CLXXXIV.—*The Interaction of the Alkylsulphates with the Nitrites of the Alkali Metals and Metals of the Alkaline Earths.*

By PRAFULLA CHANDRA RÂY and PAÑCHĀNAN NEOGI, M.A.

As silver nitrite by its interaction with the alkyl iodides yields a nitro-compound as well as an ester, it has often been taken for granted that this nitrite has a twofold constitution, namely, nitronic and oxylic. Evidence has already been adduced in favour of the latter structure (Rây and Gañguli, Proc., 1905, **21**, 278), which Dr. Divers is inclined to accept as fairly conclusive (*ibid.*, p. 281). It seemed to us that further light would be thrown on the question by studying the reaction between the alkylsulphates and the alkali nitrites, as the latter have always been supposed to have the oxylic constitution.

EXPERIMENTAL.

I. *Potassium Ethylsulphate and Sodium Nitrite.*

Lauterbach has published a brief note on the subject (*Ber.*, 1878, **11**, 1225), but a systematic investigation seemed desirable, especially as this chemist contented himself with demonstrating the formation of ethyl nitrite by its odour and inflammability, and also in view of the additional interest lent to the subject by Wade's fruitful research on the interaction between the alkylsulphates and potassium cyanide (Trans., 1902, **81**, 1596).

Dried and powdered potassium ethylsulphate and sodium nitrite were mixed in molecular proportions in a glass retort, to the neck of which was attached an inverted condenser. The upper end of the condenser was connected with a bulb provided with stop-cocks at both ends and three absorption bottles containing 90 per cent. alcohol. As the temperature of the laboratory was about 30°, the entire condensation and absorption apparatus was immersed in ice-cold water. It will be seen below that even this arrangement failed to condense the whole of the ethyl nitrite, as during the reaction a constant stream of nitric oxide was evolved, which carried off a considerable amount of it. For the same reason the air was expelled by a slow stream of carbon dioxide. The retort was heated in a glycerol bath. The reaction, which commences at 145°, is indicated by frothing, which slowly extends towards the centre from the peripheral regions. When the reaction once begins it proceeds continually, even when the temperature sinks so low as 110°. After a certain interval, the action becomes very violent and a sudden and vigorous evolution of white vapours takes place. The reaction then moderates, effervescence ceases, and the mass has the appearance of tranquil fusion. The digestion lasts from two and a half to three hours.

(a) *Ethyl Nitrite.*

Although it is "dry" ethylsulphate which is heated, much alcohol is given off at the temperature at which the reaction takes place (compare Wade, *loc. cit.*). A portion of this alcohol is carried off and condensed with ethyl nitrite in the bulb. The alcoholic solution of the ethyl nitrite in the bulb, as also in the absorption bottles, was estimated according to the method prescribed in the British Pharmacopœia. As will be shown below, the result is somewhat too low owing to the fact that a part of the nitrite escapes condensation, being carried off with the stream of nitric oxide and carbon dioxide.

(b) *Nitroethane.*

The nitroethane was now distilled off, using a small condenser, the distillation being continued as long as oily drops appeared. The distillate was shaken up with brine and the oily layer separated, washed with water, and dried over calcium chloride. Considerable difficulty was experienced here, as it was found that calcium chloride forms with the "oil" a kind of emulsion. When our work was at this stage, Wade's paper on "The Influence of Water and Alcohols on the Boiling Point of Esters" (Trans., 1905, **87**, 1656) appeared, which materially helped us. Fused sodium sulphate was used as the dehydrating agent, as potassium carbonate acts on nitroethane. When the "oil" was subjected to distillation, curious and anomalous behaviour was noticed. A considerable amount passed over below 100°; only a small fraction could be collected at a constant boiling point between 110° and 118°, whilst a minute quantity came over between 150° and 160° and the residue charred. As pointed out by Wade (*loc. cit.*, 1668), an ethereal liquid containing alcohol, when shaken up with brine, does not give up its alcohol, but, on the contrary, "shares its alcohol with it." The fraction below 100° answered to all the well-known tests of nitroethane, namely, it solidified completely on the addition of alcoholic sodium hydroxide, and the aqueous solution of the sodium compound gave with ferric chloride a red coloration, and with copper sulphate a green precipitate. Obviously the quantity of nitroethane formed cannot be determined by fractionation.* Known mixtures of

---

* A mixture made up of 5 c.c. of alcohol and 5 c.c. of nitroethane, when shaken up with brine and dried over fused sodium sulphate, gave 6·1 c.c. of "oil" which, on fractionation, gave 4·5 c.c. distilling between 75° and 100° and only 1·3 c.c. between 100° and 115°.

nitroethane and alcohol were treated with alcoholic sodium hydroxide, the precipitate washed with absolute alcohol and ultimately converted into sodium sulphate and weighed as such; but the results turned out to be too low. Consequently the nitrogen in an aliquot portion of the liquid was estimated according to Dumas' method, and from it the amount of nitroethane in the mixture deduced. The fraction between 110° and 118° was nearly pure nitroethane. The results of 3 experiments out of 27 are given below, 32·8 grams of potassium ethylsulphate and 14 grams of sodium nitrite being taken in each case.

No. of experiment.	Weight of ethyl nitrite in grams.	Weight of nitroethane in grams.
1	2·3	1·3
2	3·2	1·0
3	2·0	1·3

As has been already explained, some of the ethyl nitrite is invariably lost, and the figures for nitroethane are also a little too low, as quite an appreciable quantity of it remains mixed with the liquid of higher boiling point (see below). The yield of nitroethane is 6 to 8 per cent. of that which is theoretically possible.

(c) *Liquid of Higher Boiling Point.*

The fraction which distilled at 150—160° was very small, and not more than 0·15 gram could be recovered in each experiment. In order to study its nature and properties, the distillates from several preparations were mixed, and the crude "oil," after being treated with brine and fused sodium sulphate as above, was subjected to fractional distillation under diminished pressure in Brühl's apparatus. Four fractions were collected, namely, 40—60°, 60—65°, 65—125°, and 125—130°, the distillation taking place under a pressure of 130 mm. The ranges of temperature recorded above are only approximate; in fact, the liquid gave evidence of the properties of a homogeneous ternary mixture (compare Wade, *loc cit.*). Blank experiments showed that pure nitroethane distilled at 63—65° under the above pressure, so that the second fraction was nearly pure nitroethane. The fraction 125—130° proved to be α-nitro-n-butane with traces of a compound of a still higher boiling point. The analyses of two typical samples of different preparations are given below:

I. $C = 47·06$; $H = 8·23$; $N = 14·10$.
II.* $C = 46·06$; $H = 6·60$; $N = 13·85$.
$C_4H_9O_2N$ requires $C = 46·60$; $H = 8·73$; $N = 13·60$ per cent.

---

* This represents a fraction which distilled at 150—160° under the ordinary pressure.

The vapour density of the liquid was found by Hofmann's method to be 50·4, that required by nitrobutane being 51·50. That it has this constitution is evident from the fact that its boiling point was about 150°, and it gave with alcoholic sodium hydroxide the characteristic precipitate and with potassium hydroxide, on standing, a yellow deposit. It also responded to the nitrolic acid test.

II. *Potassium Ethylsulphate and Potassium Nitrite.*

The conditions of the experiment were similar to those previously described. The mass fused at a much higher temperature, namely, at about 165°, and the reaction proceeded without the aid of heat; white fumes and nitric oxide were evolved. The yield of nitroethane was much less than in the former experiment.

Expt. 1.—32·8 grams of potassium ethylsulphate and 17 grams of potassium nitrite gave 1·5 grams of ethyl nitrite and 0·8 gram of nitroethane. In this case also nitrobutane was formed, as will be seen below.

Expt. 2.—164 grams of potassium ethylsulphate and 85 grams of potassium nitrite yielded 8·5 c.c. of "oil" which on distillation under the ordinary pressure gave 70—100°, 5·0 c.c.; 100—150°, 1·5 c.c.; and 150—160°, 0·5 c.c.

III. *Barium Ethylsulphate and Barium Nitrite.*

Barium ethylsulphate crystallises with 2 molecules of water, and is completely dehydrated when kept for a few days over sulphuric acid under diminished pressure (see analysis given below), whilst the nitrite still retains some water (Rây, Trans., 1905, **87**, 177). The anhydrous alkylsulphate and the nitrite were mixed in equimolecular proportions. The mass did not fuse and froth up, even when the temperature of the bath was raised to 190°. A distillate passed over which was mainly alcohol. With the hydrated salts, however, fusion commenced at 120°, but the action suddenly became violent at about 130°, and white fumes were evolved with violence. The yield of nitroethane was very poor, and only a few drops could be collected, which, however, answered to all the tests of this compound.

IV. *Calcium Ethylsulphate and Calcium Nitrite.*

Calcium ethylsulphate, which also crystallises with 2 molecules of water, is completely dehydrated, like the barium salt, when kept over sulphuric acid under diminished pressure. The anhydrous salt mixed with dehydrated calcium nitrite in equimolecular proportions does not fuse on heating, but simply decomposes when the temperature is sufficiently raised. The hydrated salts were therefore used. The mixture fused at 116°, but at about 125° torrents of white fumes were evolved. The yield of nitroethane was again very poor, the last drops of the distillate responding to the reactions for this substance.

V. *Sodium Ethylsulphate and Sodium Nitrite.*

In the hope of obtaining better yields of nitroethane, the sodium salt was next tried. It crystallises with 1 molecule of water, which may be removed when kept under diminished pressure over sulphuric acid (see analysis given below). The anhydrous salt did not fuse with sodium nitrite, even when the temperature was raised to 195°. The hydrated salt, however, when similarly treated, began to fuse at so low a temperature as 80°, and the action, once begun, proceeded of itself as in the case of the potassium salt. The temperature of the bath was not allowed to rise above 120°. The sudden evolution of white fumes was never noticed. As the reaction takes place at a much lower temperature, it gave a better yield of nitroethane, and, moreover, the liquid having a higher boiling point was not formed. The results of the two experiments are given below, 33·2 grams of sodium ethylsulphate and 13·8 grams of sodium nitrite being taken in each case.

Expt. 1 gave 0·6 gram of ethyl nitrite and 2·2 grams of nitroethane. Expt. 2 gave 0·9 gram of ethyl nitrite and 2·0 grams of nitroethane. The yield of nitroethane is thus as much as 13 per cent. of the theoretical, whilst it is only about 6 to 8 per cent. when the potassium salt is used.

VI. *Sodium Ethylsulphate and Potassium Nitrite.*

This reaction began with frothing at a higher temperature than that in V, namely, at 120° when the hydrated salt was used, there being no fusion with the anhydrous salt. There was, again, no evolution of white fumes, and the reaction proceeded of itself when once started, nitrobutane not being formed. The yield of nitroethane is, however, much less, being almost equal to that obtained from potassium ethylsulphate and sodium nitrite. 33·2 grams of sodium ethylsulphate and 17 grams of potassium nitrite gave 0·9 gram of ethyl nitrite and 1·3 grams of nitroethane.

Conclusion.

The formation of nitrobutane, as noticed in I and II, is remarkable, and it is always associated with vigorous evolution of white fumes. Moreover, the interaction of sodium ethylsulphate and sodium nitrite, which takes place at a much lower temperature, does not give rise to this compound. This mode of ascent in the homologous series does not admit of an easy explanation. The alcohol which was used in the present investigation was proved to be free from impurities. It was rectified over quicklime and had a constant boiling point (78°). The analyses of the various alkylsulphates are given below.*

The argument in favour of the twofold constitution of silver nitrite simply because it yields with ethyl iodide both ethyl nitrite and nitroethane is scarcely tenable. The alkali nitrites have the constitution MO·NO, where M represents the atom of the metal, in other words, the nitrogen is not directly attached to it. Hence we should have only expected the production of ethyl nitrite in the present series of experiments, but its formation is always accompanied with that of its isomeride. The more correct view would seem to be that it is only during the substitution of the atom of the metal by the alkyl radicle that a tautomeric change takes place.†

Summary.

From the foregoing investigation, it would appear that by the interaction of the sodium, potassium, barium, and calcium salts of ethylsulphuric acid and the nitrites of the alkali metals and metals of the alkaline earths, both ethyl nitrite and nitroethane are formed. In the case of the potassium ethylsulphate and potassium or sodium nitrite small quantities of nitrobutane are also obtained.

PRESIDENCY COLLEGE,
CALCUTTA.

* $(C_2H_5SO_4)_2Ba,2H_2O$. Ba, found 32·79; calculated 32·70.
$(C_2H_5SO_4)_2Ba$. Ba, found 36·01 and 35·88; calculated 35·77.
$C_2H_5NaSO_4,H_2O$. Na, found 13·70; calculated 13·85.
$C_2H_5NaSO_4$. Na, found 15·72; calculated 15·54 per cent.

† Whether the hypothesis of tautomerism is adequate or not, there is evidently much force in what Wade urges: "It does not follow, for example, that because silver cyanate and nitrite yield alkyl*iso*cyanates and nitro-compounds respectively, the metal is necessarily linked to nitrogen; it may equally be linked to oxygen" (*loc. cit.*, p. 1612).