[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Parachors of Methyl and Ethyl Nitrites and of Nitromethane and Nitroethane

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Sugden has published the parachors of nitromethane[1] and of butyl and isoamyl nitrites.[2] The values agree so well with the calculated value, when we remember that less than one-third of the value for the compounds depends on the nitrite group, that there is no reasonable doubt that the structure of the group is $:\ddot{O}:\ddot{N}::\ddot{O}$, for which the calculated parachor is 75.7.

Sugden has reached the conclusion that the structure of the nitro group is $:\ddot{N}^{+}(:\ddot{O}:^{-})(::\ddot{O})$, with one semi-ionic ("semi-polar")[3] union and one double union. Since the semi-ionic union has only a small and irregular effect on the parachor while a double covalence increases the parachor by 23.2 units, the parachors of an alkyl nitrite and of the corresponding nitroalkyl should be very nearly the same. Methyl nitrite boils at −12°; nitromethane at 101°; ethyl nitrite at 17° and nitroethane at 114°. These four compounds are, therefore, especially adapted for a test of the validity of the parachor for the detection of double covalences. These compounds have the advantage that the parachors of the groups which we are considering furnish 58% of the parachors of the methyl compounds and 44% of the parachors of the ethyl compounds and for this reason give us a much more reliable basis for comparing the parachors of the nitrite and nitro groups.

The parachor of nitromethane is given as 132.0 by Sugden.[4] Dr. T. F. Young has been kind enough to calculate the parachor of nitroethane on the basis of a recalculation of the surface tension from the observations of Ramsay and Shields.[5] Dr. Young has given us the value 170.2. If we subtract from these values the calculated parachors of methyl 56.1, and ethyl 95.1, we find the parachor of the nitro group to be 75.9 and 75.1, respectively. Sugden[6] gives the values 75 and 73 based on results which indicate some variation in the value for different compounds.

The surface tensions of ethyl nitrite and methyl nitrite were determined by measuring with a cathetometer the difference in height of the liquids in the two arms of a U-tube made after a design furnished us by Dr. Young. The radii of the two arms of the U-tube, determined by weighing the quantity of mercury contained in a measured length of each, were 0.2231 and 0.0334 cm.

The surface tension was calculated by a formula furnished us by Dr. Young

$$\gamma = \frac{r_1 r_2 (3h + r_1 - r_2)(D - d)g}{6(r_2 - r_1)}$$

where h is difference in height, D is density of liquid at the temperature of the measurement, d is density of the mixture of the air and vapor in equilibrium with the liquid, r_1 and r_2 are the two radii in cm., and g, the gravity constant.

The density of ethyl nitrite is taken from Beilstein. The density of methyl nitrite was determined in an apparatus consisting of two bulbs having capacities of 6 and 10 cc. and connected by a narrow, heavy capillary tube and with a similar tube at the top of the 10 cc. bulb. The capacity of the smaller bulb was determined at 4° by weighing it empty and filled with water to a mark on the tube connecting the bulbs. After emptying and drying, the small bulb was filled with methyl nitrite to the mark, at −19°. The vapor of the methyl nitrite in the larger bulb was then drawn out with a small capillary tube and the end of the capillary tube above the 10-cc. bulb was sealed without the removal of any glass. The apparatus was then weighed at ordinary temperatures. The results of the determinations were

Compound, nitrite	Methyl	Ethyl
t, °C.	−19	15
h, cm.	1.024	1.014
D	1.00	0.90
γ	21	16.5
$[P]$	130.6	169.0
$[P]$ of nitrite group	74.5	73.9

If these parachors of the nitrite group are compared with those for the nitro group given earlier in this paper, it will be seen that they differ from

(1) Sugden, "The Parachor and Valency," 1930, p. 119.
(2) Sugden, Reed and Wilkins, *J. Chem. Soc.*, **127**, 1531 (1925).
(3) For nomenclature see Noyes, *Chem. Rev.*, **17**, 13 (1935).
(4) Ref. 1, p. 119.
(5) Ramsay and Shields, *J. Chem. Soc.*, **63**, 1089 (1893); "International Critical Tables," Vol. IV, p. 449.
(6) Sugden, *J. Chem. Soc.*, **125**, 1186 (1924); Ref. 1, p. 110.

those and from each other less than the values for the nitro group found by Sugden in different compounds and that the differences are insignificant in comparison with the increase in the parachor caused by a double covalence (23.2).

If we compare the structures of the nitrite and nitro groups given at the beginning of this paper, it is seen that the former has four covalences, including the one attaching it to the radical; the latter has four covalences and one semi-ionic union. Each oxygen atom of the nitrite has two covalences and the nitrogen has two unshared electrons. It is evident that these differences in the structures of the groups have only a trifling effect on the parachors of the compounds but it seems probable that the semi-ionic union in the nitro compound has a considerable effect on the boiling points.

Sugden has shown the intimate connection between surface tension and the critical temperatures of elements. Kopp introduced the determination of molecular volumes at the boiling points of compounds, or at "corresponding temperatures." His work may now be considered as an approach to the principles which led Sugden to the discovery of the parachor and there is some advantage in considering the parachor as a determination of atomic and structural volumes at the critical temperature. This point of view together with the considerations which have led Pauling to consider that the four electrons forming a double covalence between two carbon atoms have tetrahedral arrangements about the kernels of the two atoms held together gives us a simple explanation for the increase in volume of a compound having a double covalence. In spite of the fact that the kernels of the atoms must be closer together than are the atoms held by a single covalence, the positions of these four covalence electrons extending on both sides of the line from one kernel to the other must cause a considerable increase in volume and the increase would be similar for the groups, C :: C, C :: O, N :: O, N :: N. In all these cases the kernels of each atom have two electrons. It will be of some interest to know whether this generalization holds.

After reading this paper Professor Linus Pauling has written me: "I have no criticism to make of your results. On the other hand, I do not have a good enough understanding of the structural interpretation of the parachor to be able to say that I concur in your explanation of the increase in the parachor caused by the double covalence. It is true however, that the distance of closest approach in molecules containing double bonds, such as the benzene molecule, as determined by x-ray methods, seems to be somewhat larger than that for saturated molecules, in agreement with your suggestion.

"There are several determinations of carbon to carbon double bond distances which lie in the region of about 1.38 Å., the single bond distance being about 1.54 Å. In ethylene itself a band spectroscopic investigation by Badger has given the value 1.37 Å."[7]

Summary

The parachors of methyl and ethyl nitrites have been determined and these agree closely with the parachors of nitromethane and nitroethane, furnishing a strong confirmation of the value of the parachor for the determination of the presence of a double covalence in a compound.

A simple hypothesis is offered to account for the increase in the parachor caused by a double covalence.

(7) Badger, *Phys. Rev.*, **45**, 648 (1934).

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