CLXXVIII.—*Esterification Constants of Substituted
Acrylic Acids. Part I.*

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SOME few years ago attention was drawn to the rates at which various substituted cinnamic acids are esterified by means of methyl alcohol, using the hydrogen chloride catalytic method (Sudborough and Lloyd, *Trans.*, 1898, **73**, 81). The amount of acid esterified after a given time was determined by actually isolating and weighing the ester.

As we were desirous of extending the investigation to substituted acrylic acids, the esters of which are relatively volatile, we decided to determine the actual rate of esterification by using the equation for a unimolecular reaction. In the meanwhile, this method has been used for determining the esterification constants of substituted acetic acids (Trans., 1899, **75**, 467) and of the acid esters of methyl-substituted succinic acids (Trans., 1904, **85**, 534), and in both series interesting examples of the inhibiting influence of various substituents have been noted. The general method adopted has been to prepare 100 c.c. of *N*/10 solution of the acid in methyl alcohol and to titrate carefully two lots of 10 c.c. each with standard barium hydroxide, using phenolphthalein as indicator: 70 c.c. of the acid solution were then mixed, at the given temperature (15°), with an equal volume of standard hydrogen chloride in methyl alcohol. Quantities of 30 c.c. of the mixture were introduced into separate small bottles, which were then placed in a thermostat at 15° and the contents titrated, after given intervals of time, with the standard barium hydroxide.

In this paper, the constants for the following acids are given.

Saturated.—Butyric and dihydrocinnamic.

Ethylenic.—Crotonic, cinnamic, methyl hydrogen fumarate and maleate, furfurylacrylic and furfurylalloacrylic, α -chlorocrotonic, β -chlorocrotonic, β -chloroisocrotonic, α -chlorocinnamic, α -chloroallocinnamic, β -chlorocinnamic, β -chloroallocinnamic, α -bromocinnamic, α -bromoallocinnamic, β -bromocinnamic, β -bromoallocinnamic, atropic (α -phenylacrylic), α -phenylcinnamic, and α -phenylallocinnamic.

Acetylenic.—Phenylpropionic.

The results are tabulated on p. 1843, the acids being arranged in descending order according to the magnitude of their esterification constants at 15°. The third column contains the values of the dissociation constants of the various acids, and it is obvious that in this series, as in others, there is no simple relationship between the strength of an acid and its esterification constant as determined by the catalytic method.

As we are at present engaged in the preparation of other substituted acrylic acids and the determination of their esterification constants, we think that it is not advisable to discuss the present results in detail, but will merely indicate several points which deserve further investigation.

1. *Relationship between the Esterification Constant of an Acrylic Acid and its Saturated Analogue.*

<i>Unsaturated.</i>	<i>E.</i>	<i>Saturated.</i>	<i>E.</i>
Crotonic	1.28	Butyric	41.63
Cinnamic.....	0.937	Dihydrocinnamic	43.20
Methyl hydrogen fumarate	1.79	Methyl hydrogen succinate	17.25
Methyl hydrogen maleate	0.859		

The foregoing numbers indicate that an acrylic acid is esterified much less readily than its saturated analogue. Further experiments will show whether this generalisation holds in all cases and will also show in what manner the position of the double bond (for example, $\alpha\beta$, $\beta\gamma$, $\gamma\delta$) affects the rate of esterification.

2. *Relationship between the Esterification Constant of an Acrylic Acid and that of the Corresponding Acetylenic Acid.*

The only comparison we can make at present is between cinnamic and phenylpropionic acids. The numbers 0.937 and 0.640 for the ethylenic and acetylenic acids respectively show that there is not the same difference here as between the numbers for an ethylenic and a saturated acid.

3. *Comparison of the Esterification Constants of Isomeric α - and β -Substituted Acrylic Acids.*

A glance at the table shows that the β -compounds are, as a rule, esterified more readily than the α -isomerides. The position of β -chloroisocrotonic acid appears somewhat remarkable, as there is very little difference between its constant and that for α -chlorocrotonic acid.

4. *Comparison of Stereoisomerides of the Types*

(see Trans., 1898, 73, 93).

A comparison of the values for α -chloro-, α -bromo-, and α -phenylcinnamic acids and for their *allo*-isomerides confirms the conclusion previously drawn, namely, that when the substituent X (phenyl in all these cases) is in the *cis*-position with respect to the carboxylic group

the rate of esterification is slower than when the substituent is in the *trans*-position.

Acid.	$E_{MeOH}^{15^\circ}$	K .
Dihydrocinnamic	43.20	0.00227 Ostwald.
Butyric	41.63	0.00154 Billitzer.
Methyl hydrogen fumarate	1.79	
Crotonic	1.28	0.00204 Ostwald.
Cinnamic	0.937	0.00355 „
Methyl hydrogen maleate	0.859	
β -Furfurylacrylic	0.718	
Phenylpropionic	0.640	0.59 Ostwald.
β -Chlorocrotonic	0.488	0.0144 „
β -Bromoallocinnamic	0.419	
β -Bromocinnamic	0.385	
β -Furfurylalloacrylic	0.379	
β -Chloroallocinnamic	0.371	0.0272 Mulliken.
β -Chlorocinnamic	0.355	0.028 „
α -Phenylacrylic (atropic)	0.187	0.0143 Ostwald.
β -Chloroisocrotonic	0.172	0.0095 „
α -Chlorocrotonic	0.163	0.072 „
α -Phenylcinnamic	0.126	
α -Chlorocinnamic	0.101	0.097 Mulliken.
α -Bromocinnamic	0.075	1.44 ? Ostwald.
α -Chloroallocinnamic	0.028	1.07 Mulliken.
α -Bromoallocinnamic	0.00962	0.093 ? Ostwald.
α -Phenylalloccinnamic	0.00288	

Ostwald, *Zeit. physikal. Chem.*, 1889, **3**, 418; Mulliken, *Dissertation*, Leipzig, 1890; Billitzer, *Monatsh.*, 1899, **20**, 666.

The methyl alcohol used in all these experiments was Kahlbaum's No. 1 ("aceton frei"), which had been distilled twice over small amounts of sodium, and, although not pure, it is the same as was employed for the acid methyl esters of substituted succinic acids, and the constants are thus comparable. Each lot of alcohol was treated in the same manner and a determination made with crotonic or cinnamic acid in order to be quite sure that the differences in esterification constant were not due to differences in the methyl alcohol used.

EXPERIMENTAL.

Methyl hydrogen fumarate was prepared from the methyl ester by treatment with the requisite quantity of methyl-alcoholic potash, and was purified by crystallisation from benzene (m. p. 143°).

A.—Strength of the hydrochloric acid before mixing = 0.2001*N*.

15 c.c. of the alcoholic solution required 30.37 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log a/a - x$.
1	25.34	0.0786
2	21.11	0.0790
3	17.67	0.0784
5.517	10.92	0.0805

B.—Strength of the hydrochloric acid before mixing = 0.197*N*.

15 c.c. of the alcoholic solution required 30.60 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log a/a - x$.
1.5	23.74	0.0735
2	21.68	0.0748
3.16	17.66	0.0754
4.16	14.79	0.0758

Mean corrected for 0.1*N* hydrochloric acid = A, 0.0791; B, 0.0761 (mean = 0.0776).

$$E_{MeOH}^{15^\circ} = 0.0776 \times 10 \times 2.3026 = 1.79.$$

Methyl hydrogen maleate was obtained by adding a slight excess of methyl alcohol to maleic anhydride and warming for an hour on the water-bath. The liquid obtained was placed in an exhausted desiccator and analysed at intervals (by titration against standard alkali) until the result was constant. Even then the acid ester was not quite pure and apparently contained a small amount of normal ester.

Results of tests of purity of acid by titration against standard baryta.

	Weight of acid ester taken.	Vol. of <i>N</i> /20 baryta necessary to neutralise.	Vol. of <i>N</i> /20 baryta that would have been necessary if ester were pure.
(i)	0.1965 grams	28.53 c.c.	30.23 c.c.
(ii)	0.2176 „	31.58 „	33.5 „

A.—Strength of the hydrochloric acid before mixing = 0.197*N*.

15 c.c. of the alcoholic solution required 28.58 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
1	26.15	0.0386
2	24.15	0.0366
3	22.44	0.0350
4.5	19.85	0.0352

B.—Strength of the hydrochloric acid before mixing = 0.202*N*.

15 c.c. of the alcoholic solution required 28.0 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
1	25.51	0.0405
2	23.50	0.0380
3.5	21.08	0.0350

Mean corrected for 0.1*N* hydrochloric acid = A, 0.0368; B, 0.0379 (mean = 0.0373).
 $E_{\text{MeOH}}^{15} = 0.0373 \times 10 \times 2.3026 = 0.859$.

Crotonic acid (m. p. 72°) was purified by recrystallisation from ligroin (b. p. 50—70°).

A.—Strength of the hydrochloric acid before mixing = 0.1002*N*.

15 c.c. of the alcoholic solution required 30.00 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
2	26.26	0.0289
4	23.17	0.0280
6	20.58	0.0273
8	18.16	0.0273

B.—Strength of the hydrochloric acid before mixing = 0.0996*N*.

15 c.c. of the alcoholic solution required 30.19 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
2	26.47	0.0286
4	23.38	0.0277
7	19.36	0.0276
8	18.22	0.0274

C.—Strength of the hydrochloric acid before mixing = 0.1992*N*.

15 c.c. of the alcoholic solution required 30.19 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
1	26.34	0.0592
2	23.43	0.0550
3.5	19.45	0.0546
4	18.07	0.0557

Mean for 0.05*N* hydrochloric acid = A, 0.0278; B, 0.0279; C, 0.0281 (mean = 0.0279).

$$E_{\text{MeOH}}^{15} = 0.0279 \times 20 \times 2.3026 = 1.28$$

Cinnamic acid (m. p. 133°) was purified by crystallisation from benzene.

A.—Strength of the hydrochloric acid before mixing = 0.10*N*.

15 c.c. of the alcoholic solution required 29.78 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
2	26.95	0.0217
4	24.67	0.0205
6	22.68	0.0197
8	20.73	0.0197

B.—Strength of the hydrochloric acid before mixing = 0.1995*N*.

15 c.c. of the alcoholic solution required 30.16 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
1.25	26.76	0.0415
3	22.89	0.0399
4	20.90	0.0398
4.5	19.96	0.0399

C.—Strength of the hydrochloric acid before mixing = 0.20*N*.

15 c.c. of the alcoholic solution required 29.95 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
1	27.19	0.0420
2	24.79	0.0410
4	20.70	0.0401
5	18.87	0.0401

Mean corrected for 0.1*N* hydrochloric acid = A, 0.0408; B, 0.0404; C, 0.0408 (mean = 0.0407).

$$E_{\text{MeOH}}^{15} = 0.0407 \times 10 \times 2.3026 = 0.937.$$

Atropic (α-Phenylacrylic) Acid (m. p. 106°).

A.—Strength of the hydrochloric acid before mixing = 0.098*N*.

15 c.c. of the alcoholic solution required 29.67 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
12	26.61	0.00393
24	23.67	0.00409
36.5	21.26	0.00397
48	18.95	0.00406

B.—Strength of the hydrochloric acid before mixing = 0.102*N*.

15 c.c. of the alcoholic solution required 29.28 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
21.35	23.57	0.00441
45.35	18.82	0.00423
69.6	15.11	0.00413
77.56	14.40	0.00397

C.—Strength of the hydrochloric acid before mixing = 0.101*N*.

15 c.c. of the alcoholic solution required 38.67 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
24	30.60	0.00423
34.25	28.01	0.00409
46.17	25.62	0.00387

Mean corrected for 0.05*N* hydrochloric acid = A, 0.00408; B, 0.00410; C, 0.00402 (mean = 0.00407).

$$E_{\text{MeOH}}^{15} = 0.00407 \times 20 \times 2.3026 = 0.187.$$

α-Chlorocrotonic acid (m. p. 99.2°) was purified by recrystallisation from ligroin (b. p. 90—110°).

A.—Strength of the hydrochloric acid before mixing = 0.20*N*.

15 c.c. of the alcoholic solution required 29.98 c.c. of *N*/20 alkali.

in hours.	$a-x$.	$1/t \log. a/a-x$.
16	22.91	0.00730
25	19.90	0.00712
40	15.68	0.00704
49.5	13.51	0.00700

B.—Strength of the hydrochloric acid before mixing = 0.20*N*.

15 c.c. of the alcoholic solution required 29.98 c.c. of *N*/20 alkali.

t in hours.	$a-x$.	$1/t \log. a/a-x$.
16	22.91	0.00731
25	19.90	0.00712
40	15.68	0.00704
49.3	13.60	0.00697

C.—Strength of the hydrochloric acid before mixing = 0.101*N*.

15 c.c. of the alcoholic solution required 27.95 c.c. of *N*/20 alkali.

t in hours.	$a-x$.	$1/t \log. a/a-x$.
17.70	24.21	0.00353
26.88	22.32	0.00363
40.78	19.92	0.00360
50.83	18.77	0.00340

Mean corrected for 0.05*N* hydrochloric acid = A, 0.00356; B, 0.00356; C, 0.00350 (mean = 0.00354).

$$E_{\text{MeOH}}^{15^\circ} = 0.00354 \times 20 \times 2.3026 = \mathbf{0.163}.$$

β-Chlorocrotonic acid (m. p. 94—95°) was crystallised from ligroin.

A.—Strength of the hydrochloric acid before mixing = 0.200*N*.

15 c.c. of the alcoholic solution required 29.94 c.c. of *N*/20 alkali.

t in hours.	$a-x$.	$1/t \log. a/a-x$.
3	26.22	0.0192
6.5	22.61	0.0188
10.2	19.22	0.0189

B.—Strength of the hydrochloric acid before mixing = 0.103*N*.

15 c.c. of the alcoholic solution required 30.43 c.c. of *N*/20 alkali.

t in hours.	$a-x$.	$1/t \log. a/a-x$.
19.63	19.31	0.01006
22.35	18.30	0.00988
25.51	17.21	0.00971
28.67	16.07	0.00968

C.—Strength of the hydrochloric acid before mixing = 0.101*N*.

15 c.c. of the alcoholic solution required 34.95 c.c. of *N*/20 alkali.

t in hours.	$a-x$.	$1/t \log. a/a-x$.
3.02	32.75	0.00934
8.17	29.01	0.00990
10.5	27.65	0.00968

Mean corrected for 0.05*N* hydrochloric acid = A, 0.00947; B, 0.00954; C, 0.00954 (mean = 0.00952).

$$E_{\text{MeOH}}^{15^\circ} = 0.00952 \times 20 \times 2.3026 = \mathbf{0.438}.$$

β-Chloroisocrotonic acid (m. p. 61°) was purified by recrystallisation from water.

A.—Strength of the hydrochloric acid before mixing = 0·1975*N*.

15 c.c. of the alcoholic solution required 30·32 c.c. of *N*/20 alkali.

<i>t</i> in hours.	$\alpha - x.$	$1/t \log. a/a - x.$
3	28·71	0·00787
5	27·88	0·00728
8	26·42	0·00747
10	25·46	0·00759

B.—Strength of the hydrochloric acid before mixing = 0·101*N*.

15 c.c. of the alcoholic solution required 33·39 c.c. of *N*/20 alkali.

<i>t</i> in hours.	$\alpha - x.$	$1/t \log. a/a - x.$
22	27·76	0·00364
29	25·89	0·00381
46	22·69	0·00365

Mean corrected for 0·05*N* hydrochloric acid = A, 0·00382; B, 0·00366
(mean = 0·00374).

$$E_{\text{MeOH}}^{15^\circ} = 0\cdot00374 \times 20 \times 2\cdot3026 = \mathbf{0\cdot172}.$$

Furfurylacrylic acid (m. p. 141°) was prepared according to Liebermann's method (*Ber.*, 1894, 27, 286), and was purified by crystallisation from benzene.

A.—Strength of the hydrochloric acid before mixing = 0·098*N*.

15 c.c. of the alcoholic solution required 29·74 c.c. of *N*/20 alkali.

<i>t</i> in hours.	$\alpha - x.$	$1/t \log. a/a - x.$
2	27·57	0·0165
4·183	25·88	0·0148
6	24·4	0·0143
8	22·98	0·0140

B.—Strength of the hydrochloric acid before mixing = 0·0992*N*.

15 c.c. of the alcoholic solution required 29·86 c.c. of *N*/20 alkali.

<i>t</i> in hours.	$\alpha - x.$	$1/t \log. a/a - x.$
2	27·79	0·0156
4	25·87	0·0156
6	24·11	0·0155
8	22·50	0·0154

C.—Strength of the hydrochloric acid before mixing = 0·100*N*.

15 c.c. of the alcoholic solution required 30·06 c.c. of *N*/20 alkali.

<i>t</i> in hours.	$\alpha - x.$	$1/t \log. a/a - x.$
2	27·92	0·0161
4	25·94	0·0160
6	24·02	0·0162
8	22·34	0·0161

Mean corrected for 0·05*N* hydrochloric acid = A, 0·0152; B, 0·0156; C, 0·0161
(mean = 0·0156).

$$E_{\text{MeOH}}^{15^\circ} = 0\cdot0156 \times 20 \times 2\cdot3026 = \mathbf{0\cdot718}.$$

Furfurylalloacrylic Acid (m. p. 104°).—This acid was obtained at the same time as furfurylacrylic acid described above. The crude acid melting at 83—87° was purified by conversion into piperidine salt and finally by crystallisation from ligroin (b. p. 70—90°) (compare Liebermann, *Ber.*, 1895, 28, 129).

A.—Strength of the hydrochloric acid before mixing = 0.198*N*.

15 c.c. of the alcoholic solution required 29.92 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log. a/a - x$.
1	28.78	0.0169
2	27.77	0.0162
4	25.72	0.0164
4.5	25.13	0.0168

B.—Strength of the hydrochloric acid before mixing = 0.20*N*.

15 c.c. of the alcoholic solution required 29.66 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log. a/a - x$.
1.5	28.05	0.0161
2.5	27.03	0.0161
3.6	25.95	0.0161
4.5	25.01	0.0164

Mean corrected for 0.01*N* hydrochloric acid = A, 0.0167 ; B, 0.0162 (mean = 0.01645).

$$E_{\text{MeOH}}^{15} = 0.01645 \times 10 \times 2.3026 = \mathbf{0.379}.$$

Liebermann (*Ber.*, 1894, 27, 287) describes an acid melting at 83—87°, which at one time he regarded as being furfuryl*allo*acrylic acid, but which was subsequently shown (*Ber.*, 1895, 28, 129) to be a mixture of furfurylacrylic acid with the *allo*-isomeride. We have determined the esterification constants of this mixture and obtained the following numbers :

A.—Strength of the hydrochloric acid before mixing = 0.1*N*.

15 c.c. of the alcoholic solution required 29.97 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log. a/a - x$.
2	28.42	0.0115
4	27.07	0.0110
6	25.83	0.0108
8	24.74	0.0104

B.—Strength of the hydrochloric acid before mixing = 0.0998*N*.

15 c.c. of the alcoholic solution required 30.07 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log. a/a - x$.
2	28.31	0.0130
4	26.96	0.0118
6	25.72	0.0113
8	24.63	0.0108

Mean corrected for 0.05*N* hydrochloric acid = A, 0.0109 ; B, 0.0117 (mean = 0.0113).

$$E_{\text{MeOH}}^{15} = 0.0113 \times 20 \times 2.3026 = \mathbf{0.520}.$$

The result is intermediate between the values for furfurylacrylic acid and its isomeride. It is noticeable that the values of $1/t \log. a/a - x$ are not by any means constant, but diminish as *t* increases.

α-Chlorocinnamic acid was purified from benzene and melted at 139°.

A.—Strength of the hydrochloric acid before mixing = 0.10*N*.

15 c.c. of the alcoholic solution required 29.94 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log. a/a - x$.
48	23.42	0.00222
72	20.59	0.00226
96	18.31	0.00222
120.5	16.32	0.00219

B.—Strength of the hydrochloric acid before mixing = 0.0993*N*.

15 c.c. of the alcoholic solution required 29.94 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log. a/a - x$.
21.5	26.83	0.00219
46	23.70	0.00221
72.5	20.85	0.00217
98	18.49	0.00214

Corrected mean for 0.05*N* hydrochloric acid = A, 0.00221 ; B, 0.00218 (mean = 0.00220).

$$E_{\text{MeOH}}^{15} = 0.00220 \times 20 \times 2.3026 = \mathbf{0.101}.$$

α-Chloroallocinnamic Acid (m. p. 111°).

A.—Strength of the hydrochloric acid before mixing = 0·0998*N*.

15 c.c. of the alcoholic solution required 29·82 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
48	27·86	0·000617
91·5	26·19	0·000616
144	24·49	0·000594

B.—Strength of the hydrochloric acid before mixing = 0·0993*N*.

15 c.c. of the alcoholic solution required 29·77 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
56·5	27·34	0·000655
96·25	25·95	0·000619
148	24·27	0·000599

C.—Strength of the hydrochloric acid before mixing = 0·099*N*.

15 c.c. of the alcoholic solution required 29·79 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
51	27·71	0·000616
96	26·09	0·000600
145	24·74	0·000557
192	23·02	0·000583

Mean corrected for 0·05*N* hydrochloric acid = A, 0·000610; B, 0·000628; C, 0·000595 (mean = 0·000611).

$$E_{\text{MeOH}}^{15^\circ} = 0·000611 \times 20 \times 2·3029 = \mathbf{0·028}.$$

β-Chlorocinnamic acid, obtained by the action of phosphorus pentachloride on ethyl benzoylacetate, was crystallised from benzene and melted at 143°.

A.—Strength of the hydrochloric acid before mixing = 0·197*N*.

15 c.c. of the alcoholic solution required 30·32 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
1·5	28·81	0·0147
3	27·27	0·0153
4·5	25·80	0·0156
6	24·46	0·0155

B.—Strength of the hydrochloric acid before mixing = 0·198*N*.

15 c.c. of the alcoholic solution required 30·27 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a/a</i> - <i>x</i> .
1·58	28·70	0·0146
3·1	27·09	0·0155
4·5	25·66	0·0159
6·5	24·43	0·0143

Mean corrected for 0·10*N* hydrochloric acid = A, 0·0155; B, 0·0152 (mean = 0·0154).

$$E_{\text{MeOH}}^{15^\circ} = 0·0154 \times 10 \times 2·3026 = \mathbf{0·355}.$$

β-Chloroallocinnamic acid, obtained by the action of phosphorus pentachloride on ethyl benzoylacetate and also by the addition of hydrogen chloride to phenylpropionic acid, was crystallised from methyl alcohol and carbon disulphide and melted at 123·5°.

A.—Strength of the hydrochloric acid before mixing = 0.202*N*.

15 c.c. of the alcoholic solution required 29.84 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
2	27.56	0.0173
3.05	26.53	0.0167
5	24.66	0.0166
6	23.81	0.0163

B.—Strength of the hydrochloric acid before mixing = 0.214*N*.

15 c.c. of the alcoholic solution required 29.74 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
2.5	27.10	0.0162
3.5	26.10	0.0162
4.5	24.76	0.0177
6.5	23.03	0.0171

Mean corrected for 0.1*N* hydrochloric acid = A, 0.0165; B, 0.0157 (mean = 0.0161).

$$E_{\text{MeOH}}^{15^\circ} = 0.0161 \times 10 \times 2.3026 = 0.371.$$

α-Bromocinnamic Acid.—This was crystallised from benzene and melted at 130—131°.

A.—Strength of the hydrochloric acid before mixing = 0.10*N*.

15 c.c. of the alcoholic solution required 29.95 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
24	27.41	0.00160
48.5	25.08	0.00159
72	22.97	0.00160
96	21.09	0.00159

B.—Strength of the hydrochloric acid before mixing = 0.100*N*.

15 c.c. of the alcoholic solution required 29.95 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
24	27.11	0.00180
48	24.80	0.00171
72	23.08	0.00157
96	21.18	0.00157

Mean corrected for 0.05*N* hydrochloric acid = A, 0.00160; B, 0.00166 (mean = 0.00163).

$$E_{\text{MeOH}}^{15^\circ} = 0.00163 \times 20 \times 2.3026 = 0.075.$$

α-Bromoalocinnamic acid (m. p. 120°) was purified by crystallisation from ligroin (b. p. 110—130°).

A.—Strength of the hydrochloric acid before mixing = 0.0998*N*.

15 c.c. of the alcoholic solution required 29.95 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
72	28.97	0.000200
144.5	27.94	0.000209
216	26.98	0.000209
312	25.70	0.000213

B.—Strength of the hydrochloric acid before mixing = 0.10*N*.

15 c.c. of the alcoholic solution required 30.03 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
72	29.00	0.000210
144	28.04	0.000206
240	26.67	0.000215
312	25.90	0.000206

Mean corrected for 0.05*N* hydrochloric acid = A, 0.000208; B, 0.000209 (mean = 0.000209).

$$E_{\text{MeOH}}^{15^\circ} = 0.000209 \times 20 \times 2.3026 = 0.00962.$$

β-Bromocinnamic acid, when crystallised from chloroform, melted at 135°.

A.—Strength of the hydrochloric acid before mixing = 0·10*N*.

15 c.c. of the alcoholic solution required 30·15 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
3	28·26	0·00940
6	26·78	0·00858
10	24·79	0·00850
12	23·87	0·00845

B.—Strength of the hydrochloric acid before mixing = 0·1002*N*.

15 c.c. of the alcoholic solution required 29·87 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
9·25	24·78	0·00877
22·15	19·72	0·00814
26·48	18·10	0·00821

C.—Strength of the hydrochloric acid before mixing = 0·1031*N*.

15 c.c. of the alcoholic solution required 30·27 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
17·02	21·81	0·00836
20·78	20·06	0·00860
23·65	19·03	0·00852
27·62	17·81	0·00834

Mean corrected for 0·05*N* hydrochloric acid = A, 0·00851; B, 0·00836; C, 0·00821 (mean = 0·00836).

$$E_{\text{MeOH}}^{15^\circ} = 0\cdot00836 \times 20 \times 2\cdot3026 = \mathbf{0\cdot385}.$$

β-Bromoallocinnamic acid was crystallised from ethyl alcohol and from benzene and melted at 159°.

A.—Strength of the hydrochloric acid before mixing = 0·198*N*.

15 c.c. of the alcoholic solution required 30·43 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
1·5	28·61	0·0178
2·9	26·98	0·0180
4·5	25·16	0·0183
6	23·21	0·0196

B.—Strength of the hydrochloric acid before mixing = 0·202*N*.

15 c.c. of the alcoholic solution required 30·25 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
1·5	27·96	(0·0228)
3	26·73	0·0179
4·5	25·19	0·0177
6	23·43	0·0185

Mean corrected for 0·1*N* hydrochloric acid = A, 0·0186; B (last three values), 0·0178 (mean = 0·0182).

$$E_{\text{MeOH}}^{15^\circ} = 0\cdot0182 \times 10 \times 2\cdot3026 = \mathbf{0\cdot419}.$$

Phenylcinnamic Acid.—The *α*-phenyl- and *α*-phenyl-*allo*-cinnamic acids were prepared by Bakunin's method (*Gazzetta*, 1897, 27, ii, 48) by the condensation of sodium phenylacetate, benzaldehyde, and acetic anhydride. The mixture of crude acids was separated by repeated crystallisation from benzene until the crystals had the correct melting point of the *α*-phenylcinnamic acid, namely, 172°. The mother liquors when evaporated gave residues melting at 120—130°. These were transformed into the aniline salt of the *allo*-acid, which was crystallised from benzene until it had the correct melting point (128°), and was then decomposed with hydrochloric acid, and the liberated *allo*-acid crystallised from light petroleum. From 110 grams of sodium salt,

90 grams of pure α -phenyl acid and 9 grams of *allo*-acid, melting at 136—137°, were obtained.

A.—Strength of the hydrochloric acid before mixing = 0.0990*N*.

15 c.c. of the alcoholic solution required 28.44 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log a/a - x$.
22.5	25.08	0.00243
45	21.68	0.00262
69	18.64	0.00266
93	16.21	0.00262

B.—Strength of the hydrochloric acid before mixing = 0.20*N*.

15 c.c. of the alcoholic solution required 29.32 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log a/a - x$.
14	24.34	0.00578
23.5	21.22	0.00597
38	17.78	0.00571
49	15.30	0.00577

Mean corrected for 0.05*N* hydrochloric acid = A, 0.00260; B (omitting 2nd value), 0.00287 (mean = 0.00274).

$$E_{\text{MeOH}}^{15^\circ} = 0.00274 \times 20 \times 2.3026 = \mathbf{0.126}.$$

Phenylallocinnamic Acid.

A.—Strength of the hydrochloric acid before mixing = 0.198*N*.

15 c.c. of the alcoholic solution required 28.61 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log a/a - x$.
120	27.76	0.000110
187.25	27.13	0.000123
266.5	26.53	0.000124

B.—Strength of the hydrochloric acid before mixing = 0.197*N*.

15 c.c. of the alcoholic solution required 30.46 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log a/a - x$.
114	29.49	0.000124
209.25	28.56	0.000134
282	28.13	0.000123

Mean corrected for 0.1*N* hydrochloric acid = A, 0.000120; B, 0.000129 (mean = 0.000125).

$$E_{\text{MeOH}}^{15^\circ} = 0.000125 \times 10 \times 2.3026 = \mathbf{0.00288}.$$

Butyric acid was redistilled, and the portion boiling at 162° used in the following experiments:

A.—Strength of the hydrochloric acid before mixing = 0.05*N*.

15 c.c. of the alcoholic solution required 29.75 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log a/a - x$.
0.516	17.10	0.465
0.75	13.95	0.439
1.0	11.18	0.425
1.25	8.90	0.420

B.—Strength of the hydrochloric acid before mixing = 0.0491*N*.

15 c.c. of the alcoholic solution required 30.10 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log a/a - x$.
0.3	20.86	0.480
0.5	17.63	0.465
0.75	13.65	0.458
1.0	11.16	0.431

C.—Strength of the hydrochloric acid before mixing = 0.0491*N*.

15 c.c. of the alcoholic solution required 30.25 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	$1/t \log a/a - x$.
0.25	23.46	0.442
0.5	18.09	0.447
0.75	13.93	0.449
1.0	11.11	0.435

Mean corrected for 0.025*N* hydrochloric acid = A, 0.437; B, 0.467; C, 0.451 (mean = 0.452).

$$E_{\text{MeOH}}^{15^\circ} = 0.452 \times 40 \times 2.3026 = \mathbf{41.63}.$$

Dihydrocinnamic acid (m. p. 47·5°) was purified by crystallisation from ligroin (b. p. 30—50°).

A.—Strength of the hydrochloric acid before mixing = 0·049*N*.

15 c.c. of the alcoholic solution required 28·63 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
0·258	21·45	0·486
0·5	16·97	0·454
0·75	13·01	0·457
1·0	10·21	0·448

B.—Strength of the hydrochloric acid before mixing = 0·0998*N*.

15 c.c. of the alcoholic solution required 29·81 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
0·5	10·05	0·944
1·0	3·49	0·931
1·5	1·20	0·930
2	0·38	0·947

C.—Strength of the hydrochloric acid before mixing = 0·10*N*.

15 c.c. of the alcoholic solution required 29·68 c.c. of *N*/20 alcohol.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
0·5	10·14	0·933
1·0	3·59	0·917
1·5	1·18	0·934
2	0·38	0·946

Mean corrected for 0·05*N* hydrochloric acid = A, 0·941 ; B, 0·940 ; C, 0·933 (mean = 0·938).

$$E_{\text{MeOH}}^{15} = 0·938 \times 20 \times 2·3026 = 43·20.$$

Phenylpropionic Acid (m. p. 136—137°).—This acid was prepared according to instructions given in *Trans.*, 1903, 83, 1154, and was purified by crystallisation from chloroform.

A.—Strength of the hydrochloric acid before mixing = 0·10*N*.

15 c.c. of the alcoholic solution required 29·63 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
2	27·73	0·0144
4	26·04	0·0140
6	24·52	0·0137
8	23·36	0·0129

B.—Strength of the hydrochloric acid before mixing = 0·1003*N*.

15 c.c. of the alcoholic solution required 29·76 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
2	27·70	0·0156
4	25·94	0·0149
6	24·45	0·0142
8	23·13	0·0137

C.—Strength of the hydrochloric acid before mixing = 0·10*N*.

15 c.c. of the alcoholic solution required 29·74 c.c. of *N*/20 alkali.

<i>t</i> in hours.	<i>a</i> - <i>x</i> .	1/ <i>t</i> log. <i>a</i> / <i>a</i> - <i>x</i> .
2	27·91	0·0138
4	26·22	0·0137
6	24·69	0·0135
8	23·53	0·0127

Mean corrected for 0·05*N* hydrochloric acid = A, 0·0138 ; B, 0·0146 ; C, 0·0134 (mean = 0·0139).

$$E_{\text{MeOH}}^{15} = 0·0139 \times 20 \times 2·3026 = 0·640.$$

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BOWACK AND LAPWORTH :

Our thanks are due to the Government Grant Committee of the Royal Society for a grant which has helped to defray the expenses involved in this research, and also to Dr. E. Atkinson for assistance in a few of the determinations.

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