EFFECT OF TEMPERATURE ON THE ELECTROLYTIC DISSOCIATION IN STRONG ELECTROLYTES.

PART I. NITRIC ACID

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(Plate VII)

ABSTRACT. Electrolytic dissociation in nitric acid is studied at various concentrations and temperatures by the mechanism of Raman effect The degree of dissociation of the acid at various temperatures is calculated by comparing the intensity of the line of Raman frequency 1050 with that of Raman frequency 1300 in the Raman spectra of the acid at these temperatures. It is found that the dissociation of the acid decreases with increasing temperature.

INTRODUCTION

It is well known that the conductivity of electrolytes increases with temperature. This increase may be due to (1) the increase in the ionic velocity and (2) larger ionisation of electrolyte. A mere study of the conductivity of the solution which is a function of the above two factors at different temperatures does not, therefore, give a direct indication of how the degree of dissociation varies with temperature. But a study of the Raman spectrum of the electrolyte at different temperatures gives, in suitable cases, an idea of how it varies, as the intensity of a Raman line is directly proportional to the ion giving rise to it. The first attempt in this direction was made by Koteswaram (1938), who, on studying the Raman spectrum of sulphuric acid at 30°C and 200°C, concluded that the acid ionises more at 200°C than at 30°C. The present work describes a similar study in nitric acid.

FACTORS TO BE TAKEN INTO ACCOUNT IN STUDYING THE DISSOCIATION OF THE ACID BY THIS METHOD

The Raman spectrum of nitric acid consists of two sets of lines corresponding respectively to the NO_3' ions and the undissociated HNO_3 molecules. The line of Raman frequency 1050 is the most intense of the first set, while that of Raman frequency 1300 is the strongest of the second set. It was first observed by I. R. Rao (1930) that as the concentration of the acid is decreased, the first set of the lines brighten up while the intensity of the latter decreases, therby showing that the acid progressively dissociates with increasing dilution. The first set of lines were observed in the spectra of the nitrates also. It was also shown by I. R. Rao (1934) that in the case of the alkali nitrates, the intensity of the 1050 line is proportional to the concentration, if the Raman spectra for different solutions are taken with equal times of exposure, thereby showing that they are completely dissociated at all concentrations. In a paper published by the author, (Rao, N. R., 1941) in which the details of the calculations are given, this result was made use of to calculate the actual degree of dissociation of the acid at various concentrations, by comparing the intensities of the 1050 line in the spectra of the nitrate solution and the acid.

To study the variation of the degree of dissociation with temperature, one may be tempted to assume that the relative intensities of particular Raman line in the spectra taken with the acid at different temperatures are a measure of the relative proportions of the radicals giving rise to this line, similar to what was done by Rao (1941) while studying its dissociation at different dilutions. This is justified only if the specific intensity (the intensity corresponding to each molecule) of a Raman line is independent of temperature. But, it is well known that there is a variation of this intensity according to the formula (Kohlrausch, 1931).

$$I\gamma \propto (\nu - d\nu)^4 \left(1 - e^{\frac{-hd\nu}{kT}}\right)^{-1}$$

Thus, a correction is necessary for this variation, to obtain the correct value of the intensity of a Raman line as a function of the number of molecules giving rise to it.

This correction is, however, eliminated by the author from the following considerations. What is required for the estimation of the degree of dissociation is the ratio of the number of the dissociated to the total number of the molecules of the acid. As was already pointed out, there are two prominent lines in the Raman spectrum of nitric acid, one of frequency 1050 and the other of 1300 characteristic of NO_3 and the HNO_3 radicals respectively. As the temperature of the acid is increased, the ratio of the intensities of these lines varies. This variation is taken as a measure of the change in the degree of dissociation.

But this is justified only if the variation in the ratio of the specific intensities of the lines with temperature is very small as otherwise it cannot be ascertained as to what proportion of this variation in the ratio is due to the change in the relative abundance of the NO_3 and the HNO_3 radicals and what due to the intrinsic change in the specific intensities of the radicals.

Let $Id\nu$ be the intensity of the 1050 line and $Id\nu'$ that of the 1300 line, then

$$Id\nu \propto (\nu - d\nu)^4 \left(1 - e^{\frac{-hd\nu}{kT}}\right)^{-1}$$

$$Id\nu' \propto (\nu - d\nu')^4 \left(1 - e^{\frac{-hd\nu'}{kT}}\right)^{-1}$$

Since $e^{\frac{-hd\nu}{kT}}$ is small compared to 1,

$$\frac{\mathrm{I}d\nu}{\mathrm{I}d\nu'} = \left(\frac{\nu - d\nu}{\nu - d\nu'}\right)^4 \left(1 + e^{\frac{-hd\nu}{kT}} - e^{\frac{-hd\nu'}{kT}}\right)$$

Now the expression $e^{\frac{-hd\nu}{kT}} - e^{\frac{-hd\nu'}{kT}}$ which is a difference between two small quantities that are nearly equal, is much smaller than the individual expressions. So, the variation of the ratio of the specific intensities of the lines is much smaller than their individual variation with temperature and it can be safely assumed that the ratio of the specific intensities of the lines under question is independent of temperature. This is borne out by the experimental investigations carried out in this laboratory in the case of many substances and by the quantitative measurements of the intensities of the lines in crystals made by Venkateswarlu (1942). So, any variation in the relative intensities with temperature must be due only to the change in the relative abundance of the radicals NO_3 and HNO_3 and the assumption, on the basis of which the degree of dissociation is proposed to be determined, is justified.

Now, for a fairly accurate determination of the dissociation of the acid by determining the relative intensities of the lines 1050 and 1300, the lines must be of the same order of intensity. But, as the concentration of the acid is decreased, the 1300 line characteristic of the undissociated molecules, falls off rapidly in intensity and below a concentration of about 10N the intensities of the two lines are far different from each other. Therefore, solutions of concentration below 10N cannot be studied by this method. Above about 16N, the acid gets very much coloured even by a slight rise in the temperature. Therefore only concentrations intermediate between these two limits, *viz.*, 14.50N 12.58N and 10.5N are chosen for investigation. They are studied at three temperatures 30°C, 60°C and 90°C. The solution of concentration 12.58N is studied at 5°C also.

EXPERIMENTAL

The experimental arrangement is the same as that described in a previous paper (Rao, N. R., 1940). To study the acid at higher temperatures, the copper jacket surrounding the Wood's tube is heated by a burner and the rate of flow of water and the gas adjusted to get the required steady temperature varying by not more than 5°. To work at 5°C, water cooled by large quantities of powdered ice in a trough is siphoned into the copper jacket. The mist condensed on the face of the Wood's tube is found to drain off as quickly as it is formed if the face is cleaned absolutely free from grease.

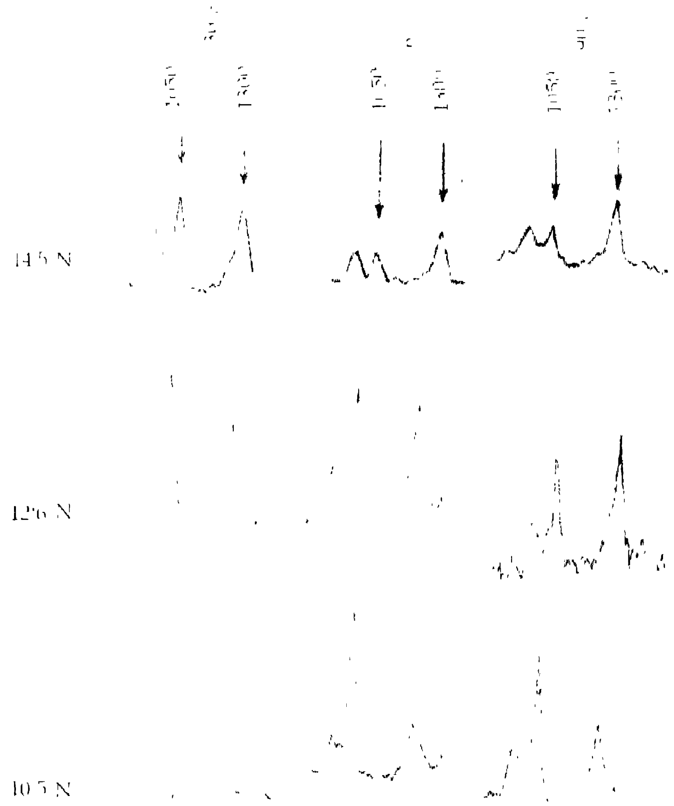
The intensities of the lines 1050 and 1300 are measured by the usual method and the degree of dissociation calculated by the following method.

CALCULATION OF THE DEGREE OF DISSOCIATION

It was suggested in a previous paper (Rao, N. R., *loc. cit.*) that the absolute degree of dissociation of the acid can be calculated by comparing the intensity of the 1050 line in the spectrum of the acid with that in an alkali nitrate solution which is assumed to be completely dissociated. If I is the intensity of the 1050 line in the spectrum of the nitrate of concentration c gm. moles. per litre, then $I/c = a$ is the intensity corresponding to one gm. mole. of NO_3 ions. If I_1, is the intensity of this line in the acid, then $I_1 / \frac{I}{c} = n_1$ gives in gram-molecules the number of NO_3 ions in the acid. Subtracting n_1 from the total number of acid molecules, the number of undissociated HNO_3 molecules n_2 is obtained. While $I_1/n_1 = a$ gives the specific intensity of the NO_3 ion, $I_2/n_2 = b$ gives the specific intensity of the HNO_3 molecule where I_2 is the intensity of the 1300 line and n_2 the number of undissociated molecules. Knowing I_1, I_2 and n_1 and n_2 for one of the concentrations of the acid (a/b) is calculated. Then, the degree of dissociation

$$\alpha = \frac{n_1}{n_1 + n_2} = 1 \Big/ \left(\frac{I_2}{I^1} \cdot \frac{a}{b} + 1 \right).$$

Now, it was shown previously that (a/b), the ratio of the specific intensities can be assumed to be independent of temperature. It can also be easily seen that it is independent of concentration of the acid or of the time of exposure. It also does not vary even if the solution is slightly coloured, since the lines are very close to each other and it can be assumed that both of them will be absorbed to the same extent. Once this ratio is determined for any one convenient concentration, the value of α for any other concentration can be calculated from the ratio I_1/I_2 for this concentration. The advantage of this method is that the spectra of the solutions of the nitrate and the acid need not be taken on the same plate, every time the degree of dissociation of the acid of any particular concentration is required, and it does not matter even if the acid is slightly coloured. But, the value of this ratio (a/b) thus determined is subjected to a small error for the following reasons. The intensity of the 1300 line falls off rapidly on dilution. Therefore, only concentrated solutions which cannot be obtained in a perfectly colourless condition must be worked with, and while comparing the intensity of the 1050 line in the acid and in the nitrate solution, an error due to absorption in the case of the acid will be incurred though this error is very small and can be practically neglected, compared to the inaccuracy involved in the determination of the intensities of the Raman lines. But the absorption in the case of the 1300 line does not bring in any error at all in the calculation of the dissociation as what matters is the relative absorptions of the 1050 and the 1300 lines. It is found by a seperate experiment that the two lines are absorbed to the same extent. The intensities of the 1050 and 1300 lines are determined and the corresponding values of α for different temperatures are calculated and given in table I.



Nitric Acid

TABLE I

Percentage degree of dissociation α at various temperatures and concentrations.

Temperature / Concentration in N.	30°C	60°C	90°C
14,50N	11.4	9.5	3.2
12.58N	21.2	15.5	10.5
10.5N	35.2	30.0	22.6

The dissociation of the acid of concentration 12.58N at 5°C is found to be 29.6%.

DISCUSSION

It is clearly seen from the table that the dissociation of the acid decreases with temperature, probably due to the decrease of dielectric constant of water with temperature. This is clearly demonstrated in the microphotometric records of the spectra of the acid of different concentrations at different temperatures reproduced in Plate VII. As the temperature of the acid is increased the line at 1050 gradually decreases in intensity while that at 1300 correspondingly gets more intense.

But it is well known that the conductivity of the acid increases as its temperature is raised at all concentrations. This increase must be due to the large increase in the ionic mobility with temperature which more than compensates for the decrease in the conductivity due to the decrease in the dissociation of the acid.

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