

Paramagnetism of Na_2NO_2

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When a solution of sodium nitrite in liquid ammonia is treated with a solution of sodium in liquid ammonia the blue colour of the solution disappears and a yellow compound of the composition Na_2NO_2 is deposited. This substance was first obtained by Maxted¹ and later prepared by Zintl and Kohn², who also studied the chemical properties of the salt. The present author investigated the magnetic properties of Na_2NO_2 in 1940 and published in 1941 the qualitative results of the measurements and discussed their chemical significance in the paper³ "Magnetochemical Studies on Free Radicals" (in Danish). Parts of this article, also that which concerns Na_2NO_2 , has been quoted by Selwood⁴. In the present note the quantitative results are reported. Klemm and Pauli⁵ published in 1951 a paper on the magnetic properties of the same compound.

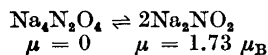
The preparation of Na_2NO_2 was carried out according to the method given by Zintl and Kohn² using an apparatus and a technique similar to those applied by these authors. The samples were extracted with liquid ammonia in order to remove NaNO_2 with which the preparations were contaminated. Seven independent speci-

mens were prepared but the magnetic measurements are given for four only. Two preparations (Nos. 1 and 2) possessed very small paramagnetic susceptibilities. The analyses proved that 1 and 2 were rather impure. One preparation (No. 5) exploded in the magnetic measuring tube.

In trying to prepare LiNaNO_2 we did not succeed in getting sufficiently pure substances.

The determination of the magnetic susceptibilities were performed by the Gouy-method as described by Christiansen and Asmussen⁶. The substances were transferred to the magnetic measuring tubes protected by an atmosphere of dry nitrogen. The results of the magnetic measurements and the chemical analyses are given in Table 1. The molar susceptibilities (column 5) were corrected for the diamagnetic contribution of the electron system of the ions Na^+ and O^{2-} . The gram ionic susceptibilities used for these ions are -3.7×10^{-6} and -11.3×10^{-6} , respectively. The total diamagnetic correction is then -30×10^{-6} neglecting the correction for N^{+2} , which doubtless is very small since the value for N^{+5} is about -0.1×10^{-6} .

Na_2NO_2 is formed in a reaction similar to that of the metal ketyls and may be considered as an inorganic ketyl. If the crystal contains Na^+ and NO_2^- ions only, the molar magnetic susceptibility should be 1271×10^{-6} (spin only; at 20°C). The observed small susceptibility values may be interpreted as being due to a certain dissociation in the crystal of the dimer $\text{Na}_4\text{N}_2\text{O}_4$, the sodium salt of a hypothetical tetraoxyhydrazine:



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Table 1. Analyses, paramagnetic susceptibilities and degrees of dissociation for four independent preparations of Na_2NO_2 .

Prep. No.	% Na		Temp. °K	$\chi_g \times 10^6$	$\chi_M \times 10^6$ for Na_2NO_2	$\chi_M \times 10^6$ for Na_2NO_2 Corr.	$\chi_M \times 10^6$ for $\text{Na}_4\text{N}_2\text{O}_4$ Corr.	$\chi_M \times 10^6$ for 100% dis. $\text{Na}_4\text{N}_2\text{O}_4$	Degree of dissociation
	Calc.	Found							
3	49.98	49.4	294	2.0	184	214	428	2 524	0.17
4	49.98	49.8	292	2.4	221	251	502	2 542	0.20
6	49.98	49.7	292	2.1	193	223	446	2 542	0.18
7	49.98	49.2	293	1.9	175	205	410	2 534	0.16

The degrees of dissociation at room temperature calculated by means of the data in columns Nos. 7 and 8 are in column 9. The mean value is 0.18. Klemm and Pauli⁵ report 0.23 at 20°C. Their susceptibility values at two lower temperatures may be interpreted as indicating a decrease in the degree of dissociation with decreasing temperature.

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Isolation of an Anti-Sclerotinia Factor, 7-Hydroxy-4'-methoxyisoflavone from Red Clover

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When investigating the antifungal substances in red clover, we isolated a new compound (A 1) the characteristics of which we have earlier reported^{1,2}. The structure elucidation of this compound is still in progress. When isolating this compound, we also came to isolate an other substance (A 2) which is found in comparatively large amounts in the leaves and the stems

of red clover. From fresh clover plants the isolation and separation of the two substances in pure form was difficult, since on paper chromatograms both substances behaved in much the same way in different solvent systems. The separation succeeded, however, using O'Keeffe fractionation. 2.69 g (m.p. 217°C) of A 1 was obtained in crystalline form from 10.75 kg of fresh red clover and 4.6 g (m.p. 262°C) of A 2, likewise in crystalline form. A large amount of the latter remained in the motherliquor, however. The total amount of A 2 was calculated on the basis of paper chromatography from the fluorescence of the spots to about 10 g per 10 kg fresh clover harvested 26.7. Since A 1 disappears on drying of the clover, the isolation of A 2 from dried clover is easy (ether extraction, extraction of the ether residue by petroleum ether and sublimation of the undissolved residue *in vacuo* at 260 to 280°C).

The structure of A 2. Elementary analysis: C 71.89; H 4.66; Calc. for C₁₆H₁₂O₄: C 71.63; H 4.51. The substance contained one hydroxy and one methoxy group. The content of the methoxy group in the substance was 11.1 %, determined by the method of Vieböck and Brecher, calculated for the compound (C₁₅H₉O₃)-OCH₃ 11.57 %.

Using Rossman's method the substance in 30 min took up an amount of bromine corresponding to one double bond. In the alkali melt (131 mg of A 2, 2.74 g of solid KOH, 230–250°C, 2 h) 2,4-dihydroxybenzoic acid and *p*-hydroxybenzoic acid were formed. When heated in BaOH₂ solution anisic acid was formed. The structure of the A 2 compound accordingly is I or II.

On heating 400 mg of the substance in NaOH solution on a water bath for 20 min a substance was obtained after neutralisation with hydrochloric acid, acidification with acidic sodium phosphate and extraction by ether. This substance crystallized in flaky crystals and melted at 164°C. The yield was 285 mg. The elementary analysis of the substance was C 69.36; H 5.61; O 24.62. If the compound formed had been a chalcone (C₁₆H₁₂O₄ + H₂O) corresponding to A 2, the calculated values

