fringence form a more satisfactory basis for quantitative study. The wave length of isotropy (at which $\epsilon = \omega$) is an important fixed point on the birefringence–wave length curve.

Crossed axial plane dispersion in the near ultraviolet can be detected and measured photographically provided the wave length of uniaxiality is longer than that of the ultraviolet cut-off of the microscope system used. Thiourea becomes uniaxial at 3780 Å. and hence is a good experimental subject. Most organic substances have absorption bands in the ultraviolet and all types of dispersion tend to be intensified as these bands are approached from the high wave length side. For this reason many substances may have strong measurable dispersion in the visible violet or ultraviolet but very little in the balance of the visible spectrum. In such cases the dispersion may acquire sudden prominence over a relatively short wave length interval as illustrated by the sudden appearance of crossed dispersion in stilbene.

Summary

1. The dispersion of the optic axial angle in *trans*-stilbene has been measured. This substance is optically positive for wave lengths above 4070 Å. and optically negative for shorter wave lengths. The rare type of dispersion giving rise to this effect has tentatively been called *axial dispersion with change of sign.* Strong crossed dispersion is also present.

2. Dispersion of the refractive indices α, β, and γ in stilbene has been determined by Merwin's method.

3. The refractive indices ϵ and ω of benzil were measured over a wide range of wave lengths. As shown by Jelley, this substance is optically isotropic at 4205 Å., optically positive above, and negative below this wave length.

4. The optical properties of thiourea have been measured. This compound exhibits crossed axial plane dispersion near 3780 Å. in the ultraviolet.

WILMINGTON, DELAWARE RECEIVED JULY 6, 194

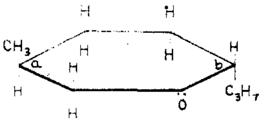
[COMMUNICATION NO. 878 FROM THE KODAK RESEARCH LABORATORIES]

The Inversion of Menthone with Trichloroacetic Acid in Aprotic Solvents

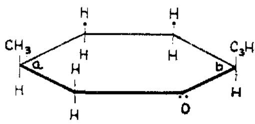
BY A. WEISSBERGER

The reaction of diazoacetic ester with trichloroacetic acid in hexane yielding the trichloroaceto-glycolic ester, $CCl_3CO_2CH_2CO_2C_2H_5$, proceeds through a reactive complex composed of one molecule of the ester and two molecules of the acid.[1,2] The reaction is slowed down considerably by the addition of certain substances like ethers, ketones and alcohols.[2] This effect was attributed to the formation of compounds of the addenda with the acid, and a spectroscopic study of the salt formation of dimethylaminoazobenzene and trichloroacetic acid in benzene[3] corroborated this interpretation. Parallel with these investigations was studied the inversion of menthone.[4] This reaction also can be measured in aprotic solvents, but it differs from the decomposition of diazoacetic ester in some respects. In the latter reaction, carried out in aprotic solvents, the acid becomes part of the reaction product, *i. e.*, it "catalyzes its own reaction,"[5] while in the menthone inversion the reaction product is a stereoisomer of the starting material. It was, therefore, of interest to see whether the reactive complex in the menthone inversion is simpler than in the diazoester decomposition, and to investigate whether addenda have the same or a different effect in both processes. The investigation of the menthone inversion itself is reported in the following.

Menthone, 1-methyl-4-isopropyl-cyclohexane-3-one, has two asymmetric carbon atoms and exists in four optically active isomers. The two pairs of antipodes differ from one another by geometrical isomerism



Menthone



Isomenthone

The *trans* formulas are attributed to menthone,

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[1] Brönsted and Bell, THIS JOURNAL, **53**, 2478 (1931).

[2] Weissberger and Högen, *Z. physik. Chem.*, **A156**, 321 (1931).

[3] Weissberger and Fasold, *ibid.*, **A157**, 65 (1931).

[4] Wonneberger, Dissertation, Leipzig, 1930; Dörken, Dissertation, Leipzig, 1934.

[5] Bell, "Acid–Base Catalysis," Oxford University Press, New York, N. Y., 1941.

the *cis* formulas to isomenthone.[6] The isomerization of *l*- and *d*-menthone under the influence of acids or bases was discovered by Beckmann,[7] and the first rate determinations were made by Vorländer.[8] Tubandt[9] showed that the same equilibrium is reached from a menthone of $(\alpha)^{20}\text{D}$ $-27.75°$ and from a "Rechtsmenthon" of $(\alpha)^{20}\text{D}$ $+27.79°$, and that the reaction velocity is identical in both cases. Tubandt assumed that "Rechtsmenthon" is a mixture of *l*-menthone and of *d*-isomenthone, while Grossman and Brauer[10] took a different view because they observed that "Rechtsmenthon" was not inverted in formic acid. We found that under identical conditions the reaction velocity and the final rotatory power of the equilibrium mixture are identical not only in the inversion of *l*-menthone, and of "Rechtsmenthon" but also of a *d*-isomenthone of $(\alpha)^{20}\text{D}$ $+85.6°$. In formic acid, this *d*-isomenthone was inverted at the same rate as *l*-menthone, and reached the same equilibrium angle as the latter compound. These observations confirm Tubandt's findings. The stability of "Rechtsmenthon" in Grossman and Brauer's experiment was caused by the accident that this menthone was a mixture of *d*-isomenthone and *l*-menthone of, or nearly of, the composition of the equilibrium in formic acid as a solvent.

The rearrangement takes place at the asymmetric carbon atom in the α-position to the carbonyl group (b). It is accompanied by a prototropic change at the other carbon atom adjacent to this group[11] while the arrangement on carbon atom (a) is untouched; the oxidation of both partners of an equilibrium leads to the same ketocarbonic acid.[12] The two diastereoisomers with the higher rotatory power are partners in one equilibrium, those with the small values partners in the other. This agrees with the theory[13] that the carbon atom adjacent to the carbonyl group makes the larger contribution to the activity of the molecule. The activity of the equilibrium mixture is caused by the asymmetry of carbon atom (a), which, in turn, keeps (b) from complete racemization through the formation of diastereoisomers. Identity of the final equilibria under varying conditions is therefore not to be expected.

The inversion proceeds as a first-order reaction[9]

$$dx/dt = kmx - k'm(1 - x) \qquad (1)$$

where m is the total concentration of menthone; x and $1 - x$ are the fractions of the isomers, and k and k′, the velocity coefficients of the opposite isomerizations. The sum k + k′ is determined from the change in rotation of the reacting solution

$$k + k' = \frac{1}{t} \log_{10} \frac{\rho_\infty - \rho_0}{\rho_\infty - \rho_t} \qquad (2)$$

ρ_0, ρ_∞, and ρ_t are, respectively, the rotation angles at the time of the first reading, at equilibrium and at a time t after the first reading.

The rate of the alkali-catalyzed menthone inversion is independent of the menthone concentration and proportional to the alkali concentration, the final equilibrium being identical for all solutions.[9] The inversion with acids is more complicated.

Tubandt[9] found, with hydrochloric and sulfosalicylic acid in ethanol, that the inversion rate falls when the menthone concentration is increased. He suggested that menthone forms compounds with the acids and showed that esterifications with acids as catalysts are slowed down by the addition of menthone. At constant menthone concentration, the inversion velocity in most solvents increases more rapidly than the concentration of the acid. The composition of the final equilibrium between *l*-menthone and *d*-isomenthone is, according to Tubandt, independent of the nature and concentration of the inverting agent and of the menthone concentration, dependent, however, on solvent and temperature. Grossman and Brauer inverted *l*-menthone by addition to various acids without a solvent and found that, after evaporation of the acid, mixtures of different activities remained.

After the completion of the present experiments, Bell and Caldin[14] investigated the menthone inversion in chlorobenzene at 100° and used it for the comparison of different acids. The reaction rate was found to vary linearly with the menthone concentration. At a constant concentration of the menthone, it increased faster or slower than the acid concentration, depending on the conditions. Cryoscopic and polarimetric measurements showed that trichloroacetic acid

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(6) Sugden and Whittaker, *J. Chem. Soc.*, **127**, 1868 (1925); Zeitschel and Schmidt, *Ber.*, **59**, 2301 (1926); Carter, *J. Chem. Soc.*, 1278 (1927); Read. *Chem. Rev.*, VII, 1 (1930).

(7) Beckmann, *Ann.*, **250**, 322 (1889).

(8) Vorländer, *Ber.*, **36**, 273 (1903).

(9) Tubandt, *Ann.*, **339**, 41 (1905); **354**, 259 (1907); **377**, 284 (1910).

(10) Grossman and Brauer, *J. prakt. Chem.*, **98**, 37, 38, 62 (1918).

(11) Bartlett and Vincent, THIS JOURNAL, **55**, 4992 (1933).

(12) Beckmann and Mehrländer, *Ann.*, **289**, 367 (1896).

(13) Freudenberg and Kuhn. *Ber.*, **64**, 703 (1931).

(14) Bell and Caldin, *J. Chem. Soc.*, 382 (1938).

and menthone form a stable complex, and that the complexes formed with other acids are the less stable, the lower the ionization constant of the acid.

Experimental

l-Menthone was prepared from *l*-menthol and distilled *in vacuo*. Four different samples were made. Two of them underwent a further rectification over boric acid.[15] Kinetically, these samples did not behave differently from the others. The rotatory power of the equilibrium mixtures, however, differed owing to the presence of some menthol in the unrectified samples. *d*-Isomenthone was prepared from *d*-isomenthol, for which we thank Messrs. Schimmel and Co., Miltitz. It was rectified over boric acid.

Trichloroacetic acid, solvents and other materials were purified as described by Weissberger and Fasold.[3]

The observations were carried out with a Lippich half-shade polarimeter, allowing readings of 0.01°, in jacketed 200-mm. polarimeter tubes. The temperature was held at 20.0 ± 0.1° by means of a thermostat, unless stated otherwise. The calculations were made according to (2). Some typical experiments are given in detail to show the reproducibility of the rate coefficients and their constancy in a given run.

TABLE I

Menthone, 0.5 mole/liter; trichloroacetic acid, 0.5 mole/liter; benzene

	$\rho_\infty - \rho_0 = 5.81$			$\rho_\infty - \rho_0 = 5.77$	
t, min.	ρ_t	$(k + k')10^4$	t, min.	ρ_t	$(k + k')10^4$
0	−1.31	..	0	−1.28	.
60	−0.83	6.2	60	−0.78	6.6
120	− .35	6.5	120	− .33	6.5
180	+ .06	6.5	180	+ .09	6.5
210	+ .25	6.5	240	+ .46	6.5
240	+ .45	6.5	360	+1.12	6.5
1440	+3.81	6.4	1440	+3.81	6.4
∞	+4.50	..	∞	+4.49	..

Menthone, 0.5 mole/liter; trichloroacetic acid, 2.0 mole/liter; benzene

	$\rho_\infty - \rho_0 = 6.56$			$\rho_\infty - \rho_0 = 6.51$	
0	−0.73	..	0	−0.64	.
20	+0.15	31.3	20	+0.25	31.9
40	+0.92	31.5	30	+0.64	31.7
60	+1.58	31.4	60	+1.66	31.6
90	+2.42	31.6	120	+3.16	31.7
120	+3.09	31.6	180	+4.11	31.6
180	+4.07	31.7	300	+5.15	31.9
∞	+5.83	..	∞	+5.87	.

With constant concentration of menthone and varying concentrations of trichloroacetic acid in benzene as a solvent, the average values of Table II and Fig. 2 are obtained.

Starting with low concentrations of the acid, the reaction velocity increases faster than proportional to the acid concentration. The increase, however, reaches a maximum and falls off with high concentrations of the acid. The maximum lies at a concentration of about two moles of acid per mole of menthone. Table III and Fig. 1 show that this relation is maintained at other menthone concentrations and in other solvents.

TABLE II

Menthone, 0.5 mole/liter; benzene

Trichloroacetic acid, mole/liter	$(k + k')10^4$	$(k + k')10^4$/conc. acid
0.10	0.31	3.1
.25	1.5	6.0
.30	2.1	7.0
.40	3.9	9.8
.50	6.5	13.0
.75	13.3	17.8
.93	17.0	18.3
1.00	18.5	18.5
1.04	19.3	18.6
1.10	20.4	18.6
1.23	22.5	18.3
1.50	26.4	17.6
2.00	31.6	15.8
3.00	39.9	13.3

TABLE III

Trichloroacetic acid, mole/liter	$(k + k')10^4$	$(k + k')10^4$/conc. acid
Menthone, 0.25 mole/liter; benzene		
0.25	4.4	17.6
.40	9.75	24.4
.50	12.7	25.5
.60	15.5	25.8
.70	17.5	25.0
.80	19.5	24.4
1.00	23.7	23.7
Menthone, 0.1 mole/liter; benzene		
0.20	6.8	34.0
.25	8.8	35.2
.30	11.5	38.3
.40	14.6	36.5
.50	16.9	33.8
1.00	26.2	26.2
Menthone, 0.5 mole/liter; hexane		
0.25	2.8	11.2
.50	10.2	20.4
1.00	24.2	24.2
Menthone, 0.25 mole/liter; hexane		
0.5	18.7	37.3
.823	26.8	32.6

The rate of inversion varies with the solvent. Under identical conditions—menthone 0.5 mole/liter, acid 0.5 mole/liter—$(k + k')10^4$ is in hexane 10.2, in benzene, 6.5, and in chloroform, 4.8. The reaction rate falls with the dielectric constant of the solvents. This may be caused by the dependence of the formation of the reactive complex (see below) on the dielectric constant of the surrounding medium. However, other factors may also contribute toward this solvent effect.[16]

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(15) Zeitschel and Schmidt, *Ber.*, **59**, 2298 (1926).

(16) Dimroth, *Ann.*, **377**, 127 (1910); H. v. Halban, "Habilitationsschrift," Würzburg, 1909; Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford, 1933.

TABLE IV

Benzene Acid 0.25 mole/liter		Benzene Acid 0.5 mole/liter		Benzene Acid 1 mole/liter		Hexane Acid 0.5 mole/liter	
Menthone, mole/liter	$(k + k')10^4$	Menthone, mole/liter	$(k + k')10^4$	Menthone, mole/liter	$(k + k')10^4$	Menthone, mole/liter	$(k + k')10^4$
0.1	8.8	0.1	16.9	0.1	26.2	0.1	23.8
.25	4.4	.25	12.7	.25	23.7	.25	18.7
.5	1.5	.5	6.5	.5	18.5	.5	10.2
		1.0	2.3	1.0	9.2		

According to Tubandt, the rate of inversion of menthone in 0.01 *N* alcoholic hydrochloric acid falls by 6% if the menthone concentration is raised from 0.26 to 1.04 moles per liter. Table IV shows that the influence of the menthone concentration on the rate of the reaction with trichloroacetic acid as a catalyst in benzene and in hexane is much more pronounced.

When the menthone concentration rises from 0.1 to 0.5 *M*, the reaction rate in benzene falls to 70.5% if the trichloroacetic acid is 1 *N*, to 38.4% if the trichloroacetic acid is 0.5 *N*, and to 17.0% if the trichloroacetic acid is 0.25 *N*. The (k + k′) values plotted against the menthone concentration lie on a straight line as long as the menthone concentration is lower than the concentration of the acid. If, however, the menthone concentration becomes higher than that of the acid, the retarding effect of the menthone is diminished.

The temperature coefficient of the reaction was determined between 20 and 50° in solutions containing 0.25 mole/liter of menthone and 0.5 mole/liter of trichloroacetic acid as shown in Table V. The activation energy calculated in the usual way is 6,200 cal.

TABLE V

Temp., °C.	ρ_∞	$(k + k')10^4$
19.95	2.56	13.5
29.90	2.44	30.6
40.01	2.34	65.8
49.32	2.27	126.8

The rotation of the equilibrium mixture, ρ_∞, rises with the concentration of the trichloroacetic acid, as shown by Table VI. The increase of the final rotation of a 0.5 molar menthone solution with increasing concentration of the acid is rather steep up to an acid concentration of 1 mole/liter, *i. e.*, an acid menthone ratio of 2. In this region, the curve becomes more flat.

TABLE VI

Menthone, 0.5 mole/liter in benzene

Acid, mole/liter	ρ_∞
0.1	+0.95°
.25	+1.51
.5	+2.22
.75	+2.51
1.0	+2.68
2.0	+2.93
3.0	+3.09

The reason for the dependence might be (1) an effect of the acid on the rotation of the components of the equilibrium, without a shift in the concentrations of the latter, and (2) a change in the position of the equilibrium itself. The following experiments give further information.

A 0.5 molar solution of a mixture of *l*-menthone and *d*-isomenthone in benzene had a rotation of +0.37° in a 100-mm. tube. This rotation increased immediately to +1.4° when the solution was made to contain 2 mole/liter trichloroacetic acid. The value of +1.4° was obtained by extrapolation to the time of mixing because the angle shifted owing to the progressing isomerization.

A completely inverted solution of 0.5 mole/liter of menthone and 0.25 mole/liter of trichloroacetic acid in benzene in a 100-mm. tube rotates +3.02°. When the same volume of 2 molar trichloroacetic acid in benzene is added, the rotation jumps to +4.58° in a 200-mm. tube. From there it shifts at a rate characteristic of the new conditions to the value appropriate for them. These experiments show that both factors mentioned above are responsible for the dependence shown in Table VI.

An idea of the shift in the concentrations of the isomers in the equilibrium mixtures with the acid concentration is given by Table VII. In these experiments the acid was extracted with aqueous sodium bicarbonate solution after equilibrium was reached. It should be noted that the results are not very accurate; small amounts of menthone are taken up by the sodium bicarbon-

TABLE VII

In 100-mm. tube; menthone, 0.5 mole/liter in benzene

Trichloroacetic acid, mole/liter	ρ_∞	ρ_∞ after extraction of the acid
0.1 normal	+0.95	+0.75
.25 normal	+1.50	+ .93
1.0 normal	+2.64	+1.12

ate solution, and the extraction of the different amounts of trichloroacetic acid changes the concentrations of the remaining solutions.

Discussion of Results

It is obvious that the reaction rate is not simply proportional to the concentration of hydrogen ions or of the undissociated acid either in its dimeric or in its monomeric state. The situation of singularities in regions where the ratio of trichloroacetic acid to menthone is 2:1 suggested that the reactive complex might have this composition. The result that the rate of inversion with hydrogen chloride in benzene is proportional to the square of the acid concentration[4] emphasized this suggestion. A number of assumptions were tried for the formation of the ternary complex, for instance, that it is formed from menthone and the dimeric acid. These deductions were not in accordance with the experiments. The evaluation,[17] however, of assumptions which resemble those made about the mechanism of the diazoacetic ester decomposition[2] gave results in good agreement with the experimental values.

Stobbe and Haertel[18] and Kendall and Gibbons[19] showed that ketones and acids form complexes. Tubandt's evidence for acid complexes with menthone was quoted above. The existence of a complex between menthone and trichloroacetic acid in hydrocarbon solution follows from cryoscopic measurements,[14] from the instantaneous effect of the acid on the rotation of menthone, and from the action of menthone in the diazoacetic ester decomposition.[2] We assume that the inversion takes place by interaction of a binary acid–menthone complex with a further molecule of the monomeric acid. Equivalent to this assumption would be the spontaneous rearrangement of an intermediary complex of one molecule of menthone with two molecules of monomeric acid. If A is the monomeric acid, A_2, the dimeric acid, M, the menthone, x, its unreacted fraction, MA, the menthone-acid complex, and [] indicates concentrations, the reaction velocity is

$$\mathrm{d}x/\mathrm{d}t = k[\mathrm{MA}][\mathrm{A}]x - k'[\mathrm{MA}][\mathrm{A}](1 - x) \qquad (3)$$

We write

$$[\mathrm{A}]^2/[\mathrm{A}_2] = K_1 \qquad (4)$$

$$[\mathrm{A}][\mathrm{M}]/[\mathrm{MA}] = K_2 \qquad (5)$$

The total concentrations of menthone (m) and of acid (a) are

$$m = [\mathrm{MA}] + [\mathrm{M}] \qquad (6)$$

$$a = [\mathrm{MA}] + 2[\mathrm{A}_2] + [\mathrm{A}] \qquad (7)$$

From (5) and (6) follows

$$[\mathrm{MA}] = m\,\frac{[\mathrm{A}]}{K_2 + [\mathrm{A}]} \qquad (8)$$

Elimination of $[\mathrm{A}_2]$ through (4) and elimination of [MA] through (8) in (7) gives

$$a = m\,\frac{[\mathrm{A}]}{K_2 + [\mathrm{A}]} + 2\,\frac{[\mathrm{A}]^2}{K_1} + [\mathrm{A}] \qquad (9)$$

Equations (1) and (3) can be written as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = m(\mathrm{k} + \mathrm{k}')\left(\frac{\mathrm{k}}{\mathrm{k} + \mathrm{k}'}\,x - \frac{\mathrm{k}'}{\mathrm{k} + \mathrm{k}'}\,(1 - x)\right) \qquad (1')$$

and

$$\frac{\mathrm{d}x}{\mathrm{d}t} = [\mathrm{MA}][\mathrm{A}](k + k')\left(\frac{k}{k + k'}\,x - \frac{k'}{k + k'}\,(1 - x)\right) \qquad (3')$$

and, since the reaction velocity in the equilibrium is zero, *i. e.*

$$K = \frac{\mathrm{k}'}{\mathrm{k}} = \frac{x}{1 - x} = \frac{k'}{k} \qquad (10)$$

as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = m(\mathrm{k} + \mathrm{k}')\left(\frac{1}{1 + K}\,x - \frac{1}{(1/K) + 1}\,(1 - x)\right) \qquad (1'')$$

and

$$\frac{\mathrm{d}x}{\mathrm{d}t} = [\mathrm{MA}][\mathrm{A}](k + k')\left(\frac{1}{1 + K}\,x - \frac{1}{(1/K) + 1}\,(1 - x)\right) \qquad (3'')$$

Division of (1″) and (3″) gives

$$\mathrm{k} + \mathrm{k}' = (k + k')\,\frac{[\mathrm{A}][\mathrm{MA}]}{m} = (k + k')\,\frac{[\mathrm{A}]^2}{K_2 + [\mathrm{A}]} \qquad (11)$$

To find out whether $(\mathrm{k} + \mathrm{k}')/a$ has a maximum in agreement with the experiment, it is differentiated with respect to a

$$\left(\frac{\mathrm{d}}{\mathrm{d}a}\left(\frac{\mathrm{k} + \mathrm{k}'}{a}\right)\right)_m = \left(\frac{\mathrm{d}((\mathrm{k} + \mathrm{k}')/a)}{\mathrm{d}[\mathrm{A}]}\right)_m \left(\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}a}\right)_m \qquad (12)$$

The second factor on the right-hand side of (12) is always positive, which can be shown by the formation of the reciprocal value $\mathrm{d}a/\mathrm{d}[\mathrm{A}]$ from (9), and it can therefore be neglected in the discussion of the maximum. Using the values for $\mathrm{k} + \mathrm{k}'$ from (11) and for a from (9), we differentiate

$$\frac{\mathrm{d}\,\frac{\mathrm{k} + \mathrm{k}'}{a}}{\mathrm{d}[\mathrm{A}]} = \frac{d}{\mathrm{d}[\mathrm{A}]}\left(\frac{(k + k')[\mathrm{A}]}{m + K_2 + [\mathrm{A}]\left(1 + 2\,\frac{K_2}{K_1}\right) + 2\,\frac{[\mathrm{A}]^2}{K_1}}\right) =$$

$$\frac{(k + k')}{[m + K_2 + [\mathrm{A}]\left(1 + 2\,\frac{K_2}{K_1}\right) + 2\,\frac{[\mathrm{A}]^2}{K_1}}\Big\{m + K_2 +$$

$$[\mathrm{A}]\left(1 + 2\,\frac{K_2}{K_1}\right) + 2\,\frac{[\mathrm{A}]^2}{K_1} - [\mathrm{A}]\left[1 + 2\,\frac{K_2}{K_1} + 4\,\frac{[\mathrm{A}]}{K_1}\right]\Big\} \qquad (13)$$

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[17] In these evaluations, I enjoyed the most valuable assistance of Dr. C. Wagner, to whom I express sincere thanks. I should also like to thank Mr. D. S. Thomas of these Laboratories for his help.—A. W.

[18] Stobbe and Haertel, *Ann.*, **370**, 106 (1909).

[19] Kendall and Gibbons, THIS JOURNAL, **37**, 149 (1915).

The term in { } must equal zero at the maximum, and, solving for $[A]_{max}$, we obtain

$$[A]_{max} = \sqrt{\frac{K_1}{2}(K_2 + m)} \qquad (14)$$

Since (14) has one real positive root, a maximum exists and a_{max} is given by (9).

K_1, the association constant of trichloroacetic acid was calculated from freezing-point determinations of G. v. Frank,[20] and E. Strasser.[21] These authors give the association factor f, *i. e.*, molecules calcd./molecules exp. for a concentration range of 0.023 mole/liter to 0.241 mole/liter. From their values K_1 was calculated according to

$$K_1 = a\frac{\left(\frac{2}{f} - 1\right)^2}{\left(1 - \frac{1}{f}\right)} \qquad (15)$$

with an average of 0.06. For a 0.25 molar solution, we found $f = 1.58$ and $K_1 = 0.048$. A higher degree of association was found by Bell and Arnold,[22] who state that dry trichloroacetic acid in benzene consists essentially of double molecules over the whole concentration range investigated, 0.01–1.5 mole/liter. From measurements of LeFèvre and Vine,[23] on the other hand, a value $K_1 = 0.04$ is obtained. According to these authors, trichloroacetic acid in benzene is less associated than the dichloroacetic acid; this, in turn, less than the monochloro compound, and only acetic acid itself is present almost completely in the dimeric form. It appears that the association of the acid in benzene is the higher, the smaller its ionization in aqueous solution. This suggestion was made by A. Hantzsch[24] and is very plausible indeed. The ionization constant of a carboxylic acid is the higher the less tightly the proton is bound in the carboxylic group. The association of the acid, on the other hand, is caused by the sharing of two protons between two acid molecules. If, in a first approximation, we neglect other factors, we may expect that an acid molecule with a low tendency to keep its proton will also have a relatively low tendency to share the proton of another acid molecule. A high, but limited, association of benzoic acid in benzene, $K = 0.0015$, was found by Wahl and Rouse.[25] Considering the fact that in aqueous solution the ionization constant of benzoic acid lies between that of acetic and monochloroacetic acid, one might surmise that trichloracetic acid is associated to an appreciably lesser degree than benzoic acid. However, in view of these uncertainties, the calculations were carried through with several values of K_1, *viz.*, 0.06, 0.04, 0.01, and even 0.001.

The equilibrium constant K_2 of the menthone acid complex—(5)—for benzene solutions at the freezing point, can be evaluated as follows from freezing-point determinations of benzene with trichloroacetic acid and menthone and with menthone alone, and the association constant of the acid: [M][A] and [MA] in (5) are calculated with m, K_1 and ΔT. σ is the concentration of that part of the acid which is not bound to menthone, Σ, the sum over all concentrations on which depends the freezing point, and C, the molecular freezing-point depression of benzene 5.13. According to (7) and (4)

$$[MA] = a - (2[A_2] + [A]) = a - \sigma \qquad (16)$$

and

$$\Sigma = [A] + [A_2] + [MA] + [M] = \Delta T/C \qquad (17)$$

We call

$$[A] + [A_2] = [A] + ([A]^2/K_1) = \varphi \qquad (18)$$

and consider φ and σ functions of A—according to (18)—with the result

$$\sigma = 1/2(K_1 + 4\varphi - \sqrt{K_1(K_1 + 4\varphi)}) \qquad (19)$$

Since, however, φ is known according to (18), (17), and (6), and because

$$\varphi = (\Delta T/C) - m \qquad (20)$$

[MA] can be calculated according to (18). The values for [M] and [A] now follow from (6) and (18). Table VIII shows the results of the freezing-point determinations in benzene and the values for K_2 obtained with several values for K_1.

According to (14) and (9) and with the values for K_1 and K_2, data for a_{max} are obtained which are compared with the experimental results in Table IX.

The agreement is best with $K_1 = 0.06$ and 0.04, but fair even with much lower values. While the position of the maximum depends strongly on the menthone concentration, it varies relatively little with K_1 and K_2 as long as these values are within the results of the experimental evidences mentioned above. Hence, the theoretical treatment of the assumption that the menthone inversion takes place in a ternary reactive complex

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(20) G. v. Frank, Dissertation, Leipzig, 1922, p. 79.

(21) E. Strasser, Dissertation, Leipzig, 1929, p. 18.

(22) Bell and Arnold, *J. Chem. Soc.*, 1432 (1935).

(23) LeFèvre and Vine, *ibid.*, 1795 (1938).

(24) Private communication.

(25) Wahl and Rouse, THIS JOURNAL, **63**, 3002 (1941).

TABLE VIII

ASSOCIATION CONSTANTS OF THE MENTHONE–ACID COMPLEX IN BENZENE

m	a	ΔT	$\Delta T/C$	φ	K_2 (K_1 = 0.06)	K_2 (K_1 = 0.04)	K_2 (K_1 = 0.01)	K_2 (K_1 = 0.001)
0.109	0.1	0.752	0.147	0.038	0.032	0.032	0.027	0.015
.15	.2	1.183	.231	.081	.035	.037	.034	.020
.25	.2	1.641	.320	.070	.060	.057	.045	.021
.111	.25	1.176	.229	.118	.030	.037	.046	.036
.257	.25	1.731	.338	.081	.041	.040	.027	.0143
.15	.3	1.496	.292	.142	.053	.060	.070	.052
.25	.3	1.849	.350	.110	.048	.046	.038	.013
.273	.5	2.402	.471	.195	.035	.037	.036	.0181

TABLE IX

POSITION OF MAXIMAL ACID REACTIVITY

m	K_1	K_2	$a_{\max\ \exp}$[a]	$a_{\max\ \text{calc}}$
0.1	0.06	0.04	0.32	0.27
	.04	.04	.32	.26
	.01	.04	.32	.21
.25	.06	.04	.55	.56
	.04	.04	.55	.52
	.01	.04	.55	.45
	.001	.014	.55	.39
.50	.06	.04	1.05	1.05
	.04	.04	1.05	1.00
	.01	.04	1.05	0.87

[a] Interpolated from Figs. 1 and 2, experimental curves.

composed of one molecule of the menthone and two molecules of the monomeric acid yields maxima for the rate-acid concentration curves for the various concentrations of menthone which agree well with the experimental results.

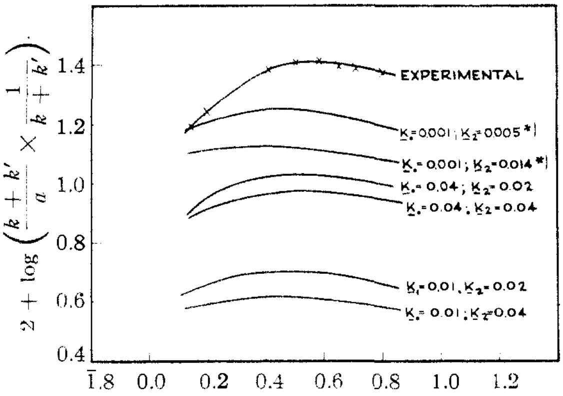


Fig. 1.—Menthone 0.25 mole/liter: xxx, experimental values; *, ordinate = 3 + log $[(k + k')/a\ (1/(k + k'))]$.

In the following, the *shape* of the dependence of the reaction rate acid concentration is studied over the whole range of the latter. The course of (k + k′)/a is investigated as a function of a, using values of K_2 of the order of magnitude just determined, and the curves are compared with the experimental values.

For the calculation, values are given to [A] as parameter. According to (11)

$$\frac{k + k'}{a} = (k + k')\frac{[MA][A]}{ma} \qquad (21)$$

a and [MA] are determined according to 4, 7 and 8. In this comparison it has to be kept in mind that the factor $(k + k')$ in (21) displaces each calculated curve by a value log $(k + k')$ which is constant for each curve. Only the shape of the curve—and the position of the maximum in respect to the abscissa—can, therefore, be considered. The calculated and the experimental values to be compared are given in Figs. 1 and 2.

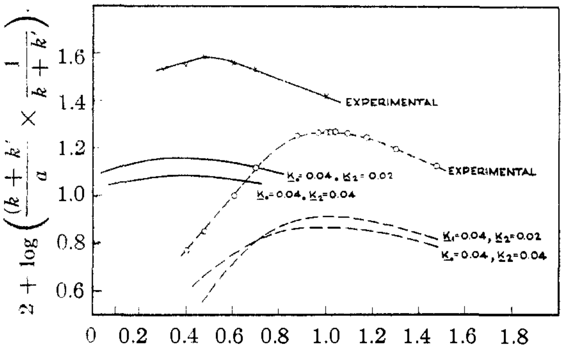


Fig. 2.—Menthone 0.1 mole/liter: xxx, experimental values; --- menthone 0.5 mole/liter: ooo, experimental values.

For m = 0.25, curves were calculated with each of the values mentioned above and the corresponding values for K_2. At higher concentrations of the acid, these curves show good agreement with the observations. The calculated curves are too flat, however, in the region of lower acid concentrations. With K_2 values which are 50% smaller, agreement of the calculated curves with the experimental is obtained over the whole range. If one considers the fact that in the calculation of K_2 the change of the association of the acid by the addition of menthone is neglected, and that small alterations in ΔT have a big effect on

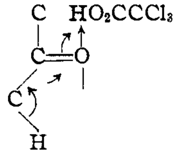
K_2—a 1% alteration of ΔT changes K_2 by almost 15%—the agreement between theory and experiment must be considered as good. Since the curves for $m = 0.25$ show in principle the same behavior with the three values of 0.04, 0.01 and 0.001 for K_1, the curves for $m = 0.1$ and $m = 0.5$ are given for $K_1 = 0.04$ only. The situation with the menthone concentration of $m = 0.5$, at which most of the experiments were made, is similar to that with $m = 0.25$. The calculated value for K_2 shows good agreement with the experimental curve at higher concentrations of the acid. With smaller values for K_2, satisfactory agreement over the whole range is obtained. For a menthone concentration of 0.1 mole/liter, a satisfactory agreement, even for the higher acid concentrations, is obtained with smaller values for K_2 only.

The agreement shown in Figs. 1 and 2 confirms that the racemization of menthone by trichloroacetic acid in hydrocarbons or halogenated hydrocarbons as solvents proceeds in a complex formed by one molecule of the menthone and two molecules of the monomeric acid. This mechanism explains not only the dependence on the acid concentration, but also the observations on the falling of the reaction rate with rising concentration of the menthone (Table III). From Equation (11) it is evident that an increase in m will, by formation of [MA], cause a decrease in [A] and $k + k'$, and furthermore that in the region of our experiments the effect on [A] will be greater for $m < a$ than for $m > a$.

When Weissberger and Högen[2] analyzed the reaction rate of diazoacetic ester with trichloroacetic acid, it was found that the assumption of a reactive complex composed of one mole of diazo ester and two moles of acid gave the best agreement with the experiment. The agreement was very good in the region of excess diazo ester but not good in the region of excess acid. This behavior is now understood because the authors neglected the association of the trichloroacetic acid. The effect of this omission is negligible as long as the diazo ester is in excess, but it becomes large when the reverse is the case. In the absence of a more active proton acceptor, the acid molecules share their protons with each other and associate to dimers. In the presence of another proton acceptor, the latter accepts the protons of the monomeric acid molecules, and the equilibrium between dimeric and monomeric acid is shifted. If the new acceptor is more avid for protons or present in sufficient excess, the dimeric acid practically disappears; *e. g.*, on addition of one mole of water to a benzene solution of trichloroacetic acid no dimeric acid could be found cryoscopically.[14] Hence, as long as the diazo ester, a good proton acceptor, is present in at least equimolar concentration to the acid, the latter can be considered as unassociated without detriment. If, however, the acid is in excess over the ester, this simplification is no longer permissible.

The observation that the reactive complex in the menthone inversion is similar to that of the reactive complex in the diazoacetic ester decomposition is particularly interesting in view of the fact that in the latter reaction the acid enters the final product. This circumstance obviously does not affect the kinetics of the process as compared with the menthone inversion.

The information about the reactive complex in the menthone inversion given above agrees with and supplements the accepted views on acid-catalyzed enolizations.[26] It is assumed that the relevant part of the binary complex has the constitution



In this complex the protons on the carbon atoms in the α position to the carbonyl group have become more mobile, the acid proton causing a shift of electrons through electrostatic attraction and through the resonance effect indicated by the arrows. These protons are therefore capable of an exchange reaction with the proton of a second acid molecule, and, if this exchange involves a replacement of the proton on the reverse side of the asymmetric carbon atom, the *l*-menthone goes over into *d*-isomenthone and vice versa.

Summary

1. The inversion of *l*-menthone to *d*-isomenthone by trichloroacetic acid in benzene, hexane, and chloroform was investigated at 20° with various concentrations of acid and menthone.

2. The catalytic activity per mole of acid has a maximum when the molar ratio of acid to menthone is about 2. This relation holds in different solvents and at all concentrations of the menthone which were investigated (0.1 to 1 mole/liter).

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(26) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.

3. With a constant concentration of the acid, the reaction rate sinks with rising concentration of the menthone. If the menthone concentration is lower than the acid concentration, the retarding effect of the menthone is more pronounced than with menthone concentrations higher than those of the acid.

4. The temperature coefficient of the reaction was determined at intervals between 20 and 50°. The heat of activation is 6200 cal.

5. The rotation of the equilibrium mixture depends on the concentration of the trichloroacetic acid for two reasons. The acid affects the specific rotation of the components of the equilibrium mixture, and, with higher concentration of the acid, the equilibrium shifts in favor of the *d*-isomenthone.

6. The analysis of the kinetic results shows that the inversion takes place by interaction of a binary acid–menthone complex with a further molecule of the monomeric acid. Equivalent to this assumption would be the spontaneous rearrangement of a complex of one molecule of menthone with two molecules of monomeric acid.

7. Freezing-point determinations were carried out on benzene solutions of menthone and trichloroacetic acid to determine the constant of the complex formation between menthone and acid, and the association constant of the acid.

8. By comparison of the reaction rate of "Rechtsmenthon," *l*-menthone and *d*-isomenthone, it was confirmed that "Rechtsmenthon" is a mixture of *l*-menthone and *d*-isomenthone.

ROCHESTER, N. Y. RECEIVED AUGUST 14, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF BACTERIOLOGY, THE SCHOOL OF MEDICINE, UNIVERSITY OF PENNSYLVANIA]

Properties of *p*-Hydroxylaminobenzenesulfonamide and a Related Molecular Complex[1]

BY M. G. SEVAG

Mayer[2] reported a crystalline substance melting at 161° but did not give either its preparation or analysis. Bratton, White and Marshall[3] obtained a product melting at 139.5–141.5° and having the composition $C_6H_8N_2SO_3$ which they regarded as *p*-hydroxylaminobenzenesulfonamide. Thorpe and Williams[4] confirmed the work of Bratton, *et al.* Burton, *et al.*,[5] obtained a substance melting at 163–164°, the analysis of which did not fully agree with that required by $C_6H_8N_2SO_3$. Burton[6] reported two substances, one melting at 139–140° and the other at 160–161°. He did not give their analyses but considered them to be dimorphic forms. Sevag and Shelburne[7] obtained two forms of hydroxylaminobenzenesulfonamide, one melting at 139–141° and the other at 161.5°. In view of the above conflicting results, a detailed study of the properties and the nature of these substances was considered necessary.

The present study confirms the findings of Bratton, White and Marshall regarding the nature of the substance melting at 141.5°. On the other hand, the substance melting at 161.5° is found to differ from it in C, H and N analyses, salt-forming and solubility properties and in the volume of oxygen they consume.

According to the findings of Bamberger[8] hydroxylamine on oxidation yields one mole of nitrosobenzene and one mole of hydrogen peroxide. One mole of nitrosobenzene is then combined with one mole of hydroxylamine forming azoxybenzene and water. The oxidation of *p*-hydroxylaminobenzenesulfonamide seems to follow the same course. The substance melting at 141.5° consumed a volume of oxygen corresponding to 92.4%, and that consumed by the substance melting at 161.5° to only 64% of the theoretical value (Fig. 1). It was evident that the latter substance contained 36% a non-oxidizable substance. The analysis of the products in the reaction mixture revealed the presence of 35% sulfanilamide (Table I, compare columns 1. 5 and 8). These results show that the substance melt-

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(1) This work started under a grant from The Commonwealth Fund, and was continued under grants from The Josiah Macy, Jr. Foundation, and Merck and Co.

(2) R. L. Mayer, *Bull. acad. med.*, **117**, 727 (1937); *Biol. med. Paris* (Suppl.), **27**, 45, 75 (1937).

(3) A. C. Bratton, H. J. White and E. K. Marshall, Jr., *Proc. Soc. Exp. Biol. Med.*, **42**, 847 (1939).

(4) W. V. Thorpe and R. T. Williams, *Biochem. J.*, **35**, 61 (1941).

(5) H. Burton, J. W. McLeod, T. S. McLeod and A. Mayr-Harting, *Brit. J. Exptl. Path.*, **21**, 292 (1940).

(6) H. Burton, *Chemistry & Industry*, **60**, 449 (1941).

(7) M. G. Sevag and M. Shelburne, *J. Bact.*, **43**, 411, 421, 447 (1942).

(8) E. Bamberger, *Ber.*, **33**, 113 (1900).