

for the regression coefficient given by equation 2, where the error is expressed to the 5% probability level.³

Measurement of the kinematic viscosity of the solution at room temperature (25.0°) gave $\nu^{25.0} = 0.8836 \pm 0.0028$ centistoke. The viscosity of the solution with density $\rho^{25.0} = 1.0008$ g./cm.³ is therefore $\eta^{25.0} = 0.8843 \pm 0.0028$ centipoise. The area of the disc electrode was measured as 3.9039 ± 0.0012 sq. cm. Calculation of the diffusion coefficient for the silver ion from equation 3 gave $D_s = (1.416 \pm 0.013) \times 10^{-5}$ cm.²/sec. All the errors indicated are expressed to the 5% probability level.⁴

Another independent experimental run at a room temperature of 25.2° gave similar linear relationships. Constants of the solution at this temperature were $\nu^{25.2} = 0.8824 \pm 0.0016$ centistoke, $\rho^{25.2} = 1.0007$ g./cm.³, and $\eta^{25.2} = 0.8830 \pm 0.0016$ centipoise. The regression coefficient was calculated as $b = 0.07644 \pm 0.00033$ and the diffusion coefficient as $D_s = (1.458 \pm 0.009) \times 10^{-5}$ cm.²/sec.

The experimental values for the diffusion coefficient of Ag^+ are in good agreement with the Onsager limiting law^{5,6} which predicts a value $D_{\text{Ag}} = 1.485 \times 10^{-5}$ cm.²/sec. at 25°.

(3) R. A. Fisher, "Statistical Methods for Research Workers," Oliver and Boyd, London, 1946, p. 135.

(4) R. A. Fisher, ref. 3, p. 122.

(5) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

(6) L. J. Gosting and H. S. Harned, *J. Am. Chem. Soc.*, **73**, 159 (1951).

THE INFRARED SPECTRUM OF SULFUR DICHLORIDE

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Sulfur dichloride is one of the few triatomic molecules not studied in either the Raman or infrared. Raman investigation is made difficult by the red color of the compound and the low frequencies of its fundamentals allow only an incomplete study by means of infrared. By the determination of sufficient overtone and combination bands, however, the fundamentals can be fairly definitely deduced.

The compound was prepared¹ by bubbling chlorine through sulfur monochloride containing a trace of iodine. It was distilled immediately before use and boiled at a constant value of 57.3° at 734 mm.

Figure 1 shows the spectrum of the liquid and vapor obtained on a Beckman IR2T (rock salt region) and a Perkin-Elmer Model 112 (CsBr region) instrument.

Absorptions at 460 cm.⁻¹ in the vapor and 445 cm.⁻¹ in the liquid are due to the very strong band of S_2Cl_2 contaminating the sample. None of the remaining bands can be assigned to this impurity.

Table I lists the more intense of the observed frequencies with an assignment of the overtones and combinations in terms of a set of fundamental modes. For this molecule all combinations and

(1) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, New York, N. Y., 1950, p. 946.

overtones are allowed by symmetry in the infrared. The strong band at 525 cm.⁻¹ in the vapor is undoubtedly a stretching fundamental. The Raman spectra² of Stammrich, Forneris and Sone indicate that this band is to be assigned to the symmetric stretching mode. The remaining fundamentals, reported from the Raman spectrum as 208 and 535 cm.⁻¹, are not observed. With these fundamentals the remaining stronger infrared bands can be satisfactorily accounted for.

Taking as gas phase fundamentals 525, 504 and approximately 200 cm.⁻¹, an SCl_2 angle of 103° ³ and a potential field of the form

$$2V = k[(\Delta r_1)^2 + (\Delta r_2)^2] + k(r_0 \Delta \alpha)^2 + k_2[\Delta r_1 + \Delta r_2]r_0 \Delta \alpha$$

the force constants are evaluated as $k = 2.46 \times 10^5$, $k\alpha = 0.30 \times 10^5$ and $k_2 = 0.16 \times 10^5$ dynes/cm. More detailed consideration of different force fields does not seem warranted in view of the uncertainty in the assignment of the symmetric and antisymmetric vibrations.

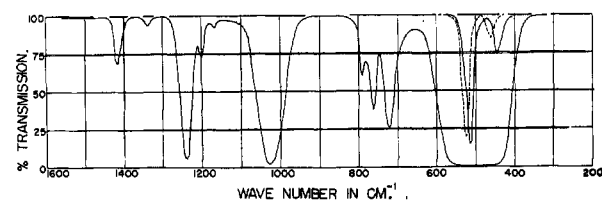


Fig. 1.—The infrared spectrum of SCl_2 : -----, vapor; ———, pure liquid.

Comparison can be made, however, with the force constant of 2.42×10^5 for the SCl bond in sulfur monochloride⁴ and the bending constant at 0.3×10^5 . Since somewhat different force fields were used exact agreement for these molecules cannot be expected.

TABLE I
FREQUENCIES AND ASSIGNMENT OF INFRARED ABSORPTION BANDS OF SCl_2 , ν (CM.⁻¹)

Vapor	Liquid	Assignment
	(208)	ν_2
525	514(vs)	ν_1
	(535)	ν_3
	719(m)	$\nu_1 + \nu_2$
	761 w	$\nu_1 + \nu_3$
	1027(s)	$2\nu_1$
	1237(m)	$2\nu_1$
	1416(w)	$2\nu_1 + 2\nu_2$

For a similar molecule Cl_2O and the frequencies of Hedberg⁵ and of Bailey and Cassie⁶ the same force field as given above gives $k = 4.75 \times 10^5$, $k = 0.46 \times 10^5$, and $k_2 = 0.32 \times 10^5$ dynes/cm. The increase in the stretching force constant and the interaction constant are to be expected for the molecule containing a first row element compared to one of the second row.

(2) Since submission of this note the Raman spectrum has been reported by Stammrich, Forneris and Sone, *J. Chem. Phys.*, **23**, 972 (1955). Their reported Raman bands are used here to aid in the assignment of the infrared overtone bands.

(3) D. P. Stevenson and J. Y. Beach, *J. Am. Chem. Soc.*, **60**, 2872 (1938).

(4) H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 1018 (1950).

(5) K. Hedberg, *J. Chem. Phys.*, **19**, 509 (1951).

(6) C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc. (London)*, **142A**, 129 (1933).

Finally one can notice the variation in the frequencies of the SCl bond stretching vibrations in the set of molecules SCl_2 , OSCl_2 ,⁷ and O_2SCl_2 ,⁸ where the average SCl frequency (for the liquid) decrease from 525 to 466 to 396 cm^{-1} . Interaction with the SO frequency of the thionyl and sulfuryl chloride might be expected to increase rather than to decrease the "SCl" frequency. In this case the frequency decrease would be associated with a weakening of the S-Cl bonds in the series. This result is not readily understood in terms of the increased formal charge on the sulfur atom,⁹ and a simple explanation based on the use of d orbitals by the sulfur atom follows only if it is assumed that in SCl_2 there are contributing structures involving use of the chlorine d orbitals also.

(7) C. A. McDowell, *Trans. Faraday Soc.*, **49**, 371 (1953).

(8) Vogel-Hogler, *Acta Phys. Austriaca*, **1**, 323 (1948).

(9) C. C. Price and R. G. Gillis, *J. Am. Chem. Soc.*, **75**, 4750 (1953).

A NOTE ON VISCOSITY OF MIXTURES. PART I (LIQUID-LIQUID BINARY MIXTURE)

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A viscosity function of the form

$$(\eta_m)^{1/3} = \frac{d(x_1R_1 + x_2R_2 + \dots + x_nR_n)}{M_m}$$

where η_m is the viscosity, M_m the mean molecular weight, "d" the density of the mixture, and "x," the mole fraction and "R" the rheochor of the component, has been tested with viscosity data on binary liquid-liquid pairs.^{1,2}

The above equation for viscosity can be obtained from the equation of Smith and co-worker,³ in the following manner.

The above authors³ have shown that F , the additive-constitutive property

$$F = \sum x_i F_i = (x_1 F_1 + x_2 F_2 + \dots + x_n F_n) \quad (1)$$

and also

$$F = f(\eta) \sum x_i M_i / d = f(\eta) \times (x_1 M_1 + x_2 M_2 + \dots + x_n M_n) / d \quad (2)$$

where x_i is the mole fraction of the i^{th} component of the mixture. Now by equating "F" in the two equations

$$f(\eta) = d \sum x_i F_i / \sum x_i M_i = \frac{(x_1 F_1 + x_2 F_2 + \dots + x_n F_n) \times d}{x_1 M_1 + x_2 M_2 + \dots + x_n M_n}$$

The values of F_1 , F_2 , etc., can be calculated from the additivity of the groups or the atomic values of the molecules and corresponds to the rheochor of the components. If R_1 , R_2 , etc., are the rheochor of the components 1, 2, etc., and $(x_1 M_1 + x_2 M_2 + x_3 M_3 + \dots) = M_m$, the mean molecular weight; η_m , the viscosity of the mixture can be obtained from the equation

$$(\eta_m)^{1/3} = \frac{(x_1 R_1 + x_2 R_2 + \dots + x_n R_n) \times d}{M_m} \quad (3)$$

(1) F. W. Lima, *J. Am. Chem. Soc.*, **56**, 1052 (1952).

(2) Katz, *et al.*, *Ind. Eng. Chem.*, **35**, 1091 (1943); **35**, 239 (1943).

(3) C. P. Smith, *et al.*, *J. Am. Chem. Soc.*, **51**, 1736 (1929).

Following are the comparative results of viscosity as calculated from equation three and viscosity observed by Silawat,⁴ *et al.*

TABLE I

(The detailed calculations may be published elsewhere at a later date.)

Systems	Deviations, %	
	Maximum	Minimum
Toluene-acetic acid	3.50	0.52
Benzene-acetic acid	2.75	.03
Chloroform-acetic acid	3.12	.02
Carbon tetrachloride-acetic acid	4.40	.045
Toluene-acetone	3.57	.48

As will be seen from the table the standard deviation between the calculated and experimental viscosities is approximately 1%, while the maximum deviation being 4.4%. In the equation suggested by Lima¹ there is a maximum deviation of 15% and generally an error of 12%. Further work of binary solid-liquid and ternary liquid mixtures is being carried out.

(4) H. G. Silawat, *et al.*, *J. Ind. Chem. Soc.*, **27**, 345 (1950).

SYNTHESIS OF *n*-BUTANE-2,3-*d*₄ BY THE PHOTOLYSIS OF α, α' -DIETHYL KETONE-*d*₄

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In agreement with the work of Wijnen and Steacie,¹ we found that deuterium from heavy water exchanged with hydrogen in diethyl ketone exclusively in the α -positions. Nine ml. of D_2O containing 0.1 g. of K_2CO_3 was added to 10 ml. of redistilled diethyl ketone. The partially miscible system was refluxed gently at one atmosphere for 8-16 hours in a closed system. Sufficient K_2CO_3 was added to saturate the water layer. The ketone layer was separated and the procedure repeated ten times. The resulting ketone was distilled from an excess of K_2CO_3 and freed of dissolved air by repeated freezing and melting under vacuum. Mass spectrometric analysis showed about 98-99% α, α' -diethyl ketone-*d*₄, the remainder being the trideutero compound.

The marked ketone was photolyzed in a water cooled 200-ml. fused silica reaction vessel at 33 mm. initial pressure and at 30°, using a Hanovia Alpine burner. The photolysis was continued for about two hours or until the pressure had risen to 45 mm. The entire contents of the photolysis vessel were pumped into a 2-liter flask. This procedure was repeated 35 times. The flask containing the heavy products of the photolysis in addition to CO was sealed off.

According to the work of Kutschke, Wijnen and Steacie,² the main products of the photolysis in the region of room temperature are butane, ethylene, ethane and carbon monoxide. The mechanism of

(1) M. H. J. Wijnen and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1092 (1951).

(2) K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, *J. Am. Chem. Soc.*, **74**, 714 (1952).