[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Parachor of NO_3F[1]

BY DOUGLAS G. HILL AND LUCIUS A. BIGELOW

The compound NO_3F, originally discovered by Cady,[2] has been studied since by Ruff and Kwasnik[3] as well as by Yost and Beerbower.[4] It is an unusual compound, whose structure is of much interest, and at the suggestion of Professor W. A. Noyes we have measured its surface tension and calculated the parachor. Our experience has amply confirmed that of others, to the effect that the substance is highly explosive, sometimes from unknown causes, so that it is not only difficult but may also be dangerous to handle. All of our later operations were carried out behind a large wire glass screen or a section of bullet proof glass, and we consider these precautions to be essential.

Experimental Part

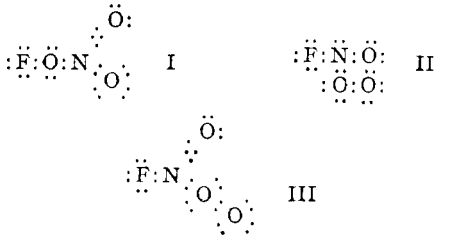
The compound was synthesized by passing pure fluorine, prepared according to Miller and Bigelow,[5] through very concentrated nitric acid, made by distilling sodium nitrate with sulfuric acid and removing the oxides of nitrogen with a current of dry air. Our procedure was similar in general to that already described,[3] but different in that the reaction was carried out in an upright aluminum cylinder 4.5 × 14.5 cm., closed by a cone held in place by springs, as a safety valve. Sodium fluoride, contained in an aluminum tube 38 × 3 cm., was used to absorb the by-products. The connecting lines (6.3 mm. o. d.) as well as the cores of the compression couplings were made of the same metal, which proved to be completely resistant. The fluorine was supplied at the rate of 2 liters per hour at atmospheric pressure, and the crude product was condensed by means of liquid air as a faintly orange solid, about 10 cc. being collected in ten hours.

This was then condensed into a Pyrex glass still modeled on that described by Ruff and Menzel.[6] It differed from theirs, however, in that it was surrounded by asbestos packing, and that the thermocouple was inserted in a deep well at the head of the column. The still was sealed to a system provided with magnetic break seals, and maintained at constant pressure by a regulator. The product, which never came into contact with anything but glass after first being condensed, was separated into three fractions. The middle fraction, which was collected, had a volume of about 3 cc., came over in nine minutes, and boiled from −78 to −80° at 103 mm. It solidified within 0.2° at −181° (freezing curve). According to Ruff and Kwasnik,[3] NO_3F boils at −79° at 99 mm., and melts at −175°. The difference in actual melting point was probably not significant, since our sample was quite small.

The purified material was then distilled into a carefully calibrated apparatus for determining the surface tension by capillary rise, similar to that described by Bowden.[7] This was immersed in a bath contained in an unsilvered Dewar flask thermostat, maintained at a constant temperature within 0.3° by a regulator. The liquid levels were adjusted by means of a magnetically operated plunger, and finally read to 0.05 mm. through a telescope mounted on a measuring microscope stand. The values obtained for the surface tension were 21.5 and 23.4 dynes per cm. (±0.2) at −64.1 and −80.4°, respectively.

Discussion

There seem to be three lines of evidence which should be considered in an attempt to determine the structure of NO_3F, namely, the physical and chemical properties of the compound, the electron diffraction studies of Pauling and Brockway[8] and the parachor. There also appear to be three fairly reasonable formulations for this molecule, which are



The method of preparation of NO_3F is most in accord with Formula I unless considerable rearrangement is assumed in the reaction. The boiling point, however, (−45°) is twenty degrees higher than that of NO_2F, although nitrates usually boil lower than nitro compounds. If Formula I is to be maintained, a change in the normal order of boiling points must have occurred, due to the electronegative nature of fluorine. In addition, the stability of NO_3F is much less than that of either nitric acid or oxygen fluoride, which contain linkages formally similar to I. Formulas II and III should presumably represent unstable molecules.

Pauling and Brockway[8] have presented the electron diffraction data for NO_3F, which agree well with their theoretical curve for I, although they

(1) Presented before the Division of Physical and Inorganic Chemistry at the Chapel Hill Meeting, April 14, 1937.

(2) G. H. Cady, THIS JOURNAL, **56**, 2635 (1934).

(3) O. Ruff and W. Kwasnik, *Z. angew. Chem.*, **48**, 238 (1935).

(4) D. M. Yost and A. Beerbower, THIS JOURNAL, **57**, 782 (1935).

(5) W. T. Miller, Jr., and L. A. Bigelow, *ibid.*, **58**, 1585 (1936).

(6) O. Ruff and W. Menzel, *Z. anorg. Chem.*, **190**, 257 (1930).

(7) S. T. Bowden, *J. Phys. Chem.*, **34**, 1866 (1930).

(8) L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 13 (1937).

have conceded that the experimental difficulties encountered were considerable. We have calculated similar curves for II and III, and have illustrated them all together in Fig. 1 for comparison. From this it appears that the curves for I and III agree well with each other (and therefore with the observed values), while that corresponding to II is quite different.

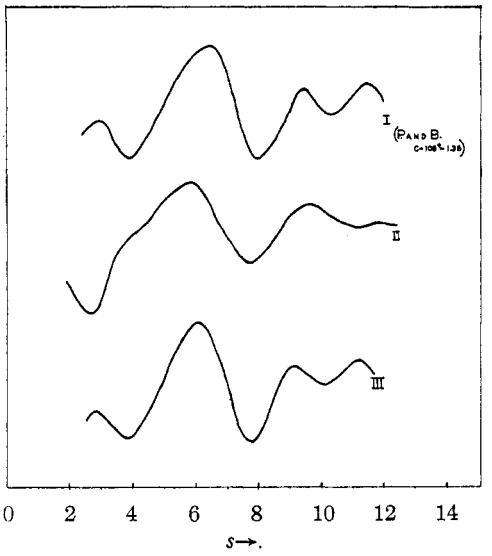


Fig. 1.—Theoretical s-curves for NO_3F.

We have calculated the parachor of NO_3F, using our own values for the surface tension, and those of Ruff and Kwasnik[3] for the density. It is 111.5 and 110.2 at -64.1 and -80.4[4], respectively, which means that the value may be taken as 111 independent of temperature in this range. Considerable confidence is felt in this figure, since preliminary measurements with a different preparation had given the values 111.5, 110.2 and 111.8 at -76.8, -71.6 and $-61.8°$, respectively. The calculated parachors corresponding to the three formulas are 122 (I), 110.2 (II) and 122 (III), using Sugden's[9] values for N (12.5), O (20) and the double bond (23.3) together with Desreux's[10] newer figure for F (26.1). Consequently only (II) agrees well with our results.

(9) S. Sugden, "The Parachor and Valency," Knopf, New York, 1930.

(10) V. Desreux, *Bull. soc. chim. belg.*, **44**, 249 (1935).

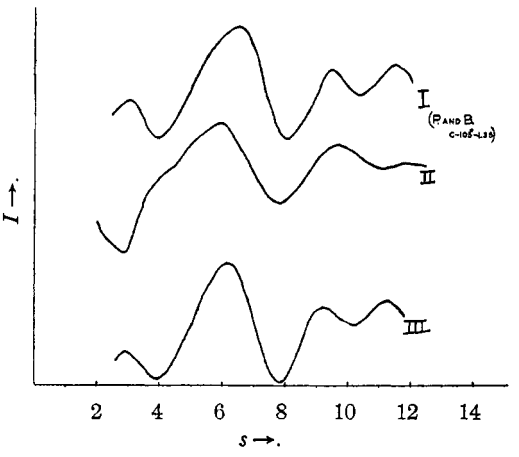


Fig. 2.—Theoretical s-curves for NO_3F.

Consideration of this evidence shows that each of the three formulas has something to recommend it; but (I) demands particular assumptions if it is to accord with the physical and chemical properties and with the parachor, (II) does not agree with the electron diffraction measurements and represents a strained ring structure, while (III) is opposed by the parachor. These facts may demand a reconsideration of the structure as determined by Pauling and Brockway. They may, on the other hand, imply that the additive nature of atomic parachors is not valid in this case. The reversal of polarity demanded when two highly negative groups are combined (Formula I) may so change the atomic volumes that parachors determined in more conventional molecules do not apply. Ouchakov and Chistov[11] have postulated that $ClNO_3$ and $BrNO_3$ may be ionized. If this were true of NO_3F, it should yield a positive nitrate ion of unknown parachor. Further studies of similar highly electronegative molecules might furnish an explanation for the discrepancy.

Summary

The surface tension of liquid NO_3F has been determined and the parachor calculated. The structure of the compound has been discussed.

DURHAM, N. C. RECEIVED AUGUST 2, 1937

(11) M. V. Ouchakov and W. O. Chistov, *Bull. soc. chim.*, [5] **3**, 2142 (1936); *Ber.*, **68**, 824 (1935).