# 384. *Hyponitrites. Part II : Metallic Salts. Part III : Esters.*

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## PART II.

CALCIUM, strontium, and barium hyponitrites have been previously prepared in pure crystalline forms (Divers, J., 1899, **47**, 97; Maquenne, *Compt. rend.*, 1889, **108**, 1303; Kirschner, *Z. anorg. Chem.*, 1898, **16**, 424), the first and last occurring as tetrahydrates, the second as a pentahydrate. We obtained all three in the cryst. form by pptn. on adding excess of a solution of the corresponding nitrate to $Na_2N_2O_2$ aq., washing with $H_2O$ (at 40°), EtOH, and $Et_2O$, and drying on a porous plate (in the case of the Ca salt in a desiccator). The analyses of the products confirmed the formulæ stated.

We were unable to obtain the alleged basic lead hyponitrite, $PbO,PbN_2O_2$ (Kirschner, *loc. cit.*), or $Pb(OH)_2,PbN_2O_2$ (Neogi and Nandi, J., 1928, 1449), under any conditions, the normal salt, $PbN_2O_2$, prep. by Divers (*loc. cit.*), Kirschner (*loc. cit.*), and Thum (*Inaug. Diss.*, Prague, 1893; *Monatsh.*, 1893, **14**, 294), being always obtained in a pale yellow form by pptn. as in the case of alkaline-earth salts, and drying in a vac. If, instead of $Pb(NO_3)_2$, $Pb(OAc)_2$

is used, the ppt. is deep sulphur-yellow, and the salt detonates more violently when heated than that obtained from the nitrate. No attempt should be made to dry the Pb salt by heating. The other properties and the chemical composition of the two forms are the same.

A basic copper hyponitrite, $Cu_2(OH)_2N_2O_2$ (Divers; Thum; Kirschner; *locc. cit.*), could not be obtained. The ppt. formed on adding $CuSO_4$ aq. to $Na_2N_2O_2$ aq. was found (by Cu and N detmtn.) to have the composition $CuN_2O_2$.

*Analyses.*—N was determined as described in Part I (J., 1931, 2071). The metal in Ca, Sr, Ba, and Pb hyponitrites was determined as sulphate, and in Cu hyponitrite as oxide by maintaining the salt at a red heat for some time. Ca salt (Found : Ca, 23·21; N, 16·32. Calc. for $CaN_2O_2,4H_2O$ : Ca, 23·29; N, 16·29%). Ba salt (Found: Ba, 51·37; N, 10·9. Calc. for $BaN_2O_2,4H_2O$ : Ba, 50·97; N, 10·40%). Sr salt (Found: Sr, 36·9; N, 11·5. Calc. for $SrN_2O_2,5H_2O$ : Sr, 36·86; N, 11·79%). Pb salts (Found, for yellow product: Pb, 77·32; N, 10·45. Found, for pale yellow product : Pb, 77·85; N, 10·3. Calc. for $PbN_2O_2$ : Pb, 77·57; N, 10·49%). Cu salt (Found : Cu, 50·97; N, 22·4. Calc. for $CuN_2O_2$ : Cu, 51·44; N, 22·67%).

*Action of Air.*—According to Kirschner, barium hyponitrite is decomp. by dry $CO_2$, while calcium hyponitrite is said by Divers to be very stable and a good hyponitrite to stock. Maquenne found that the alkaline-earth hyponitrites do not completely lose $H_2O$ of crystn. at 100°. Copper hyponitrite was found by Kirschner to be slightly hygroscopic. We found that these hyponitrites, when exposed to dry air or $CO_2$, remained practically unchanged in wt., whilst on exposure to air saturated with water vapour, there was a slight increase. The alkaline-earth hyponitrites retained their cryst. structure as seen under the microscope, even on exposure to ordinary air for several days, and the analysis of the salts exposed to air for a week did not show any change.

Scott (*J. Amer. Chem. Soc.*, 1927, **49**, 986) states that the Na salt prep. by him was non-hygroscopic, but this seems to have been based on appearance only. We exposed weighed amounts of the salt, prep. by our modification of Divers's method (J., 1931, 2075), to air, dry $CO_2$, and $CO_2$-free air saturated with water vapour. When exposed to air the salt at first rapidly absorbs moisture and increases in wt.; after about 3 days it begins to lose wt. When exposed to air saturated with water vapour in a desiccator, the increase in wt. continues for a considerable time, but the wt. immediately falls on exposure to the free air. The wt. of the dry salt remains unaffected on exposure over conc. $H_2SO_4$ in an atm. of $CO_2$. A sample of sodium hyponitrite after exposure to air for a fortnight gave no characteristic yellow ppt. with $AgNO_3$. It appears that the dry salt is unaffected by $CO_2$ and is hygroscopic; in contact with water vapour or in solution it is slowly converted into the carbonate on exposure to ordinary air. The external appearance of the salt remains like that of anhyd. $MgSO_4$, even absorption by the salt of twice its own wt. of $H_2O$.

*Thermal Decomposition.*—The thermal decomp. of the alkaline-earth salts has not been examined previously. Divers found that $CuN_2O_2$ gave $H_2O$, $CuO$, $Cu_2O$, $N_2O$, and NO.

The thermal decomp. of these salts cannot be represented by one equation, as in the case of $Na_2N_2O_2$, for although $N_2O$ forms the major portion of the gaseous reaction products, it is always accompanied by NO and N. The alkaline-earth salts behave similarly and decompose at a temp. higher than 320°. The principal gaseous products are $N_2O$ and N, with some NO. The solid residue is alk. and contains some nitrate and an amount of nitrite, which, although it can be detected qualitatively, is too small for determination. The following equations, in which R = Ca, Sr, or Ba, probably represent the decomposition :

$$RN_2O_2 = RO + N_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$5RN_2O_2 = R(NO_3)_2 + 4RO + 4N_2 \quad . \; . \; . \; . \quad (2)$$

$$2RN_2O_2 = 2RO + 2NO + N_2 \quad . \; . \; . \; . \; . \; . \quad (3)$$

During the decomp. of lead and copper hyponitrites, $N_2O$ is likewise the main product, but no nitrite or nitrate can be detected in the solid residue. The Pb salt is so explosive that the gaseous products could not be examined, but the greyish-yellow solid residue was PbO. Lead hyponitrite appears to be unstable even at 100°, at which temp. it slowly turns brown and loses wt., with evolution of $N_2O$. Since no nitrite or nitrate is found in the residue, it appears that the decomp., which is slow at lower temps. and occurs explosively at 150—160°, proceeds according to equation (1).

TABLE I.

| Reagent. | Wt. of substance, g. | $N_2$, c.c. | $N_2O$, c.c. | NO, c.c. | % of total N as | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | $N_2$. | $N_2O$. | NO. | $HNO_3$. |
| | $CaN_2O_2,4H_2O$. | | | | | | | |
| Heat | 0·1088 | 2·8 | 9·2 | 1·7 | 20 | 65 | 6 | 9 |
| ,, | 0·1360 | 3·9 | 11·0 | 2·3 | 22 | 62 | 6 | 8 |
| Dil. HCl | 0·0954 | 0·9 | 4·0 | 1·7 | 7 | 32 | 7 | 0 |
| Dil. $H_2SO_4$ | 0·0994 | — | 1·3 | — | 0 | 10 | 0 | 0 |
| Conc. $H_2SO_4$ | 0·1007 | 2·9 | 6·1 | 0·9 | 22 | 47 | 34 | — |
| ,, | 0·1235 | 3·2 | 7·9 | 1·0 | 20 | 49 | 31 | — |
| Acid $KMnO_4$ | 0·0970 | 0·2 | 4·2 | — | 2 | 33 | 0 | 65 |
| $KMnO_4$ + acid | 0·1146 | 0·8 | 3·2 | — | 5 | 21 | 0 | 74 |
| ,, | 0·1082 | 0·8 | 3·0 | — | 6 | 21 | 0 | 73 |
| | $BaN_2O_2,4H_2O$. | | | | | | | |
| Heat | 0·1376 | 3·8 | 6·7 | 2·4 | 33 | 59 | 10 | — |
| ,, | 0·1032 | 3·0 | 5·1 | 1·9 | 35 | 59 | 8 | — |
| Dil. HCl | 0·1003 | 0·7 | 5·2 | 1·3 | 8 | 62 | 8 | 0 |
| Conc. $H_2SO_4$ | 0·1001 | 2·3 | 4·1 | 2·1 | 27 | 53 | 13 | — |
| Acid $KMnO_4$ | 0·1113 | 0·4 | 4·7 | — | 4 | 51 | 0 | — |
| $KMnO_4$ + acid | 0·1042 | 0·7 | 3·2 | — | 8 | 37 | 0 | — |
| | $SrN_2O_2,5H_2O$. | | | | | | | |
| Heat | 0·1270 | 3·8 | 6·8 | 2·7 | 31 | 56 | 11 | — |
| ,, | 0·1010 | 3·0 | 5·4 | 2·1 | 31 | 57 | 11 | — |
| $KMnO_4$ + acid | 0·1078 | — | 3·5 | — | 0 | 34 | 0 | — |
| | $PbN_2O_2$. | | | | | | | |
| Dil. $HNO_3$ | 0·1347 | — | 7·8 | — | 0 | 69 | 0 | 0 |
| | $CuN_2O_2$. | | | | | | | |
| Heat | 0·1042 | 1·1 | 16·8 | 2·0 | 6 | 89 | 5 | 0 |
| ,, | 0·0830 | 0·3 | 13·5 | 0·7 | 2 | 90 | 3 | — |
| Dil. $H_2SO_4$ | 0·1256 | — | 19·1 | — | 0 | 84 | 0 | 0 |
| ,, | 0·1137 | — | 17·4 | — | 0 | 84 | 0 | 0 |
| Dil. HCl | 0·0938 | — | 14·2 | — | 0 | 83 | 0 | 0 |
| ,, | 0·1029 | — | 15·4 | — | 0 | 83 | 0 | 0 |
| Conc. $H_2SO_4$ | 0·1020 | 4·2 | 10·8 | 3·5 | 23 | 58 | 10 | — |
| ,, | 0·0803 | 3·0 | 8·2 | 2·8 | 21 | 56 | 10 | — |
| Acid $KMnO_4$ | 0·1256 | — | 7·5 | — | 0 | 33 | 0 | — |

Unlike the Pb salt, copper hyponitrite is not explosive. It decomposes at 225—230°, and the gaseous products of decomp. are $N_2O$, NO, and N. The residue was shown by analysis to be CuO. Equations (1) and (3) represent the decomp.

*Action of Water and Alkalis.*—Water has no apparent action on the alkaline-earth, lead, or copper salts, and no gas is evolved when they are treated with water in a vac. 5*N*-NaOH aq., when added to the salts, causes no evolution of gas, but hyponitrite can be detected in the solution. In the case of $PbN_2O_2$, which becomes perfectly white, the reaction is probably $PbN_2O_2 + 2NaOH = Pb(OH)_2 + Na_2N_2O_2$. Even in this case the conversion is not complete, for the insol. residue contains some hyponitrite. For studying the action of heat and various reagents in a vac., the apparatus described in Part I (*loc. cit.*) was used. The results are given in Table I.

*Action of Acids.*—Our expts. on the reaction of dil. $H_2SO_4$ and HCl with $Na_2N_2O_2$ (*loc. cit.*) indicated that $N_2O$ was the main product, and those now described are in general agreement with those of Cambi (*Gazzetta*, 1929, **59**, 770) on the action of 7*N*-$H_2SO_4$ on $PbN_2O_2$ and 4*N*-acid on $Na_2N_2O_2$ in an atm. of $CO_2$, but not with his results in the case of the action of 7*N*-acid on $CuN_2O_2$. All the five hyponitrites behave towards acids like the Na salt; with the Ca, Sr, Ba, and Pb salts, the decomp. by $H_2SO_4$ is only slight, the Pb salt losing its colour very slowly. As in the case of the Na salt, no nitrate or nitrite is formed. Conc. $H_2SO_4$ completely decomposes all the salts at room temp., the products being similar.

*Action of Oxidising Agents.*—The action of $KMnO_4$ aq. on $H_2N_2O_2$ has been previously described (*loc. cit.*). Cambi (*loc. cit.*) has also studied the action of $KMnO_4$, I, and $K_3Fe(CN)_6$ on $Na_2N_2O_2$, and finds that nearly 50% of the hyponitrite N escapes as $N_2O$. He states that the amount of I absorbed depends on the $p_H$ of the medium, and upon the order in which the reagents are added.

*Potassium permanganate.* Our results show that the nature of the acid has an influence on the amount of $KMnO_4$ consumed, the results being always high with HOAc and HCl. In the titration with $KMnO_4$ a weighed amount of the salt was added to dilute acid, followed by excess of $KMnO_4$ aq. After 15 mins., standard $H_2C_2O_4$ was added and the excess determined by titration with $KMnO_4$.

| Salt. | C.c. of 0·1*N*-$KMnO_4$ required for 1·0 g. of the salt. | Equivs. of $\frac{1}{2}O$ required. | Acid. |
|---|---|---|---|
| $CuN_2O_2$ | 267·8 | 3·3 | $H_2SO_4$ |
| | 275·3 | 3·4 | $HNO_3$ |
| | 338·4 | 4·2 | HCl |
| $CaN_2O_2,4H_2O$ | 379·8 | 6·5 | HCl |
| | 267·8 | 4·6 | $HNO_3$ |
| | 268·5 | 4·6 | $H_2SO_4$ |
| | 269·5 | 4·6 | HOAc + $H_2SO_4$ |
| | 344·2 | 5·9 | AcOH |
| $BaN_2O_2,4H_2O$ | 270·7 | 7·3 | $H_2SO_4$ |
| | 287·3 | 7·7 | $HNO_3$ |
| | 292·4 | 7·9 | HCl |
| | 290·2 | 7·8 | HOAc |
| $SrN_2O_2,5H_2O$ | 189·2 | 4·5 | $H_2SO_4$ |
| | 198·6 | 4·9 | $HNO_3$ |
| | 259·3 | 6·2 | HCl |
| | 259·5 | 6·2 | HCl (excluding air) |
| | 233·3 | 5·5 | HOAc |

$PbN_2O_2$ gave varying results. Some values obtained with $HNO_3$ are given, the figures in the last line corresponding with 1·0 g. of salt.

| Wt., g. …… | 0·0990 | 0·1129 | 0·1302 | 0·1336 | 0·1475 | 0·1645 | 0·1717 | 0·1773 |
|---|---|---|---|---|---|---|---|---|
| Vol. required, c.c. ……… | 9·6 | 8·2 | 10·7 | 12·9 | 12·9 | 11·5 | 12·5 | 11·0 |
| Vol. per g. … | 97·0 | 72·6 | 82·2 | 96·6 | 87·5 | 69·9 | 72·8 | 62·0 |

*Iodine.* The iodine titrations were carried out exactly in the manner described by Raschig ("Schwefel- und Stickstoffstudien," 1924, p. 103) (figures in parentheses give atoms of I per mol. of salt):

| Amount of substance. | 0·1*N*-I absorbed, c.c. | 0·1*N*-I liberated by $H_2SO_4$, c.c. |
|---|---|---|
| 10 c.c. 0·1335*N*-$Na_2N_2O_2$ | 4·0 (3·0) | 3·5 (2·6) |
| 0·1 g. $CaN_2O_2,4H_2O$ | 10·8 (1·9) | 5·9 (1·0) |
| 0·1 g. $SrN_2O_2,5H_2O$ | 8·5 (2·0) | 5·0 (1·2) |
| 0·1 g. $BaN_2O_2,4H_2O$ | 9·6 (2·6) | 5·1 (1·4) |

The results were very discordant, and it is very doubtful whether the reactions proceed as represented by Raschig (*op. cit.*), *viz.*,

$$H_2N_2O_2 + I = HN_2O_2 + HI \quad (1)$$
$$HN_2O_2 = HNO_2 + N \quad (2)$$
$$HN_2O_2 = NO + NOH$$
$$2NOH = N_2O + H_2O \quad (2a)$$
$$HNO_2 + HI = NO + I + H_2O \quad (3)$$

(1) represents the absorption of I in HOAc solution, and (3) the liberation of I in presence of $H_2SO_4$. If the reaction proceeds smoothly according to (1), (2), and (3), all the I used in the first stage should be liberated in the third. Raschig found that only one-half is liberated, and hence suggested that (2) may occur in either of the two ways, the alternative being (2*a*).

*Sodium hypochlorite.* Oxidation by NaOCl gave the same results as that by $KMnO_4$. The action was investigated by adding excess of the reagent. After 5 mins., $H_2SO_4$ was added, and then an excess of KI aq. The liberated I was titrated with $Na_2S_2O_3$.

| Amount of substance. | 0·1*N*-NaOCl, c.c. |
|---|---|
| 10·0 c.c. 0·05*N*-$Na_2N_2O_2$ | 33·7 (6·7) |
| 0·1 g. of $CaN_2O_2,4H_2O$ | 40·1 (6·9) |
| 0·1 g. of $SrN_2O_2,5H_2O$ | 26·7 (6·3) |
| 0·1 g. of $BaN_2O_2,4H_2O$ | 28·5 (7·7) |

The figures in parentheses give atoms of active Cl per mol. of salt.

## PART III.

*Esters of Hyponitrous Acid.*—Ethyl hyponitrite, prep. by Zorn (*Ber.*, 1878, **11**, 1630) by the action of $Ag_2N_2O_2$ on EtI in presence of dry ether, is described by him as a liquid, stable at room temp. but explosive at higher temps., having the normal vapour density [mol. formula $(C_2H_5)_2N_2O_2$] below 61°. He found that on reduction with Sn and HOAc or HCl, or Na–Hg, traces of amino-compounds are formed. In presence of $H_2O$, the ester decomposed slowly at ordinary temps., rapidly at 40° and upwards, according to the equation $(C_2H_5)_2N_2O_2 = C_2H_5{\cdot}OH + CH_3{\cdot}CHO + N_2$.

Benzyl hyponitrite, described as fairly volatile at room temp., was prepared in a similar way by Hantzsch and Kaufmann (*Annalen*, 1896, **292**, 329); it decomposed similarly in presence of $H_2O$, forming Ph·CHO.

We describe the preparation of very pure silver hyponitrite, from which we prepared the ethyl, *n*-propyl, *n*-butyl, and benzyl esters by the same method, the first three being liquids and the last a solid. Cryoscopic determination of their mol. wts. in $C_6H_6$ solution showed them to possess the formula $R_2N_2O_2$. Attempts to determine the vapour density showed that even as low as 15° and at correspondingly low pressures, the liquid esters decompose, giving a gaseous product. A rapid determination of the vapour density of ethyl hyponitrite at 46° in the apparatus described below gave the value 46 (calc.: 59, H = 1).

Reduction of the esters with KOH and Devarda's alloy did not give any amino-compounds. The benzyl ester remained unchanged when treated with Al–Hg in alc. solution at room temp., but at higher temps. (60—70°), reduction to benzyl alcohol occurred. Since $H_2O$ rapidly decomposes the ester at this temperature according to the equation :

$$(C_7H_7)_2N_2O_2 = C_7H_7OH + C_6H_5{\cdot}CHO + N_2 \quad . \quad . \quad (1)$$

the aldehyde first formed is no doubt reduced to the alcohol.

The three liquid esters are readily decomposed by $H_2O$ at 40° according to equation (1), but the benzyl ester only above its m. p. Even in presence of 50% KOH aq., the reaction appears to take the same course, since, after hydrolysis either at room temp. or at 0°, no hyponitrite can be detected.

The benzyl ester, when heated at 70—80° with an HOAc solution of phenylhydrazine, gave an 80% yield of benzaldehydephenylhydrazone (m. p. 157°), so that even in acid solution the reaction takes the course of equation (1).

All the esters are unstable. The liquids on standing become slightly yellow, sometimes deep yellow, but the colour disappears on shaking. If the ester is kept for more than a week, however, the colour does not so disappear. The esters possess the normal cryoscopic mol. wts. even after a week, although the density of the liquid ethyl ester increases from 0·953 to 1·047. The benzyl ester becomes yellow and pasty, and after a week forms a liquid. On account of its low m. p. it is very difficult to prepare in hot weather.

*Silver Hyponitrite.*—Great care is necessary in the preparation of this salt, since otherwise the product is grey, or even black (cf. Divers, J., 1899, **47**, 97; Coblens and Bernstein, *J. Physical Chem.*, 1925, **29**, 750). 10 G. of $Na_2N_2O_2$ are dissolved in $H_2O$, the filtered solution made up to 200 c.c., and slightly less than the theoretical amount of 10% $AgNO_3$ aq. added drop by drop (stirring). If the solution is added rapidly, or a more conc. solution used, a considerable amount of a brown ppt. is formed, which requires vigorous shaking before it becomes pure canary-yellow. The ppt. is allowed to settle, the supernatant liquid is decanted, and divided into two equal parts. To one, the $AgNO_3$ solution is slowly added till the ppt. becomes *slightly* discoloured. The volume added is measured and the two portions mixed. An amount of $AgNO_3$ aq. 5 c.c. less than the amount required in the previous operation is then slowly added and the whole is mixed with the main ppt. and shaken. After the ppt. has settled, the liquid is decanted and 1% $AgNO_3$ aq. added until the colour of the liquid begins to change from bright yellow to pale yellow. This liquid is then shaken with the main ppt., and the remaining solid is washed 6—8 times by decantation, filtered off, and dried for 2—3 days in vac. over $H_2SO_4$ in the dark, during which it must retain its bright yellow colour. It is then powdered, and on standing over-night in a vac. desiccator over $P_2O_5$ it becomes perfectly dry (Found : Ag, 78·1; N, 10·7. Calc. for $Ag_2N_2O_2$ : Ag, 78·21; N, 10·16%).

*Ethyl,* n-*Propyl, and* n-*Butyl Hyponitrites.*—5·0 G. of EtI (or 5·5 g. of $Pr^{\alpha}I$, or 6·0 g. of *n*-BuI) are added to 20 c.c. of dry $Et_2O$ in a freezing mixture, and 5·0 g. of dry powdered $Ag_2N_2O_2$ slowly added. The flask is closed with a cork carrying a $CaCl_2$ tube and left in the refrigerator for 24 hrs. The solution is filtered into a large test-tube, through which a current of dry air is slowly drawn until all smell of ether is removed. The ester is kept for 2 hrs. over anhyd. $CaCl_2$ and filtered. The esters cannot be distilled even at low pressures. The amount of nitrogen evolved on hydrolysis by $H_2O$ showed them to be pure.

All the esters are easily sol. in EtOH, $Et_2O$, and $C_6H_6$, but practically insol. in $H_2O$. Ethyl hyponitrite when heated begins to decompose rapidly at 80—82° and explodes, but not very violently, whilst according to Zorn (*loc. cit.*) it is as explosive as $NCl_3$. The propyl and the butyl ester detonate when heated rapidly, but with slow rise in temp. the decomp. is smooth and without detonation.

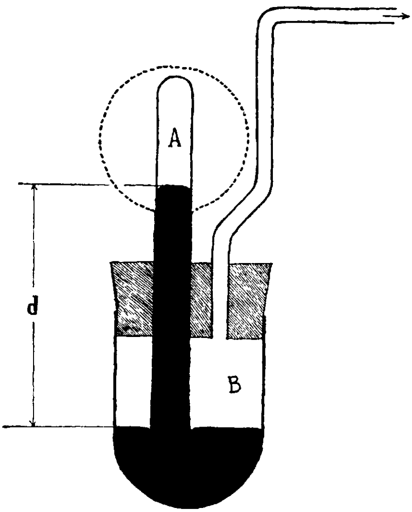
*Benzyl Hyponitrite.*—From $CH_2PhI$ (6·0 g.) and $Ag_2N_2O_2$ (4·5 g.), this ester is prepared as in the preceding cases, the ether being evaporated in a vac. over $H_2SO_4$. When nearly all the $Et_2O$ has been removed, the solid is washed with dry light petroleum, redissolved in the minimum of dry $Et_2O$, and pptd. by the former solvent. It is then left on a porous plate in a partly evacuated desiccator containing $H_2SO_4$ and solid paraffin; m. p. 48—49° (Found : N, 11·9. Calc. for $C_{14}H_{14}N_2O_2$ : N, 11·57%).

*Action of Aqueous Alcohol on the Esters.*—A weighed amount of ester was dissolved in 10 c.c. of EtOH and diluted with $H_2O$ to 25 c.c. in a flask fitted with two delivery tubes, one connected with a nitrometer and the other with a $CO_2$ generator. The flask was placed in a freezing mixture, and the air expelled by a current of $CO_2$. The flask was then heated at 40—50°, or, in the case of the benzyl ester, at 70—75°. The gas collected was insol. in EtOH and was N. Gas evolution ceased after about 45 mins.

| | Ester, g. | Gas at N.T.P., c.c. | $N_2$, %. Found. | $N_2$, %. Calc. |
|---|---|---|---|---|
| Ethyl hyponitrite | 0·1205 | 22·0 | 22·83 | 23·73 |
| ,, ,, | 0·0937 | 17·1 | 22·82 | |
| Propyl ,, | 0·1180 | 17·5 | 18·54 | 19·18 |
| Butyl ,, | 0·1095 | 13·7 | 15·64 | 16·10 |
| ,, ,, | 0·0823 | 10·1 | 15·34 | |
| Benzyl ,, | 0·1020 | 9·0 | 11·04 | 11·57 |
| ,, ,, | 0·0923 | 8·2 | 11·11 | |
| ,, ,, | 0·1527 | 13·5 | 11·05 | |

*Action of Phenylhydrazine on Benzyl Hyponitrite.*—To 0·0677 g. of the ester, dissolved in EtOH, a solution of $NHPh{\cdot}NH_2$ in HOAc was added, the solution heated at 70—80° for 15 mins., and diluted with $H_2O$. The pptd. benzaldehydephenylhydrazone, 0·0426 g. (77·7% of theory), was recryst. from EtOH (m. p. 156—157°).

FIG. 1.



*Hydrolysis of* n-*Butyl Hyponitrite.*—0·5 G. of the ester was added to alc. KOH, the solution kept at room temp. for 5 hours, and then diluted with $H_2O$. The liquid had no smell of the ester. On addition of a little dil. $AgNO_3$ aq., only a brown ppt. was obtained, whereas yellow hyponitrite is first pptd. even in presence of a large excess of alkali. When the solution was left in the refrigerator, the smell of the ester could be detected after dilution for 3—4 days, but at no time, even after a week, when it no longer smelt of the ester, did the solution give any yellow ppt. with $AgNO_3$.

*Reduction of Benzyl Hyponitrite by Aluminium Amalgam.*—0·5 G. of the ester was dissolved in dil. aq. EtOH and 1 g. of freshly prepared Al–Hg added. After standing for ½ hr. at room temp., the solution was poured into a large vol. of $H_2O$ and extracted with $Et_2O$; the extract on evaporation at reduced press. deposited unchanged benzyl hyponitrite. When the solution was kept at 60° for ½ hr., the ethereal extract gave a non-nitrogenous liquid, b. p. 204°, *viz.*, benzyl alcohol.

*Reduction of Ethyl Hyponitrite by Devarda's Alloy.*—About 1 g. of the ester was added to 25 c.c. of 50% KOH solution with 2 g. of Devarda's alloy. The distillate was very slightly alk. (requiring 0·1 c.c. of 0·1*N*-HCl) and showed a trace of $NH_3$. It gave no carbylamine test.

*Vapour Density.*—In the determination with ethyl hyponitrite in the Hofmann apparatus, the mercury column, on cooling, did not return to the original level, indicating decomp. at the reduced press. The modified Hofmann apparatus shown in Fig. 1 was then used in an attempt to determine the vapour pressure, but the instability of the esters rendered it useless in this case. The tube A is filled with dry Hg, and a small amount of substance introduced into it. It is then transferred in a deep mercury trough to the tube B, and the rubber stopper pressed in. The whole apparatus is then immersed in a water-bath. When the bath attains the desired temp., B is connected with a Sprengel pump. When the mercury in A begins to fall, the pump is stopped and the manometer reading taken. The difference (*d*) in the mercury levels is measured by a cathetometer and, after temp. correction, is added to the manometer reading. After each reading the vac. can be released, whereupon, if no decomp. occurs, no gas will be found in A.

For the determination of vapour density A is substituted by a 50-c.c. flask as shown dotted. After the apparatus has been heated to the desired temp., the pump is started, and the Hg in the neck of the flask adjusted to the graduation mark. Decomp. can be detected as in the previous case.

*Molecular weights of the esters in benzene solution.*

| | | | | | |
|---|---|---|---|---|---|
| *Ethyl hyponitrite* ($M$ = 118). | | | *Propyl hyponitrite* ($M$ = 146). | | |
| $C_6H_6$ = 13·26 g. | | | $C_6H_6$ = 13·15 g. | | |
| *w.* | *d.* | *M.* | *w.* | *d.* | *M.* |
| 0·0468 | 0·151° | 119·9 | 0·0281 | 0·076° | 144·2 |
| 0·0964 | 0·322 | 115·8 | 0·0658 | 0·179 | 143·4 |
| 0·1286 | 0·429 | 116·1 | 0·0469 | 0·121 | 151·2 |
| | | Mean 117·3 | | | Mean 146·3 |
| *Butyl hyponitrite* ($M$ = 174). | | | *Benzyl hyponitrite* ($M$ = 242). | | |
| $C_6H_6$ = 13·50 g. | | | $C_6H_6$ = 14·27 g. | | |
| 0·0577 | 0·127 | 172·6 | 0·0813 | 0·121 | 241·5 |
| 0·0643 | 0·140 | 174·6 | 0·0602 | 0·089 | 243·2 |
| 0·1030 | 0·226 | 173·2 | 0·0907 | 0·135 | 241·5 |
| | | Mean 173·5 | | | Mean 242·1 |

Measurements of the parachors and dipole moments of the esters, and the dipole moment of nitramide, have been made and will be published. The parachors of the esters are not in agreement with the usual formula if the usual values for the constants are used, but the dipole moments show that the formula $RO{\cdot}N{:}N{\cdot}OR$ is very probably correct. The dipole moment of nitramide is large and throws some light on its constitution.

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