α-Phenyl-α-carbethoxy-γ-methyl Thiourea, $C_6H_5N(COOC_2H_5)C(SCH_3)NH$, is formed from the interaction of γ-methylphenylthiourea, ethyl chlorocarbonate and alkali. It melts at 128° and on thiohydrolysis breaks down into thiocyanic acid mercaptan and phenylurethan.

Anal. Calcd. for $C_{11}H_{14}N_2O_2S$: N, 11.76. Found: N, 11.57.

Summary

1. The chlorohydrins, their esters and ethers react with thiourea giving γ-thio ethers, which are easily hydrolyzed, the hydroxy derivatives being especially unstable. The thio ethers yield with amines guanidines, with acyl chlorides diacyl derivatives and with phenyl isocyanate the phenyl amide derivatives of α,β-thioureadicarboxylic acids.

2. A method has been described for the thiohydrolysis of the thio ether ethers.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE PARACHORS OF TWO ISOMERIC CHLORODINITROBENZENES

BY D. V. SICKMAN AND ALAN W. C. MENZIES

RECEIVED MAY 3, 1930 PUBLISHED AUGUST 5, 1930

It has been found by Sugden and his collaborators[1] that the parachors of isomerides which differ in structure only by the position of groups or linkages in the molecule are identical within the limits of experimental error. On examining the published data for surface tension, it was noticed that the values for the two isomers (A) 1-chloro-3,4-dinitrobenzene and (B) 1-chloro-2,4-dinitrobenzene differed very widely, the value for the latter being more than three times that for the former at like temperature. The reported densities differ by only a few per cent. As a consequence, the parachors of these two isomers, as computed from the available experimental data, show a wide divergence, namely, 258.7 for (A) and 346.4 for (B). The parachor computed from the atomic and structural parachors given by Sugden[2] is 358.3, and is, of course, identical for both substances.

Now the chloro-dinitrobenzenes differ considerably in reactivity, and they are known to exist in a number of different crystalline forms, so that a difference of parachor was not *a priori* unthinkable. Furthermore, it seemed hardly possible that experimental error could account for the enormous discrepancy found in surface tension. It therefore seemed worth while to redetermine the surface tensions and densities of the substance (A).

The existing values of surface tension and density for the two isomers (A)

[1] (a) Sugden and Wilkins, *J. Chem. Soc.*, **127**, 2517 (1925); (b) Sugden, "The Parachor and Valency," **1930**, p. 33.

[2] Ref. 1b, pp. 38, 114.

and (B) are due, respectively, to Müller[3] and to Jaeger;[4] and these are the values recorded, for example, in "International Critical Tables." On studying the work of Müller, who worked with both isomers although he reported density and surface tension only for (A), a curious confusion became apparent. Müller's literature references for the preparation of the two isomers are interchanged. The three melting points which he found for the substance (A) are those of the substance (B); but the density, 1.471, at 60° which he reports as that of (A) is closer (difference 1.60%) to that found by us, 1.495, than it is (difference 2.65%) to that found by Jaeger, 1.511, for (B). It is therefore uncertain upon which isomer Müller's measurements of density and surface tension were carried out. In either case, however, the resulting experimental values for the parachor would be expected to be identical, which they are not.

The substance (A) was, accordingly, prepared[5] following the directions of Laubenheimer[6] and had a corrected melting point, for the α-form, of 36.3°, which is precisely that reported by Laubenheimer. We employed the capillary rise method for measuring surface tension in air, using a U-form apparatus of which one limb was of capillary core. Our experimental arrangements were such that, assuming the values given in "International Critical Tables" (1928) for benzene at 40, 50 and 60° as correct, we were able to confirm those given there for water at these temperatures within 0.3%. On account of its higher viscosity, the experimental values tabulated below for the substance (A) may be in error by perhaps 1%. Density was measured by a dilatometric method, with an estimated error within 0.1%. We tabulate our results below, along with those of Müller, adding the resulting values for the parachor.

TABLE I

SURFACE TENSIONS, DENSITIES AND PARACHORS OF 1-CHLORO-3,4-DINITROBENZENE

Temp., °C.	Surface tension dynes/cm.	Specific volume		Parachor Obs.	Parachor Calcd.	Observer
40	13.281	0.6712		259.5	358.3	Müller
50	12.782	.6757		258.7	358.3	Müller
60	12.301	.6803		258.0	358.3	Müller
			Av.	258.7	358.3	Müller
		Density				
40	45.1	1.516		346.0	358.3	S. and M.
50	44.6	1.505		347.8	358.3	S. and M.
60	44.2	1.495		349.3	358.3	S. and M.
			Av.	347.4	358.3	S. and M.

[3] Müller, *Z. physik. Chem.*, **86**, 224 (1914).

[4] Jaeger, *Z. anorg. allgem. Chem.*, **101**, 117 (1917).

[5] We are indebted to Mr. A. E. Rainsford for his services in this connection.

[6] Laubenheimer, *Ber.*, **8**, 1623 (1875); **9**, 760, 1826 (1876).

Our average value for this parachor is, therefore, 347.4 at a temperature of 50°. We are obliged to conclude that Müller's surface tension measurements are seriously in error, or that his specimen was impure.

For the substance (B), Jaeger[4] obtained in his lower temperature range the values noted below, using for surface tension the method of maximum bubble pressure. We have inserted the values for the resulting parachors.

TABLE II

SURFACE TENSIONS, DENSITIES AND PARACHORS OF 1-CHLORO-2,4-DINITROBENZENE

Temp., °C.	Surface tension dynes/cm.	Density	Parachor Obs.	Parachor Calcd.	Observer
60.4	45.5	1.515	347.1	358.3	Jaeger
76.2	43.9	1.497	348.1	358.3	Jaeger
95	42.2	1.477	349.4	358.3	Jaeger
		Av.	348.2		

The average value, 348.2, is for a temperature near 77°. Corrected for the drift of parachor with temperature, this would become 346.4 at 50°, a value not very different from 347.4, which is our experimental value for the other isomer.

Neither one of these values is especially close to the "calculated" value yielded by Sugden's adopted constants. The latter have been recalculated by Mumford and Phillips.[7] By using these newer constants, the discrepancy is not diminished, and the whole matter will be dealt with elsewhere.

From our comparison we conclude that the parachors at 50° of these two isomers are identical within the experimental error, while both fall short of the parachor calculated as the sum of the atomic and structural parachor terms of Sugden by 3.2%.

Summary

1. The experimental data found in the literature yield for two isomeric chloro-dinitrobenzenes values of the parachor which are very widely divergent, while these would be expected to be identical.

2. By redetermination of densities and surface tensions, this discrepancy is shown to be due to experimental error.

3. The values of the two corrected parachors are shown to be very concordant, but to differ from the value calculated according to Sugden in a degree requiring explanation.

PRINCETON, NEW JERSEY

[7] Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929).