In the experiments with trichloroacetic acid, none of the addenda tested caused an acceleration of the reaction rate. With hydrogen chloride in benzene, Tubandt[9] showed that small amounts of alcohols accelerate the inversion of *l*-menthone. A few experiments with hydrogen chloride (Table III) show that ether lowers the activity of this acid, while phenol, like the aliphatic alcohols, causes a strong increase of the reaction rate and of the rotation of the final equilibrium.[4] According to Tubandt, the reaction rates sink again if larger amounts of the alcohols are added. The evidence available at present appears insufficient for an adequate interpretation of these effects.

TABLE III

Hydrogen chloride 0.032 mole/liter; menthone 0.5 mole/liter; benzene; temperature 20.0 ± 0.1°

Addendum, 0.5 mole/liter	ρ_∞ (100-mm. tube)	$(k + k')10^4$
...	−1.58°	198
Phenol	−2.84°	795
Ethyl ether	−1.41°	101

Summary

The inversion of *l*-menthone with trichloroacetic acid in benzene was studied in the presence of small amounts of various protophilic compounds. The results are compared with those obtained by adding such compounds to solutions of diazoacetic ester or dimethyl yellow and trichloroacetic acid in aprotic solvents.

All of these addenda, including benzoic acid, retard the rate of reaction. This effect is explained with the elimination of part of the catalyzing acid by compound formation with the addendum. The addenda method represents an additional means for the determination of the proton affinity of weak bases. The elimination of part of the acid is also indicated by the rotation of the equilibrium mixtures.

The inversion of *l*-menthone with hydrogen chloride is retarded by ether and accelerated by phenol.

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[9] Tubandt, *Ann.*, **354**, 259 (1907).

[COMMUNICATION NO. 893 FROM THE KODAK RESEARCH LABORATORIES]

The Inversion of *l*-Menthone and the Reaction of Diazoacetic Ester with the Chloroacetic Acids

BY A. WEISSBERGER

Hantzsch attributed both the catalytic activity and the ionization of acids to their salt formation, in the former case with the substrate, in the latter case with the solvent.[1] As a substrate for the investigation of the activity of acids in non-aqueous solvents, diazoacetic ester was chosen. The work of other authors agrees with the fundamental idea.[2] A connection between the catalytic activity of acids and their ionization, other than the untenable assumption of an exclusive activity of free hydrogen ions, had been suggested by Taylor,[3] and was most successfully formulated in the Brönsted relation.[4] However, the use of the decomposition of diazoacetic ester in non-aqueous solvents for the comparison of different acids encountered unabated criticism,[5] because the reaction product varies with the acid HX

$$HX + N_2CHCO_2C_2H_5 \longrightarrow XCH_2CO_2C_2H_5 + N_2$$

The inversion of *l*-menthone to *d*-isomenthone, on the other hand, was accepted for the comparison of different acids.[6] In the latter reaction, the product is qualitatively independent of the catalyst, inasmuch as it is always *d*-isomenthone. However, *l*-menthone and *d*-isomenthone are not true optical antipodes, but diastereoisomers and the final equilibrium between the isomers shifts with the concentration and the nature of the catalyzing acid.[7] Therefore, the difference between the decomposition of diazoacetic ester and the inversion of *l*-menthone is not one of principle but only of degree of deviation from the ideal.

The mechanism of both reactions,[7,8] as revealed by their kinetics, is of a striking similarity. In both cases, the reactive complex is built up of one molecule of the substrate, menthone or ester, and two molecules of the monomeric acid. This similarity seemed to indicate that the above-mentioned criticism of the use of the diazo ester

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[1] Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923).

[2] Hammett, THIS JOURNAL, **50**, 2666 (1928).

[3] Taylor, *Z. Elektrochem.*, **20**, 201 (1914).

[4] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[5] R. P. Bell, "Acid-Base Catalysis," Oxford, 1941.

[6] Bell and Caldin, *J. Chem. Soc.*, 382 (1938).

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

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

decomposition by Hantzsch might not be justified. Measurements undertaken to compare different acids in the diazoacetic ester decomposition and in the menthone inversion were interrupted by political conditions. Because there is little likelihood that they will be continued by the present author, the results obtained, although relating to three acids only, are presented in the following.

The techniques of the measurements and calculations were those described previously.[7,8] The menthone inversion was carried out at 70°, the decomposition of diazoacetic ester at 20°. All reacting compounds were in 0.1 molar solution in benzene.[9] Each experiment was made in duplicate and the average values of the runs are given in the table.

The inversion of *l*-menthone by the three chloroacetic acids is in accord with the Brönsted relation.[6] In Fig. 1, the logarithm of the rate constant of the diazoacetic ester reaction is plotted against the logarithm of the rate constant of the menthone inversion, for each acid. The straight-line relationship shows that the Brönsted relation applies as well to the diazo ester decomposition as to the menthone inversion.

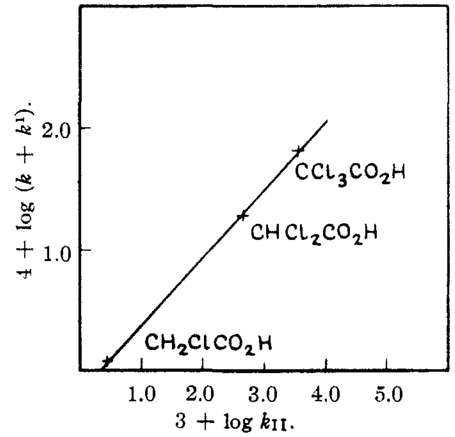

Fig. 1.

REACTION RATES WITH CHLOROACETIC ACIDS

	Inversion of *l*-menthone $(k + k')10^4$	Decomposition of diazoacetic ester K_{II}
Monochloroacetic acid	1.1	0.0026
	1.3	.0028
Dichloroacetic acid	18.9	.44
	19.0	.42
Trichloroacetic acid	63.1	3.6
	63.2	3.1

The scant experimental material does not warrant far-reaching conclusions. However, the result agrees with the observation that in both reactions the limiting phase lies in the protolytic reaction of the acid with the substrate.[7,8] The subsequent fate of the reactive complex, even if it involves the entrance of the acid into the reaction product in the case of the diazoacetic ester, does not seem to affect the kinetics, except by the disappearance of acid for which allowance is made in the calculations.

Summary

The decomposition of diazoacetic ester by the three chloroacetic acids in benzene agrees with the Brönsted relation as well as does the inversion of *l*-menthone by these acids. As far as this result can be generalized, the use of the diazoacetic ester reaction by Hantzsch to determine the strength of acids is as sound as the use of the menthone inversion for the same purpose.

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[9] For these measurements I am indebted to Dr. A. Dörken.