# 435. *The Rotatory Power of* D-(+)-*Tartaric Acid* * *and the Tartrates.*

By M. K. Hargreaves and P. J. Richardson.

The relation of the rotatory power of tartaric acid to its structure is discussed. Further measurements of the rotatory dispersion of D-tartaric acid * and its salts are reported. An attempt is made to use these results to combine the available data into a comprehensive picture.

*The Solid State.*—Peerdeman, van Bommel, and Bijvoet [1] showed, by an *X*-ray diffraction technique, that the conventional Fischer projection represents, fortuitously, the absolute configuration of (+)-tartaric acid. The correctness of the absolute configuration is assumed in the discussion that follows; the term " conformational isomers " refers to " rotational " isomers of the same configuration.

The relation between the rotatory power of tartaric acid in the crystalline and in the super-cooled state has recently been discussed by Levy.[2] This is of interest for the light which it might throw on the persistence of partial crystalline character in solution and the phenomena associated with " seeding " by crystals. Astbury [3] suggested that the rotatory power of tartaric acid under different conditions could be explained in terms of the persistence in solution of a spiral arrangement which he found in the crystal structure. More recent determinations by Beevers and Stern [4] do not confirm the detailed Astbury

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* *I.e.*, Fischer's *d* acid.

[1] Peerdeman, van Bommel, and Bijvoet, *Proc. k. ned. Akad. Wetenschap.*, 1951, **54**, *B*, 16.

[2] Levy, *Compt. rend.*, 1949, **229**, 419.

[3] Astbury, *Proc. Roy. Soc.*, 1923, *A*, **102**, 506.

[4] Beevers and Stern, *Nature*, 1948, **162**, 854; *Acta Cryst.*, 1950, **3**, 341.

structure though their unit cell is similar. They found the space group to be $P2_1$. This implies the lack both of a centre and of planes of symmetry and the presence of a screw-diad axis. Levy [5] has argued from this that the crystal structure itself will not give rise to optical activity, and that the high rotatory power of crystalline tartaric acid is due to alignment of the individual optically active acid molecules. This argument is based on the assumption that there is no sense of screw in a screw-diad axis. This is strictly correct. But when the axis operates upon certain arrangements of points or atoms a sense of screw is produced. Fig. 1 shows that with three or more different elementary points, *e.g.*, atoms, in a unit cell the presence of a screw-diad axis gives a sense of screw provided that these points do not all lie in a plane perpendicular to the screw axis and that at least two of them do not lie on a line parallel to the screw axis. When more points of the same kind are added the symmetry conditions are altered.

Fig. 1.

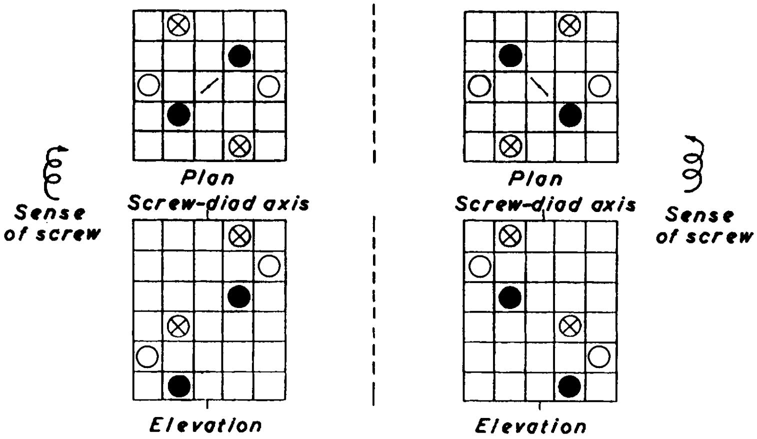

Fig. 2.

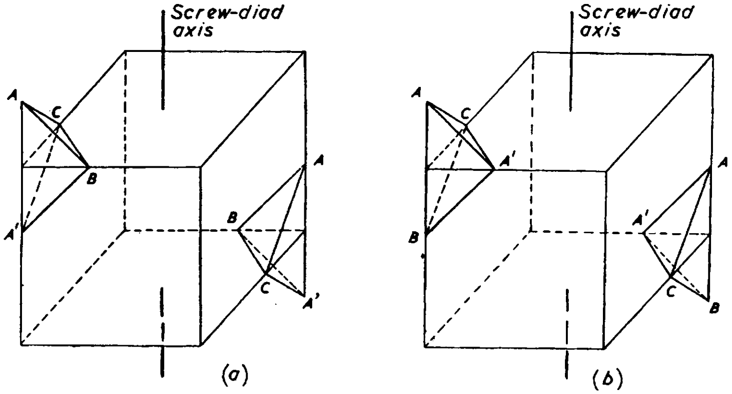

Fig. 2 shows the operation of a screw-diad axis on a tetrahedron in which two of the apices are the same ($A = A'$). In the first case, (*a*), there is no optical activity in the resultant structure since the two equivalent apices lie on a line parallel to the screw axis, giving rise to a plane of symmetry in the crystal. In the second case, (*b*), the structure should be optically active; Beevers and Stern's results show that the crystal of tartaric acid corresponds to this case. If $A$ is not identical with $A'$, the overall symmetry of the

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[5] Levy, *J. Phys. Radium*, 1950, **2**, 80.

crystal of this type is not altered, so that arguments that apply to the case $A = A'$ should also apply when $A \neq A'$. Levy assumed, on the basis of the crystal structure, that the crystal of tartaric acid had no rotatory power due to the crystal framework itself; since it has been shown above that this is most unlikely, Levy's arguments would appear to be based on a misconception. A Referee has kindly pointed out that Levy's argument is disproved by the existence [6] of optically active $MgSO_4,7H_2O$ ($\alpha_{579}$ 1·98°; $\alpha_D \approx 1{\cdot}8°$, per mm. orthorhombic, $D_2$), whose structure has only diad or screw-diad axes, and lithium sulphate monohydrate [7] ($\alpha_D$ 1·8° per mm., $P2_1$) which has the same space group as tartaric acid. We shall therefore not consider this theory further in this paper. Some of the criticisms of Astbury's hypothesis made by Lowry [8] and by Austin [9] are no longer valid in the light of modern theory. An adaptation of his hypothesis might therefore possibly explain the variation of the rotatory power of tartaric acid under different conditions. If the hypothesis is correct it should be possible to apply the equilibrium method to the variation of the rotatory power of tartaric acid with temperature and to obtain values for the energy difference between the crystalline form and that which is most prevalent in dilute solutions or at high temperatures.

Application of this method to Bruhat's results [10] for the super-cooled acid gives reasonable agreement in the values of $\Delta H$ and $\Delta S$ for the different wavelengths (Table 1; the method of calculation is that described earlier [11]). This is in agreement either with Levy's orientational hypothesis or with one which ascribes rotatory power to the crystal structure, provided that the absorption bands associated with the optical activity of the crystal are similar to those of the low-temperature form of the supercooled acid. The

TABLE 1. *Calculation of thermodynamic quantities from the variation of the rotatory power of super-cooled tartaric acid with temperature.**

Temp. (°K) : $T_1$ = 288·16°, $T_2$ = 317·16°, $T_3$ = 340·76°, $T_4$ = 383·03°.
$T_1'$ = 288·16°, $T_2'$ = 317·76°, $T_3'$ = 332·92°, $T_4'$ = 373·16°.

| λ (Å) | $\alpha_1$, $\alpha_1'$ | $\alpha_2$, $\alpha_2'$ | $\alpha_3$, $\alpha_3'$ | $\alpha_4$, $\alpha_4'$ | $a$ | $b$ | $\Delta H$ (kcal./mole) | $\Delta S$ (E.U./mole) |
|---|---|---|---|---|---|---|---|---|
| 5840 | 0·71° | 5·27° | 8·22° | 11·65° | 21·83 | −32·88 | 2282 | 8·8 |
| | 0·71 | 5·27 | 7·30 | 10·90 | | | | |
| 5840 | 0·71 | 5·24 | 8·22 | 11·65 | 20·56 | −24·17 | 2620 | 9·6 |
| | 0·71 | 5·24 | 7·25 | 10·90 | | | | |
| 5450 | −0·27 | 5·06 | 8·47 | 12·75 | 27·29 | −38·65 | 2115 | 8·0 |
| | −0·27 | 5·06 | 7·40 | 11·90 | | | | |
| 5450 | −0·30 | 5·17 | 8·55 | 12·75 | 24·12 | −31·96 | 2538 | 9·3 |
| | −0·30 | 5·17 | 7·50 | 11·90 | | | | |
| 4680 | −5·05 | 2·95 | 8·07 | 14·50 | 37·16 | −66·50 | 1955 | 7·6 |
| | −5·05 | 2·95 | 6·40 | 13·08 | | | | |
| 4680 | −5·05 | 2·95 | 8·07 | 14·50 | 28·43 | −32·95 | 3228 | 10·9 |
| | −5·05 | 2·95 | 6·30 | 13·08 | | | | |
| 4680 | −5·70 | 2·95 | 8·07 | 14·50 | 32·18 | −65·84 | 2419 | 9·3 |
| | −5·70 | 2·95 | 6·30 | 13·08 | | | | |
| 4470 | −7·00 | 1·20 | 6·45 | 14·35 | 61·96 | −65·60 | 2687 | 8·4 |
| | —7·00 | 1·20 | 4·80 | 12·80 | | Mean | 2480 | 9·0 |

* The 6650 Å line yielded $\Delta H$ and $\Delta S$ as 3700 kcal./mole and 15·9 E.U./mole respectively. The results for this line are the least accurate since the values of $\alpha$ used above were interpolated from Bruhat's results by plotting $\alpha/\lambda$ and $\alpha/T$. Thus the extreme points in the dispersion curve and the extreme temperatures will give less accurate results.

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[6] Longchambon, *Compt. rend.*, 1921, **173**, 89; Barker, "Index of Crystals," Vol. I (2), Heffer, Cambridge, 1951, O. 486.

[7] Johnsen, *Zentralblatt Mineralogie*, 1915, 233—243. Ziegler, *Z. Krist.*, 1934, **89**, 456.

[8] Lowry, "Optical Rotatory Power," Longmans, Green & Co., London, 1935, p. 292.

[9] Austin, *Trans. Faraday Soc.*, 1930, **26**, 413.

[10] Bruhat, *ibid.*, 1914, **10**, 89.

[11] Hargreaves, *J.*, 1957, 1071.

mean of the values obtained for the constant $b$ for each wavelength follows approximately the same dispersion curve as that given by Longchambon [12] for the crystalline acid (see Table 2).

Though the rotatory constants, $a$ and $b$, obtained by this method are liable to wide variation as a result of minor errors in the dispersion curve,[11] the order of magnitude obtained in this case is uniform and so probably correct. Table 1 shows that the " lower-temperature form " has a rotatory power, $b$, some twenty time smaller than that of the crystalline acid, and that the dispersion is similar to that of the crystalline acid. It appears, therefore, that there are at least two forms or conformations of the acid other than that of the crystal; this is in agreement with the views first expounded by Arndtsen.[13] It is notewothy that the values of $\Delta H$ lie close to those obtained by Kauzmann, Walter, and Eyring [14] for the esters of tartaric acid. Probably, therefore, at least so far as ordinary temperatures are concerned, Astbury's hypothesis must be rejected. Thus in the discussion below the crystalline form has been neglected since, as it has little influence on the super-cooled acid, it may be expected to have even less on its solutions. The results are interpreted in terms of two forms or conformations associated with high and low temperatures respectively. A similar interpretation will apply to a larger number of forms provided that they fall into two groups in terms of energy.

TABLE 2.

| Wavelength (Å) | 5840 | 5450 | 4680 | 4470 |
|---|---|---|---|---|
| $[M]$ of cryst. acid * | 934° | 1120° | 1735° | 1930° |
| $b$ (molar) ($=1{\cdot}5b$) (mean) | 42·8 | 53·0 | 74·8 | 98·4 |
| Ratio, $[M]/b$ (molar) | 21·8 | 21·6 | 21·1 | 19·6 |

* Interpolated from Longchambon's results.[12]

*Rotatory Power of Solutions of Tartaric Acid.*—In considering the factors which may influence the rotatory power of tartaric acid first place must be given to its dissociation. Britton and Jackson [15] studied the effect of dilution and consequent ionisation on the rotatory power of solutions of tartaric acid, obtaining $[M]_D^{25} = 20{\cdot}0°$, $45{\cdot}0°$, and $60°$ for the acid, the hydrogen tartrate, and the tartrate ion respectively. They also studied the effect of adding sodium chloride to sodium tartrate solutions. They considered that the reduction in the rotatory power which they observed was due to the hydration of the sodium or chloride ions resulting in a reduction of the " free " water available for the dissolution of the tartrate. In this way the rotatory power should approximate to that observed in more concentrated solutions. Quantitatively this explanation is difficult to maintain since the change in rotatory power of 0·1M-sodium tartrate solution for a change in sodium chloride concentration from zero to 2·0M corresponds to a two-fold change in concentration [16] whilst primary solvation numbers [17] correspond to a change in concentration of 17%, and other values for the solvation numbers [18] do not alter the order of magnitude. An alternative explanation of this phenomenon is given below in the section on tartrates.

Lowry and Austin [16] have shown that the effect of increasing the concentration of a concentrated aqueous solution is to reduce the positive rotatory power in the visible region although at those concentrations the degree of ionisation is very small. Fig. 3 and Table 3 show that increase in temperature increases the positive rotatory power in the same region. Dissolution in alcohol or acetone reduces this rotatory power whilst the solutions in dioxan and ether yield negative rotations. Lowry and Austin showed that

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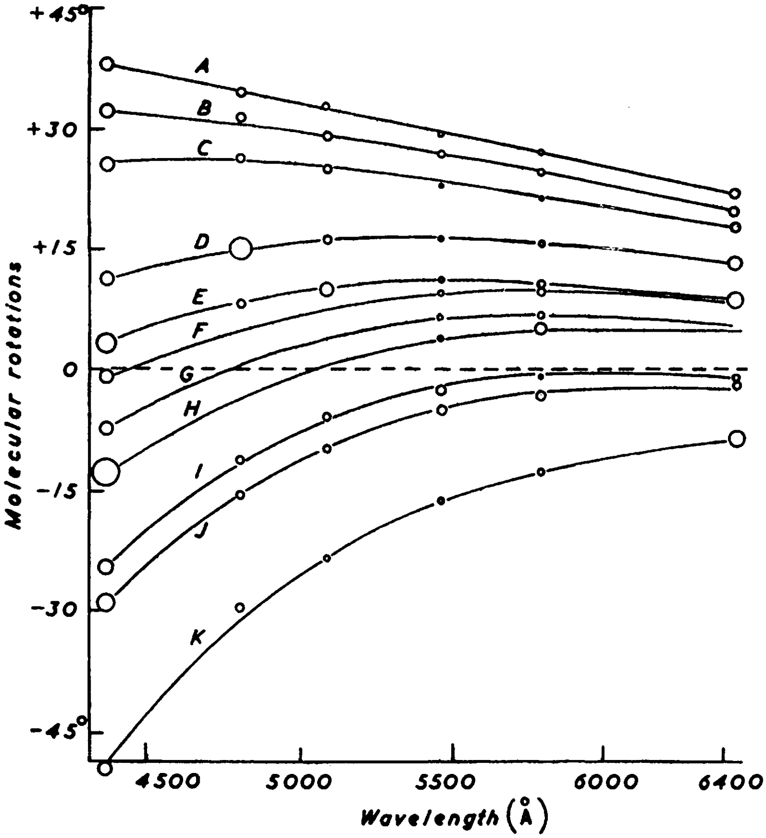
[12] Longchambon, *Compt. rend.*, 1924, **178**, 951.
[13] Arndtsen, *Ann. Chim. Phys.*, 1858, **54**, 403.
[14] Kauzmann, Walter, and Eyring, *Chem. Rev.*, 1940, **26**, 375.
[15] Britton and Jackson, *J.*, 1934, 998.
[16] Lowry and Austin, *Phil. Trans.*, 1922, **222**, *A*, 249.
[17] Bockris and Conway, " Modern Aspects of Electrochemistry," Butterworths, London, 1954, p. 62.
[18] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955, pp. 121, 320.

the positive rotation constant $B$ of the Drude equation, $[\alpha] = A/(\lambda^2 - \lambda_a^2) + B/(\lambda^2 - \lambda_b^2)$, is associated with absorption in the Schumann region and that the band nearest the visible is negative is sign. The rotation constants of the two-term Drude equation are given in Table 4. Since measurements in solution are unlikely to be accurate enough for a direct derivation of the Drude equation the values in Table 4 are obtained by using the absorption wavelengths selected by Lowry and Austin as the most likely. The Table shows that, although the observed rotatory powers vary widely with solvent, concentration, and temperature, there is a systematic and sensible variation in the rotation constants of much smaller magnitude.

FIG. 3.



*A*; 70·3°, water. *B*; 46·5°, water. *C*; 24·7°, water. *D*; 54·5°, alcohol. *E*; 37·0°, alcohol. *F*; 94·0°, dioxan. *G*; 24·0°, alcohol. *H*; 74·5°, dioxan. *I*; 57·5°, dioxan. *J*; 50·4°, dioxan. *K*; 24·0°, dioxan. The diameters of the circles represent the estimated experimental errors.

Table 4 shows that not only the rotatory power but also the dispersion varies with the solvent, implying that the proportions of the constituent species in solution also change. If the change in the rotatory dispersion is to be explained in terms of a small number of forms (or conformational isomers) of the acid, then intramolecular hydrogen bridges must play an important part in stabilising these conformations. For example, in dilute solution in ether or dioxan (Table 3) intermolecular bonding would give a random orientation which would not provide the basis for the observed variation of the rotatory power with temperature, since increase in temperature may be expected to result in greater freedom of rotation about all single bonds. The calculation, above, based on Bruhat's results,

TABLE 3. *Variation of the molecular rotatory power of tartaric acid solutions with temperature.*

| | | | Wavelength (Å) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Solvent | Temp. | *c* | 6438 | 5893 | 5780 | 5461 | 5086 | 4800 | 4358 |
| Water | 24·7° | 10·00 | +17·5° | — | +21·3° | +22·8° | +24·9° | +26·1° | +25·4° |
| | 46·5 | 10·00 | +19·5 | — | +24·6 | +26·9 | +28·6 | +31·0 | +32·0 |
| | 70·3 | 10·00 | +21·7 | — | +27·1 | +29·2 | +32·7 | +34·3 | +37·8 |
| Alcohol | 24·0 | 10·00 | — | — | + 6·6 | + 6·0 | — | — | − 7·2 |
| | 37·0 | 10·00 | + 8·8 | — | +10·6 | +11·0 | + 9·7 | + 8·1 | + 3·2 |
| | 54·5 | 10·00 | +13·3 | — | +15·8 | +16·2 | +15·9 | +15·0 | +11·2 |
| Dioxan | 24·0 | 10·00 | − 8·7 | — | −12·9 | −16·5 | −23·5 | −29·7 | −50·0 |
| | 50·4 | 10·00 | − 1·8 | — | − 3·3 | − 5·1 | −10·0 | −15·7 | −29·2 |
| | 57·0 | 10·00 | + 1·0 | — | − 0·9 | − 2·5 | − 6·2 | −11·4 | −24·6 |
| | 74·5 | 10·00 | — | — | + 5·1 | + 4·0 | — | — | −12·8 |
| | 94·0 | 10·00 | — | — | +10·8 | +10·3 | — | — | −0·7 |
| | 24·8 | 5·00 | −10·5 | −12·3° | −13·7 | −17·3 | −24·2 | −31·9 | −52·2 |
| | 24·8 | 2·50 | −10·5 | −13·7 | −14·5 | −17·8 | −24·8 | −33·7 | −54·4 |
| Acetone | 24·6 | 3·00 | + 4·3 | + 4·5 | + 4·3 | + 3·0 | + 2·2 | − 1·6 | −13·6 |
| Ether | 25·2 | 0·2 | — | — | −14 | −18 | — | — | −54 |
| Dimethylformamide | 25·3 | 10·00 | + 1·8 | + 0·8 | + 0·3 | − 1·1 | − 4·4 | − 8·4 | −20·4 |
| | 47·7 | 10·00 | + 4·8 | — | + 4·0 | + 3·2 | + 0·04 | − 2·7 | −12·0 |
| | 68·3 | 10·00 | + 7·4 | — | + 7·5 | + 7·2 | + 5·4 | + 2·8 | − 4·1 |

*Densities.* The expansion of the solutions necessitates a small correction for the higher temperatures, based on the ratio of the densities at that temperature and at 25°. Standard values for the pure solvent were used except for the following which were determined directly :

Soln. in dioxan (*c* 10), $d_4^{24\cdot0}$ 1·0680, $d_4^{50\cdot0}$ 1·0404, $d_4^{70\cdot0}$ 1·0197.
Soln. in $H\cdot CO\cdot NMe_2$ (*c* 10), $d_4^{20\cdot0}$ 0·9970, $d_4^{45\cdot0}$ 0·9738, $d_4^{69\cdot1}$ 0·9512.

TABLE 4. *Constants for a two-term Drude equation of tartaric acid.*

$\lambda_a^2 = 0{\cdot}030$, $\lambda_b^2 = 0{\cdot}074$.

The lettering refers to Tables 5 & 6. The values used were those for the 5461 and the 4358 Å line.

| Solvent | *c* | Temp. | *A* | −*B* | | *c* | Temp. | *A* | −*B* |
|---|---|---|---|---|---|---|---|---|---|
| Water | 10 | 24·7° | 19·51 | 11·20 | Acetone–water | G | 24·8° | 19·68 | 11·83 |
| | | 46·5 | 20·80 | 11·35 | | H | 24·8 | 18·88 | 12·06 |
| | | 70·3 | 19·49 | 9·71 | | I | 24·8 | 18·49 | 12·51 |
| | | | | | | J | 24·8 | 17·88 | 12·44 |
| Ethanol | 10 | 24·0 | 19·64 | 15·07 | | K | 25·2 | 18·50 | 13·67 |
| | | 37·0 | 19·93 | 13·35 | | | | | |
| | | 54·5 | 21·22 | 14·11 | Pyridine–water | C | 24·5 | 29·37 | 5·55 |
| | | | | | | D | 23·0 | 29·54 | 5·62 |
| Acetone | 3 | 24·6 | 20·26 | 16·26 | | E | 24·5 | 31·24 | 6·92 |
| | | | | | | F | 24·5 | 30·40 | 6·26 |
| Ether | 0·2 | 25·2 | 30·61 | 21·64 | | | | | |
| | | | | | Dioxan–water | A | 25·3 | 18·50 | 11·80 |
| Dioxan | 10 | 24·0 | 18·90 | 19·50 | | | 49·2 | 19·67 | 11·68 |
| | | 50·4 | 20·14 | 17·98 | | | 72·5 | 18·48 | 10·01 |
| | | 74·5 | 21·37 | 16·98 | | B | 25·3 | 18·27 | 12·50 |
| | | 94·0 | 21·50 | 15·67 | | | | | |
| | 5 | 24·8 | 19·70 | 20·39 | Aq. $CaCl_2$ | L | 25·3 | 8·43 | 10·90 |
| | 2·5 | 24·8 | 21·29 | 21·81 | | | 39·9 | 13·09 | 12·91 |
| | | | | | | M | 25·2 | 14·90 | 11·95 |
| Dimethyl-formamide | 10 | 25·3 | 19·06 | 16·19 | | | 42·8 | 15·34 | 10·97 |
| | | 47·7 | 18·97 | 15·14 | | | 54·6 | 15·54 | 10·45 |
| | | 68·3 | 18·86 | 14·15 | | | | | |

*Tartrates.*

| Salt | Solvent | *c* | Temp. | *A* | −*B* | Salt | Solvent | *c* | Temp. | *A* | −*B* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | Water | 3·2 | 25·3° | 28·40 | 11·80 | Na | Water | 10 | 25° | 25·04 | 5·66 |
| | | | 40·0 | 27·48 | 7·21 | | Aq. dioxan | P | 25 | 25·45 | 6·34 |
| | | | 56·5 | 27·57 | 7·20 | | | Q | 25 | 24·62 | 5·98 |
| | | | 73·3 | 28·27 | 7·67 | | | | | | |
| | Aq. LiCl | N | 25·3 | 6·67 | 10·26 | | | | | | |
| | | | 47·1 | 4·71 | 7·68 | | | | | | |
| | | | 75 | 6·65 | 7·83 | | | | | | |
| | | | 96·1 | 11·72 | 10·56 | | | | | | |

shows that the difference in the heat content of the proposed conformations is 2—3 kcal./mole, *i.e.*, less than that of one hydrogen bond (4—8 kcal.). In view of the number of possible inter- and intra-molecular hydrogen bonds this energy difference possibly corresponds rather to a difference in conformational potential energy than to a difference in the number of hydrogen bonds.

A clue as to how these bonds are distributed is given by the rotatory behaviour of the acid and its derivatives. The rotatory power of the acid varies widely with its concentration in water [16] (see also Table 3) as does that of ethyl tartrate,[19] whilst the rotatory powers of alkali tartrates, and of the acid in pyridine (Tables 5 and 6) vary much less with concentration [15] and very little with temperature. Further, the dispersion of the alkali tartrates is quite different from that of the acid, except when the latter is dissolved in a solvent such as pyridine, the rotational constant, in these cases, being markedly reduced for the shorter wavelengths (Table 4).

The similarity between the behaviour of the acid and that of the ester, and the agreement between the values of $\Delta H$ obtained for the acid (above) and the esters,[14] suggest that the factors determining their dispersion are similar, being both different from that of the salts. Thus if restriction of rotation resulting from intramolecular hydrogen bonding is the cause of the rotatory behaviour, this bonding appears to be present in the acid and the ester but not in the salt. The determining hydrogen bonding must therefore involve the hydrogen of the hydroxyl group and not necessarily that of the carboxyl group. Failure of the salts to show a similar effect may be due to hydration of the carboxylate ion. Examination of a model shows that two forms of intramolecular hydrogen bonding are possible in addition to any between $\alpha$-hydroxyl and the carboxyl groups (cf. Lowry and Austin [20]). Interaction between the $\alpha$-hydroxyl and the $\alpha'$-carboxyl group, and the $\alpha'$-hydroxyl and $\alpha$-carboxyl group, gives a double link with the molecule held in an extended conformation rather similar to that of the crystal [4] (Plate 2). This presumably will be the form favoured at low temperature. Alternatively, interaction between the two carboxyl groups can give rise to one, and with some strain to two, hydrogen bonds, the molecule being held in a folded form (Plate 1).

Increasing the temperature of an aqueous solution of the acid appears to break the hydrogen bonds holding the molecule in the low-temperature conformation, there being formed, on the average, an almost equal number of alternative bonds; there will thus be an interchange of intra- and inter-molecular hydrogen bonds. The energy exchange of the process may also be attributed to the difference in energy of equal numbers of intra- and inter-molecular hydrogen bonds. Interchange would be facilitated by dilution with hydroxylic solvents, which partly explains the higher specific rotations obtained on dilution of an aqueous solution. Tartaric acid is unfortunately almost completely insoluble in most non-hydroxylic solvents, but in dioxan and in ether the acid is preferentially held in the low-temperature form. This behaviour is paralleled by that of keto–enol tautomers in which there is a greater proportion of the hydrogen-bridged enol form in hydrocarbon than in hydroxylic solvents, ether behaving as a hydrocarbon solvent.[21] Tartaric acid is insoluble in the higher ethers, so the effect of temperature on ethereal solutions cannot be studied. In dioxan increasing the temperature promotes more positive rotatory power in the visible region (Fig. 3; Table 3), *i.e.*, the effect is in the same direction as in the homogeneous acid or in hydroxylic solvents. On the other hand, whilst dilution with the latter increases the positive rotation in the visible region, dilution with dioxan makes it more negative.

Table 7 shows that the rotatory power (for 5461 and 4358 Å) of tartaric acid follows the same order as the dielectric constant of the solvent, except for pyridine, where it behaves as a salt, and for dimethylformamide. This relation between the rotatory power

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[19] Patterson, *J.*, 1901, **79**, 180.

[20] Lowry and Austin, *Nature*, 1924, **114**, 431.

[21] Meyer, *Annalen*, 1911, **380**, 212.

PLATE 1.

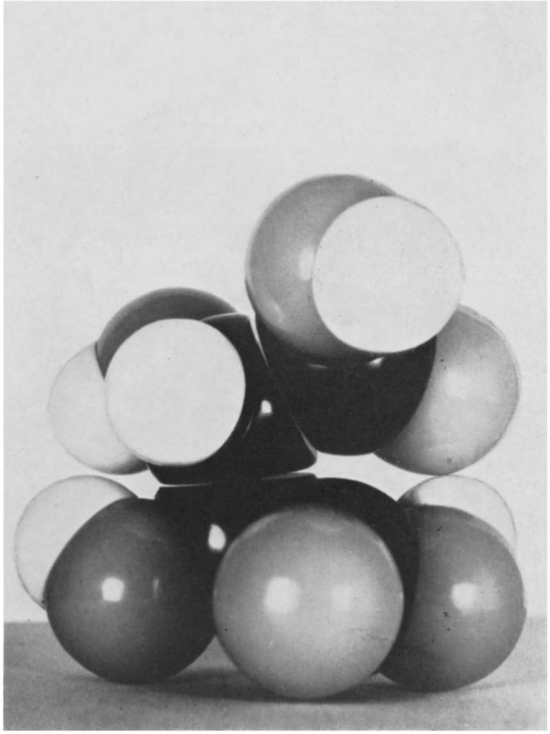
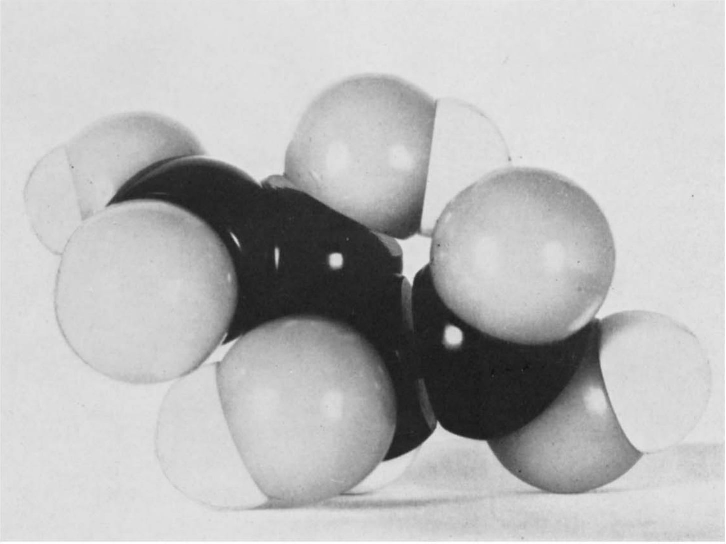


PLATE 2.



White = hydrogen, black = carbon, grey = oxygen.

[*To face p.* 2266.

and the dielectric constant must be regarded as that between two effects with a similar cause, rather than that of cause and effect. Thus dimethylforamide, which can form only one hydrogen bond apparently has a similar isolating effect on the tartaric acid molecule as dioxan. The other hydrogen-bonding solvents, in which the rotatory power varies in the order of the dielectric constant, all have possibility of forming hydrogen-bridged chains or aggregates, since they can form more than one hydrogen bond per molecule. The almost identical rotatory powers shown in ether (*c* 0·2) and in dioxan (*c* 2·5) are in agreement with this series since the dilution effect in ether may be expected to be similar to that in dioxan.

TABLE 5. *Molecular rotatory powers of solutions of tartaric acid* (0·66M) *in mixed solvents.*

| | Solution | Concn. (M) | Temp. | Wavelength (Å) 6438 | 5893 | 5780 | 5461 | 5086 | 4800 | 4358 |
|---|---|---|---|---|---|---|---|---|---|---|
| A | Dioxan<br>Water | 1·6<br>42·2 } *a* | 25·3° | +13·3° | +15·2° | +15·5° | +16·4° | + 17·1° | + 16·5° | + 13·9° |
| | | | 49·2 | +16·3 | — | +19·5 | +21·2 | + 22·4 | + 22·7 | + 22·2 |
| | | | 72·5 | +18·6 | — | +22·4 | +24·3 | + 26·7 | + 28·2 | + 29·2 |
| B | Dioxan<br>Water | 3·2<br>35·9 } *b* | 25·3 | +10·5 | +11·8 | +12·0 | +12·4 | + 12·2 | + 11·4 | + 6·5 |
| C | Pyridine<br>Water | 2·32<br>43·3 | 24·5 | +59·4 | — | +75·1 | +84·8 | + 98·9 | +111·7 | +135·8 |
| D | Pyridine<br>Water | 3·41<br>38·6 | 23·0 | +60·1 | — | +75·8 | +85·1 | + 99·2 | +111·3 | +136·2 |
| | | | 44·0 | +59·4 | — | +74·2 | +84·0 | + 98·4 | +110·6 | +134·2 |
| | | | 67·0 | — | — | +73·4 | +82·2 | + 94·8 | +107·4 | — |
| E | Pyridine<br>Water | 3·90<br>36·4 | 24·5 | +59·9 | — | +75·9 | +85·6 | + 99·8 | +112·4 | +135·6 |
| F | Pyridine | 6·10 | 24·5 | +60·5 | — | +75·7 | +85·4 | +100·0 | +112·4 | +136·0 |
| G | Acetone<br>Water | 1·72<br>46·00 | 24·8 | +16·0 | +18·6 | +19·2 | +20·6 | + 22·2 | + 22·9 | + 21·0 |
| H | Acetone<br>Water | 3·57<br>39·13 | 24·8 | +13·2 | +15·3 | +15·9 | +16·6 | + 17·5 | + 16·4 | + 14·0 |
| I | Acetone<br>Water | 5·47<br>32·08 | 24·8 | +10·5 | +12·7 | +12·9 | +13·2 | + 13·1 | + 12·5 | + 7·7 |
| J | Acetone<br>Water | 6·67<br>27·22 | 24·8 | + 9·2 | +10·9 | +11·0 | +11·2 | + 11·1 | + 9·9 | + 4·5 |
| K | Acetone<br>Water | 7·85<br>22·61 | 25·2 | + 8·4 | + 9·4 | + 9·6 | + 9·3 | + 8·2 | + 6·4 | + 0·4 |

*Densities.* A, $d_4^{22\cdot8}$ 1·1130, $d_4^{36\cdot3}$ 1·1052, $d_4^{49\cdot4}$ 1·0974, $d_4^{63\cdot9}$ 1·0878, $d_4^{79\cdot5}$ 1·0761.
D, $d_4^{25\cdot0}$ 1·0644, $d_4^{54\cdot0}$ 1·0452, $d_4^{62\cdot0}$ 1·0397.

[a, b] Concns. of tartaric acid, (*a*) 1·3M, (*b*) 1·2M.

The dilution effect in dioxan points to the importance of intramolecular association in determining the rotatory power, since in this case the effect of rising temperature may be expected to be opposite to that of dilution, as is found (Table 3). On the other hand, dilution with a hydroxylic solvent has the same effect as rising temperature. If the determining factor were intermolecular association, however, the effect of dilution with a non-polar solvent should be similar to that of a rise in temperature. Tartaric acid is not sufficiently soluble in hydrocarbon solvents to test this, but in dioxan the effect of dilution is of opposite sign to that of rise of temperature. Since ether behaves similarly to the non-polar group in the case of keto–enol tautomerism, the behaviour of dioxan may be expected to simulate that of the non-polar group in this case (see below).

In view of the relation between the dielectric constant of hydroxylic solvents and the rotatory power of the solutions it might be expected that the effect of the addition of neutral salts to aqueous solutions of tartaric acid would follow the same law. So far as calcium chloride is concerned (Tables 6 and 7), the observed change is greater than would be expected on the basis of the depression of the dielectric constant alone, *i.e.*, by comparison with alcohol, etc. It seems probable that similar factors are involved to those which produce complicated behaviour in the metallic tartrates. It is noteworthy that the dispersion of the acid in calcium chloride solution and of calcium tartrate·in the same medium are distinct, that of the acid resembling rather its dispersion in alcohol.

Table 5 shows that the rotatory behaviour of tartaric acid in mixed solvents is intermediate between that shown in each separately.

TABLE 6. *Molecular rotatory powers of lithium and sodium tartrate, and of tartaric acid in calcium chloride solution.*

| | Soln. (aq.) | Concn. (M) | Temp. | Wavelength (Å) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 6438 | 5893 | 5780 | 5461 | 5086 | 4800 | 4358 |
| M | Acid<br>$CaCl_2$ | 0·67<br>1·0 | 25·2° | — | — | + 3·0° | + 2·2° | — | — | − 10·0° |
| | | | 42·8 | — | — | + 8·2 | + 8·2 | — | — | + 1·2 |
| | | | 54·6 | — | — | +11·0 | +11·3 | — | — | + 7·0 |
| L | Acid<br>$CaCl_2$ | 0·67<br>1·93 | 25·3 | — | — | −12·9 | −17·2 | — | — | − 41·3 |
| | | | 39·9 | — | — | − 6·7 | − 8·8 | — | — | − 28·5 |
| | Li tartrate | 0·20 | 25·3 | — | — | +62·0 | +69·3 | — | — | +106·8 |
| | | | 40·0 | — | — | +62·5 | +70·3 | — | — | +109·6 |
| | | | 56·5 | — | — | +63·2 | +70·7 | — | — | +110·3 |
| | | | 73·3 | — | — | +63·3 | +71·2 | — | — | +110·6 |
| N | Li tartrate<br>LiCl | 0·05<br>12·0 | 25·3 | — | — | — | −20 | — | — | − 46 |
| | | | 47·1 | — | — | — | −17 | — | — | − 37 |
| | | | 75 | — | — | −10 | −10 | — | — | − 26 |
| | | | 96·1 | — | — | − 6 | − 3 | — | — | − 18 |
| | Na tartrate | 0·68 | 25 | +47·7° | +58·2° | +60·6 | +68·1 | +79·5° | +89·4° | +107·7 |
| P | Na tartrate<br>Dioxan | 0·68<br>1·45 | 25 | +47·1 | +56·7 | +59·1 | +66·6 | +77·1 | +86·7 | +104·4 |
| Q | Na tartrate<br>Dioxan | 0·68<br>2·43 | 25 | +46·2 | +55·5 | +58·5 | +65·1 | +75·9 | +85·2 | +102·3 |

*Rotatory Power of Solutions of Metallic Tartrates.*—The rotatory behaviour of the tartrates is superficially much simpler than that of the acid; this simplicity disappears, however, when the tartrates are dissolved in solutions of neutral salts, particularly those of the multivalent metals. The results quoted below are those of Darmois [22] unless given in Table 6 or otherwise stated. So far as the alkali tartrates are concerned the rotatory powers follow the same order as the molar depression of the dielectric constant of water by the alkali chlorides (Table 8). This order is the same as that of the ionic field, so that any effect which is purely electrical in origin may be expected to follow it.

Darmois has shown, however, that for the alkaline-earth tartrates the negative rotatory power increases in the order $Mg < Ca < Sr < Ba$, which is the reverse order to that of the alkali series. Thus, whilst the field effect no doubt influences the rotation, it is not the sole determining factor. Further, salts of the groups Zn, Cd, and Hg give rotations similar to that of sodium although their ionic fields will be quite different. In this group a mutarotation was observed, though not so marked as that of the aluminium salt. This fact, coupled with the existence of compounds of the acetylacetone-complex type [23] and with observations on the conductance of tartrates,[24] suggests that complex formation is one of the chief factors governing the rotations of these salts, and that it also influences those of the alkaline earths and possibly those of lithium and sodium. In fact, if the basis of the variation in the rotatory power of the alkali tartrates with concentration were a simple electrical-field effect, then this effect would have to be of opposite sign for the potassium, rubidium, and cæsium salts to that for the lithium and sodium salts.

If Darmois's results for the alkali tartrate series are extrapolated to zero concentration, the values $[M]^{18}_{5780}$ +62·2°, 63·0°, 64·5°, 65·7°, 64·5°, 65·1° are obtained for the Li, Na, $NH_4$,

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[22] Darmois, *Ann. Physique*, 1928, **10**, 70.
[23] Morgan and Moss, *J.*, 1914, **105**, 195.
[24] Davies and Topp, *J.*, 1940, 87.

K, Cs, and Rb salt respectively. Each of these values should also correspond to the "molecular" rotation of the tartrate ion. Thus the alkali tartrates all give values very close to the $[M]^{25}_{5893}$ +60·0° obtained by Britton and Jackson[15] for the tartrate ion. The results for lithium tartrate (Table 6), when extrapolated to 5893 Å, give $[M]^{25\cdot3}_{5893}$ +60·3°, whilst the value $[M]^{25\cdot3}_{5461}$ +70·2° is also in agreement with the value of 70·0° given by Britton and Jackson for the tartrate ion. Thus the molecular rotatory powers of the alkali tartrates in dilute solution may be considered to be those of the tartrate ion.

TABLE 7. *Molecular rotatory powers of tartaric acid solutions and the dielectric constant* (ε) *of the solvent.*

| Solvent | $\varepsilon^{28}$ | *c* | Temp. | $[M]_{5461}$ | $[M]_{4358}$ | $\frac{[M]_{4358}}{[M]_{5461}}$ |
|---|---|---|---|---|---|---|
| Water ..................... | 78·5 | 10 | 24·7° | +22·8° | + 25·4° | + 1·11 |
| Ethanol .................. | 24·2 | 10 | 24·0 | + 6·0 | − 7·2 | − 1·19 |
| Acetone .................. | 20·4 | 3 | 24·6 | + 3·0 | − 13·6 | − 4·54 |
| Ether ..................... | 4·3 | 0·2 | 25·3 | −18 | − 54 | + 3·08 |
| Dioxan .................. | 2·2 | 10 | 24·0 | −16·5 | − 50·0 | + 3·03 |
| Aq. pyridine (D) ...... | 59·5 | 10 | 23·0 | +85·1 | +136·2 | + 1·60 |
| Dimethyl formamide... | 36·7 | 10 | 25·3 | − 1·1 | − 20·4 | +18·5 |
| Aq. $CaCl_2$ 1M ............ | 51 | 10 | 25·2 | + 3·0 | − 10·0 | − 3·33 |
| 1·93M ...... | 25 | 10 | 25·3 | −12·9 | − 41·3 | + 3·20 |

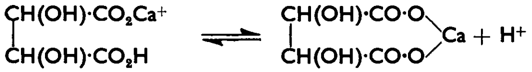
TABLE 8. *Molar depression* (δ) *of the dielectric constant* (ε) *of water by metal chlorides, and the rotatory powers of aqueous solutions of tartrates.* (*δ is determined from the equation* $\varepsilon = \varepsilon_M + 2\delta c$, *where c is the molar concentration.*)

| Salt | RbCl | KCl | NaCl | LiCl | $BaCl_2$ | $MgCl_2$ |
|---|---|---|---|---|---|---|
| δ * ..................... | −5 | −5 | −5·5 | −7 | −14 | −15 |
| *c* ........................ | 0·54 | 0·51 | 0·44 | 0·43 | 0·60 | — |
| $[M]^{25}_{5461}$ † .............. | 67·8° | 67·3° | 61·8° | 59·1° | 34·0° | 60° |

* From Robinson and Stokes (ref. 18, p. 19; cf. Hasted, Ritson, and Collie, *J. Chem. Phys.*, 1948, **16**, 1). † From Darmois.[22]

If the depression due to $CaCl_2$ is similar to that of $MgCl_2$ or $BaCl_2$, the dielectric constant of 1M- and 1·93M-calcium chloride should be 51 and 25 respectively (cf. Table 7).

In considering the rotations of the alkaline-earth tartrates it is interesting that potential measurements by Cannan and Kibrick[25] appear to show the preponderance of the form on the left in the equilibrium :



$$\begin{matrix}CH(OH)\cdot CO_2Ca^+\\ |\\ CH(OH)\cdot CO_2H\end{matrix} \rightleftharpoons \begin{matrix}CH(OH)\cdot CO\cdot O\diagdown\\ |\qquad\qquad\quad Ca\\ CH(OH)\cdot CO\cdot O\diagup\end{matrix} + H^+$$

Since the hydrogen-ion concentration of solutions of calcium tartrate will be low, the form on the left cannot be attained in the normal way. Also Davies and Topp[24] have shown by conductance measurements that calcium tartrate is only 75% dissociated in 0·001M-solution, whilst in the 0·025M-solutions used by Darmois the degree of dissociation is only about 4%. Davies has also attributed[26] the weak dissociation of calcium lactate to stabilisation of un-ionised complexes by co-ordination. It is clear that if the left-hand form, above, exists it has something of the hydrogen tartrate structure, but in 0·025M-solution its rotatory power is similar to that of the free tartrate ion. It is also clear from the conductivity measurements that it must exist as an ion pair with the hydroxyl group.

If this type of equilibrium exists it must involve some form of hydrolysis the degree of normal hydrolysis in these solutions being only of the order of $10^{-5}$. Harned and Owen[27] have, however, used the concept of local hydrolysis to explain differences in the activites

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[25] Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 3074.

[26] Davies, *J.*, 1938, 277.

[27] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Inc., New York, 1950, p. 385.

[28] Ref. 18, p. 448; Weissberger, "Organic Solvents," Interscience Publ. Inc., New York, 1955; Leader and Gormley, *J. Amer. Chem. Soc.*, 1951, **73**, 5732.

of the alkali-metal halides and their hydroxides and acetates. A similar scheme should be even more certainly applicable to the tartrates than to the acetates :

$$\mathrm{M^+ + OH^-\cdots H^+} \longleftarrow \mathrm{M^+\cdots OH^-\cdots H^+}$$

and in the presence of a proton acceptor :

$$\mathrm{M^+ + OH^-\cdots H^+ + A^-} \longrightarrow \mathrm{M^+\cdots OH^-\cdots H^+\cdots A^-}$$

where the dotted lines represent " linkages " due to ion–ion or ion–molecule forces. In the tartrates the equilibrium may take the form :

$$\begin{array}{l}\mathrm{CH(OH)\cdot CO_2^-}\\ |\\ \mathrm{CH(OH)\cdot CO_2^-}\end{array} + \mathrm{HOH} + \mathrm{Na^+} \rightleftharpoons \begin{array}{l}\mathrm{CH(OH)\cdot CO_2^-\cdots H^+\cdots OH^-}\\ | \qquad\qquad\qquad\qquad\qquad \vdots\\ \mathrm{CH(OH)\cdot CO_2^-\cdots\cdots\cdots Na^+}\end{array}$$

The proximity of a proton to one carboxyl group presumably renders the other less basic, so that it remains almost completely ionised. The difference between the higher alkali-metal tartrates and those of the alkaline-earth metals appears to be that, whilst the former are completely ionised at the highest concentrations, the latter are only fully free as ions in dilute solutions and in more concentrated solutions the metal is retained by the carboxylate ion partly by co-ordination.

The increase in the rotatory powers of potassium, rubidium, and cæsium tartrate on addition of the corresponding chlorides has been attributed to hydration of the cations,[15] which reduces the " free " water available for the dissolution of the tartrate ion, thus increasing its effective concentration. This theory does not explain, however, why the molecular rotatory powers of potassium, rubidium, and cæsium tartrate increase with concentration whilst those of sodium and lithium tartrate diminish with increasing concentration. This discrepancy is particularly important since the hydration number of the lithium ion is greater than that of cæsium.[16] It seems probable that the explanation must be sought in terms of two opposing effects. Analogy with the alkaline-earth series suggests that the factor which tends to give negative rotations in the visible region is complex formation. The opposing factor may be more directly due to the ionic field. Both will increase from cæsium to lithium. In cæsium the tendency to form complexes will be very small, so that as the solution is concentrated the field effect, giving more positive rotations, may become more important. In lithium the tendency to form complexes will be greater, and is in fact dominant, so that as the concentration is increased the negative rotatory power also increases. Lithium and sodium thus represent an intermediate case. Table 6 shows that lithium tartrate in a concentrated solution of lithium chloride has a negative rotation; if this solution is heated the rotatory power tends to become more positive. A purely electrical effect would not be expected to be so temperature-sensitive. This suggests that the presence of excess of lithium ions encourages the formation of the complex, giving rise in extreme cases to a negative rotation in the visible region; this complex is partially disrupted by increasing the temperature.

In the alkaline-earth series the tendency to complex formation is even more marked so that in this case also the rotatory power becomes more negative as the concentration is increased.[22] The field and complex effects will both be greater with calcium than with barium, but their relative magnitudes may be different, giving rise to the reversal of the order observed in the alkali series.

It is not proposed to specify the mechanism of the " field effect." The field of a cation will influence the properties of the solution in several ways, one of which will be a direct deformation of the polarisable anion, with a resultant variation in its electron distribution and so in its rotatory power.

*Conclusion.*—Analysed in terms of hydrogen-bridged molecular conformations of a more or less rigid nature the behaviour of the rotatory dispersion of tartaric acid is seen to be relatively simple. The formation of complexes with the cation provides a similar explanation of the behaviour of the tartrates.

*Experimental.*—Observational error was less than 0·01° for 5461 and 5780 Å, and about ±0·03° for the other lines.

The tartaric acid, recrystallised from water, had m. p. 178·5—179·5°.

Solvents. These were dried as follows: acetone, $CaCl_2$; pyridine, KOH; alcohol, CaO; ether, Na; dimethylformamide, $CaH_2$; dioxan, refluxed over Na and freshly distilled before use.

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