entropy with the dehydration of the carboxylate ion in the activated state.

The rate of decomposition in the solid state of the brucine salts of *d,l*-α-bromopropionylglycine and *d,l*-α-bromopropionylglycylglycine was followed by means of titration of the bromide ion. From the former substance the lactone of *d,l*-lactylglycine was isolated. The decomposition followed an S-shaped curve. Addition of brucine hydrobromide to the brucine salt resulted in the elimination of the induction period.

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The Inversion of Menthone with Hydrogen Chloride in Benzene

By A. Weissberger and D. S. Thomas, Jr.

In a preceding paper it was shown that the rather complex kinetics of the inversion of menthone by trichloroacetic acid are adequately understood if we assume that the sterical rearrangement takes place by interaction of a binary menthone-acid complex with a further molecule of the monomeric acid.[1] The results of some experiments with hydrogen chloride[2] as a catalyst are in agreement with a similar assumption.

Dry solutions of menthone and of hydrogen chloride in benzene were mixed, the rotations (ρ) measured at certain times (t) and the reaction rates ($k + k'$) calculated as stated before.[1] The concentration of the acid in the reaction mixtures was determined after the completion of the reaction. The constancy of the rate coefficients is illustrated by Table I.

Table I

Menthone 0.5 mole/liter; benzene 20.0 ± 0.1°

HCl 0.024 mole/liter			HCl 0.047 mole/liter		
t	ρt	$(k + k')10^4$	t	ρt	$(k + k')10^4$
0	−1.79	. . .	0	−0.66	. . .
5.0	−1.38	119	4.9	+0.08	354
13.1	−0.81	120	8.2	+0.40	337
30.2	+0.01	118	13.3	+0.78	335
49.9	+0.62	121	18.4	+1.04	332
64.9	+0.88	119	27.0	+1.31	335
99.8	+1.22	118	38.3	+1.49	353
∞	+1.42	. . .	∞	+1.59	. . .

Table II gives the results for a series of concentrations of hydrogen chloride. They agree with similar measurements by Tubandt covering part of the range of the acid concentrations,[3] and show that the reaction rate is proportional to the *square* of the concentration of the catalyst.

Table II

Menthone 0.5 mole/liter; benzene, 20.0 ± 0.1°

[HCl] mole/liter × 10^3	$(k + k')10^4$	$((k + k')/[\text{HCl}]^2)10$
4.8	6.7	29.1
12.0	21.5	14.9
16.6	46.3	16.8
24.0	119.9	20.8
32.0	197.8	19.3
47.0	335.0	15.2
92.0	1329.0	15.7

The inversion with trichloroacetic acid proceeded the more slowly, the higher the concentration of the menthone. Table III shows that the inversion with hydrogen chloride is not affected in a similar way by the menthone concentration.

Table III

[HCl] mole/liter × 10^3	Menthone mole/liter	$(k + k')10^4$
26.5	0.5	144
26.5	0.75	155
26.4	1.00	154
26.7	1.50	155

To discuss the results, we write M for the menthone, A for the acid, MA for their binary complex, [ ] to indicate concentrations, and m and a for the total concentrations of menthone and of acid. For convenience, we consider the sterical rearrangement as going in one direction only, $(k + k') = \kappa$. If the inversion takes place by interaction of the binary menthone–acid complex with a further molecule of the acid, the inversion rate $r = \kappa[\text{MA}][\text{A}]$.[1] At variance with the experiments with trichloroacetic acid, the experiments with hydrogen chloride were carried out with low concentrations of the acid and a large *excess of menthone* over the latter. This technique was necessary to keep the reaction rates low enough and the angles of rotation high enough for observation. With trichloroacetic acid, the association of the catalyst had to be

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(1) Weissberger, This Journal, **65**, 245 (1943).

(2) A. Dörken, Dissertation, Leipzig, 1934.

(3) Tubandt, *Ann.*, **339**, 41 (1905); **354**, 259 (1907).

taken into consideration. With hydrogen chloride, we can neglect the association of the acid,[1] particularly in the presence of excess menthone. Then, $a = [\mathrm{MA}] + [\mathrm{A}]$; $[\mathrm{MA}] = K[\mathrm{M}][\mathrm{A}]$, and, because $m \gg a$, $[\mathrm{MA}] = Km[\mathrm{A}]$. Hence, $\mathrm{A} = a/(1 + Km)$; $[\mathrm{MA}] = Kma/(1 + Km)$, and $r = Kma^2/(1 + Km)$.

From the last equation follows the dependence of the reaction rate on the square of the acid concentration which is shown in Table II. The dependence on the menthone concentration is more complex. At high concentrations of the menthone, the rate should become independent of the substrate concentration. When the menthone concentration is lowered beneath a certain value, the rate should fall with increasing rapidity as the menthone concentration becomes smaller. The value of the menthone concentration above which the rate is practically independent of the menthone concentration and below which the rate sinks markedly with this concentration depends on K. If K is about equal to or greater than 10, a sinking of the rate with the menthone concentration will be unmistakable only at menthone concentrations which are lower than those reported in Table III. In view of the strong complex formation of trichloroacetic acid with menthone[4] and the still greater protolytic activity of hydrogen chloride, such a high value of K is to be expected. The results of Table III are therefore in agreement with the suggested mechanism.

It may be noted in Table III that the rate in the experiment with 0.5 mole/liter of menthone is somewhat lower than with the higher menthone concentrations, but this difference is not well enough established to be significant. In other experiments, the menthone concentration was lowered to 0.25 and to 0.1 mole/liter,[2] and a more pronounced sinking of the rate was noted—by about 20 and 40%, respectively. This dependence would roughly agree with a value for K of about 15. However, the isolated experiments in which relatively small changes of rotation were observed, would need checking before they could be considered as reliable.

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Summary

1. The rate of inversion of *l*-menthone by hydrogen chloride in benzene was studied in its dependence on the concentration of both compounds.

2. The results confirm that the inversion occurs by interaction of a binary acid menthone complex with a further molecule of the acid.

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[4] Weissberger, THIS JOURNAL, 65, 102 (1943).

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Lead Tetraacetate Oxidations in the Sugar Group. III.[1] Triphenylmethyl Ethers of β-Methyl-D-arabinopyranoside and of α-Methyl-L-fucopyranoside. The Determination of their Structures[2]

BY ROBERT C. HOCKETT AND DWIGHT F. MOWERY, JR.[3]

The extraordinarily numerous glucose derivatives which have been recorded in the literature were prepared, one supposes, with the purpose of revealing the laws of substitution in the sugar molecule. The ultimate object of such work is presumably to provide a roster of reference compounds for use in studies of structure and as intermediates for controlled syntheses. This task has proved more difficult in the sugar group than, for example, it was in the study of substitutions in benzene. No simple statistical method comparable to Körner's absolute method of distinguishing the ortho, meta and para disubstituted benzenes[4] can be applied to the analogous problem of differentiating the disubstitution products

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[1] Number II of this series, THIS JOURNAL, 61, 1667 (1939). *Cf.* Hockett and Maynard, *ibid.*, 61, 2111 (1939).

[2] This paper was read before the Division of Sugar Chemistry at the St. Louis meeting of the American Chemical Society in April, 1941. It is taken from a thesis submitted by Dwight F. Mowery, Jr., to the Graduate School of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy in November, 1940.

[3] Mr. Mowery was Louis Francisco Verges Fellow in Chemistry in 1939–1940.

[4] Körner, *Gazz. chim. ital.*, 4, 305 (1874); Cohen, "Organic Chemistry for Advanced Students," London, 1923, Vol. II, p. 408.