.2844	0.87346	106.7
.004316	2.2927	.87436	99.7
.007355	2.3054	.87548	100.8
.010838	2.3210	.87666	102.9
.000000	2.2755	.87274	
.003087	2.2888	.87377	105.5
.007210	2.3056	.87517	103.4
.008913	2.3109	.87586	100.2

TABLE II

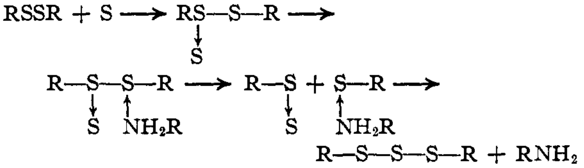
MOLAR REFRACTIONS, POLARIZATIONS, P_∞ (25°), AND DIPOLE MOMENTS

	MR_D	P_∞(25°)	μ(× 10^{18})
$(C_2H_5)_2S_2$	36.61[11]	118.3	1.99
$(C_2H_5)_2S_3$	47.48[12]	102.7	1.64

The Rearrangement of Disulfides to Trisulfides.—The fact that the trisulfides as well as disulfides appear to be linear requires that a rearrangement take place during the transformation of the latter into the former. This interconversion has been confirmed by preparing diethyl disulfide by the Bunte salt method,[13] which unequivocally gives the disulfide. This was converted to diethyl trisulfide by the method of Olin.[8] Diethyl trisulfide was also prepared by Chakravarti from ethyl mercaptan and sulfur monochloride,[13] S_2Cl_2,[2] giving a product identical with that obtained from the disulfide, as well as with that described in the literature

MacMillan and King,[14] in a recent discussion of the mechanism of the Willgerodt reaction, discarded one alternative step in their proposed mechanism on the ground that sulfur does not attack disulfides in the presence of catalytic amounts of amines. Our observation that, while a reaction does take place, it does not involve attack on the carbon, strengthens the argument for the alternative which requires an amine-sulfur addition product to attack the disulfide.

It is possible to suggest a mechanism by which a linear disulfide becomes a linear trisulfide. It would logically begin by the addition of a sulfur atom to one of the disulfide sulfurs. The resulting positive charge on the latter, attracting some of its neighbor's electrons and aided by the approach of the amine group to the neighboring sulfur, would induce the splitting of the S–S disulfide bond and the recombination of the fragments into a linear chain of three sulfurs. This may be written, schematically, as



$$\mathrm{RSSR + S \longrightarrow R\underset{\underset{S}{\downarrow}}{S}—S—R \longrightarrow}$$

$$\mathrm{R—\underset{\underset{S}{\downarrow}}{S}—\underset{\underset{NH_2R}{\uparrow}}{S}—R \longrightarrow R—\underset{\underset{S}{\downarrow}}{S} + \underset{\underset{NH_2R}{\uparrow}}{S}—R \longrightarrow}$$

$$\mathrm{R—S—S—S—R + RNH_2}$$

Such a route, while unsupported except for the structures of the initial and final materials, does represent a logical explanation of the observed phenomenon. A free radical mechanism, in which the disulfide first splits, possibly because of the influence of the amine, into R–S– fragments which then pick up free sulfur and recombine, is also a possibility.

The reaction in the reverse direction is probably only another example of the well-known hydrolytic cleavage of the S–S bond in the presence of alkali. The fact that no residue was observed on distilling the isolated product showed that the transformation had already occurred. The only unusual result was that no mercaptan was found in the alkaline solution. Whether this was due to the small amounts of reactants or to a peculiarity of the hydrolytic cleavage of trisulfides was not determined. The general effect of heating the tri-

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[9] Donohue and Schomaker, *J. Chem. Phys.*, **16**, 92 (1948).

[10] Lewis and Smyth, *ibid.*, **7**, 1085 (1939).

[11] Nasini, *Ber.*, **15**, 2878 (1882).

[12] Baroni, *Atti accad. Lincei*, **14**, 28 (1931).

[13] Westlake and Dougherty, THIS JOURNAL, **64**, 149 (1942).

[14] MacMillan and King, *ibid.*, **70**, 4143 (1948).

sulfide with aqueous alkali appeared to be the formation of sodium polysulfides and the degradation to the disulfide.

Preparation of Ethyl Disulfide.[12]—A mixture of 500 g. of sodium thiosulfate, 220 g. of ethyl bromide, 500 cc. of water and 40 cc. of alcohol was refluxed with stirring for twenty-two and one-half hours. Two hundred and fifty grams of iodine was added in small batches to the hot mixture. After all the iodine was added, the mixture was decolorized with aqueous sodium bisulfite. The crude disulfide was separated. The aqueous layer was extracted with ether and the extract was combined with the crude product. The solution was washed with aqueous sodium bisulfate, dried over calcium chloride, and distilled. The fraction boiling at 145–155° was collected. It weighed 67.7 g. (55.4% yield).

Anal. Calcd. for $(C_2H_5)_2S_2$: S, 52.46. Found: S, 52.84, 52.48.

The ethyl disulfide was redistilled through a small fractionating column, a middle fraction boiling at 152.5–154° being collected. The refractive index of this sample was checked to determine purity: $n^{20}D$ 1.5078; (*cf.* Nasini[11]: $n^{20}D$ 1.50633, b. p. 153–154°; Nekrassow and Melkinow[15]: $n^{20}D$ 1.503).

Preparation of Ethyl Trisulfide.[2,6]—Seventy grams of freshly distilled water-white sulfur monochloride, S_2Cl_2, was dissolved in 50 g. of carbon bisulfide. This solution was slowly added through a reflux condenser to a flask containing a solution of 100 g. of ethyl mercaptan (Eastman Kodak Co.) in 50 g. of carbon bisulfide. The flask was kept cold during the addition. Freshly precipitated calcium carbonate was prepared from soda ash and calcium chloride and dried at 105°. Ten grams was added to the reaction mixture. After the evolution of carbon dioxide had ceased, the mixture was filtered. The carbon bisulfide was distilled from the filtrate on a water-bath in an atmosphere of nitrogen. The reaction products were fractionated under reduced pressure (26 mm.) in a stream of nitrogen, the following fractions being obtained: (1) b. p. 89–100° (26 mm.), $n^{13}D$ 1.5685; (2) b. p. 100–115° (26 mm.), $n^{13}D$ 1.5700; (3) b. p. 123–129° (26 mm.), $n^{13}D$ 1.5888.

Levi and Baroni[6] found for the trisulfide, $n^{13}D$ 1.56890, and b. p. 85° and for the tetrasulfide $n^{13}D$ 1.58436. The middle fraction (2) was redistilled at b. p. 92–97°. Its refractive index was found to be $n^{13}D$ 1.5689. After standing several months this had dropped to 1.5683. Although the boiling point reported here differs appreciably from that reported by Levi and Baroni, it is believed to be correct since it was observed repeatedly. The refractive index coincides with that found by Levi and Baroni, and both boiling point and refractive index are in satisfactory agreement with the values for fraction 2B described in the next paragraph and found by analysis to have the correct composition.

Reaction of Ethyl Disulfide with Sulfur.—A mixture of 15 g. of ethyl disulfide, 7.8 g. of sulfur and 1.5 g. of dibutylamine was heated to 85–90° for three hours and then to 120–128° for five hours. The mixture was cooled, dissolved in ether, and washed with dilute hydrochloric acid and water. After drying the mixture with calcium chloride, the ether was evaporated. The residual liquid was fractionated at a pressure of 16 mm.: (1) b. p. 20–70° (16 mm.), 1.0 g.; (2) b. p. 70–100° (16 mm.), 7.9 g.; (3) b. p. 100–110° (16 mm.), 3.0 g.

Fractions 2 and 3 were combined and redistilled at 18 mm.: (2A) b. p. 83–87° (18 mm.); (3A) b. p. 92–97° (18 mm.).

These were analyzed for sulfur. *Anal.* Calcd. for $(C_2H_5)_2S_3$: S, 62.4. Found: 2A, S, 60.23, 60.08; 2B, S, 62.69, 62.33.

Fraction 2B was redistilled at 26 mm. Most of it came over at 96–97°. The refractive index was found to be $n^{13}D$ 1.5683.

Desulfurization of Diethyl Trisulfide.—A mixture of 5 g. of ethyl trisulfide, 1.6 g. of sodium hydroxide and 20 cc. of water was stirred one and one-half hours at reflux. After cooling, it was extracted with ether. The extract was dried and the ether evaporated. The residual liquid boiled at 152–154° leaving no residue ($n^{20}D$ 1.5080). The aqueous layer was acidified with dilute sulfuric acid and the gases evolved were passed through an ice-trap. Only a trace of ether was trapped but hydrogen sulfide was evolved. Sulfur precipitated from the solution.

Summary

The preparation of ethyl disulfide and ethyl trisulfide and the conversion of each compound into the other have been described. The mechanisms of the conversions are discussed.

The dielectric constants and densities of dilute benzene solutions of diethyl disulfide and trisulfide have been measured and used to calculate the dipole moments of the molecules. The moment values, in excellent agreement with additional data shortly to be interpreted and published, are 1.99×10^{-18} for diethyl disulfide and 1.64×10^{-18} for diethyl trisulfide.

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(15) Nekrassow and Melkinow, *Ber.*, **62**, 2091 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

A New Polarographic Diffusion Current Equation

BY JAMES J. LINGANE* AND BRIAN A. LOVERIDGE†

The Ilkovic equation[1,2,3] for the diffusion current observed with the dropping mercury electrode

$$i_d = 607nD^{1/2}Cm^{2/3}t^{1/6} \text{ (at 25°)} \qquad (1)$$

although approximately correct is not completely satisfactory. Lingane and Loveridge[4] demonstrated that the diffusion current "constant," $i_d/Cm^{2/3}t^{1/6}$, of lead ion varies significantly with changing values of $m^{2/3}t^{1/6}$, whereas according to the Ilkovic equation it should be truly constant and independent of the electrode characteristics m and t. Loveridge[5] observed an exactly similar behavior with tetramminozinc ion. The nature and extent of these variations are shown in Fig. 1,

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† Harvard University Ph.D. 1947.

(1) D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934); *J. chim. phys.*, **35**, 129 (1938).

(2) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, Chap. II and Chap. IV.

(4) J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1944); **68**, 395 (1946).

(5) B. A. Loveridge, Ph.D. Thesis, Harvard University, 1947.