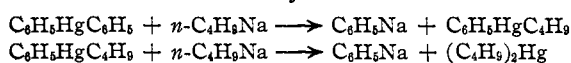


when amyl chloride was added to a mixture of sodium and dimethylaniline in ligroin.

Diphenylmercury.—From a reaction between *n*-butylsodium and diphenylmercury in petroleum ether there was obtained after carbonation a 40% yield of benzoic acid and a 48% recovery of diphenylmercury. The large yield of benzoic acid could not have come from the action of sodium (used to prepare *n*-butylsodium) and diphenylmercury, because the excess sodium was removed by free mercury prior to adding the diphenylmercury. This interchange reaction of organometallic compounds might have involved the intermediate formation of an unsymmetrical mercurial.



Sodium Phenoxide.—There was no evidence of metalation when sodium phenoxide was treated with *n*-butylsodium in a medium of petroleum ether, for three days at room temperature.

General Considerations.—(1) Where comparisons can be made, the extent of metalation increases with the reactivity of the RM compound. This is particularly true when there are possibilities of mono- and polymetalation, the moderately reactive types rarely showing polymetalation. (2) The best solvents, of those so far examined, are the simple ethers.¹⁹ Unfortunately, the more

(19) The effect of ethers with higher oxygen content will be re-

reactive RM compounds cleave ethers. An examination of some of the results now reported reveals that this cleavage reaction may be of secondary importance where the rate of metalation is more rapid than the rate of cleavage, and where the new RM compound formed subsequent to metalation is known to cleave ethers to a limited extent. Although tri-*n*-butylamine was used successfully in some cases as a medium, it appears to suffer the disadvantages of ethers. For example, in an experiment with *n*-butylsodium the yield of *n*-octane was in excess of 100%, and this indicates definite cleavage of the amine by the RNa compound. (3) There are marked correlations between rates of metalation and the rates of cleavage of RM compounds by hydrogen chloride. These will be presented later together with mechanisms correlating metalation with other substitution reactions.

Summary

A series of compounds has been metalated by different organometallic compounds in various media. Interpretations and generalizations of the reactions have been presented.

ported later. Ethers like dimethylglycol ether have been found very effective for addition of alkali metals [Scott, Walker and Hansley, *THIS JOURNAL*, **58**, 2442 (1936)]. The authors are grateful to Dr. Scott for a supply of this particular ether.

AMES, IOWA

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, DICKINSON COLLEGE]

The Viscosity of Solutions of Sulfur Dioxide in Organic Liquids

BY H. E. ADAMS AND H. E. ROGERS

Research on the viscosity of solutions of gases and liquids has been almost entirely neglected. Lewis¹ investigated solutions of sulfur dioxide in carbon tetrachloride, methyl alcohol, benzene, acetone, toluene and ether and found that the viscosities of liquids are changed by saturating with gases.

This paper presents additional data concerning the effect of dissolved sulfur dioxide on the viscosity of carbon tetrachloride, chloroform and bromoform.

Experimental Part

The carbon tetrachloride was dried over anhydrous calcium chloride and fractionated: b. p. 76.7°; d_{25}^4 1.5845.

(1) J. R. Lewis, *THIS JOURNAL*, **47**, 626 (1925).

The chloroform was washed three times with concentrated sulfuric acid, followed by a solution of sodium hydroxide and finally water. It was then dried over anhydrous potassium carbonate and fractionally distilled, the fraction boiling within a 0.1° interval being collected: b. p. 61.2°; d_{25}^4 1.480.

The bromoform was shaken five times with concentrated sulfuric acid, followed by sodium hydroxide solution and water. It was dried over anhydrous potassium carbonate and distilled at reduced pressure: d_{25}^4 2.864. A slight yellow color developed.

Sulfur dioxide was obtained, in cylinders, from the Fisher Scientific Company. It was passed over anhydrous calcium chloride and through cotton before being used.

Apparatus.—The viscosimeter used was a modification of the Ostwald type. It was made according to details given by Lewis¹ (p. 633) in the second part of his paper. Carbon tetrachloride was used for standardizing the viscosimeter. Since, in adding the sulfur dioxide to the vis-

cometer to make up the mixtures, it was found very difficult to add the same working volume each time, a calibration curve was determined. The times for different volumes to transpire were determined and a curve was constructed by plotting times of flow against the volumes of carbon tetrachloride added. It was found that 13.35, 11.62, 12.91, 11.11, 11.81 and 9.98 ml. of carbon tetrachloride transpired in 183.2, 174.1, 179.4, 172.4 and 168.8 seconds, respectively.

To make a determination, the following operations were conducted. The viscometer was cleaned, dried and accurately weighed. A certain amount of organic liquid was introduced and the viscometer was weighed again. The instrument was next placed in a Dewar vessel containing toluene cooled to about -20° with dry ice. Sulfur dioxide was then introduced into the viscometer. After filling the viscometer to the approximate volume, it was then quickly sealed off. The instrument, plus contents, was weighed again. The filled viscometer was next placed in a large, well-stirred, constant temperature bath maintained at $25 \pm 0.04^{\circ}$. After coming to the temperature of the bath, the viscometer was inverted, causing the liquid to equalize itself in the two arms, thus filling the small bulb. It was then returned to an upright position, being careful that there were no air bubbles at the end of the capillary and that no liquid was sticking at the top of the sealed-off arm. The time of transpiration was determined with a stop watch reading to 0.2 of a second. It was checked against a good watch for accuracy.

TABLE I
VISCOSITY DATA AT 25°

Wt. % of SO ₂	Vol. % of SO ₂	Density of solns.	Viscosity centipoises	Fluidity, rhes.	ΔV Change in vol. per unit vol.
Carbon Tetrachloride					
0.00	0.00	1.584	0.8840	113.1	0.0000
11.64	13.10	1.544	.5956	167.9	.0074
16.07	17.91	1.529	.5317	186.2	.0108
24.70	27.10	1.501	.4532	220.6	.0157
55.50	58.17	1.434	.3143	318.2	.0156
77.32	78.86	1.395	.2672	374.3	.0120
100.00	100.00	1.368	.2501	399.8	.0000
Chloroform					
0.00	0.00	1.480	0.5235	191.0	0.0000
14.15	15.04	1.454	.4343	230.3	.0062
29.73	31.12	1.432	.3709	269.3	.0089
38.20	39.71	1.422	.3455	289.5	.0092
43.35	44.86	1.416	.3326	300.7	.0094
61.02	62.32	1.397	.2955	338.5	.0089
79.05	79.86	1.382	.2707	369.4	.0085
100.00	100.00	1.368	.2501	399.8	.0000
Bromoform					
0.00	0.00	2.860	1.864	53.65	0.0000
10.88	20.27	2.548	1.072	93.29	.0033
16.52	29.18	2.416	0.8753	114.3	.0031
38.66	56.63	2.004	.4775	209.4	.0038
65.58	79.80	1.665	.3259	294.4	.0017
73.02	84.86	1.590	.3025	330.6	.0023
100.00	100.00	1.368	.2501	399.8	.0000

Density determinations were made with a pycnometer somewhat similar to the one described by Bingham.² It was an elongated bulb having a neck graduated in mm., that could be sealed off. It had a capacity of approximately 10 ml. A calibration curve was determined for the pycnometer, using water as a standardizing liquid.

Calculations of Viscosities.—In calculating the values of viscosities, the following formula was used

$$\eta = \eta_0 \frac{dt}{d\phi_0} + \frac{m\delta v}{8\pi l} \left(\frac{t^2}{t_0^2} - 1 \right)$$

where η , d , t are the viscosity, density and time of flow of the liquid, respectively. η_0 , d_0 , t_0 are the viscosity, density and time of flow of the standard liquid, respectively. m equals 1.12, l the length of the capillary, which was 7.5 cm., v the volume of flow, being 5.6 ml. In these calculations, 0.8840 centipoise was the value used for the viscosity of carbon tetrachloride at 25° . Lewis¹ gave a value of 0.8876 centipoise at 25° . Linebarger³ gave 0.8834. Thorpe and Rodger⁴ list 0.9009. Values in the International Critical Tables vary considerably. Viscosity and density data are shown in Tables I and II.

TABLE II
DENSITY DATA AT 25°

Wt. % of SO ₂	Vol. % of SO ₂	Density of solns.	ΔV Change in vol. per unit vol.
Carbon Tetrachloride			
0.00	0.00	1.584	0.0000
23.13	25.46	1.506	.0147
35.91	38.64	1.471	.0183
62.54	64.92	1.420	.0152
85.36	86.34	1.384	.0085
100.00	100.00	1.368	.0000
Chloroform			
0.00	0.00	1.480	0.0000
16.08	17.07	1.451	.0061
38.06	39.57	1.422	.0094
56.67	58.08	1.402	.0088
69.14	70.22	1.389	.0084
100.00	100.00	1.368	.0000
Bromoform			
0.00	0.00	2.860	0.0000
20.11	34.34	2.337	.0037
36.39	54.20	2.037	.0051
56.60	72.79	1.766	.0015
76.14	86.87	1.559	.0022
100.00	100.00	1.368	.0000

Discussion

Viscosity data in Table I for solutions of sulfur dioxide in carbon tetrachloride, chloroform and

(2) Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922, p. 308.

(3) Linebarger, *Am. J. Sci.*, [4] **11**, 331 (1896).

(4) Thorpe and Rodger, *J. Chem. Soc.*, **71**, 364 (1897).

bromoform are plotted in Fig. 1. For the carbon tetrachloride-sulfur dioxide mixtures, our viscosities are lower than given by Lewis. The equation used in this paper to calculate the viscosities contains a factor, in the kinetic energy term, not used by Lewis. For the viscosity of pure sulfur dioxide, Lewis¹ (p. 636) gives 0.2559 centipoise. The value determined in this work was 0.2501.

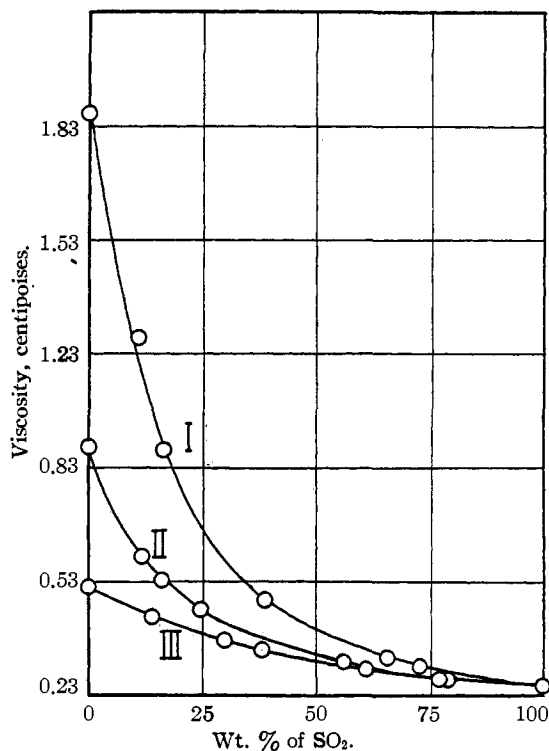


Fig. 1.—I, Bromoform; II, carbon tetrachloride; III, chloroform.

The viscosity curves appear to be typical. The chloroform curve is moderately sagged, while the carbon tetrachloride curve is considerably sagged and that of the bromoform even more so.

In Fig. 2, volume per cent. and weight per cent. have been plotted against the fluidities of the solutions. For carbon tetrachloride and chloroform, volume per cent.-fluidity and weight per cent.-fluidity curves are concave downward and are practically coincident. For this reason, volume per cent.-fluidity curves were not plotted. In the case of bromoform, the curvature of the weight per cent.-fluidity curve is very slightly concave downward and almost linear, while the volume per cent.-fluidity curve is concave upward and is considerably sagged.

In Fig. 3, the density has been plotted against

weight per cent. and volume per cent. for bromoform. The volume per cent.-density curves for carbon tetrachloride and chloroform are coincident with the weight per cent. curves. For this reason the volume per cent. curves are not plotted for these two liquids. It is interesting to note that for bromoform, the density-volume per cent. curve is a straight line, while the same curves for carbon tetrachloride and chloroform deviate from a straight line. This deviation is probably due to a change in volume on mixing.

Change in volume per unit volume (ΔV) has been plotted against volume per cent. in Fig. 4. ΔV was calculated by using the expression

$$\Delta V = (V_a - V_b)/V_a$$

where V_a is the weight of the solution divided by the density of the solution and V_b is the sum of the volumes of the two components. An expansion, on mixing, was found in all cases. It is observed that the change in volume per unit volume is greatest for carbon tetrachloride, chloroform being next and bromoform the least. This is the same order as observed for the density-volume per cent. curves in Fig. 3. The deviation from a straight line in the density curves is proportional to the change in volume per unit volume.

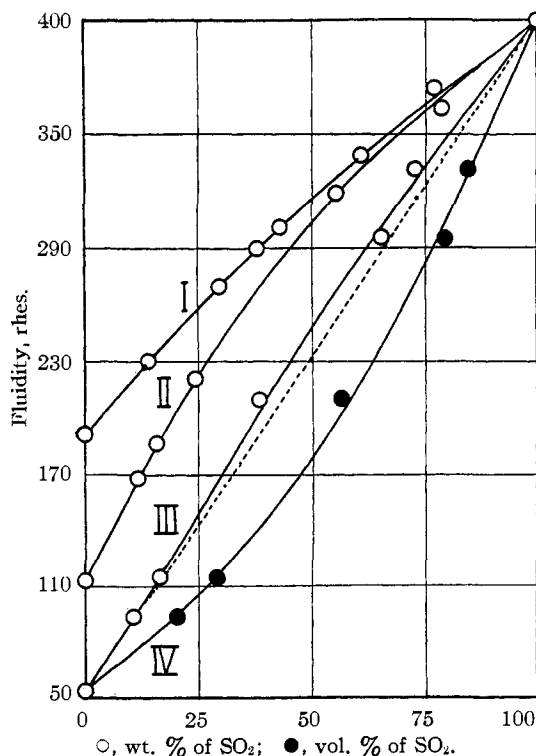


Fig. 2.—I, chloroform; II, carbon tetrachloride; III and IV, bromoform.

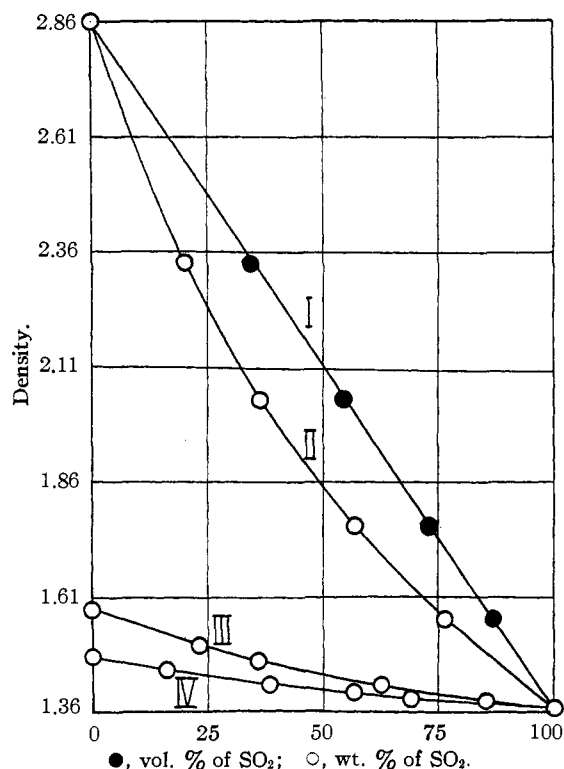


Fig. 3.—I and II, bromoform; III, carbon tetrachloride; IV, chloroform.

In Fig. 2, the order of decreasing magnitude of the deviation from a straight line in the case of the weight per cent.-fluidity curves is carbon tetrachloride, chloroform and bromoform. This is the same order as obtained from the change in volume data and furnishes evidence that the fluidity is directly proportional to the free volume. Bingham² (p. 142) has pointed out that the Batschinski relation between free molecular volume and fluidity may be expressed as follows: the fluidity varies directly as the free volume. Consequently fluidity and density data should go hand in hand. It is well known that when liquids

show an expansion in volume, on mixing, the fluidity of the mixture is greater than the fluidity calculated from the fluidities of the pure liquids. Bingham and Rogers⁵ concluded from a study of one hundred and thirty-one non-aqueous mixtures that there is a parallelism between the volume change on mixing and the deviation of the fluidity from the linear. Further evidence for this is offered by the data plotted in Fig. 2 and Fig. 4.

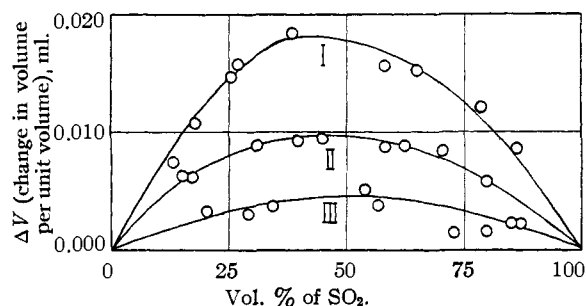


Fig. 4.—I, carbon tetrachloride; II, chloroform; III, bromoform.

Summary

1. Using a sealed, modified Ostwald viscometer, the viscosities of solutions of sulfur dioxide in carbon tetrachloride, chloroform and bromoform were measured at 25°.
2. Densities for these same solutions were determined at 25°.
3. Viscosity and fluidity curves for these solutions have been determined.
4. Density curves were also determined for the same solutions.
5. Expansion in volume, on mixing, was found in each case.
6. Evidence is furnished which shows that the fluidity is proportional to the free volume.

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(5) Bingham and Rogers, *J. Rheology*, **3**, 113 (1932).