447. *The Salt-forming Characteristics of Doubly- and Singly-linked Elements of the Oxygen Group. Part V. The Rotation of Camphor in Strong Mineral Acids.*

By John W. Baker.

The observation that solutions of *d*-camphor in concentrated sulphuric acid are strongly lævorotatory was first made by Landolt and his collaborators (Vogel, *Diss.*, Berlin, 1892) and has been confirmed by Lucas (*Ann. Physique*, 1928, **9**, 444, where references to earlier observations are cited) and Patterson, Dunn, Buchanan, and Loudon (this vol., p. 1715). These investigators, however, concluded that the change in sign of rotation ($[\alpha]_D$ — 60°) is to be ascribed to a purely physical solvent effect. Lucas gave the following reasons for his conclusion that the change in rotation cannot be the result of any chemical interaction between camphor and sulphuric acid : (1) the rotation of the solution remains constant, combination with the enol form thus being excluded; (2) camphorsulphonic acids are formed only by heating at 95—100°, and, moreover, when formed are dextrorotatory; (3) camphor is regenerated on dilution of the acid solution with water; and (4) it is possible to obtain intermediate values for the rotation by using mixtures of solvents such as sulphuric–acetic acids or sulphuric acid–water.

The investigations described in earlier parts of this series (J., 1931, 307, 314; this vol., p. 1226, preceding paper), however, have supplied definite evidence for the view that the formation, in sulphuric acid solution, of oxonium salts of the type $\mathrm{ArC}\overset{\oplus}{\overbrace{\mathrm{R{:}OH}}}\}\mathrm{H}\overset{\ominus}{\mathrm{S}}\mathrm{O_4}$ is a general property of the carbonyl group, and during the discussion on one of these communications (*Chem. and Ind.*, 1932, 231) Professor Lowry suggested that similar salt formation is responsible for the observed change in sign of rotation of *d*-camphor in sulphuric acid solution, a view which could be tested by application of the methods developed in this series of investigations.

Carr and Reynolds (J., 1910, **97**, 1328) have already directed attention to the large changes in rotation, often involving changes in sign, which result from the conversion of certain alkaloids into their salts, the rotation in neutral solvents being that of the free base, whereas in acid solution or in solutions of the salts it is the rotation of the ammonium kation which is under observation. Thus in aqueous solutions the specific rotations of aconine, nicotine, and *l-sec.*-butylamine (Pope and Gibson, J., 1912, **101**, 1704) are $[\alpha]_D$ + 23·0°, − 77·9°, and − 5·0°, respectively, and the corresponding values for the ammonium kations are, respectively, − 8·8°, + 23·1°, and + 2·8°. Similarly in chloroform the free base hydrastine has $[\alpha]_D$ − 63·8°, whereas for the sulphate in the same solvent the value is + 7·44°. It seems reasonable to suppose, therefore, that the lævorotation of solutions of *d*-camphor in concentrated sulphuric acid is due, not to the free camphor molecule, but to either the oxonium kation $\mathrm{C_9H_{16}}\overset{\oplus}{\overbrace{\mathrm{C{:}OH}}}$ or the corresponding ψ-salt $\mathrm{C_9H_{16}C(OH){\cdot}O{\cdot}SO_3H}$, the condition of the ketone in this solvent being represented by equilibria precisely analogous to those previously postulated for various aromatic carbonyl derivatives:

$$\begin{matrix}\mathrm{HO{\cdot}SO_3H}\ + \\ \mathrm{C_9H_{16}C{:}O}\end{matrix} \rightleftharpoons \mathrm{C_9H_{16}C(OH){\cdot}O{\cdot}SO_3H} \rightleftharpoons \begin{matrix}\mathrm{C_9H_{16}}\overset{\oplus}{\overbrace{\mathrm{C{:}OH}}} + \\ \overset{\ominus}{\mathrm{O}}\mathrm{{\cdot}SO_3H}\end{matrix}$$

Soluble ←——— Insoluble in ligroin ———→

Considerable support for this hypothesis has been obtained by the application of the partition methods previously employed. The results for the partition of *d*-camphor between ligroin (b. p. 100—

120°) and sulphuric acid are in Table I. The camphor in the ligroin layer was determined by measurements of the optical rotation (see p. 2927).

TABLE I.

Partition of *d*-camphor between ligroin (20 c.c.) and sulphuric (5 c.c.) or phosphoric (5 c.c.) acid at 19°.

Camphor, g.	Conc. of acid, %.	*d*-Camphor, %, in the ligroin layer, without NH_4 salt.	with NH_4 salt.
0·9102	H_2SO_4 100	0·7	0·9
(1·2682	100	0·2	0·9) *
0·9102	90	0·5	9·0
0·9102	85	1·3	26·9
(1·2682	85	1·1	22·2) *
0·9102	78	12·9	90·1
(1·2682	78	12·1	94·5) *
0·3641	100	1·8	1·9
0·3641	90	1·3	11·5
0·3641	85	2·7	65·4
0·0910	100	1 †	4 †
0·0910	90	5 †	20·9
0·0910	85	4 †	60·4
0·9102	H_3PO_4 98	10·5	43·0
0·9102	88	58·6	100·0

* Values obtained with the same sample of *d*-camphor but before purification.

† These values are only approximate owing to the small concentration of camphor and rotation values.

The close similarity of these results to those previously obtained with aromatic carbonyl derivatives is at once apparent, the equilibria being displaced from right to left either by dilution of the sulphuric acid or by the common-ion effect of added ammonium sulphate. Moreover, the observation that the partition coefficient between ligroin and sulphuric acid of any particular concentration varies with the concentration of the camphor is additional evidence that the solution in the acid is not a purely physical one.

It is evident that none of the arguments brought forward by Lucas (*loc. cit.*) against the possibility of chemical combination is valid if oxonium salt formation is involved. Thus (1) and (2) are obviously irrelevant, and with regard to (3) and (4), addition of either water or the very weak acid, acetic, would displace the equilibria in favour of free camphor—a specimen so recovered from sulphuric acid solution, after washing and drying but without further purification, had a dextrorotation identical with that of the original sample.

Lucas also observed a small but definite lævorotation ($[\alpha]_D$ — 1·5°) of *d*-camphor in solution in 87% phosphoric acid. That this results from a precisely analogous salt formation (cf. preceding paper) is confirmed by the similar results obtained in the partition of *d*-camphor between ligroin and phosphoric acid which are included in the table above. In this case, moreover, a crystalline camphor phosphate [probably the ψ-salt $C_9H_{16}C(OH){\cdot}O{\cdot}PO_3H_2$] can actually be isolated. The much lower value of the lævorotation and the relatively larger proportion remaining in the ligroin layer both suggest that, under the experimental conditions employed, the salt-forming power of phosphoric acid is much less than that of sulphuric (cf. Part III, *loc. cit.*).

From the above results it is evident that the dissymmetry of the force field around the asymmetric carbon atom in *d*-camphor, causing dextrorotation of the plane of polarisation, is reversed by conversion of the $C{:}O$ group into the kation $\cdot\overset{\oplus}{\overbrace{C{:}OH}}$, and it would be expected, therefore, that the opposite dissymmetry present in *l*-camphor would be similarly inverted on salt-formation and that a solution of *l*-camphor in sulphuric acid would be dextrorotatory. This is actually the case, a sample having $[\alpha]_{5461}$ − 70·9° in ligroin giving a value $[\alpha]_{5461}$ + 75·4° in 95% sulphuric acid.

If this explanation of the change in sign of rotation of camphor in sulphuric acid solution is correct, it would be expected that a similar change would be observed in esters of active camphoric acids, but that the magnitude of such a change would be smaller owing to the more weakly basic character of carbonyl oxygen when present in an ester group. It was found that the effect of salt formation is not sufficient actually to reverse the sign of rotation, but the large dextrorotation, $[\alpha]_{5461}$ + 60·3°, of methyl *d*-camphorate in ligroin solution is reduced to + 7·5° in sulphuric acid solution.

In view of these results, the interesting observation of Carr and Reynolds (*loc. cit.*) that the rotation of hydrastine changes from + 115·0° in 50% alcohol, through zero in 95% alcohol, to − 49·8° in absolute alcohol (similar changes being observed in acetone) suggests that possibly a definite chemical compound, readily hydrolysed by water is formed between the base and the solvent and that it is this compound which is responsible for the lævorotation observed in the anhydrous solvent.

EXPERIMENTAL.

Preparation of Materials.—A.R. Camphor supplied by British Drug Houses Ltd. was purified by Lucas's method (*loc. cit.*) and sublimed. The author thanks Professor C. K. Ingold, F.R.S., for the gift of a small specimen of *l*-camphor, which was of sufficient purity to give a colourless solution in H_2SO_4 and was used without further purification. Methyl *d*-camphorate was prepared by esterification of *d*-camphoric acid with MeOH and H_2SO_4, removal of the large quantity of acid ester formed with Na_2CO_3 aq., and repeated fractionation. The sample used had b. p. 109°/2 mm. The H_2SO_4 and H_3PO_4 were prepared and their concns. determined as described in previous papers.

Rotation of d-*Camphor in Ligroin Solution.*—In agreement with Lucas it was found that, although the sp. rotation of *d*-camphor is independent of the concn. over a considerable range (from $c = 4·5$ to $c = 1$), it increases rapidly at low concns. The following vals. were obtained in a 2 dcm. tube for the Hg green line, the usual precautions being taken.

c (g./100 c.c.)	4·5511	3·6409	1·8204	0·9102
$\alpha^{22°}_{5461}$	6·69°	5·42°	2·68°	1·39°
$[\alpha]^{22°}_{5461}$	73·5°	74·4°	73·6°	76·4°
c (g./100 c.c.)	0·4551	0·2276	0·1138	0·0228
$\alpha^{22°}_{5461}$	0·72°	0·40°	0·20°	0·04°
$[\alpha]^{22°}_{5461}$	79·1°	87·9°	90·1°	87·8°

In the partition expts. the amount of *d*-camphor in the ligroin layer was determined by measurement of the rotation of the solution and reference to the smoothed curve obtained from these observations.

The rotations of *l*-camphor and methyl *d*-camphorate in various solvents (2 dcm. tube) are summarised below.

	Solvent.	c (g./100 c.c.).	α_{5461}.	$[\alpha]_{5461}$.
l-Camphor	Ligroin	3·6402	−5·16°	−70·9°
	95·4% H_2SO_4	3·4904	+5·26	+75·4
Methyl *d*-camphorate	Ligroin	3·3980	+4·10	+60·3
	95·4% H_2SO_4	3·3984	+0·51	+ 7·5

Partition Experiments.—Partition between ligroin (b. p. 100—120°, free from aromatic hydrocarbons) and either H_2SO_4 or H_3PO_4 was effected in a manner exactly similar to that described in previous parts of this series. The results, at room temp. (19° ± 0·5°), are in Table II, whence the results in Table I are obtained.

TABLE II.

Partition of *d*-camphor between ligroin and H_2SO_4 or H_3PO_4.

Ligroin = 20 c.c. H_2SO_4 = 5 c.c. $(NH_4)_2SO_4$ = 2 g.

		Data relating to the ligroin layer.			
		α_{5461} (2 dcm. tube).		Wt. of camphor, g.	
Camphor, g.	Conc. of H_2SO_4, %.	(a) Without Am_2SO_4.	(b) With Am_2SO_4.	(a).	(b).
0·9102	99·8	0·05°	0·07°	0·006	0·008
(1·2682	99·8	0·02	0·09	0·002	0·011) *
0·3641	99·8	0·05	0·06	0·006	0·007
0·0910	99·8	0·01	0·03	0·001	0·003
0·9102	90·1	0·04	0·66	0·005	0·082
0·3641	90·1	0·04	0·37	0·005	0·042
0·0910	90·1	0·05	0·17	0·006	0·019
0·9102	85·3	0·10	1·85	0·012	0·245
(1·2682	85·3	0·12	2·12	0·014	0·282) *
0·3641	85·3	0·08	1·80	0·010	0·238
0·0910	85·3	0·03	0·47	0·003	0·055
0·9102	78·1	0·91	6·06	0·1175	0·8202
(1·2682	78·1	1·19	8·62	0·153	1·120) *
0·9102	97·8 †	0·76	2·91	0·096	0·391
0·9102	88 †	3·96	6·69	0·533	0·9102

* Unpurified sample of camphor. † H_3PO_4 and $(NH_4)_2HPO_4$ used.

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THE UNIVERSITY, LEEDS.

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