If equation (9) is valid, it follows that the radical formed in equation (5) should be able to dimerize also

$$2CF_3CO\cdot \longrightarrow CF_3COCOCF_3 \qquad (10)$$

This compound has not yet been isolated, but it is significant that in the distillations a portion was always obtained boiling around −9° the molecular weight of which was *higher* than that of hexafluoroacetone. There are only two presumably low boiling possibilities here, hexafluorodiacetyl and octafluoropropane. The latter, however, boils at −36° and so is eliminated as a possibility.

From all these considerations it becomes increasingly clear that vapor phase fluorinations in all probability proceed by a free radical, non-ionic mechanism.

Summary

The simple and convenient apparatus previously used for the direct fluorination of organic gases has been adapted to the vapor phase fluorination of volatile organic liquids, thereby greatly increasing its usefulness.

Acetone has been fluorinated without difficulty. The principal products were hexafluoroacetone CF_3COCF_3, monofluoroacetone CH_2FCOCH_3, trifluoroacetyl fluoride CF_3COF, oxalyl fluoride $(COF)_2$, carbonyl fluoride COF_2 and carbon tetrafluoride.

The results have been explained on the basis of a free radical, non-ionic mechanism.

DURHAM, NORTH CAROLINA

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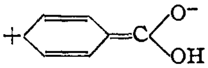
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Dissociation Constants in the Cinnamic Acid Series[1]

BY R. D. KLEENE, F. H. WESTHEIMER AND G. W. WHELAND

It has been known for some time that the acid strength of benzoic acid is increased by practically any substituent ortho to the carboxyl group, regardless of the effect which that substituent exerts when in the meta or para position. To explain this "ortho effect," the suggestion[2] has been made that the ortho substituent inhibits resonance with such quinoid structures as



This suggestion seemed reasonable since such resonance would be expected to stabilize the acid more than it would the corresponding negative ion. A similar explanation can be offered for the fact that *cis* cinnamic acid, for which a completely planar configuration is not possible, is appreciably stronger than the *trans* isomer.

In an investigation of the above hypothesis, the strengths of a series of substituted cinnamic acids have been determined. On account of the insolubility in water of some of the compounds studied, the measurements were made in an acetone–water mixture containing 40% acetone by volume. This had the effect of making the measured dissociation constants more or less uniformly lower than in pure water.[3] The experimental results, which are summarized in the accompanying table, leave something to be desired in the way of precision, but they are sufficiently accurate to show that the strengths of the acids in question can*not* be accounted for on the basis of an inhibition of resonance. Thus *trans*-2,4,6-trimethyl cinnamic acid is stronger than the *cis* isomer by a factor of about 2½, even though the former is probably, and the latter is certainly not entirely planar. The fact that the dissociation constants of *cis* and *trans*-α-methylcinnamic acids are in the ratio of approximately 10:1 is even more difficult to explain since it seems quite probable that neither of these acids can achieve planarity. This failure of the theory of inhibition of resonance to account for the strengths of the cinnamic

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(1) Part of a thesis presented by R. D. Kleene to the faculty of the Division of Physical Sciences of the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy, December, 1940.

(2) Baddeley, *Nature*, **144**, 444 (1939). See also Allan, Oxford, Robinson and Smith, *J. Chem. Soc.*, 401 (1926), and Ives, Linstead and Riley, *ibid.*, 561 (1933). A further suggestion, involving the idea of steric hindrance, has been made by Flürscheim (*ibid.*, **95**, 718 (1909)). This will not be considered here since its theoretical basis seems questionable. The chelation theory of Dippy, Evans, Gordon, Lewis and Watson (*ibid.*, 1421 (1937)) and of Smith (THIS JOURNAL, **61**, 1176 (1939)) will also not be considered here, since, in its application to the acids discussed below, it requires the formation of a hydrogen bond between an oxygen and a carbon atom. The supposition that such a hydrogen bond can exist in cases like the present ones, in which the carbon atom does not carry negative substituents, requires independent confirmation. *Cf.* Zellhoefer, Copley and Marvel, THIS JOURNAL, **60**, 1337 (1938).

(3) See, for example, Goldschmidt, *Z. physik. Chem.*, **99**, 116 (1921).

acids (and perhaps, by inference, of the ortho substituted benzoic acids) cannot, however, be taken as a reflection upon the validity of the theory in certain other types of problem in which it has been found to apply and in which it has been definitely established.[4]

TABLE I

	Dissociation constant ($K \times 10^6$)[a]	
Acid	A[b]	B[b]
cis-Cinnamic		5.25
		5.86
		5.56
		5.80
trans-Cinnamic	2.46	2.81
	2.51	2.75
	2.50	
	2.62	
	2.48	
	2.63	
Hydrocinnamic	1.24	1.27
	1.30	1.15
	1.32	1.13
	1.28	
cis-2,4,6-Trimethylcinnamic	0.77	0.73
	.79	.70
	.80	
trans-2,4,6-Trimethylcinnamic	2.11	1.89
	1.99	1.86
	2.01	1.76
	2.30	
	2.01	
	2.22	
	2.05	
2,4,6-Trimethylhydrocinnamic	1.27	1.32
	1.25	1.34
	1.25	
cis-α-Methylcinnamic	10.0	10.2
	10.6	10.7
	10.4	
trans-α-Methylcinnamic	1.07	0.97
	1.07	.98
	1.06	

[a] In a solvent consisting of 40% acetone by volume.

[b] In the two columns, A and B, are listed separately the values obtained in two series of measurements made at different times upon different samples. The reason for the discrepancies in certain cases is not known.

Experimental

Preparation of Acids.—*trans*-2,4,6-Trimethylcinnamic acid[5] melted at 177.6–178.0° (cor.). *trans*-Cinnamic acid melted at 134°, *cis*-cinnamic acid at 68°,[6] and hydrocinnamic acid at 48.5–49°.[7] *trans*-α-Methylcinnamic acid melted at 80.5–82°,[8] and *cis*-α-methylcinnamic acid at 91–92°.[9]

Dibromide of Ethyl 2,4,6-Trimethylcinnamate.—The ethyl ester of *trans*-2,4,6-trimethylcinnamic acid[5] (2.00 g.) was dissolved in 10 cc. of distilled carbon tetrachloride and cooled to −10°. To this was added 15.3 cc. of a 0.60 *M* solution of bromine in carbon tetrachloride in nine portions at twenty minute intervals. The solution was then poured into an evaporating dish and allowed to stand at room temperature overnight. In the morning, the remainder of the solvent was driven off by a current of air. The viscous, colorless residue crystallized when left for twenty-four hours in a vacuum desiccator over calcium chloride. The product, after purification by several recrystallizations from absolute alcohol, formed small colorless crystals melting at 51.5–52°. The yield of purified material was 1.5 g.

Anal. Calcd. for $C_{14}H_{18}O_2Br_2$: C, 44.47; H, 4.80; Br, 42.28. Found: C, 44.49; H, 4.99; Br, 42.47.

2,4,6-Trimethylphenylpropiolic Acid.—The above dibromide (7.6 g.) without purification was dissolved in 40 cc. of 90% alcohol containing 5 g. of potassium hydroxide. The mixture was refluxed for six hours and then poured into water. The resulting emulsion was extracted with ether, warmed to expel the ether, and acidified. The propiolic acid which precipitated was purified by crystallization from carbon tetrachloride. It formed colorless crystals melting at 160–161°. The yield was 50–60% of the theoretical.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.55; H, 6.44. Found: C, 76.04; H, 6.49.

***cis*-2,4,6-Trimethylcinnamic acid** was prepared by half hydrogenation of the above propiolic acid with the use of the catalyst of Paal and Hartmann.[6] The propiolic acid (0.415 g.) was dissolved in a slight excess of sodium carbonate, and the catalyst (0.15 g.) was added as a suspension in dilute sodium carbonate. The calculated volume of hydrogen was taken up in the course of one hour. After the catalyst had been removed by filtration, the product was precipitated by acidifying the solution, and dried over calcium chloride. After crystallization from ligroin, the purified material melted at 147.6–147.9° (cor.).

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37. Found: C, 76.09; H, 7.61.

That the material obtained in this way was the *cis*-2,4,6-trimethylcinnamic acid was inferred from the fact that the unsubstituted phenylpropiolic acid gives the known *cis*-cinnamic acid when hydrogenated by the same procedure as above.[6] Confirmatory evidence is provided by the reactions described below.

2,4,6-Trimethylhydrocinnamic Acid.—The *trans*-2,4,6-trimethylcinnamic acid was hydrogenated by the same procedure as above. The product, after separation from the reaction mixture and crystallization from ligroin, melted at 111–112°, in agreement with the value of 113° reported by Hoch.[10]

The *cis*-2,4,6-trimethylcinnamic acid was also hydrogenated in the same manner. The product again melted

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[4] For examples, see Birtles and Hampson, *J. Chem. Soc.*, 10 (1937); Brown, Widiger and Letang, THIS JOURNAL, **61**, 2597 (1939); Spitzer and Wheland, *ibid.*, **62**, 2995 (1940).

[5] Böck, Lock and Schmidt, *Monatsh.*, **64**, 399 (1934).

[6] Paal and Hartmann, *Ber.*, **42**, 3930 (1909).

[7] Gabriel and Zimmermann, *ibid.*, **13**, 1680 (1880).

[8] Edeleano, *ibid.*, **20**, 616 (1887).

[9] Stoermer and Voht, *Ann.*, **409**, 52 (1915).

[10] Hoch, *Compt. rend.*, **192**, 1464 (1931).

at 111–112°, and a mixed melting point with the above acid showed no depression.

Amide of 2,4,6-Trimethylcinnamic Acid.—The *trans* acid was refluxed with thionyl chloride, and the reaction mixture was then poured into concentrated aqueous ammonia. The substance, after recrystallization from alcohol, formed needles melting at 187–188°.

Anal. Calcd. for $C_{12}H_{15}ON$: N, 7.41. Found: N, 7.52.

The *cis* acid was transformed into an amide in the same way. The product again melted at 187–188°, and a mixed melting point with the amide prepared from the *trans* acid showed no depression.

Anal. Calcd. for $C_{12}H_{15}ON$: N, 7.41. Found: N, 7.76.

The fact that the two trimethylcinnamic acids give the same amide confirms the belief that they are stereoisomers, since the conditions of the experiment are such that a *cis–trans* conversion might be anticipated. Hydrolysis of the amide with aqueous sodium hydroxide gave the *trans* acid. It seems probable that the amide is the *trans* isomer, in view of general considerations of stability.

Amide of Cinnamic Acid.—For comparison with the results obtained with the trimethylcinnamic acids, *cis* and *trans* cinnamic acids were transformed into the amides by the same procedure as above. In both cases, the known *trans* amide, melting at 144–145°, was obtained.

Amide of 2,4,6-Trimethylhydrocinnamic Acid.—The acid was transformed into the amide as in the preceding cases. The product formed colorless leaflets when crystallized from dilute alcohol, and it melted at 159–160°.

Anal. Calcd. for $C_{12}H_{17}ON$: N, 7.33. Found: N, 7.57.

Melting points are uncorrected unless otherwise noted. The analyses reported in this paper were made by Dr. T. S. Ma.

Conductivity Measurements.—The conductivity measurements were made with a Leeds and Northrup bridge, using a Clough–Brengle oscillator as the source of current. The circuit was in general similar to that of Jones and Josephs.[11] The conductivity cell, designed as suggested by Jones and Bollinger,[12] had electrodes of about 1 sq. cm. in area and about 1 cm. apart. The cell constant was 0.2161.

The "classical" ionization constants were obtained from the degree of ionization, and the latter was computed by dividing the equivalent conductance of the acid by its computed limiting conductance. It was not regarded as worth while, on the basis of the measurements performed, to attempt a computation of thermodynamic constants.

The conductivity of potassium chloride, measured in 40% acetone, agreed with the values given by Brownson and Cray[13] to 0.3%. The conductivity of hydrogen chloride was taken from Brownson and Cray.

The equivalent conductivity of the potassium salt of each acid was obtained from measurements of solutions prepared by adding corresponding quantities of the acid and potassium hydroxide. The limiting values were obtained graphically from a plot of the equivalent conductivity against the square root of concentration. The plots were satisfactorily linear, and the limiting conductivities obtained were as follows: potassium *cis*-cinnamate 70.7 ohms^{-1} mols^{-1} cm.$^{-1}$; potassium *trans*-cinnamate 69.0; potassium hydrocinnamate 70.0; potassium *cis*-2,4,6-trimethylcinnamate 66.2; potassium *trans*-2,4,6-trimethylcinnamate 66.5; potassium 2,4,6-trimethylhydrocinnamate 67.0; potassium *cis*-α-methylcinnamate 68.4; and potassium *trans*-α-methylcinnamate 67.5.

The measurements were made in an oil thermostat maintained at a temperature of 25 ± 0.1°.

The solvent was prepared by adding to each 100 cc. of purified dry acetone enough conductivity water to bring the volume to 250 cc.

Summary

1. The dissociation constants of a series of substituted *cis* and *trans* cinnamic acids have been measured in 40% acetone.

2. The values of these dissociation constants cannot be accounted for, even qualitatively, on the basis of an inhibition of resonance in those acids in which a planar configuration is impossible.

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[11] Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

[12] Jones and Bollinger, *ibid.*, **53**, 411 (1931).

[13] Brownson and Cray, *J. Chem. Soc.*, **127**, 2923 (1925).