THE DIELECTRIC CONSTANT OF FORMIC, ACETIC, AND PROPIONIC ACIDS, AND THE ELECTRIC MOMENT OF COMPLEX MOLECULES

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Abstract

The *temperature and pressure variation of the dielectric constant of formic and propionic acid vapors* has been studied experimentally. The behavior is similar to that previously found for acetic acid. For formic acid it is possible to calculate from Coolidge's vapor density measurements the amount of association into double molecules, and to explain the apparent departures from Debye's theory in terms of such association. It is then seen that the apparently linear pressure curves can be explained by the compensation of several factors in the measurements. By assuming that the optical part of the polarization is doubled on association and taking this value from refractivity measurements, values for the electric moment of the single and double molecules of formic acid are obtained, 1.51×10^{-18} and 0.99×10^{-18} c.g.s.e.s.u., respectively. Although no reliable vapor density measurements exist for acetic acid it is assumed that the anomaly in this case also is due to association rather than to the previously suggested effect of vibrational quantization. The previous data are re-interpreted accordingly. By using the optical refractivity as before a value is obtained from the high temperature measurements for the *electric moment of the single molecule* of acetic acid, 1.73×10^{-18}; and similarly for propionic acid, 1.74×10^{-18} c.g.s.e.s.u. *The electric moment of complex molecules* is then discussed with reference to directed valence and to internal free rotation around single bonds. The possibility of the importance of interaction between external rotation and internal free rotation is suggested. The question of the interpretation of measured electric moments is raised for the case where free rotation causes a time variation of electric moment. In this connection the experimental values of electric moment are discussed. The values of the electric moment of these acids indicate that the OH group is tightly bound as supposed by Eucken and Meyer. A structure for the double molecule of formic acid is suggested, with the four oxygen molecules at the corners of a rectangle, the planes of the two constituent single molecules at an angle of about 120°, and the OH groups bound tightly in positions of minimum potential energy. This structure does not seem to be inconsistent with the observed electric moment.

IN A previous communication[1] measurements of the dielectric constant of acetic acid vapor were published. These measurements indicated that there is a change of the electric moment of the acetic acid molecule with temperature, and it was suggested as a possible explanation that the effect is due to a transition in vibrational quantum state of the OH group. The possibility that the apparent change in electric moment could be due to association was considered excluded by the fact that the variation of dielectric constant with pressure was linear within the limits of experimental error. The presence of association could not be further tested since there exist no

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[1] C. T. Zahn, Phys. Rev. **35**, 1047 (1930).

reliable measurements of the vapor density of acetic acid. It was decided to make a further study of this effect by making measurements of the dielectric constant of formic acid and propionic acid vapors. In the case of formic acid excellent vapor density measurements have been made recently by Coolidge,[2] who has shown that his measurements can be explained by the existence of double molecules and has given satisfactory equations for the calculation of the degree of association. A study of these data shows that there is a considerable amount of association in the region of temperature and pressure available for convenient dielectric constant measurements. This suggests that the anomaly in the previous acetic acid measurements might be due to association in spite of the apparently linear pressure curves. For example, this might be possible if the shape of the vapor density curve were such as to effect the linearity of the pressure curve only very slightly throughout the measured range of pressure, and particularly if the molecular polarizations of the single and the double molecules were not greatly different.

FORMIC ACID

The present data on formic acid show the same general characteristics as those on acetic acid. The pressure curves are apparently linear and the electric moment apparently decreases with the temperature. This being a partial confirmation of the above suggestion of association, an attempt was made to explain the anomaly in formic acid quantitatively in terms of association and to calculate the electric moment of the single and double molecules. The percentage of associated molecules was calculated from Coolidge's equations for the points of maximum pressure on the curves and at the four different temperatures included by the data. At the highest temperature there was found 9 percent association and at the lowest temperature 58 percent. A

TABLE I. *Formic acid data.*

$T°K$	p cm Hg	$3(\epsilon-1)/(\epsilon+2)v$	$3(\epsilon-1)/(\epsilon+2)vT$	P
344.63	18.62	5547	1.912	41.43
386.91	28.32	5542	2.144	41.40
403.10	28.27	5536	2.231	41.34
423.43	28.36	5525	2.338	41.26

rough calculation from the data of Table I shows that if the effect is due to association the associated molecule cannot have zero electric moment as it would have in case the two associating moments were antiparallel. This also is in confirmation of the above suppositions.

In Table I the data were calculated from the readings at the highest pressures only. An example of a pressure curve is shown in Fig. 1. For economy in space the individual pressure data were not included in the table. In column 3 of Table I the value of the specific volume was calculated from the ideal gas equation and refers therefore to the normal ideal value. Therefore the values in column 3 represent the apparent polarization referred to a normal ideal

[2] A. S. Coolidge, Jour. Amer. Chem. Soc. **50**, 2166 (1928).

number of gas molecules. The values in column 5 represent the molecular polarization, or the polarization referred to a mol of the molecules. The values in column 4 plotted against the absolute temperature would give a Debye line if the molecules were of one kind only. The absolute values of ϵ used here are the values corrected as described later for the extrapolation to zero pressure under the assumption of association.

In order to determine the molecular polarization of the single and double molecules individually, it was assumed that the constant, or so-called optical, part of the polarization is doubled on association. This is probably justified by the well-known principle of the additivity of refractivity, particularly since the energy of association is not great. In any case the optical part is the smaller part of the electric polarization under the available experimental con-
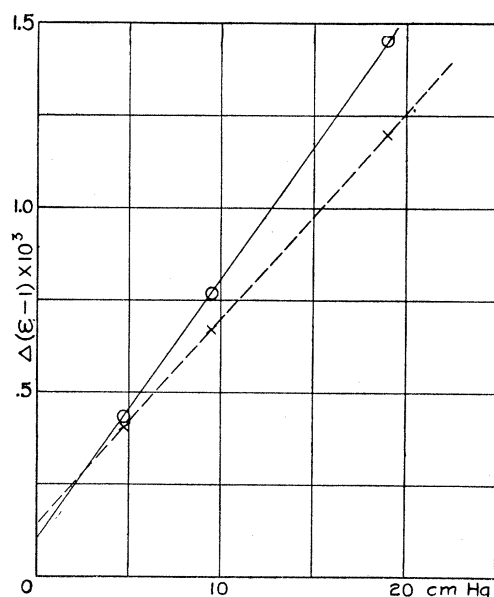

Fig. 1. Pressure Curve.

ditions. The two molecular polarizations are set respectively equal to $A + B_1/T$ and $2A + B_2/T$ according to the Debye theory. Hence the measured molecular polarization is

$$P = n_1(A + B_1/T) + n_2(2A + B_2/T)$$

where n_1 and n_2 are the respective mol fractions. B_1 and B_2 are proportional to the squares of the two electric moments. An approximate idea of the magnitude of the effect of association can be obtained by assuming that the association is negligible at the highest temperature, and then calculating $2A + B_2/T$ from the data at the lowest temperature and maximum pressure. If the pressure curves are then corrected so as to correspond to the single molecule alone, it is found that these curves are still apparently linear. This

can be seen in Fig. 1, where the uncorrected points are shown by crosses and the corrected points by circles.

It can therefore be stated that so far as the linearity of the pressure curves is concerned the assumption of association is justified. It remains only to see whether the constants can be chosen so as to fit all the data satisfactorily. The more accurate calculations are slightly complicated by the fact that it is never possible in a pressure curve to measure accurately the vacuum value of the experimental condenser capacity. This is true because inequalities in the temperature of the condenser plates arise on evacuation.[3] It is therefore necessary to extrapolate to zero pressure in order to obtain absolute values of the dielectric constant. Fig. 1 shows that the extrapolated value differs slightly for the corrected and the uncorrected curves. (This shows that the greatest departure from linearity exists at the very low pressures and partially explains why it was not originally detected.) These curves were first corrected roughly as above stated in order to locate the zero, and then new absolute values of the dielectric constant and molecular polarization were determined.

Because of the complicated nature of the calculations and the smallness of the association effect, no attempt was made to determine A, but it was taken from the molecular refractivity of formic acid in the liquid state as given in Landolt Börnstein, 8.53. This value is probably a little too small because of infrared terms in the refractivity, and the resulting calculations are subject therefore to a small error. Appropriate values of B_1 and B_2 were obtained by choosing the value of B_1 which gives on subsequent calculation the most nearly constant value for the ratio B_1/B_2. The value chosen for B_1 is 14160. Table II shows the corresponding values of B_1/B_2 with a weighted

TABLE II. *Formic acid: calculation of molecular constants.*

$B_1 = 14160$ $\qquad\qquad A = 8.53$

$\mu_1 = 1.51 \times 10^{-18}; \ \mu_2 = 0.99 \times 10^{-18}$

$T°K$	cm Hg	Mol fraction association	P	B_1/B_2
344.63	18.62	0.580	41.43	0.45
386.91	28.32	0.275	41.40	0.40
403.10	28.27	0.171	41.34	0.37
423.43	28.36	0.092	41.26	0.50
				0.43 mean

mean of 0.43. From these values it can be seen that while the reduction in the electric moment is considerable the doubling of the optical term masks a considerable portion of the effect. Further, in order to show how nearly the data for the four different temperatures and maximum pressures are consistent with these constants A, B_1, and B_2, the values of the electric polarization were calculated and compared with the experimental values. This is shown in Fig. 2. The upper straight line is the Debye line for single molecules, and the lower line, for double molecules. The product of the polarization and the absolute temperature is plotted against the absolute temperature. For con-

[3] C. T. Zahn, Phys. Rev. **35**, 848 (1930).

venience the values of the polarization here refer not to a mol but to the ideal number of molecules per cc under normal conditions of a gas. The crosses represent the experimental values and the circles the calculated values for the maximum pressures. The deviations are seen to be of the order of one percent. This agreement is almost better than one could expect in view of the nature of the calculations and the possibility of small errors due to absorption on the condenser plates.

Finally it seems that the anomaly for formic acid can be satisfactorily explained by association and the values of the electric moment for the single
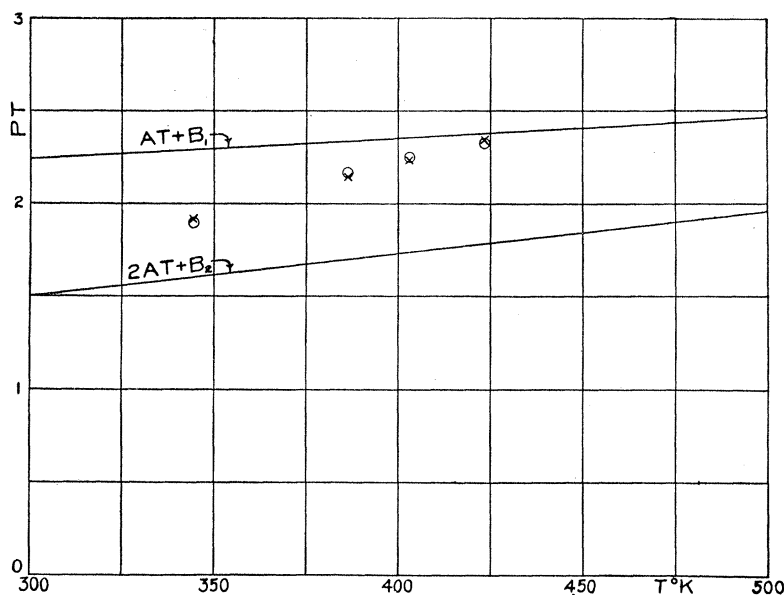

Fig. 2. Debye Lines.

and double molecules can be calculated. The above values of B_1 and B_2 correspond to electric moments of 1.51 and 0.99×10^{-18} c.g.s.e.s.u., respectively.

In order to obtain a good specimen of formic acid for these tests Kahlbaum formic acid was distilled at $0°C$ as described by Coolidge in the paper cited above.

ACETIC AND PROPIONIC ACIDS

In view of the above results of the calculations for *formic* acid it seems more than probable that the previous data on *acetic* acid should also be interpreted in terms of association rather than the previously suggested temperature variation of electric moment. The same can be said for the data here presented on propionic acid, which shows a similar but somewhat smaller effect. The fact that the effect is smaller in propionic acid may be due to a greater masking of the moment reduction by the doubling of the optical term on association; or it may also be due to a smaller amount of association.

For these two acids the calculations cannot be carried out as in the case of formic acid since their vapor densities are unknown at present. Still if it is assumed that the effect is due to association the data can be used to obtain a fairly accurate value of the electric moment of the single molecules.

In Table III are shown the previously published data on acetic acid and also the present data on propionic acid together with calculated values of the apparent electric moment, μ. The values of apparent molecular polarization

TABLE III.

Acetic acid $A = 12.9$ $\mu = 1.73 \times 10^{-18}$				Propionic acid $A = 17.4$ $\mu = 1.74 \times 10^{-18}$		
$T°K$	P	μ		$T°K$	P	μ
297.51	55.0	1.42		356.12	61.4	1.59
320.85	50.7	1.40		373.42	59.7	1.60
341.13	50.8	1.45		374.41	59.8	1.61
357.78	51.2	1.49		389.86	59.8	1.63
360.37	51.6	1.50		404.64	59.1	1.65
389.64	53.7	1.60		418.44	59.4	1.69
410.84	53.5	1.64		429.57	60.3	1.73
450.09	53.3	1.72		455.37	58.4	1.74
471.42	52.3	1.73		485.81	56.0	1.74
491.44	50.2	1.72				
493.86	50.3	1.73				

are calculated from the uncorrected pressure curves and are subject to small errors due to incorrect extrapolation to zero pressure. At the higher temperatures this error is negligible since the association effect is very small. Values for A are taken as before from refractivity data. The values of μ should approach a constant value as the temperature is increased since the association then becomes negligible. From Table III it is seen that in both cases μ becomes practically constant above 440°K. The asymptotic values may be taken as 1.73 for acetic acid and 1.74×10^{-18} c.g.s.e.s.u. for propionic acid. Because of the danger of decomposition the highest safe temperature for formic acid was about 425°K and there was still 9 percent association. Fig. 2 shows, however, that the association should become negligible at approximately the same temperature as for the other two acids, at 440°K.

In the previous article[1] on acetic acid it was stated that there was evidence at high pressures indicating association in which the polarization is increased. This effect was noticed at pressure beyond the apparently linear portions of the pressure curves near to saturation, and is probably now to be considered as due to surface adsorption on the condenser plates.

The purified propionic acid was obtained by fractional distillation of a specimen from the Eastman Kodak Company.

ELECTRIC MOMENT OF COMPLEX MOLECULES

In recent years a number of authors, chiefly Eucken and Meyer, and Wolf,[4] have made attempts to calculate the electric moment of molecules,

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[4] H. Sack, Ergebnisse der Exakten Naturwissenschaften, Band VIII, 337 (1930).

assuming that the total electric moment can be obtained by adding vectorially electric moments characteristic of each chemical bond and directed approximately along the valence directions given by the tetrahedral theory. These calculations have in some cases been complicated by the fact that whenever there is a single bond between two atoms there is a possibility of free rotation of two atomic groups relative to one another. In such cases the molecules cannot be regarded as rigid in the sense that the average relative positions of the nuclei are practically fixed. In fact, atomic groups having their own characteristic vector electric moments can rotate relatively to one another and cause a time variation of the electric moment. (Hojendahl first used this idea to explain difficulties which had arisen from the fact that certain molecules of the type CR_4 have an electric moment different from zero.) In these complicated molecules the question arises as to how one should regard such molecules in interpreting the apparent measured values of electric moment. Various attempts have been made in this direction. First attempts were made by assuming that the electrostatic interaction between the two rotating groups is negligible and that the rotation is therefore truly free. In this case it was assumed that the measured value of the square of the electric moment was the average square of the moment taken over a random distribution of the angle of free rotation. For example, two electric moments, μ, perpendicular to the axis of free rotation would give rise to an apparent or resultant moment $2^{1/2}\mu$.

Hojendahl has also pointed out that these internal rotations are never truly free but are hindered to some extent by electrostatic interaction; e.g., dipole interaction. In many cases this interaction may be considerable. Meyer[5] has made an extension of Debye's *classical* theory of the dipole polarization for certain non-rigid molecules, assuming dipole interaction. These calculations indicate an appreciable temperature variation of apparent electric moment when the innermolecular potential exceeds $(1/10)kT$; and that if the rotation is truly free the apparent moment is as if μ^2 were averaged over a random motion of the internal rotation as mentioned above. Certain objections may be raised to these conclusions. If the internal rotational energy were not too great the actual motions of the rotating parts would certainly be affected appreciably by centrifugal action due to the external rotations of the molecules as a whole and these rotating parts might be deformed by electrostatic interaction in varying degrees depending on the kinetic energies of the various parts of the molecule. Then the individual rotating parts of the molecule could not be considered as rigid and Meyer's calculations might be invalid. An idea of the importance of dipole deformation can be gotten from the electric moments of the substitution products of methane.

On the quantum theory it is found that deviations from the classical dipole theory are appreciable only at very low temperatures. Van Vleck has derived the classical formula of Debye to a close approximation from general quantum-mechanical considerations having to do chiefly with the relative values of possible energy transitions in the molecules and spectroscopic

[5] L. Meyer, Zeits. f. Phys. Chem. (B) **8**, 27 (1930).

principles. It is assumed that the energy levels of the molecule are such that $h\nu$ is never of the order of kT, but is either much larger or much smaller than kT. Then the dipole term in μ^2/T arises from possible transitions for which $h\nu \ll kT$; and the optical term from transitions for which $h\nu \gg kT$. There arises in the calculations a quantity μ^2 which is interpreted as being associated with the fixed electric moment of the molecule. The theory is developed for the case of rigid molecules and has not been explicitly stated so as to include the possibility of internal free rotation. It seems probable that in this latter case there will arise a quantity which is to be interpreted as an average μ^2 but just how this should be averaged would require further consideration of the theory. Whether this μ^2 appreciably depends on temperature or not will probably depend on the magnitude of the interaction between the rotating parts, and possibly not in the same way as it would on the classical theory.

Strictly speaking Van Vleck's theory applies to the cases where all the transitions in energy can be separated into the above two cases relative to kT. When $h\nu$ is of the order of kT difficulties may arise. Actually this condition may exist for some of the ordinary vibration states, but Van Vleck states that, under his assumptions of invariant fixed moment, these states, which correspond to linear oscillators would cause no temperature variation in the electric polarization. Now in complex molecules there may be certain other types of motion for which $h\nu$ is of the order of kT and a temperature variation does result. In this connection it is interesting to consider the internal rotation of the OH group in organic molecules. Since this group has a large electric moment there exists the possibility of strong electrostatic interaction, for example, with the $C=O$ bond in the COOH group. The quantized motions of the OH group might be similar to those for the physical pendulum as described by Condon.[6] The lower states correspond to vibration and the higher states to non uniform rotation. The motions of the OH group might be considerable and the corresponding changes in electric moment quite large. Then the assumption of fixed electric moment would be invalid and some kind of average should be taken. This average might depend upon temperature, as was originally suggested to explain the data on acetic acid vapor.[7]

With regard to the interpretation of experimental values of μ three possibilities suggest themselves for the internal rotation here discussed. (1) If the interaction energy were sufficiently small the rotation could be regarded as truly free. Then the corresponding energy levels would be closely spaced and according to Meyer's classical derivation one would expect the apparent μ^2 to be an average over random internal rotational angle. (2) If the interaction energy were large, the lower states might correspond to oscillations of the rotator and have large energy separations. At ordinary temperatures practically all the molecules would be in the lowest state and this

[6] E. U. Condon, Phys. Rev. **31**, 891 (1928).

[7] It seems now that such a temperature variation is not necessary to explain the data on acetic acid; still the effect may exist to an appreciable extent but be undetectable as a departure from the linearity of a Debye line, for example if the deviations were approximately linear in temperature in the experimental interval.

oscillation would not contribute to the temperature variation of electric polarization, but would contribute a small amount to the atomic, or infrared, part of the constant polarization. In this ground state the corresponding motions of the oscillator would be fast compared to the external rotations and the apparent fixed electric moment μ should probably be regarded as a *vector* average over the oscillation as for the electronic motions, rather than a root mean square value as for the case of slow internal rotation. (3) The previous two cases are the extreme cases of Van Vleck's theory, for which the Debye equation holds. In the intermediate case where the energy separations are of the order of kT the temperature variation in electric polarization would be very complicated. This variation would now be due not only to the distribution of states of external rotation but also to the distribution in the states of internal rotation. Further because of the combined centrifugal and electrostatic interaction the perturbations of the individual states would no longer be like those of a simple dipole rotator. As regards the interpretation of experimental data, if such an effect exists in any actual molecules, it might be regarded as an apparent variation of electric moment with temperature. Such a variation with temperature will not necessarily be detectable as a deviation from the Debye equation $P = A + B/T$; for it is easily seen that a variation in apparent B which is linear with temperature is equivalent to a different but constant B together with a change in the constant A. If the effect is relatively small it may easily be such that the apparent B is approximately linear in the experimental interval. Then the experimental data would lead to a spurious value of the optical part A. For example, this possibility may be of interest in connection with Sänger's[8] abnormal value of A for ethylene chloride. Meyer[9] seems to think that a temperature variation in μ really exists in spite of the linearity of the Debye line.

There exists another serious difficulty in any quantitative treatment of free rotation in that the electrostatic interaction cannot be expressed accurately. Attempts have been made to consider this interaction as due to dipoles concentrated and located in various ways, but such models cannot give anything more than the roughest approximation to the facts, since the atoms are separated by distances comparable to atomic radii. The difficulties seem at present unsurmountable, whether one regards the interaction as a dipole effect, or as due to residual valence and van der Waals' forces as in London's theory.

Tetrahedral symmetry: The assumption of tetrahedral symmetry cannot be accurately true as is seen, for example, from the values of the electric moment of the chlorine substitution produces of methane. The discrepancies are usually explained by saying that the valence directions tend toward tetrahedral symmetry in the absence of dipole interaction and that this interaction produces a bending of the valence directions. This seems to be consistent with experimental data. A recent article by Slater[10] is especially interesting in this

[8] R. Sänger, Phys. Zeits. **32**, 21 (1931).

[9] L. Meyer, Phys. Zeits. **32**, 260 (1931).

[10] J. C. Slater, Phys. Rev. **37**, 481 (1931).

connection. On the basis of the quantum theory it is suggested that in the carbon atom the valence directions tend toward tetrahedral symmetry, while in the nitrogen and oxygen atoms they tend to be mutually perpendicular. The case of oxygen is of special interest here since it has been assumed by Eucken and Meyer that the undistorted valence angle for oxygen is the tetrahedral angle of about 110°. This is of importance in the original determination of the characteristic electric moments of the various chemical bonds.

STRUCTURE OF THE CARBOXYL GROUP

From the previous calculations it is seen that the electric moments of acetic and propionic acids are of practically the same value, 1.73 and 1.74 $\times 10^{-18}$, but that of formic acid is smaller, 1.51×10^{-18}. It would be of interest to know whether this difference arises chiefly in the carboxyl group or in the alkyl group. If it arises in the alkyl group one could regard it as due to simple dipole induction which increases with the length of the carbon chain. Such an effect is well known in the series methyl, ethyl, propyl, to butyl chloride, where the moment increases by about 0.2×10^{-18}. This would indicate that the moment of the alkyl group changes from 0.4 to 0.6×10^{-18} by induction. Since the observed change in moment from formic to acetic acid is 0.22×10^{-18} it seems probable that this is also due to induction; particularly in view of the fact that the moment of COOH is not greatly different from that of C-Cl. The only observed difference in the two cases is that the transition is more abrupt in the fatty acid series.

It is, of course, possible that the transition may be at least in part due to a motion of the OH group of the type discussed under the above case (3) of relatively small interaction energy; but the values of the electric moment seem to indicate that the OH group is bound relatively tightly, either oscillating or rotating nonuniformly as in case (2). This is suggested by Meyer's calculated limiting values of the moment of the COOH group for the extreme positions of the OH group allowed by free rotation, 3.5 and 1.1×10^{-18}, corresponding to maximum and minimum potential energy, respectively. Because of the uncertainty in the calculations of electric moment, particularly in the valence directions, one cannot be certain whether these values indicate that the OH group has a considerable oscillation or not. The experimental values may be consistent with a very tightly bound OH group and a simultaneous bending of the valence directions, for example. We can, however, say with some degree of certainty that the motion of the OH group is not free since the expected moment would be much larger than the observed moment, about 3×10^{-18}. This is in agreement with the chemical evidence responsible for the supposition of the existence of a chelate ring in the carboxyl group.

THE DOUBLE MOLECULE OF FORMIC ACID

As regards the structure of the double molecule of formic acid, of moment 0.99×10^{-18}, this value of the electric moment excludes the possibility of the antiparallel type of association. Taking into consideration the relative sizes of the C and O atoms and assuming tetrahedral symmetry for the carbon

atoms, it is almost possible geometricaly to fit the molecules together in such a way that the four O atoms lie at the corners of a square and the C atoms on a line perpendicular to the square. The planes of the two associating HCOOH molecules would then be mutually perpendicular. If this is the approximate structure of the double molecule, the OH group of one of the original molecules of HCOOH would tend to be directed toward the doubly bound O atom of the other molecule and would be attracted toward it, distorting the square into the form of a rectangle. The OH group would then be quite near to the $C = O$ group and the interaction woud probably bind the OH group relatively tightly in the ground state. It is, of course, impossible to make an accurate calculation of the electric moment of the double molecule, but a rough estimate after the manner of Eucken and Meyer is perhaps of some interest. The sizes of the atoms permit of a distortion of the square by interaction such that the planes of the two HCOOH atoms subtend an angle a little less than 120°. In the position of minimum potential energy the OH groups would lie approximately in the plane of the oxygen rectangle and at an angle of 60° relative to one another. Using the values of Eucken and Meyer for the characteristic moments one obtains a value of about 1.1×10^{-18} for the electric moment of the double molecule. Finally, one can say that the experimental value 0.99×10^{-18} does not seem to be inconsistent with the proposed type of structure so far as this rough estimate is concerned.

At present it is not possible to calculate the electric moment of the double molecule of acetic or propionic acid. These values would be particularly interesting in connection with the interpretation of the transition in electric moment from formic to acetic acid.