341. *The Relationship between the Three Forms of* cis-*Cinnamic Acid.*

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Meyer and Pukall (*Z. physikal. Chem.*, 1929, **145**, 360) observed important differences in the rates of addition of bromine to the three *cis*-cinnamic acids, and concluded that these acids were isomeric and not merely polymorphic.

The type of reaction studied by these authors has also been investigated in these laboratories, and it has been shown by Williams and James (J., 1928, 343) that the addition of bromine to unsaturated acids and esters in the dark in non-hydroxylic solvents is an autocatalytic reaction, evidence being brought forward to show that the catalyst is hydrogen bromide.

Cinnamic acid has been shown to belong to a class of substance to which bromine, after a preliminary inhibition period, is added very slowly at first, but with an increasing velocity. By addition of hydrogen bromide to substances of this class, the inhibition period disappears, the rate of addition is considerably increased, and the reaction becomes bimolecular. Under the conditions of working, cinnamic acid showed an inhibition period of about 22 hours and *cis*-cinnamic acid one of about 7 hours (Hanson and Williams, J., 1930, 1062).

The rates of addition of bromine to solutions of the various forms of *cis*-cinnamic acid have now been determined in the dark, and under strictly equivalent conditions no differences can be detected. The three forms have been examined in pairs, each of the less stable forms being directly compared with the *allo*-cinnamic acid (m. p. 68°).

Experimental.

The three forms of *cis*-cinnamic acid were prepared by hydrogenating phenylpropiolic acid by Paal and Hartmann's method (*Ber.*, 1909, **42**, 3930). A first preparation gave Liebermann's

*iso*cinnamic acid, m. p. 58°: subsequent preparations in the same laboratory gave the *allo*-acid, m. p. 68°.

Erlenmeyer's *iso*cinnamic acid (m. p. 42°) was prepared as follows: A small portion of the 68° acid was heated about 20° above its m. p. in a sealed capillary tube for ½ hour and then allowed to cool slowly. The contents of the tube ultimately solidified, and subsequently melted at 42°. A larger mass of *allo*-cinnamic acid was then melted in a sealed tube, and kept at 80° for 3 hours. After cooling, the melt remained liquid for several weeks. The tube was then opened and inoculated with the contents of the capillary (m. p. 42°). Solidification took place immediately, and a product with m. p. 42° was obtained. The acid was stored in a sealed vessel in a dark cupboard; its m. p. remained constant over a period of 6 weeks, and it was then used for the present investigation.

M/20-Solutions of the different forms of *cis*-cinnamic acid were made in pure carbon tetrachloride, to which a definite volume of a solution of hydrogen bromide in the same solvent had been added, *viz.*, 1·00 c.c. of an approx. 0·2% hydrogen bromide solution per 100 c.c. of solvent. An *M*/20-solution of bromine in the same solvent was added in equivalent amount, and the mixture kept in the dark at 16°. The volume of bromine absorbed after definite intervals of time was measured by titration with standard sodium thiosulphate solution.

The rate of addition of bromine to *trans*-cinnamic acid under identical conditions was determined, and is included for purposes of comparison.

The results are tabulated below, together with the bimolecular constant, $k = 1/t \,.\, x/a(a - x)$, where t is the time in hours, a is 10, and x is the amount of change expressed in c.c.

Comparisons of (A) allo- *and* iso-(*m. p.* 58°) *with* trans-*cinnamic acid*;
(B) allo- *with* iso(*m. p.* 42°)-*cinnamic acid* (more concentrated catalyst than in A).

	A.						B.			
	$a - x$.			$k \times 10^4$.			$a - x$.		$k \times 10^4$.	
t, hrs.	*trans.*	*allo.*	*iso.*	*trans.*	*allo.*	*iso.*	*allo.*	*iso.*	*allo.*	*iso.*
0	10	10	10	—	—	—	10	10	—	—
1	9·26	7·83	7·91	79·9	277	264	6·65	6·53	504	531
1·5	—	7·12	7·10	—	270	279	5·60	5·48	524	551
2	—	6·50	6·44	—	269	276	4·79	4·73	544	557
2·25	8·49	—	—	79·2	—	—	—	—	—	—
2·5	—	5·98	6·03	—	269	263	4·22	4·34	548	522
3	8·18	5·39	5·60	74·2	285	262	3·83	3·93	537	515
3·5	—	4·95	5·19	—	291	265	3·49	3·54	533	521
4	7·81	—	—	76·1	—	—	3·24	—	522	—

SUMMARY.

The rates of addition of bromine to the three forms of *cis*-cinnamic acid in solution in carbon tetrachloride, with hydrogen bromide as catalyst, have been determined, and are such as to indicate that, in solution, the three forms are identical.

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