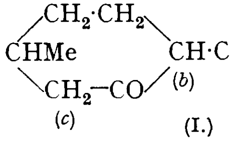
77. *Acid Catalysis in Non-aqueous Solvents. Part V. The Inversion of Menthone in Chlorobenzene Solution.*

By R. P. Bell and E. F. Caldin.

The inversion of *l*-menthone in chlorobenzene at 99·4° has been studied kinetically in presence of the following acids : mono-, di-, and tri-chloroacetic, *o*-nitrobenzoic, benzoic, and picric. For the carboxylic acids there is a relation between the catalytic power in chlorobenzene and the dissociation constant in water, but the catalytic power of picric acid is much less than predicted from this relation. The degree of complex formation between menthone and mono-, di-, and tri-chloroacetic, phenylpropiolic, *m*-nitrobenzoic, benzoic, and acetic acids was investigated in chlorobenzene solution at room temperature, partly by cryoscopic measurements, and partly by observing the instantaneous change of rotation on adding the acid. There is an approximate correlation between the degree of complex formation and the dissociation constant of the acid in water, indicating that the complex formation is a protolytic reaction. The existence of this initial protolytic equilibrium is in harmony with previous views on the mechanism of prototropic reactions of this type.

Previous parts of this series (I, Bell, *Proc. Roy. Soc.*, *A*, 1934, **143**, 377 ; II, Bell and Levinge, *ibid.*, 1935, **151**, 211 ; III, Bell and Brown, J., 1936, 1520 ; IV, Bell, Lidwell, and Vaughan-Jackson, *ibid.*, p. 1792) have dealt with migrations in the *N*-halogenoacylanilide series and with the depolymerisation of paraldehyde. It was desired to extend the work to prototropic reactions of the type $>CH-C=O \rightleftharpoons >C=C-OH$, which have already proved of great interest in the study of general acid–base catalysis (cf. Dawson *et al.*, J., 1926—1936; Pedersen, *J. Physical Chem.*, 1933, **37**, 751; 1934, **38**, 581, 601). In most of the kinetic work on this system the rate of prototropic change has been measured in aqueous solvents by the rate of halogenation of the substances concerned. This method is not practicable in non-dissociating solvents on account of the enormous catalytic effect of the halogen acid produced in the reaction (which in water or similar solvents is converted into the less active solvated hydrogen ion). We have therefore used the rate of change of optical activity, which in the case of the racemisation of various ketones has been shown to equal the rate of halogenation (Ingold and Wilson, J., 1934, 773 ; Bartlett and Stauffer, *J. Amer. Chem. Soc.*, 1935, **57**, 2580 ; Hsü and Wilson, J., 1936, 623).

Menthone (I) contains two centres of asymmetry, (*a*) and (*b*). Prototropic changes may occur between the carbonyl group and either of the carbon atoms (*b*) or (*c*), but of these only the former will lead to inversion. [Comparisons of the rates of inversion and of bromination (Bartlett and Vincent, *J. Amer. Chem. Soc.*, 1933, **55**, 4992) have in fact shown that 80% of the total prototropic change involves atom (*b*), though this figure is not of importance in the present work.] The kinetics of this inversion have been investigated by Tubandt (*Annalen*, 1905, **339**, 41 ; 1907, **354**, 259 ; 1910, **377**, 303), whose results deal chiefly with alcoholic solvents and basic catalysts and do not establish the presence of general acid or basic catalysis. The present work deals with catalysis by a number of acids



(I.)

in chlorobenzene solution at 99·4° : in these solutions there are no complications due to protolytic reactions between the catalyst and the solvent. Complex formation between the acids and the ketone has also been studied.

EXPERIMENTAL.

Materials.—*l*-Menthone was prepared by the oxidation of *l*-menthol (" Organic Syntheses," Vol. I, 333) and purified by fractional distillation in a vacuum. A product of b. p. 83—84°/9—10 mm. was obtained in 65% yield. The pure liquid had $[\alpha]_D$ = − 28·6° (Beilstein gives − 28°), and an alcoholic solution $[\alpha]_D$ = − 25·0° (Tubandt gives − 24·8°).

Chlorobenzene was dried over phosphoric oxide and fractionally distilled, the final product boiling within 0·2°. *p*-Chlorotoluene was redistilled twice in an all-glass apparatus and boiled within 0·1°.

Di- and tri-chloroacetic and *m*-nitro- and *m*-chloro-benzoic acids were pure commercial specimens. *o*-Nitrobenzoic acid was recrystallised from aqueous alcohol, benzoic acid from toluene, and monochloroacetic acid twice from benzene. Phenylpropiolic acid was prepared from cinnamic acid (" Organic Syntheses," Vol. XII, 37, 60) and recrystallised from water. All materials and solutions were kept in desiccators.

Measurement of Reaction Velocity.—The rotation was measured with a Schmidt and Haensch polarimeter, a sodium lamp being used as a source of light. Each reading was the mean of 4—6 settings, and was accurate to about 0·01°. The value of $[\alpha]_D$ for solutions of *l*-menthone in chlorobenzene was found to be independent of concentration. It was also shown by Tubandt (*loc. cit.*) that the rotations of *l*-menthone and *d*-*iso*menthone are additive.

The table of the polarimeter was removed to accommodate a small metal thermostat containing medicinal paraffin, controlled to 99·4° ± 0·05°. Two polarimeter tubes (100 mm. with adhesed ends) were cemented into short copper tubes soldered into the front and back of the thermostat. Considerable difficulty was experienced in finding a cement which would adhere to glass and copper and also be unaffected by paraffin at 100° over long periods. The proprietary cement " Semmentum " (left to harden for a few hours and then baked at 110°) was eventually found to be satisfactory. The same cement was used to attach a vertical glass tube to the filling aperture of the polarimeter tube, which could be closed below thermostat level by a ground-in glass plug. The whole thermostat could be moved laterally by a rack-and-pinion device in order to bring one or other of the two tubes into the field of view of the polarimeter.

Tests with a thermocouple showed that the temperature did not vary by more than 0·1° from one part of the polarimeter tube to another, and it was found that a solution acquired thermostat temperature to within 0·1° about 10 minutes after being introduced into the polarimeter tube. Some of the slowest experiments were carried out in the vessels previously described by Bell and Levinge (*loc. cit.*), which were periodically removed from the thermostat and cooled, polarimeter measurements being made at room temperature. By observing the rates of heating and cooling, it was possible to allow approximately for the amount of reaction occurring during this period : the time correction amounted only to about one minute for each reading.

In each reaction 20—40 readings were taken, and the first-order velocity constant calculated by Guggenheim's method (*Phil. Mag.*, 1926, **2**, 538). The first set of readings normally covered 60—90% of the reaction, and no significant deviations from a unimolecular course were observed. Table I gives the individual readings for a typical reaction, the calculated values of Δr being given by $\log_{10} \Delta r = 0{\cdot}412 - 0{\cdot}00311t$.

Kinetic results. Stability tests showed that, in the absence of acid, chlorobenzene solutions of menthone exhibit no change in rotation over the longest period employed in the catalytic experiments. The results obtained in acid solutions are given in Tables II and III. Table II

TABLE I.

0·0201N-Trichloroacetic acid; 6·90% menthone.

Time (mins.).	Δr.		Diff.	Time (mins.).	Δr.		Diff.	Time (mins.).	Δr.		Diff.
	Calc.	Obs.			Calc.	Obs.			Calc.	Obs.	
20	2·24°	2·22°	+0·02°	95	1·31°	1·33°	−0·02°	169	0·77°	0·77°	±0·00°
32	2·06	2·02	+0·04	108	1·19	1·23	−0·04	180	0·71	0·72	−0·01
46	1·86	1·87	−0·01	120	1·10	1·09	+0·01	182	0·70	0·69	+0·01
60	1·68	1·70	−0·02	130	1·02	1·05	−0·03	190	0·66	0·67	−0·01
75	1·51	1·51	±0·00	142	0·94	0·94	±0·00	202	0·61	0·59	+0·02
87	1·39	1·41	−0·02	156	0·85	0·83	+0·02				

contains results for various menthone concentrations, while for results in Table III the menthone concentration was kept constant at 6·2 ± 0·2%. The symbols used are : x = menthone concentration, weight %; c = acid concentration, moles per 1000 g. of solution; k = first-order velocity constant, mins.$^{-1}$, $\log_{10}$.

TABLE II.

Dichloroacetic acid.				*Trichloroacetic acid.*			
c.	*x.*	10^4k (obs.).	10^4k (calc.).	*c.*	*x.*	10^4k (obs.).	10^4k (calc.).
0·053	0·0	(31·5)	—	0·020	0·0	(49·3)	—
	3·48	27·9	25·2		4·52	33·9	36·6
	6·25	20·4	20·1		5·40	37·5	34·1
	8·77	13·7	15·7		6·15	27·0	32·1
0·069	0·0	(44·6)	—		6·90	31·6	30·2
	4·36	38·4	33·4		7·80	29·6	27·7
	6·00	26·4	29·5	0·029	0·0	(84·8)	—
	7·71	24·9	25·0		4·68	56·9	61·8
	9·57	19·3	20·1		6·24	49·9	54·2
0·107	0·0	(94·5)	—		7·35	54·9	49·2
	3·41	81·8	76·3		8·75	44·5	42·4
	6·30	65·7	60·7	0·051	0·0	(180)	—
	8·80	39·8	47·5		4·61	128	134
0·138	0·0	(140)	—		6·15	116	117
	3·49	117	112		7·92	104	99·2
	4·91	99·5	101				
	6·40	96·0	88·5				
	7·40	76·0	81·2				
	8·75	66·7	70·0				

TABLE III.

Benzoic acid.							
c	0·068	0·199	0·304	0·400	0·654		
10^4k (obs.)	1·11	2·43	3·02	4·36	5·38		
10^4k (calc.)	1·15	2·35	3·16	3·85	5·44		
m-*Chlorobenzoic acid.*							
c	0·111	0·156	0·218	0·258	0·288	0·391	
10^4k (obs.)	3·20	3·90	4·82	5·80	6·02	7·30	
10^4k (calc.)	3·17	3·93	4·90	5·50	5·95	7·38	
Monochloroacetic acid.							
c	0·110	0·163	0·214	0·252	0·276	0·336	0·371
10^4k (obs.)	5·3	8·3	13·0	14·8	24·3	22·9	33·2
10^4k (calc.)	4·8	8·2	12·3	15·9	18·4	25·1	29·5
o-*Nitrobenzoic acid.*							
c	0·112	0·172	0·207	0·256	0·275	0·297	
10^4k (obs.)	12·1	21·4	27·5	28·1	34·1	41·7	
10^4k (calc.)	11·5	19·7	25·2	33·6	37·1	41·4	
Dichloroacetic acid.							
c	0·0097	0·0212	0·0295	0·0395	0·0526	0·0594	0·068
10^4k (obs.)	1·8	8·2	9·6	19·2	19·9	24·0	25·0
10^4k (calc.)	2·2	5·8	9·6	13·4	20·2	24·3	29·8
c	0·078	0·103	0·138				
10^4k (obs.)	35·5	61·4	93·8				
10^4k (calc.)	37·0	58·0	89·8				
Trichloroacetic acid.							
c	0·0104	0·0194	0·0288	0·0384	0·0485	0·0505	
10^4k (obs.)	11·4	25·8	56·7	89·0	106·5	90·0	
10^4k (calc.)	11·3	27·1	49·3	78·1	114	122	
Picric acid.							
c	0·099	0·149	0·194	0·245			
10^4k (obs.)	10·5	20·5	28·0	49·0			
10^4k (calc.)	10·4	20·1	31·6	48·0			

Effect of Menthone Concentration.—The results in Table II show a linear variation of velocity constant with menthone concentration. Moreover, all the results can be expressed approximately by

$$k = k_0(1 - \gamma x) \qquad (1)$$

where γ is independent of the acid concentration and is given the same value for catalysis by trichloro- and dichloro-acetic acids. The last column of Table II contains the values of k calculated from equation (1) with $\gamma = 0{\cdot}057$ throughout. The extrapolated values of k_0 are shown in parentheses.

Effect of Acid Concentration.—Since the menthone was found to exert a constant "medium effect" in catalysis by both tri- and di-chloroacetic acids at different concentrations, the remainder of the catalytic experiments were carried out at a constant menthone concentration of about 6%, giving a total change in rotation of about 2°. The velocity constants thus obtained should be comparable, and can be used to determine the effect of the nature and concentration of the catalyst.

It is clear from Table II that the velocity is not in general proportional to the acid concentration, varying sometimes more and sometimes less rapidly than a linear relation demands. This behaviour has not been fully accounted for, but for the purpose of comparing the catalytic power of different acids we have expressed the results by one of the two following equations :

$$k = k_A c + a\sqrt{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$k = k_A c + bc^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where k_A, a, and b are all positive constants. The best values of these constants were determined graphically and are given in Table IV, together with the dissociation constants of the acids.

TABLE IV.

Acid.	10^4a.	10^4k_A.	b.	K_A. 25°.	K_A. 100°.
Benzoic	3·3	4·4	—	$6{\cdot}6 \times 10^{-5}$	$4{\cdot}5 \times 10^{-5}$
m-Chlorobenzoic	6·8	8·0	—	$1{\cdot}6 \times 10^{-4}$	—
Monochloroacetic	—	28	0·014	$1{\cdot}6 \times 10^{-3}$	$4{\cdot}7 \times 10^{-4}$
o-Nitrobenzoic	—	80	0·020	$6{\cdot}3 \times 10^{-3}$	$1{\cdot}6 \times 10^{-3}$
Dichloroacetic	—	200	0·35	$5{\cdot}5 \times 10^{-2}$	(5×10^{-3})
Trichloroacetic	—	740	3·4	8×10^{-1}	—
Picric	—	58	0·062	—	—

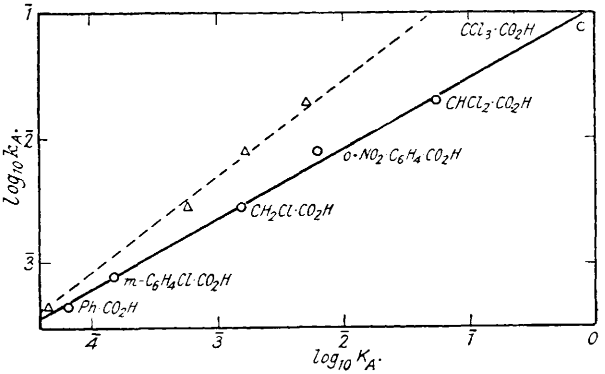
The values of k calculated from these equations are given in Table III. There are no systematic discrepancies, though in a few cases the deviations are considerably greater than the expected experimental error.

Equations (2) and (3) must be regarded as largely empirical, though it is possible to obtain some sort of justification for the non-linear terms. For instance, carboxylic acids are known to exist largely as double molecules in hydrocarbon solvents, and if the prototropic change involves the interaction of menthone with a single acid molecule, a term proportional to $\sqrt{c}$ will result. Similarly, the term in c^2 may be interpreted as a linear medium effect. It is probable that the complete theoretical expression for the variation of k with c would involve at least three terms, especially in view of the results on complex formation described below. However, the kinetic data are not sufficiently accurate or extensive to warrant the use of a more complicated expression, and it should be emphasised that the value of the coefficient k_A in the linear term will not be much affected by the form adopted for the rest of the equation. We may therefore use the k_A coefficients for comparing the catalytic power of different acids.

The Relation between Catalytic Power and Acid Strength.—Recent work on protolytic equilibria in aprotic solvents (cf. Bell, *Ann. Reports*, 1934, **31**, 79) indicates that the dissociation constants in water can be used as an approximate measure of the relative strengths of acids in these solvents. [There is in any case some justification for using the values in water as a measure of the "intrinsic" strength : cf. Wynne-Jones, *Proc. Roy. Soc.*, 1933, *A*, **140**, 440 : Bell, *Ann. Reports*, 1934, **31**, 78.] These dissociation constants (at 25°) are given in col. 5 of Table IV. For all the carboxylic acids studied there is clearly a correlation between the catalytic constant k_A and the dissociation constant K_A, and the plot of $\log_{10} k_A$ against $\log_{10} K_A$ (Fig. 1; circles) shows that this relation is a quantitative one of the type first proposed by Brönsted and Pedersen (*Z. physikal. Chem.*, 1924, **108**, 185). The slope of the heavy straight line in Fig. 1 is 0·6.

[It would be more satisfactory to use dissociation constants relating to the temperature of the kinetic experiments (*ca.* 100°) in place of those at 25°. Actual measurements at or near 100° are available only for benzoic and *o*-nitrobenzoic acids (cf. Landolt–Börnstein's "Tabellen"), but for monochloroacetic acid there are accurate measurements in the range 0—40° (Wright, *J. Amer. Chem. Soc.*, 1934, **56**, 314) which can be extrapolated to 100° with some confidence by means of the empirical relation proposed by Harned and Embree (*ibid.*, p. 1050). For dichloroacetic acid a tentative value at 100° can be derived by extrapolating the values given up to 45° by Bell and Baughan (*Proc. Roy. Soc.*, 1937, *A*, **158**, 464) on the basis of catalysis by the dichloroacetate ion. These four values are given in the last column of Table IV and are plotted as triangles in Fig. 1. It appears that the use of dissociation constants at 100° would increase the exponent of the Brönsted relation, the broken line in the figure having a slope of 0·75.]

FIG. 1.



Picric acid has a very much smaller catalytic effect than would be expected from its strength in water. The same behaviour has been observed in other catalysed reactions in non-aqueous solvents (Brönsted and Bell, *J. Amer. Chem. Soc.*, 1931, **53**, 2478; Bell, *Proc. Roy. Soc.*, 1934, *A*, **143**, 377; where the causes of this anomaly are discussed).

The Reaction Mechanism.—The mechanism of the prototropic change may be represented by the scheme

$$>\!CH{\cdot}CO\!- + HA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left\{\begin{matrix} >\!CH{\cdot}C(OH^+)\!- \\ >\!CH^+{:}C(OH)\!- \end{matrix}\right\} + A^- \quad . \quad . \quad . \quad . \quad (4)$$

$$\xrightarrow{k_3} >\!C{:}C(OH)\!- + HA$$

where the ion represented in brackets is a single species having a configuration intermediate between the two formulæ given: k_1, k_2, and k_3 are the bimolecular velocity constants for the processes concerned. For a reaction taking place in aqueous solution, the base which removes a proton from the ion is most likely to be a water molecule, but in an aprotic solvent like chlorobenzene the only base available is the anion of the catalyst acid; moreover, owing to the low dielectric constant of the medium this anion will not exist in a free state but will be associated with the cation formed from the ketone. Lowry's view that prototropic change demands the simultaneous presence of an acid and a base thus requires a special interpretation in the present case, since the addition of an acid alone serves to effect both the addition and the removal of a proton.

The removal of a proton from the cation may take place from either the oxygen or the carbon atom, and it is only in the latter case that racemisation will take place. If $k_2 \ll k_3$ the rate of racemisation will be determined by the rate of formation of the cation, and we are dealing with a true general acid catalysis. If, on the other hand, $k_2 \gg k_3$ the cation will be in equilibrium with the ketone and the rate is determined by the rate at which it loses a proton from the carbon atom; *i.e.*, we are actually measuring general basic catalysis of the cation. These possibilities have been considered by various authors (Pedersen, *J. Physical*

Chem., 1934, **38**, 581; *Trans. Faraday Soc.*, 1938, **34**, 237; Bonhoeffer and Reitz, *Z. physikal Chem.*, 1937, *A*, **179**, 135), who conclude that the latter case is the one applicable to prototropy in ketones, since the electronic structure of the cation will be nearly the same as that of the keto-form (cf. also Nathan and Watson, J., 1933, 217). The observed acid catalytic constant k_{A} can thus be written in the form

$$k_{\mathrm{A}} = k_1k_3/k_2 = Kk_3 \qquad (5)$$

where K is the equilibrium constant for the protolytic equilibrium between acid and ketone, and k_3 a catalytic constant for reaction of the ketone cation with the basic anion A^-. If K_{A} is the dissociation constant of the acid in water, then for a series of similar acids we should expect the following relations to hold approximately

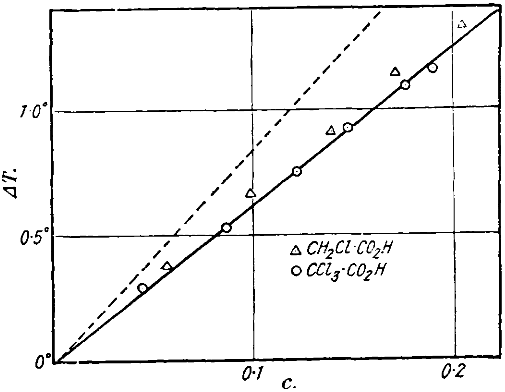
$$K \propto K_{\mathrm{A}};\; k_3 \propto (1/K)^{\alpha}\ (\alpha < 1) \qquad (6)$$

leading to the observed relation between catalytic power and acid strength

$$k_{\mathrm{A}} \propto K_{\mathrm{A}}^{1-\alpha} \qquad (7)$$

Study of Complex Formation.—It has also been found possible to observe directly the initial protolytic equilibrium between the ketone and the acid. It is usually assumed that in reactions of this kind the amounts of the intermediate cation present are very small, and this is probably the case in aqueous solution; however, in the present case there were indications of appreciable interaction with strong acids even at 99·4°, since if the rotations of menthone solutions containing tri- or di-chloroacetic acid were extrapolated back to zero time, the values obtained were always smaller than the value for pure menthone in chlorobenzene. This extrapolation was, however, inaccurate, and investigations were therefore carried out at lower temperatures, where the inversion is very slow and the reaction between ketone and acid will take place to a greater extent.

FIG. 2.



In a solvent of low dielectric constant the cation and anion shown in equation (4) will not exist independently, but will be present as an ion-pair. It should therefore be possible to detect this complex formation by cryoscopic measurements. Chlorobenzene itself melts at — 45°, and measurements were therefore made in the very similar solvent *p*-chlorotoluene (m. p. 6·86°), using the method previously described (Bell, Baughan, and Vaughan-Jackson, J., 1934, 1969). The results obtained are given in Table V.

TABLE V.

Trichloroacetic acid + menthone; equimolecular proportions.							
c	0·044	0·086	0·121	0·147	0·176	0·190	
ΔT	0·29°	0·53°	0·75°	0·92°	1·09°	1·15°	
Monochloroacetic acid + menthone; equimolecular proportions.							
c	0·056	0·098	0·138	0·171	0·204		
ΔT	0·37°	0·66°	0·91°	1·14°	1·33°		
Trichloroacetic acid + menthone; proportions M + 2A.							
c	0·090	0·128	0·156	0·181	0·218	0·242	0·274
ΔT	0·33°	0·45°	0·56°	0·64°	0·76°	0·86°	0·98°
ΔT (calc.) (*a*)	0·27	0·38	0·46	0·54	0·65	0·72	0·81
ΔT (calc.) (*b*)	0·41	0·58	0·70	0·81	0·98	1·09	1·24

The freezing-point depressions for mixtures of menthone with equivalent quantities of tri- and mono-chloroacetic acids are plotted in Fig. 2, and the full and the broken line represent the theoretical relations for complete and zero association respectively. It is clear that complex formation is complete with trichloroacetic and less complete with monochloroacetic acid. However, the carboxylic acids are present almost exclusively as double molecules at the concentrations studied (cf. Bell, Baughan, and Vaughan-Jackson, *loc. cit.*), so these results do not distinguish between the two types of association :

$$\left.\begin{array}{l}(a)\ 2\mathrm{M} + (\mathrm{HA})_2 \longrightarrow \mathrm{M} + \mathrm{M(HA)}_2\\ (b)\ 2\mathrm{M} + (\mathrm{HA})_2 \longrightarrow 2\mathrm{M(HA)}\end{array}\right\}3\text{ mols.} \longrightarrow 2\text{ mols.} \quad . \quad . \quad (8)$$

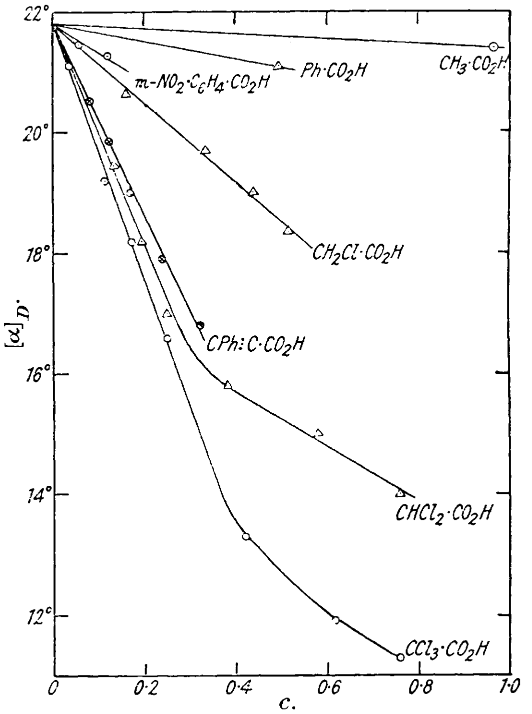
It was hoped to decide this point for trichloroacetic acid by experiments with 2 mols. of this acid per mol. of menthone, the two types of association giving

$$(a)\ \mathrm{M} + (\mathrm{HA})_2 \longrightarrow \mathrm{M(HA)}_2\ (2\text{ mols.} \longrightarrow 1\text{ mol.})$$

$$(b)\ 2\mathrm{M} + 2(\mathrm{HA})_2 \longrightarrow 2\mathrm{M(HA)} + (\mathrm{HA})_2\ (4\text{ mols.} \longrightarrow 3\text{ mols.})$$

The results are given in the last section of Table V, together with the freezing-point depressions calculated on the two assumptions (*a*) and (*b*). The experimental results are always intermediate between the two theoretical possibilities. This may indicate that both types of complex are formed; on the other hand, it must be remembered that if the complexes consist of ion-pairs they will deviate considerably from simple thermodynamic behaviour in a medium of low dielectric constant (cf. Fuoss, *J. Amer. Chem. Soc.*, 1934, **56**, 1027), thus making it difficult to interpret the cryoscopic data quantitatively.

Fig. 3.



For comparing the degree of complex formation with a series of acids, we have used the depression of the optical rotation; this is experimentally more convenient and accurate than cryoscopy, and will be less affected by thermodynamic abnormalities. This depression is instantaneous, confirming the view advanced in the last section that the initial transfer of a proton from the acid to the menthone does not determine the rate of inversion. Table VI contains the results obtained in chlorobenzene solution at room temperature, and they are shown graphically in Fig. 3.

TABLE VI.

(Menthone concentration = 6·1 ± 0·2% throughout.)

Trichloroacetic acid.

c	0·036	0·112	0·171	0·252	0·420	0·616	0·762
$[\alpha]_D$	21·1°	19·2°	18·2°	16·6°	13·3°	11·9°	11·3°

Dichloroacetic acid.

c	0·133	0·194	0·256	0·383	0·590	0·760
$[\alpha]_D$	$19{\cdot}4_5^{\circ}$	18·2°	16·8°	15·8°	15·0°	14·0°

Phenylpropiolic acid.

c	0·080	0·120	0·168	0·237	0·322
$[\alpha]_D$	20·5°	$19{\cdot}8_5^{\circ}$	19·0°	17·9°	16·8°

Monochloroacetic acid.

c	0·158	0·332	0·438	0·514
$[\alpha]_D$	$20{\cdot}6_5^{\circ}$	19·7°	19·0°	18·35°

m-*Nitrobenzoic acid.*

c	0·056	0·118
$[\alpha]_D$	$21{\cdot}4_5^{\circ}$	21·3°

Benzoic acid.

c	0·492
$[\alpha]_D$	21·1°

Acetic acid.

c	0·965
$[\alpha]_D$	21·4°

It will be seen that the depressions in $[\alpha]_D$ increase in the same order as the dissociation constants of the acids : this will also be true of the degree of complex formation provided that the rotation of the complex formed be roughly independent of the nature of the acid. This fact agrees with the supposition that complex formation is due to a protolytic equilibrium. As might be expected from the cryoscopic results, both the equilibrium constants calculated on the basis of equation (8) were found to vary considerably with concentration.

The somewhat complicated state of affairs found in these experiments may account partly for the absence of any simple relation between the rate of inversion and the acid concentration, though the degree of complex formation will be considerably smaller at 100° than at room temperature.

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