210. *The Analysis of Rotatory Dispersion: 2 : 3-Epoxypropyl Phenyl Ether.*

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The method of analysis of rotation–temperature curves in terms of an equilibrium mixture of isomeric forms or conformations is examined and the accuracy required for its use discussed. An attempt has been made to resolve the rotatory dispersion of 2 : 3-epoxypropyl phenyl ether into those of two forms by analysis of the specific rotation–temperature curves. Calculations show that the difference in the heat content of two such forms is of the order 2·5—3 kcal./mole.

KAUZMANN, WALTER, and EYRING [1] have calculated "rotatory constants" *a* and *b* for three esters of tartaric acid from the variation of the specific rotation with temperature. These "rotatory constants" represent the rotatory power, at a given wavelength, of two presumed forms or conformations, A and B, of the molecule, the proportions of each form present in the equilibrium mixture varying with the temperature. These forms may be chemically different isomers or merely "rotational" isomers. This method of analysis should have considerable application in the study of rotatory dispersion. An attempt has therefore been made to repeat the calculations which were based on experimental work by Winther.[2] Kauzmann, Walter, and Eyring do not give their method of solution and since there are discrepancies between their results and those now obtained a brief account of the method now used is given.

Form of Solution.—The expression for the equilibrium of two forms B $\rightleftharpoons$ A may be written

$$(b - \alpha)/(\alpha - a) = \exp(\Delta S/\boldsymbol{R} - \Delta H/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where α, for simplicity, is the specific rotation.

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[1] Kauzmann, Walter, and Eyring, *Chem. Reviews*, 1940, **26**, 339.

[2] Winther, *Z. phys. Chem.*, 1902, **41**, 161.

A solution to equation (1) can be obtained by using a pair of temperatures to eliminate ΔS, giving

$$\ln\left(\frac{b-\alpha_1}{\alpha_1-a}\cdot\frac{\alpha_2-a}{b-\alpha_2}\right)=-\frac{\Delta H}{\boldsymbol{R}}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\quad . \quad . \quad . \quad . \quad . \quad (2)$$

The right-hand side of this equation may be eliminated by choosing two temperatures T_3 and T_4, such that $(T_4 - T_3)/T_4T_3 = (T_2 - T_1)/T_2T_1$. We then obtain

$$\frac{b-\alpha_1}{\alpha_1-a}\cdot\frac{\alpha_2-a}{b-\alpha_2}=\frac{b-\alpha_3}{\alpha_3-a}\cdot\frac{\alpha_4-a}{b-\alpha_4}\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation can be developed into the form

$$b=-\left(\frac{Z+pa}{p+qa}\right)\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $p = (\alpha_2\alpha_3 - \alpha_1\alpha_4)$, $q = (\alpha_1 + \alpha_4 - \alpha_2 - \alpha_3)$,
and $Z = (\alpha_1\alpha_3\alpha_4 + \alpha_1\alpha_2\alpha_4 - \alpha_2\alpha_3\alpha_4 - \alpha_1\alpha_2\alpha_3)$

The solution of this equation requires a further set of values p', q', and z', obtained from α'_1, α'_2, α'_3, and α'_4 (corresponding to temperatures T'_1, T'_2, T'_3, and T'_4), of which at least one value differs from the previous set. Thus, although there are only four unknowns at least five values are required for a solution :

$$a=\sqrt{\left[\frac{p'z-z'p}{p'q-q'p}+\frac{1}{4}\left(\frac{z'q-q'z}{p'q-q'p}\right)^2\right]}-\frac{1}{2}\left(\frac{z'q-q'z}{p'q-q'p}\right)\quad . \quad . \quad . \quad (5)$$

Substitution in equation (4) then gives b and in equation (2) ΔH; ΔS is obtained from equation (1).

The author is indebted to Dr. R. G. Taylor for an alternative method which involves differentiation of equation (1) to give $\boldsymbol{R}(a - b)/\Delta H \,.\, d\alpha/dT \,.\, T^2 = -\alpha^2 + (a + b)\alpha - ab$. By reading $d\alpha/dT$ from a graph for three values of T, a solution is possible, though this requires an accuracy in the estimation of $d\alpha/dT$ which is not usually obtainable.

Attempts to calculate the difference in the heat content of the two forms, ΔH, the entropy difference, ΔS, and the rotatory constants, a and b, for dimethyl tartrate from the optical rotation–temperature curve for light of wavelength 5890 Å yield imaginary results. It is shown below that small variations in experimental values, or possibly, in this case, variations in method of calculation may produce very large variations in the results, though a and b are generally more affected than ΔH. The corresponding curve for $\lambda = 5890$ Å appears to be accurate but its form results in terms in the solution being of almost vanishing magnitude. The other curves do not give such a good plot and in these cases also no solution was obtainable by our method. Kauzmann, Walter, and Eyring found for dimethyl tartrate :

for $\lambda = 5890$ Å; $\Delta H = 2280$ cal./mole, $\Delta S = 10{\cdot}6$ e.u./mole, $a = 10{\cdot}2$, $b = -30$
for $\lambda = 4703$ Å; $\Delta H = 2280$ cal./mole, $\Delta S = 10{\cdot}6$ e.u./mole, $a = 10{\cdot}9$, $b = -61$
for $\lambda = 4445$ Å; $\Delta H = 2280$ cal./mole, $\Delta S = 10{\cdot}6$ e.u./mole, $a = 11{\cdot}1$, $b = -81$

It would seem that the constants they calculated must all have been obtained from the 5890 Å curve so that the other curves do not provide an independent check. Another possibility is that the values of ΔH, etc., are arbitrary. The fit of the calculated to the observed values is, however, impressive. With diethyl tartrate a similar divergence of results is found, and if the previous results were derived directly from the experimental points it must be assumed that some method of selection was used which was not given.

Experimental Error and the Accuracy of the Solution of the "Two-form" Equation.—A precise arithmetical analysis of the solutions of these equations is required to determine the circumstances in which those solutions are valid; such an analysis is outside the scope of the present work. It is emphasised that the solution given below is an exact algebraic solution; difficulties arise only when the experimental values are substituted in the equation. The final error appears not to be related in any simple way to the error of observation but depends on the position of the observed point on the specific rotation–temperature curve. The difficulties are almost exactly those encountered in the solution of two-term Drude equations where also the products of small numbers with the differences of their powers occur. The error in ΔH is likely to be less than that of the " constants " a and b from which it is derived. For example, one of the points in the specific rotation–temperature curve for $\lambda = 6438$ Å for 2 : 3-epoxypropyl phenyl ether (see below) is clearly seen to be in error when the experimental results are plotted on a large scale. The curve can be drawn so as to give, *e.g.*, $\alpha_4 = 11{\cdot}75$ and $\alpha'_3 = 12{\cdot}56$ or $\alpha_4 = 11{\cdot}77$ and $\alpha'_3 = 12{\cdot}58$, from which are calculated the values $a = 45{\cdot}2$, $b = 0{\cdot}63$, $\Delta H = 3194{\cdot}2$, and $a = 108$, $b = -6{\cdot}0$, $\Delta H = -1624$ cal./mole, respectively. On the other hand the reduction of α_1, α_2, α'_1 and α'_2 all by 0·01 reduces ΔH by 200 cal./mole, *i.e.*, 6%, and a by 8%, while b increases by 120%. The permissible variation or random error appears to vary with the form of the specific rotation–temperature curve and with the way in which the points enter into the solution, but in the cases studied accuracy to 0·01° seems to ensure a solution, whilst when the optical rotations are accurate only to 0·1° there is little chance of a result. Probably the percentage error is the better criterion, the figures being *ca.* 0·05 and 0·5%, respectively.

The way in which ΔH varies with a and b can be shown artificially by assuming errors in p', q', and z' of the solution so as to give, for the example with $\Delta H = -1624$ cal./mole and $a = 108$, with new values $a = 1000$, and $a = 10{,}000$; the values $b = -11{\cdot}7$ and $-12{\cdot}3$, $\Delta H = -1073$ and -908, respectively, are obtained. Thus variation by a factor of 100 in a produces variation by a factor of 2 in ΔH, which is consonant with their logarithmic relationship. Since a and b tend to have rather arbitrary values as a result of random errors in the curve of α against temperature this method may have greater value in the determination of ΔH than of a and b. Where results of sufficient accuracy are available, this method does make possible a true analysis of the rotatory dispersion. In fact, an analysis of a rotatory dispersion in terms of the Drude equation can only be considered to be of fundamental value when the large variations of rotation with temperature, due to the existence of the various isomeric forms, have been eliminated.

Scope of the Method.—Bernstein and Pedersen [3] have treated the rotatory power of *sec.*-butyl alcohol as that of a mixture of three forms due to rotational isomerism about a single bond, the observed value being that due to an equilibrium mixture of these three forms which are assumed to have quite different rotatory powers. This theory apparently leads to the rather surprising conclusion [4] that simple compounds of this type should not exhibit rotatory power in the absence of rotational isomerism. Although it is difficult to accept this conclusion, in view of this and other work on rotational isomerism of molecules containing an asymmetric group joined to a hydrocarbon skeleton by a single bond, any calculations relating variations of rotatory power with temperature to the proportions of various forms should be based on at least three such forms. The present work shows that complexity renders the success of such a calculation unlikely since whilst the solution of the " two-form " equation appears to depend on the smoothness of the curve of $(\mathrm{d}\alpha/\mathrm{d}T)/T$, in the " three-form " equation the corresponding criterion will be the smoothness of $[\mathrm{d}^2\alpha/(\mathrm{d}\lambda\,.\,\mathrm{d}T)]/T$ which is much more critical. It is doubtful whether any measurements at present available are accurate enough.

The expression for two forms in equilibrium can thus obviously only be rigidly applied in the absence of rotational isomerism due to the presence of single bonds It should also be applicable to those systems (*a*) which consist of isomers of two groups widely separated

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[3] Bernstein and Pedersen, *J. Chem. Phys.*, 1949, **17**, 885.

[4] *Idem, ibid.*, p. 888.

in terms of energy, and (*b*) in which one form is a ring structure with a relatively large rotatory power and the other a mixture of open-chain rotational isomers for which $\mathrm{d}[\alpha]/\mathrm{d}T$ will be small.

2 : 3-*Epoxypropyl Phenyl Ether.*—The " two-form " equation can be used for 2 : 3-epoxypropyl phenyl ether since this ether exhibits considerable variation of rotatory power with temperature, and its rotatory dispersion can be explained in terms of the suggested ring formation.[5] Thus, analysis of optical rotation–temperature curves should provide information on the energy difference between the two forms and enable the dispersion to be simplified.

The results, when reported previously,[6] were rounded off so as to be well within the experimental error, with consequent loss of vital accuracy. The original results are therefore given in Table 1. The individual experimental error represents 2½ units in the second decimal place for the 5780 and 5461 Å lines and rather more than twice that figure for the other two. The mean experimental error should be rather less than this. Temperatures were read to 0·1° so that, in terms of absolute temperature, this accuracy is comparable with that of the polarimetric readings.

There is no difficulty in obtaining solutions for the 5780, 5461, and 4358 Å curves from the values given in Table 1 together with interpolated values (Table 2). The plot of specific rotation against temperature for light of wavelength 5086 Å showed that the results were not sufficiently accurate. For the 6438 Å line the 353·16° K point is probably in error; interpolation between 334·16° K and 371·16° K for this curve gives varying results some of which are quoted. Apart from these variations it is interesting to note that changes in interpolation of α_4 from 11·75° to 11·775° and α'_3 from 12·56° to 12·585° result in the change of *a* from 45 almost to infinity, the solution being unstable at this point, whilst with $\alpha_4 = 11{\cdot}80°$ and $\alpha'_3 = 12{\cdot}61°$ the solution is imaginary. Attempts to obtain suitable values as a basis for calculation are therefore useless, and the justification of the method lies in the agreement or otherwise of the results obtained directly from the experimental values. However, it is reasonable to eliminate results which can be shown to be improbable. The values obtained for the two highest temperatures are useful in this way though they are not

TABLE 1. *Observed and calculated specific rotatory powers of* 2 : 3-*epoxypropyl phenyl ether.* [The calculated values, given as differences, were obtained by using the values $\Delta H = -2625$ cal./mole and (*a*) $\Delta S = -8{\cdot}3$ e.u./mole or (*b*) $\Delta S = -8{\cdot}6$ e.u./mole.]

T°, K		Wavelength, Å				
		6438	5780	5461	5086	4358
298·7		19·53	24·04	26·86	31·09	43·55
	(*a*)	−0·86	−0·01	−0·10	−0·18	−0·32
	(*b*)	−0·09	−0·40	+0·58	+0·43	−0·02
315·9		16·69	20·82	23·49	26·98	37·20
	(*a*)	−0·28	−0·02	−0·31	−0·23	−0·09
	(*b*)	−0·01	−0·54	−0·01	−0·00	−0·01
334·2		14·13	17·75	19·82	22·83	31·32
	(*a*)	0·00	0·00	0·00	+0·01	0·00
	(*b*)	0·00	−0·60	−0·01	−0·01	0·00
353·2		11·76	14·98	16·70	19·58	25·95
	(*a*)	+0·29	0·00	+0·06	−0·36	+0·10
	(*b*)	+0·08	−0·62	−0·16	−0·46	+0·11
371·2		10·37	12·71	14·26	16·35	21·76
	(*a*)	0·00	0·00	−0·01	0·00	−0·01
	(*b*)	−0·37	−0·60	−0·36	−0·22	+0·07
414		—	7·9	8·3	—	11·9
	(*a*)	—	+0·6	+1·3	—	+1·8
	(*b*)	—	+0·1	+0·8	—	+2·2
447		—	5·3	5·5	—	6·8
	(*a*)	—	+0·8	+1·4	—	+2·3
	(*b*)	—	+0·5	+0·9	—	+4·6

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[5] Hargreaves, Thesis, London, 1949.

[6] Balfe, Hargreaves, and Kenyon, *J.*, 1950, 1861.

accurate enough to be used in the solution itself. Thus values over 5·5 for b at 5461 Å can be eliminated. It is more difficult to obtain an upper limit for a, but the calculated plot of α against T for $\Delta H = -2625$ cal./mole shows that the curvature becomes reversed below *ca.* 270° K. The increased slope between 315° and 270° K will be more than balanced by the reversed curvature below that temperature so that it is reasonable to use values at room temperature together with an expression, $[\alpha] = a + cT$, to obtain a rough upper limit for a. This method is only justifiable if the inflexion point is near to room temperature; it seems reasonable to eliminate the value for a at 6438 Å, $\Delta H = -1624$ cal./mole, on this ground. The solution giving $\Delta H = -5229$ cal./mole can also be eliminated because of the unsuitability of the corresponding value of a and b.

TABLE 2. *Calculated constants for 2 : 3-epoxypropyl phenyl ether.* (α_4 and α'_3 are interpolated values from Table 1.)

		Specific rotations [(+)-isomer]				
Wavelength	$n =$	1	2	3	4	
6438 (*a*)	α_n	+19·53°	+16·69°	+14·13°	+11·75°	$\Delta H = -3416$, $\Delta S = -12·05$
	α'_n	19·53	16·69	12·56	10·37	$a = 45·21$, $b = 0·63$
(*b*)	α_n	19·53	16·69	14·13	11·77	$\Delta H = -3194$, $\Delta S = -11·07$
	α'_n	19·53	16·69	12·58	10·37	$a = 41·32$, $b = 1·493$
(*c*)	α_n	19·52	16·68	14·13	11·77	$\Delta H = -1624$, $\Delta S = -7·72$
	α'_n	19·52	16·68	12·58	10·37	$a = 108·0$, $b = -6·004$
5780	α_n	24·04	20·82	17·75	14·62	$\Delta H = -2625$, $\Delta S = -8·30$
	α'_n	24·04	20·82	15·75	12·71	$a = 47·56$, $b = -6·04$
5461	α_n	26·86	23·49	19·82	16·29	$\Delta H = -5229$, $\Delta S = -15·90$
	α'_n	26·86	23·49	17·52	14·26	$a = 36·19$, $b = 5·63$
4358	α_n	43·55	37·20	31·32	25·28	$\Delta H = -3833$, $\Delta S = -11·89$
	α'_n	43·55	37·20	27·42	21·76	$a = 73·38$, $b = 0·5654$

The negative sign of ΔH (in cal./mole) and ΔS (in e.u./mole) indicates that the roots of the equation have been taken so that form A is the low-temperature form.

The temperatures corresponding to the rotations are :

n	1	2	3	4
T_n	298·66°	315·91°	334·16°	355·90°
T'_n	298·66	315·91	347·65	371·16

The values of ΔS are determined by those obtained for ΔH, a, and b. This is one of the factors militating against an averaging of results. The solution of equation (1) gives a and b for one wavelength; the values at other wavelengths may be obtained from the corresponding ΔH and ΔS values, any pair of temperatures being used. The rotatory

TABLE 3. *Dispersions of " constants " a and b, derived from the following values.*

		A		*B*		*C*		*D*	
ΔH (calc./mole)		−2625		−2625		−3194		−3600	
ΔS (e.u.)		−8·3		−8·6		−11·07		−11·8	
λ	Series	a	b	a	b	a	b	a	b
6438	1	40·29	−6·98	41·98	−4·96	41·28	1·53	35·63	1·24
	2	37·17	−6·85	41·31	−4·38	33·66	6·22	35·38	1·57
	3	36·41	−3·65	38·86	−2·71	44·62	1·79	34·46	2·00
5780	1	47·58	−6·01	49·49	−3·72	48·69	3·63	42·29	3·30
	2	47·78	−6·21	50·35	−5·45	41·17	8·27	43·24	2·68
	3	47·62	−6·08	50·89	−4·72	58·62	1·20	44·98	1·50
5461	1	51·41	−4·51	53·50	−2·19	52·67	5·50	45·96	5·16
	2	55·72	−8·82	58·78	−6·72	47·82	8·48	50·29	1·81
	3	52·77	−6·47	56·38	−5·08	64·91	1·57	49·91	1·87
5086	1	61·14	−7·27	63·58	−4·34	62·56	5·04	54·39	4·62
	2	63·43	−9·27	66·89	−7·18	54·49	10·01	57·28	2·46
	3	61·24	−7·81	65·44	−6·19	75·38	1·56	57·90	1·91
4358	1	89·97	−15·72	93·74	−11·19	92·18	3·30	79·55	2·66
	2	88·84	−14·58	93·75	−11·20	76·19	13·16	80·14	2·47
	3	87·98	−13·89	94·19	−11·50	108·85	−0·07	83·05	0·46

Series 1 were calculated from values at 298·7° and 315·9°, series (2) from values at 315·9° and 334·2° and (3) from values at 334·2° and 371·2° K. Column *D* was calculated for a mean of the higher values from Table 2.

dispersions of *a* and *b* determined for three pairs of temperatures and four values of ΔH are given in Table 3.

The nature of these dispersions may help in selection of the possible values of ΔH; but in this case the dispersions are not accurate enough to permit an unambiguous selection. However, when $1/a$ is plotted against λ^2 (the rough test for *simple* dispersion), a straight line is produced as in the plot of $1/[\alpha]$ against λ^2. But the plot of $1/b$ against λ^2 is markedly curved except for the values $\Delta H = -3194$, $\Delta H = -2625$ cal./mole, and $\Delta S = -8{\cdot}6$ e.u./mole). Of these the first and the last give the best agreement with a linear plot. In the first case the intercept on the wavelength axis, corresponding to $\lambda_0^2 = 0{\cdot}007$ ($\lambda_0 = 800$ Å) in the one-term Drude equation, is identical for *a* and *b* and is equal to that given by the $1/[\alpha]$-λ^2 plot. This implies an identity of the dispersions of *a*, *b*, and $[\alpha]$, as would be expected if the dispersion of each form were truly simple since in this case the rotation constant does not affect the dispersion but only the magnitude of the rotation. If, however, the dispersions are only pseudo-simple, as the value of λ_0 shows them to be, then λ_0 can vary even when the isomers are chemically identical, since the relative values of the different rotation constants of the Drude equation will affect the dispersion. Thus the linearity of the plot is not an absolute criterion, though other things being equal the simpler plot is naturally to be preferred.

The intercepts of the $1/a$-λ^2 plot for the first and the last case above correspond, whilst the intercept of the $1/b$-λ^2 plot corresponds to an absorption wavelength of 2200 Å. Since the dispersion of each form seems to be complex, other series showing a maximum in *b* may equally be correct, though it is likely that this maximum is in fact due to experimental error. Thus, examination of the dispersion here gives little help in selecting possible values of ΔH.

Greater assistance is obtainable from the study of the rotatory dispersion of 2 : 3-epoxypropyl phenyl ether in *n*-butyl ether.[6] It is clear from this that if the proposed explanation of the dispersion is to be maintained *b* should now have a negative value greater than 3·2 for the 4358 Å line. Thus the value $\Delta H = -2625$ cal./mole is preferred to $\Delta H = -3194$ cal./mole which also gives too large a value for *b*. From the values of Table 3, set *A*, rotatory powers were calculated for the whole field of observation; the differences from the observed values are given in Table 1, series (*a*). A satisfactory fit is obtained up to 373° K but above that the fit is not good. An attempt to improve this fit by inserting in equation (1) the value of α_{5461} at 447° K gives a new value for ΔS; *a* and *b* were then recalculated for each wavelength (Table 3, set *B*) and the figures given in Table 1, series (*b*), then obtained. Again the fit is not good at higher temperatures, the differences being outside the limit of probable error, but a better plot is obtained for the dispersion. Further fitting of the expressions to the experimental values might yield a better correlation, but the orders of magnitude are correct so that there is little doubt as to the essential validity of the results.

Thus a difference in heat content between the two postulated forms of the order of 2·5—3 kcal./mole gives the best fit to the dispersion. It has been suggested [5] that one form of 2 : 3-epoxypropyl phenyl ether is a ring structure. This ring structure (having a heat content 2·5—3 kcal./mole less than the open form) may be considered in the light of the rearrangement of phenyl allyl ether [7] and the suggestion of the ethylenic character of the epoxide ring.[8,9] It may be noted, however, that at 174° C the proportion of the ring form of 2 : 3-epoxypropyl phenyl ether is reduced to *ca.* 20%. It is not surprising, therefore, that the ether does not rearrange even at its boiling point when heated in nitrogen.

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[7] Tarbel, *Chem. Reviews*, 1940, **27**, 495.
[8] Walsh, *Nature*, 1947, **159**, 165.
[9] Linnett, *ibid.*, 1947, **160**, 162.