LETTERS TO THE EDITORS

The Editors do not hold themselves responsible for opinions expressed by their correspondents. No notice is taken of anonymous communications

Cryoscopic Proof of the Formation of Nitronium Ion

As the result of work on the optical absorption and electrical conductivity of mixtures of nitric and sulphuric acids, and on the depression of the freezing point of sulphuric acid by added nitric acid, Hantzsch concluded that in such solutions nitric acid is largely converted into two cations, $H_2NO_3^{+}$ and $H_3NO_3^{++}$, the latter being the principal form present in excess of sulphuric acid[1]. The optical and electrical work showed essentially that the nitric acid is converted into an altered form, and that this consists of or contains ions. The cryoscopic work furnished a specific argument in favour of the bivalent ion. For the univalent ion corresponds to a two-fold, and the bivalent ion to a three-fold, depression by nitric acid of the freezing point of the sulphuric acid solvent: the van't Hoff *i*-factors would be as shown. Experimentally, Hantzsch found a three-fold depression ($i = 3$):

$$HNO_3 + H_2SO_4 = H_2NO_3^{+} + HSO_4^{-} \quad (i = 2)$$
$$HNO_3 + 2H_2SO_4 = H_3NO_3^{++} + 2HSO_4^{-} \quad (i = 3)$$

The remaining evidence of a specific nature consists in Hantzsch's claim to have isolated crystalline perchlorates corresponding to each of his ions, namely, the salts $(H_2NO_3^{+})(ClO_4^{-})$ and $(H_3NO_3^{++})(ClO_4^{-})_2$ (cf. the following note).

The purpose of this note is to record a revision of the freezing point evidence; for when corrected it provides an unambiguous proof that the cation into which nitric acid is actually converted in sulphuric acid is neither of Hantzsch's ions, but the nitronium ion, NO_2^{+}.

Hantzsch's conclusion in favour of a three-fold depression of freezing point was later supported by Robles and Moles[2]; but the methods employed were not accurate, nor were the results concordant. However, the technique of cryoscopy in sulphuric acid has since been much improved by Hammett[3]; and, using essentially his methods, we have established that the depression produced by nitric acid is four-fold, that is, that each molecule of nitric acid added to the sulphuric acid solvent produces four solute particles. Only one interpretation is possible, namely, that NO_2^{+} is formed according to the equation

$$HNO_3 + 2H_2SO_4 = NO_2^{+} + H_3O^{+} + 2HSO_4^{-} \quad (i = 4)$$

We also find that each of the oxides of nitrogen, N_2O_5, N_2O_4 and N_2O_3, produces a six-fold depression of the freezing point of sulphuric acid. The corresponding equations are

$$N_2O_5 + 3H_2SO_4 = 2NO_2^{+} + H_3O^{+} + 3HSO_4^{-} \quad (i = 6)$$
$$N_2O_4 + 3H_2SO_4 = NO_2^{+} + NO^{+} + H_3O^{+} + 3HSO^{-} \quad (i = 6)$$
$$N_2O_3 + 3H_2SO_4 = 2NO^{+} + H_3O^{+} + 3HSO_4^{-} \quad (i = 6)$$

Furthermore, Mr. D. J. Millen has confirmed the presence in the relevant solutions of all the ions represented in these equations by the method of Raman spectroscopy—excepting for H_3O^{+}, which, as is well known, cannot be detected by this means.

Our experimental values for the *i*-factors of van't Hoff are as follows:

HNO_3	10	determinations	$i = 3{\cdot}82$
N_2O_5	10	,,	$5{\cdot}85$
N_2O_4	6	,,	$5{\cdot}84$
N_2O_3	5	,,	$5{\cdot}85$

Hammett's results for H_2O lead to $i = 1{\cdot}92$. The small deviations of all these figures from integral values give mean activity coefficients of $0{\cdot}96 \pm 0{\cdot}01$ for the formed binary electrolytes, $(H_3O^{+})(HSO_4^{-})$, $(NO_2^{+})(HSO_4^{-})$ and $(NO^{+})(HSO_4^{-})$.

R. J. GILLESPIE
J. GRAHAM
E. D. HUGHES
C. K. INGOLD
E. R. A. PEELING

Sir William Ramsay and Ralph Forster Laboratories,
University College, London.

Sept. 2.

---

[1] Numerous papers (1907–32).

[2] *Anal. Fis. Quim.*, **32**, 474 (1934).

[3] *J. Amer. Chem. Soc.*, **55**, 1900 (1933); **59**, 1708 (1937).

Isolation of Salts of the Nitronium Ion

HANTZSCH[1] has claimed to have prepared, from anhydrous nitric and perchloric acids, two nitracidium perchlorates, and to have established their compositions by analysis. He represents their formation as follows:

$$HNO_3 + HClO_4 = (H_2NO_3^{+})(ClO_4^{-})$$
$$HNO_3 + 2HClO_4 = (H_3NO_3^{++})(ClO_4^{-})_2.$$

He states that either salt could be obtained by using the acids in the appropriate proportions, while with intermediate proportions mixtures were produced, which by crystallizing from warm nitric acid could be converted into the pure monoperchlorate or by crystallization from warm perchloric acid could be completely transformed into the diperchlorate.

Hantzsch's experimental methods, however, were not wholly suitable for the treatment of such sensitive compounds. We have therefore repeated the work, employing a vacuum technique designed completely to exclude atmospheric moisture, and using temperatures low enough to prevent decomposition of the pure acids, with the consequent production of such contaminants as nitrosonium perchlorate, $(NO^{+})(ClO_4^{-})$.

We find that it is readily possible to obtain a solid product of the approximate composition of $(H_3NO_3^{++})(ClO_4^{-})_2$; it is not even necessary that the two acids should be used in the theoretical proportions. However, this product is a mixture, separable by fractional crystallization from nitromethane into two components. The less soluble has been shown to be nitronium perchlorate, $(NO_2^{+})(ClO_4^{-})$; the other is the salt $(H_3O^{+})(ClO_4^{-})$, well known as the hydrate of perchloric acid.

We have not been able to prepare any dry salt, or dry mixture, of the composition of $(H_2NO_3^{+})(ClO_4^{-})$. However, we find that adhering nitric acid is somewhat difficult to remove from $(NO_2^{+})(ClO_4^{-})$ by pumping, and it is possible that Hantzsch, who dried his preparations only on porous tile, may have obtained compositions approximating to that of $(H_2NO_3^{+})(ClO_4^{-})$ from certain of his mixtures of $(NO_2^{+})(ClO_4^{-})$ and $(H_3O^{+})(ClO_4^{-})$ which by chance contained roughly the right amount of adhering nitric acid.

The separation of $(NO_2^{+})(ClO_4^{-})$ from $(H_3O^{+})(ClO_4^{-})$ by crystallization from nitromethane is tedious, and can be avoided by decomposing the $(H_3O^{+})(ClO_4^{-})$ by means of N_2O_5. The reaction is conveniently conducted in nitromethane, with such concentrations that the formed $(NO_2^{+})(ClO_4^{-})$ crystallizes.

Nitronium perchlorate has almost certainly been prepared before, Gordon and Spinks[2] having obtained a deposit of the composition $NClO_6$, which with water gave nitric and perchloric acids, by mixing gas-streams containing ozone, nitrogen dioxide and chlorine dioxide. An analysis of our salt may be quoted: acid equivalent, 73·0 (calc., 72·7); chlorine, 24·3 (calc., 24·4); nitrogen, 9·52 (calc., 9·63 per cent). The salt has a very low vapour pressure, scarcely fumes in air, and dissolves in water with but slight liberation of heat. The constitution of the solid salt has been established by Mr. D. J. Millen by the observation of its Raman spectrum, which consists simply of the combined known spectra of the ions NO_2^{+} and ClO_4^{-}. Other physical properties of the salt are being examined, and other nitronium salts, including the bisulphate, biselenate and bipyrosulphate, are being studied.

Our failure to isolate nitracidium perchlorate, $(H_2NO_3^{+})(ClO_4^{-})$, is consistent with the following note, which shows that the immediate effect of adding a small amount of perchloric acid to nitric acid is to produce the NO_2^{+} ion. Thus it appears that any ion $H_2NO_3^{+}$ formed with the aid of perchloric acid is largely converted into NO_2^{+} in an anhydrous nitric acid medium. The ion $H_2NO_3^{+}$ itself is probably not detectable by the Raman effect, just as the ion H_3O^{+} is not detectable by this means.

D. R. GODDARD
E. D. HUGHES
C. K. INGOLD

Sir William Ramsay and Ralph Forster Laboratories,
University College, London.

Sept. 2.

---

[1] *Ber.*, **58**, 958 (1925).

[2] *Canadian J. Res.*, B, **18**, 358 (1940).

Spectroscopic Identification of the Nitronium Ion

EXTENSIVE studies of the Raman spectra of mixtures of nitric and sulphuric acids have been made by Chédin[1]. He showed that such spectra were characterized by the appearance of two prominent, polarized lines, at 1,050 and 1,400 cm.$^{-1}$, which did not belong to the spectrum of either the nitric acid or the sulphuric acid molecule. The same two lines appeared if he added either nitrogen pentoxide or phosphorus pentoxide to pure nitric acid. He therefore assigned these lines to nitrogen pentoxide; but, since solutions of this substance in organic solvents gave a different Raman spectrum, he supposed that the nitrogen pentoxide, when in solution in nitric or sulphuric acid, exists in some special form.

Bennett and Williams have interpreted these results on the basis that Chédin's special form is an ionized form[2]. In particular, they have assigned the line at 1,400 cm.$^{-1}$ to NO_2^{+}, comparison with the iso-electronic molecule CO_2 having shown that a polarized Raman frequency would be expected to appear in this region. They have attributed the line at 1,050 cm.$^{-1}$ to NO_3^{-}, or, in the presence of sulphuric acid, to HSO_4^{-}, assignments which are consistent with the known spectra of these ions.

The purpose of this note is to supply a spectroscopic demonstration of the correctness of Bennett and Williams's suggestion concerning the origin of the frequency 1,400 cm.$^{-1}$: it is an important suggestion, because it renders Raman spectroscopy the most convenient and certain method for the identification of NO_2^{+}.

With the mixtures mentioned, Chédin had always obtained his two lines, 1,050 and 1,400 cm.$^{-1}$, together, and roughly in proportion to each other as regards intensity. Neither he nor anyone else[3] has hitherto observed the line 1,400 cm.$^{-1}$ without the other line. Chédin naturally assumed the two to originate in the same molecular source. The spectroscopic selection rules show, however, that, if two such lines should come from the same source, that source could not be NO_2^{+}; for this belongs to the small class of molecules which cannot have more than one strong Raman line. It is permissible to avoid the difficulty by assigning the other line to either NO_3^{-} or HSO_4^{-}; but the decisive experiment to determine whether the source of the line 1,400 cm.$^{-1}$ has in fact one or two lines in its Raman spectrum would, of course, be to produce the line 1,400 cm.$^{-1}$ without its hitherto constant companion, by mixing nitric acid with any other acid which (*a*) has no line in the neighbourhood of 1,050 cm.$^{-1}$, (*b*) gives an anion which has no line near 1,050 cm.$^{-1}$, and (*c*) is a strong enough acid to destroy nitrate ion. Both perchloric acid and selenic acid fulfil these conditions; and we find that the addition of each of these acids to