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XLV.—*Etherification* * *Constants of Substituted Acetic Acids.*

By JOHN J. SUDBOROUGH and LORENZO L. LLOYD.

THE classical researches of Menschutkin have led to several generalisations with regard to the influence of constitution on the rate of etherification of different fatty acids and of different alcohols (*Annalen*, 1879, **195**, 334; 1879, **197**, 193; *Ann. Chim. Phys.*, 1881, [v], **23**, 14). These indicate, speaking generally, that acids of the type $CR_1R_2R_3 \cdot COOH$, in which $R_1R_2R_3$ are alkyl radicles, are not so readily etherified as acids of the type $CHR_1R_2 \cdot COOH$, and these, in turn less readily than acids of the type $CH_2R \cdot COOH$. The size of the substituting group also plays an important part, as the single large group present in caprylic acid is shown to retard the formation of etheric salt almost as much as the two smaller groups present in isobutyric acid.

The more recent work of Meyer and Sudborough (*Ber.*, 1894, **27**, 510, 1580, and 3146), of V. Meyer (*Ber.*, 1895, **28**, 182, 1254, 2773, and 3197), of Goldschmidt (*Ber.*, 1895, **28**, 3218), and of Kellas (*Zeit. physikal. Chem.*, 1897, **24**, 221) on the etherification of substi-

* [The authors prefer the terms "esterification" and "ester," but have consented to "etherification" and "etheric salt" being used in this paper.—C. E. G.]

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tuted benzoic acids, indicates that, in this series also, the amount of etheric salt formed from a given acid largely depends on the constitution of the acid. It has been shown that diortho-substituted benzoic acids yield little or no etheric salt when their alcoholic solutions are treated in the usual manner with dry hydrogen chloride. When the substituting radicles are large, for example, Cl, Br, I, NO_2, COOH, no appreciable amount of etheric salt is formed, even when hydrogen chloride is passed through the boiling alcoholic solution for a considerable length of time; on the other hand, when the substituting radicles are relatively small, for example, CH_3, OH, or F, small amounts of etheric salt may be obtained under these conditions. The relationship between the amount of salt formed and the weight or volume of the substituting group does not appear to be a very simple one, since Kellas has shown that the nitro-group has a greater retarding influence than either bromine or iodine. The results obtained with ortho-substituted benzoic acids indicate that the following groups, Cl, CH_3, Br, I, NO_2 (Kellas), and Br, CH_3, NO_2 (Goldschmidt), stand in the order given as regards their retarding influence. Arranged according to their relative weights, the order would be CH_3, Cl, NO_2, Br, I, and according to atomic volumes, CH_3, Cl, Br, NO_2, I (compare Graham-Otto I, 3, 449, &c).

Still more recently, we have investigated the series of substituted acrylic acids (Trans., 1897, 73, 81), and here also we have been able to indicate relationships between the constitutions of the various acids and the amount of etheric salt formed; for example, acids of the types,

$$\begin{array}{l} H\cdot C\cdot X \\ \quad\;\; \| \\ Y\cdot C\cdot COOH \end{array}, \quad \text{or} \quad \begin{array}{l} Z\cdot C\cdot X \\ \quad\;\; \| \\ Y\cdot C\cdot COOH \end{array},$$

are difficult to etherify by the usual method with hydrogen chloride, and α-substituted acrylic acids also are more difficult to etherify than the isomeric β-compounds. The results we have already published were made with acids in which the substituting groups were relatively large, for example, C_6H_5, I, Br, and Cl; since then, further investigations have been made with methyl derivatives of acrylic acid; the results of these we hope soon to be able to lay before the Society.

The results obtained with substituted benzoic acids indicate that the nature of the substituting group, that is, its positive or negative nature, is of very little influence, as both negative (NO_2, Br, COOH, &c.) and positive (CH_3, &c.) groups cause a retardation. The chief factor appears to be the size of the substituting groups, although, as already stated, it is not clear what is the relationship between the relative weight or volume of the substituting group and its retarding influence.

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As interesting results have been obtained in both the benzoic and acrylic acid series, our attention was drawn naturally to the acetic acid series, and we undertook experiments in order to determine whether acids of the general type, $CX_1X_2X_3 \cdot COOH$, are not also somewhat difficult to etherify as compared with acetic acid itself. The results obtained by Menschutkin, and already referred to, only apply to alkyl derivatives of acetic acids, and, what is of still greater importance, were obtained without employing a catalytic agent, such as hydrogen chloride; in fact, Menschutkin used the method of etherification usually spoken of now as "autocatalysis." In order that our results might be comparable with those obtained with benzoic and acrylic acids, we determined to employ the hydrogen chloride method and to include halogen, as well as alkyl, derivatives of acetic acid. The only experiments of a general kind, in addition to Menschutkin's, which appear to have been made in this series are those of Lichty (*Amer. Chem. Journ.*, 1895, **17**, 27, and 1896, **18**, 590), which indicate that, when the autocatalytic method is employed with acetic, chloracetic, dichloracetic, and trichloracetic acids, acetic acid is the least readily, and trichloracetic acid the most readily etherified, although the limits of etherification do not differ to any very great extent.

These results show clearly that, when the autocatalytic method is employed, a broad generalisation with regard to the influence of substituting groups on the retardation of etherification cannot be drawn, as, according to Menschutkin, three methyl groups retard the formation of etheric salt, and, according to Lichty, three chlorine atoms facilitate etherification. We therefore determined to see whether this generalisation held good when hydrogen chloride was introduced as a catalytic agent. The acids selected for this purpose were acetic, propionic, dimethylacetic (isobutyric), trimethylacetic, mono-, di-, and tri-chloracetic, mono-, di-, and tri-bromacetic, iodacetic, tri-iodacetic, phenylacetic, diphenylacetic, dimethylbromacetic (α-bromisobutyric), and methyldibromacetic ($\alpha\alpha$-dibromopropionic). The method employed in the investigation of the benzoic and acrylic series could not be adopted with these acids, as most of the etheric salts are so readily volatile; the method of direct titration with a standard solution of alkali was therefore used, although it is only applicable at temperatures below 25°, as above this limit part of the hydrogen chloride reacts with the alcohol (methylic alcohol) forming an alkylic chloride with consequent loss of acid (Kellas, *loc. cit.*).

In none of the other series have the actual etherification constants been determined, merely the amount of etheric salt formed at the end of definite intervals of time when a hydrogen chloride solution of definite strength is employed.

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Goldschmidt (*Ber.*, 1895, **28**, 3218) has shown that, although the reaction between alcohol and acid, in the presence of hydrogen chloride, is bimolecular, yet when a large excess of alcohol is present it may be regarded as monomolecular, and in all the cases which he investigated, an etherification constant could be obtained readily. He has also shown that the velocity of etherification depends on the catalytic agent employed, the constant being almost identical when etherification is brought about either by hydrogen chloride or by hydrogen bromide, but is less when an equivalent quantity of picric acid is employed. In dilute alcoholic solutions, the velocity is proportional to the concentration of the hydrogen chloride.

Still more recently (*Zeit. physikal. Chem.*, 1898, **27**, 250), Kistiakowsky has investigated both the etherification of several fatty acids in mixtures of alcohol and water, and the hydrolysis of the etheric salts of the same acids in mixtures of alcohol and water, by the aid of hydrogen chloride. The results show that, provided the conditions are the same, identical constants are obtained for the etherification of an acid and also for the hydrolysis of its etheric salt, and that in the presence of hydrogen chloride the constants are directly proportional to the amount of hydrogen chloride present. Most interesting of all, from our point of view, is the fact that he has shown that acetic acid has a smaller constant than formic acid, a phenomenon he attributed to the smaller dissociation constant for the former, and further, in the case of the chloracetic acids, that the constants decrease with the increase in the number of chlorine atoms, although the actual constant was established in the case of chloracetic acid alone.

Our results were practically complete when Kistiakowsky's paper appeared, and they confirm, and in many respects amplify, some of his points.

As our experiments were made with pure ethylic alcohol, dried over sodium, we have used the equation for a monomolecular reaction, $K = \frac{1}{t} \log \frac{a}{a-x}$, in which t is the time in hours, and a the initial concentration of the acid.

According to both Goldschmidt and Kistiakowsky, the constant, K, is directly proportional to the amount of hydrogen chloride present, at any rate, in dilute solutions; to confirm this, we have made experiments with phenylacetic acid in ethylic alcohol, using hydrogen chloride of different strengths, namely, N/20, N/40, and N/60. The method adopted was that used in all the other cases, and described on page 471. The strength of the phenylacetic acid solution was practically N/10 in all cases.

The constants found are 0·01494 with N/60 acid, 0·02246 with N/40 acid (see p. 478), and 0·04468 with N/20 acid. Assuming the constant

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A.			B.		
Using N/20 HCl in ethylic alcohol. 30 c.c. of the solution required 60 c.c. of N/20 alkali to neutralise the organic acid present.			Using N/60 HCl. 30 c.c. of the solution required 60 c.c. of N/20 alkali to neutralise the organic acid present.		
t in hours.	$a-x$.	$\frac{1}{t}log_{10}\frac{a}{a-x}$.	t in hours.	$a-x$.	$\frac{1}{t}log_{10}\frac{a}{a-x}$.
1	54·1	0·0450	2	56·0	0·0150
2	48·9	0·0444	4	52·3	0·0149
3	44·1	0·0446	6	48·8	0·0150
4	39·8	0·0446	8	45·6	0·0149
5	35·8	0·0449	10	42·6	0·0149
6	32·4	0·0446			
		Mean = 0·04468			Mean = 0·01494

to be proportional to the amount of hydrogen chloride present, the values should be 0·01494, 0·02241, and 0·04482.

The general method we adopted was as follows. In each case, the acid was purified by crystallisation or distillation, and an amount sufficient to give 150 c.c. of N/5 solution was then weighed out. As most of the acids are extremely hygroscopic, they were placed overnight in a desiccator over sulphuric acid, and in the morning dissolved in absolute ethylic alcohol which had been distilled over sodium, the solution being made up to 150 c.c. Two lots of 15 c.c. each were then titrated with N/20 sodium hydroxide solution, using phenolphthalein as an indicator, and the mean of the two results taken. One hundred c.c. of the acid solution was then mixed with 100 c.c. of N/20 HCl in ethylic alcohol which had also been distilled over sodium, so that the solution contained N/40 HCl. All the experiments were carried out with N/40 HCl, as it was found that acetic and propionic acids were etherified too readily when stronger solutions were employed. The mixture was well shaken for a minute or two in a flask kept as nearly as possible at the same temperature as that at which the actual etherification occurred; quantities of 30 c.c. were then measured from a burette into small bottles of about 150 c.c. capacity, which were afterwards stoppered and placed in a bath at constant temperature. All the bottles employed had been previously filled with concentrated hydrochloric acid, and left for several days to remove any soluble alkalis from the surface of the glass. The bath employed for our determinations was a large sink, through which a stream of water from the main was kept running, and in which the bottles were im-

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mersed nearly to their necks. It was found that, for several months in summer, a constant temperature of 14—15° could be maintained. We have taken 14·5° as the mean temperature. During the cooler months, a small stream of warm water was mixed with the cold water passing through the sink, so that the temperature was kept at 14—15°.

At the end of a given time, t, which varied with the different acids, and which could only be determined by actual experiment, one of the bottles was removed, and its contents titrated by first running in N/10 and then finishing the titration with N/20 sodium hydroxide, using phenolphthalein as indicator.

In this way, we obtained the factors required for the equation $K=\frac{1}{t}\log_e \frac{a}{a-x}$; a is the initial concentration of the acid, and may be denoted by the amount of N/20 alkali required to neutralise 15 c.c. of the original acid solution before being mixed with its own volume of N/20 HCl in ethylic alcohol; $a-x$ is the concentration of the acid after the time t, and may be represented by the number of c.c. of alkali (calculated as N/20) required to neutralise the contents of a bottle after remaining for the time t, and subtracting the number of c.c. of N/20 alkali required to neutralise the HCl present. The expression $\frac{1}{t}\log_{10}\frac{a}{a-x}$ can then be readily calculated; this, multiplied by 2·3026 and by 40, gives the etherification constant for the acid at the given temperature when normal hydrogen chloride is employed in ethylic alcoholic solution.

We suggest that the letter E should be used to denote the etherification constant of an organic acid when normal hydrogen chloride is employed. As the constant is proportional to the concentration of the hydrogen chloride, it follows that this constant can be calculated when hydrogen chloride solutions of different strengths are employed. As the constant varies, moreover, with the temperature and also with the different alcohols, we suggest the use of the expressions $E^{10°}_{MeOH}$, $E^{15°}_{EtOH}$, &c., to represent the etherification constants, so that the temperature and the specific alcohol may also be indicated.

The alcohol we employed was Kahlbaum's 99·8 per cent. ethylic alcohol, which we distilled over sodium; its sp. gr. was then d 15·5°/15·5° = 0·7946.

In connection with the determination of the constant for tribromacetic acid, we found that when the bottles were left exposed to daylight for several hours, their contents became brownish-red, and on titration a larger amount of acid was found than was originally added; in fact, the amount of acid increased, instead of diminishing

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with an increase in the length of time during which the solutions were left:—

30 c.c.,	after	24	hours,	required	62·6	c.c.	N/20	alkali.
30 „	„	48	„	„	65·9	„	„	„
30 „	„	96	„	„	69·1	„	„	„
30 „	„	144	„	„	111·3	„	„	„

This increase in the amount of acid can only be due to the decomposition of the tribromo-acid yielding hydrogen bromide, and, probably, bromine. The decomposition does not occur when the bottles are kept in the dark, as was proved by estimating the amount of hydrogen chloride (+ bromide, if any) after the lapse of several hours. The solution was poured into water acidified with nitric acid, and then precipitated with silver nitrate, when the amount of silver chloride found was practically identical with that required for the hydrogen chloride originally added.

As alcoholic solutions of the tribromo-acid are decomposed so readily when exposed to sunlight, it was considered advisable to conduct the other determinations for halogen acids also in the dark, with, of course, the exception of the final titrations.

A slight difficulty was also met with in titrating the alcoholic solutions of the halogen acids after they had been allowed to remain for some time with the hydrogen chloride solution, as it was found that the pink coloration with the phenolphthalein solution was extremely evanescent, undoubtedly due to the fact that the etheric salts of these acids are hydrolysed so readily by alkalis (see p. 482). The reading taken in all cases was that at which the pink colour remained for 2—3 seconds.

Experimental.

Acetic Acid.—Schuchardt's pure acetic acid melting at 16·5° was submitted twice to fractional distillation, using a fractionating column and collecting the fractions in a Brühl receiver, the air in which was kept dry by the aid of sulphuric acid. The portion boiling at 118° was employed for our experiments, using an alcoholic solution.

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A.			B.		
15 c.c. of the alcoholic solution required 60·4 c.c. N/20 alkali. 15 c.c. of the alcoholic solution required 60·4 c.c. N/20 alkali.			15 c.c. of the alcoholic solution required 60·1 c.c. N/20 alkali. 15 c.c. of the alcoholic solution required 60·2 c.c. N/20 alkali.		
t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$.
1	55·1	0·0399	1	54·9	0·0397
2	50·3	0·0397	2	50·1	0·0397
3	45·9	0·0397	3	45·7	0·0398
4	41·9	0·0397	4	41·7	0·0398
5	38·2	0·0398	5	38·1	0·0397
6	34·9	0·0397	6	34·7	0·0398

Mean of A and B = 0·3975.

$$E_{EtOH}^{14\cdot5^\circ} = 0\cdot03975 \times 40 \times 2\cdot3026 = 3\cdot661.$$

Propionic Acid.—Kahlbaum's propionic acid was fractionated in a similar manner to the acetic acid, and the fraction passing over at 140° was employed.

A.			B.		
15 c.c. required 60·2 c.c. N/20 alkali. 15 c.c. ,, 60·2 c.c. ,, ,,			15 c.c. required 60 c.c. N/20 alkali. 15 c.c. ,, 60 c.c. ,, ,,		
t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$.
1·5	53·7	0·0331	1·5	53·4	0·0337
3	47·9	0·0331	3	47·7	0·0332
4·5	42·7	0·0331	4·5	42·5	0·0333
6	38·1	0·0331	6	37·9	0·0333
7·5	34·1	0·0329	7·5	34·2	0·0325
9	30·5	0·0328	9	30·3	0·0330

Mean of A and B = 0·0331.

$$E_{EtOH}^{14\cdot5^\circ} = 3\cdot049.$$

Isobutyric Acid.—This was twice redistilled, and the portion boiling at 155·5° was used.

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A.			B.		
15 c.c. required 60·1 c.c. N/20 alkali. 15 c.c. ,, 60·1 c.c. ,, ,,			15 c.c. required 59·8 c.c. N/20 alkali. 15 c.c. ,, 59·8 c.c. ,, ,,		
t in hours.	$a-x$.	$\frac{1}{t}log\frac{a}{a-x}$.	t in hours.	$a-x$.	$\frac{1}{t}log\frac{a}{a-x}$.
2	57·1	0·0111	2	56·8	0·0112
4	54·2	0·0112	4	53·9	0·0113
6	51·6	0·0110	6	51·2	0·0112
8	49·1	0·0110	8	48·8	0·0110
10	46·8	0·0109	10	46·6	0·0108
12	44·4	0·0110	12	44·2	0·0109

C.

15 c.c. required 61·0 c.c. N/20 alkali. 15 c.c. ,, 61·0 c.c. ,, ,,		
t in hours.	$a-x$.	$\frac{1}{t}log\frac{a}{a-x}$.
2	57·9	0·0113
4	55·1	0·0110
6	52·3	0·0111
8	49·7	0·0111
12	44·9	0·0111

Mean of A, B, and C = 0·01107.

$E^{14\cdot5^\circ}_{EtOH} = 1\cdot0196.$

Trimethylacetic Acid.—This acid was prepared by the oxidation of pinacolin by Friedel and Silva's method (*Ber.*, 1873, **6**, 146, and 826), and was purified by repeated fractionation, being finally obtained as a colourless, crystalline solid melting at 35° and boiling at 163·5—164°.

A.			B.		
15 c.c. required 60·2 c.c. N/20 alkali. 15 c.c. ,, 60·3 c.c. ,, ,, Mean = 60·25.			15 c.c. required 60·0 c.c. N/20 alkali. 15 c.c. ,, 60·0 c.c. ,, ,,		
t in hours.	$a-x$.	$\frac{1}{t}log\frac{a}{a-x}$.	t in hours.	$a-x$.	$\frac{1}{t}log\frac{a}{a-x}$.
6	59·4	0·001028	24	56·8	0·000992
24	57·1	0·000972	48	53·7	0·001004
48	54·1	0·000974	72	50·8	0·001004
72	51·2	0·000982	96	48·2	0·000991
96	48·6	0·000972	120	47·5	0·000985
144	43·8	0·000962	168	41·1	0·000978

Mean of A and B = 0·000987.

$E^{14\cdot5^\circ}_{EtOH} = 0\cdot0909.$

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Chloracetic Acid.—This acid was purified by distillation under reduced pressure; it passed over at 104—105° under 20 mm. pressure, and then melted at 63°. Tollens (*Ber.*, 1884, 17, 665) gives 62·5—63·2°.

A.
15 c.c. required 60·6 c.c. N/20 alkali.
15 c.c. ,, 60·6 c.c. ,, ,,

B.
15 c.c. required 60·3 c.c. N/20 alkali.
15 c.c. ,, 60·3 c.c. ,, ,,

	No. of experiments.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$			$E^{14\cdot5°}_{EtOH}$.
		Extremes.	Extremes.	Max.	Min.	Mean.	
A.	6	1—7	57·0—39·7	0·0266	0·0262	0·0264	2·432
B.	6	1—6	56·7—41·8	0·0268	0·0264		

Dichloracetic Acid.—After fractional distillation, this acid was obtained as a colourless liquid boiling at 190·5°.

A. 15 c.c. required 59·8 c.c. N/20 alkali.
B. 15 c.c. ,, 60·1 c.c. ,, ,,
C. 15 c.c. ,, 62·2 c.c. ,, ,,

	No. of experiments.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$.			$E^{14\cdot5°}_{EtOH}$.
		Extremes.	Extremes.	Max.	Min.	Mean.	
A.	5	48—168	55·4—45·6	0·000705	0·000691	0·000695	0·064
B.	6	24—168	57·8—46·0	0·000706	0·000691		
C.	6	48—288	57·6—39·4	0·000695	0·000687		

Trichloracetic Acid.—This, when purified by distillation under atmospheric pressure, passed over at 195—195·5° under a pressure of 754 mm., and melted at 57°. Clermont gives 55° (*Ann. Chim. Phys.*, 1885, [vi], 6, 135).

A.
15 c.c. required 60·5 c.c. N/20 alkali.
15 c.c. ,, 60·5 c.c. ,, ,,

B.
15 c.c. required 60·1 c.c. N/20 alkali.
15 c.c. ,, 60·2 c.c. ,, ,,

	No. of experiments.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$			E.
		Extremes.	Extremes.	Max.	Min.	Mean.	
A.	6	12—120	59·8—54·2	0·000421	0·000393	0·000403	0·03712
B.	6	24—168	58·8—51·6	0·000411	0·000396		

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Bromacetic Acid.—This distilled at 117—118° under a pressure of 15 mm., and melted at 49—50°. Kachler gives 50—51° (*Monats.*, 1869, **2**, 559).

A.	B.
15 c.c. required 60·3 c.c. N/20 alkali.	15 c.c. required 59·9 c.c. N/20 alkali.
15 c.c. ,, 60·3 c.c. ,, ,,	15 c.c. ,, 59·9 c.c. ,, ,,

	No. of experiments.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$.			E.
		Extremes.	Extremes.	Max.	Min.	Mean.	
A.	6	1—7	57·3—42·7	0·0222	0·0214	0·02165	1·994
B.	6	1—6	56·9—44·5	0·0223	0·0213		

Dibromacetic Acid.—After several distillations under diminished pressure, this was obtained in colourless prisms melting at 48°. Schäffer gives 45—50° (*Ber.*, 1871, **4**, 368).

A.	B.
15 c.c. required 60·1 c.c. N/20 alkali.	15 c.c. required 59·8 c.c. N/20 alkali.
15 c.c. ,, 60·1 c.c. ,, ,,	15 c.c. ,, 59·8 c.c. ,, ,,

	No. of experiments.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$.			E.
		Extremes.	Extremes.	Max.	Min.	Mean.	
A.	5	24—144	58·3—50·0	0·000559	0·000550	0·000554	0·051
B.	5	24—144	57·9—49·7	0·000584	0·000514		

Tribromacetic Acid.—As obtained from Kahlbaum, this acid melted at 131°, and even after repeated crystallisation from light petroleum melted at the same temperature. Analysis proved it to be pure. Gal (*Annalen*, 1864, **129**, 56) gives 135°.

A.	B.
15 c.c. required 60·1 c.c. N/20 alkali.	15 c.c. required 60 c.c. N/20 alkali.
15 c.c. ,, 60·1 c.c. ,, ,,	15 c.c. ,, 60·1 c.c. ,, ,,

	No. of experiments.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$.			E.
		Extremes.	Extremes.	Max.	Min.	Mean.	
A.	6	24—168	59·6—56·8	0·000151	0·000142	0·000146	0·01345
B.	6	24—168	59·6—56·8	0·000149	0·000136		

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Iodacetic Acid.—Ethylic iodacetate, obtained by heating ethylic chloracetate with potassium iodide and alcohol, is a colourless liquid boiling at 178—179°, and having an extremely pungent, acrid odour. The ethylic salt was hydrolysed by shaking it in a separating funnel with an excess of concentrated barium hydroxide solution until all the oil had disappeared; the solution was then rendered acid with hydrochloric acid, extracted with ether, and the crude acid obtained on distilling off the ether was purified by crystallisation from light petroleum. It forms long, colourless, prismatic needles melting at 82°.

A.

15 c.c. required 60·4 c.c. N/20 alkali.
15 c.c. ,, 60·4 c.c. ,, ,,

No. of experiments.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$.			E.
	Extremes.	Extremes.	Max.	Min.	Mean.	
5	1·5—8	56·6—43·6	0·0190	0·0177	0·0186	1·713

Triodacetic Acid.—The etherification constant of this acid could not be determined, as, although it dissolves fairly readily in alcohol, the solution immediately becomes deep brown owing to the liberation of iodine; this decomposition takes place even when the solution is kept in the dark.

Phenylacetic Acid.—After several recrystallisations from light petroleum, this acid melted at 76°.

A.

15 c.c. required 60·1 c.c. N/20 alkali.
15 c.c. ,, 60·1 c.c. ,, ,,

B.

15 c.c. required 60·2 c.c. N/20 alkali.
15 c.c ,, 60·2 c.c. ,, ,,

	No. of experiments.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$			E.
		Extremes.	Extremes.	Max.	Min.	Mean.	
A.	6	1·5—9	55·6—37·8	0·0226	0·0224	0·02246	2·068
B.	6	1—8	57·2—39·8	0·0226	0·0222		

Diphenylacetic Acid.—This acid, obtained by reducing benzylic acid with hydriodic acid and phosphorus, was obtained in the form of well-developed, colourless prisms melting at 146°. Jena (*Annalen,*

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1870, **155**, 84) gives 145—146°; Friedel and Balsohn (*Bull. Soc. Chim.*, 1880, **33**, 590) give 148°.

A.	B.
15 c.c. required 59·9 c.c. N/20 alkali.	15 c.c. required 60·1 c.c. N/20 alkali.
15 c.c. ,, 59·7 c.c. ,, ,,	15 c.c. ,, 60·1 c.c. ,, ,,
Mean = 59·8.	

	No. of experiments.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$.			E.
		Extremes.	Extremes.	Max.	Min.	Mean.	
A.	6	24—168	57·9—47·3	0·000619	0·000584	0·0006065	0·05586
B.	5	24—168	58·1—47·5	0·000612	0·000603		

Triphenylacetic Acid.—Heyl and Meyer (*Ber.*, 1895, **28**, 2789), who investigated the etherification of this acid with methylic alcohol at its boiling point, have shown that when the boiling alcoholic solution is kept saturated with hydrogen chloride for 3 hours, only 20 per cent. of the theoretical amount of etheric salt is formed. We have not attempted to determine the etherification at 14·5° with N/40 HCl, as from Heyl and Meyer's results, the amount of salt formed under these conditions would be practically nil.

αα-Dibromopropionic Acid, $CMeBr_2 \cdot COOH$.—The crude acid, which we obtained from Schuchardt, was purified by distillation under reduced pressure; the pure acid distils at 126° under a pressure of 20 mm., and then solidifies to colourless crystals melting at 61°. It was found impossible to recrystallise the acid, as it is so readily soluble in all the usual solvents.

A.	B.
15 c.c. required 60·3 c.c. N/20 alkali.	15 c c. required 61·6 c.c. N/20 alkali.
15 c.c. ,, 60·3 c.c. ,, ,,	15 c.c. ,, 61·6 c.c. ,, ,,

	No. of experiments.	t in hours.	$a-x$.	$\frac{1}{t}\log\frac{a}{a-x}$			E.
		Extremes.	Extremes.	Max.	Min.	Mean.	
A.	6	24—168	59·4—54·2	0·000276	0·000255	0·000263	0·0242
B.	6	48—264	59·8—52·7	0·000268	0·000256		

α-Bromisobutyric Acid, $CMe_2Br \cdot COOH$.—This acid was also purified by distillation under diminished pressure; it passed over at 115°

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under 24 mm. pressure, and formed colourless crystals melting at 47—48° and extremely readily soluble in all the usual solvents.

A.	B.
15 c.c. required 60·1 c.c. N/20 alkali.	15 c.c. required 59·8 c.c. N/20 alkali.
15 c.c. ,, 60·0 c.c. ,, ,,	15 c.c. ,, 59·8 c.c. ,, ,,
Mean = 60·05.	

	No. of experiments.	t in hours.	$a-x$.		$\frac{1}{t}\log\frac{a}{a-x}$.			E.
		Extremes.	Extremes, corresponding to extremes t.	Max.	Min.	Mean.		
A.	6	12—120	59·4—53·9	0·000394	0·000377	0·000387		0·0356
B.	6	24—168	58·5—51·5	0·000398	0·000386			

The following table gives a list of the constants found, arranged in descending order, the value K (dissociation constant) is also given where it is known.

Acid.	Formula.	$E^{14\cdot5°}_{EtOH}$.	K.
Acetic	$CH_3\cdot COOH$	3·661	0·00180 [O]
Propionic	$CH_2Me\cdot COOH$	3·049	0·00134 [O]
Chloracetic	$CH_2Cl\cdot COOH$	2·432	0·155 [O]
Phenylacetic	$CH_2Ph\cdot COOH$	2·068	
Bromacetic	$CH_2Br\cdot COOH$	1·994	0·138 [O]
Iodacetic	$CH_2I\cdot COOH$	1·713	0·075 [O]
Isobutyric	$CHMe_2\cdot COOH$	1·0196	0·00144 [O]
Trimethylacetic	$CMe_3\cdot COOH$	0·0909	0·000978 [P]
Dichloracetic	$CHCl_2\cdot COOH$	0·0640	5·14 [O]
Diphenylacetic	$CHPh_2\cdot COOH$	0·05586	
Dibromacetic	$CHBr_2\cdot COOH$	0·0510	
Trichloracetic	$CCl_3\cdot COOH$	0·0372	121·0 [O]
α-Bromisobutyric	$CMe_2Br\cdot COOH$	0·0356	
αα-Dibromopropionic	$CMeBr_2\cdot COOH$	0·0242	3·3 [W]
Tribromacetic	$CBr_3\cdot COOH$	0·01345	

O = Ostwald, *Zeit. phys. Chem.*, 1889, **3**, 176. P = Pomeranz, *Monats.*, 1897, **18**, 575. W = Walden, *Zeit. phys. Chem.*, 1892, **10**, 651.

The following conclusions may be drawn.

1. It appears that all substituted acetic acids have smaller etherification constants than acetic acid itself, when the etherification is brought about by the aid of hydrogen chloride.

A glance at the table indicates that the etherification constant is independent of the strength of the acid, and merely or mainly depends

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on the number of substituting groups introduced into the acetic acid molecule, and also on the relative "sizes" of these groups.

These results are interesting when compared with those previously obtained by the autocatalytic method. According to Lichty (*loc. cit.*), a strong acid, like any of the chloracetic acids, is more readily etherified than a feeble acid, such as acetic; in fact, acetic and the chloracetic acids, when arranged according to their initial velocity of etherification as given by Lichty, follow the same order as when arranged according to their strength, namely, acetic, chloracetic, dichloracetic, trichloracetic. It is then obvious that the two processes of etherification give very different results, since when using hydrogen chloride the main factor is the constitution of the acid, and when no direct catalytic agent is employed the main factor appears to be the strength of the organic acid. Goldschmidt and Kistiakowsky have already drawn attention to the difference in the results obtained by the catalytic and by the autocatalytic methods.

2. In a series of substituted acetic acids of the type (*a*) $CH_2X{\cdot}COOH$, (*b*) $CHX_2{\cdot}COOH$, (*c*) $CX_3{\cdot}COOH$, it appears that the mono-substituted acid is always more readily etherified than the di-substituted acid, and the latter than the tri-substituted acid. This generalisation holds for all the series investigated, namely, methyl-, chlor-, brom-, and phenyl-acetic acids; it does not, however, always follow that an acid of the type $CX_3{\cdot}COOH$ has a smaller etherification constant than one of the type $CHY_2{\cdot}COOH$. From the table on page 480, it is seen that dichlor-, dibrom-, and diphenyl-acetic acids have lower constants than trimethylacetic acid. It may, however, be taken as a general rule that acids of the type $CX_1X_2X_3{\cdot}COOH$ have low etherification constants.

3. An interesting point on which our researches throw but little light is the relationship between the retardation of etherification and the size of the group or radicle bringing about the retardation. In the acetic series, it appears that the introduction of a methyl group has the least influence on the lowering of the etherification constant, then follow Cl, Ph, Br, I, but, on the other hand, we have the fact that triphenylacetic acid is not nearly so readily etherified as tribromacetic acid (compare Heyl and Meyer, *Ber.*, 1895, **28**, 2789). The question whether the groups CH_3, Cl, C_6H_5, Br, I, &c., when introduced into an acid molecule, always produce a similar effect on the etherification constant, can only be determined by further investigations, which are in progress.

Another interesting point is the remarkable difference between the etherification constants of acids of the benzoic and acetic series. We show in the present communication that the introduction of three bromine atoms in place of three hydrogen atoms in acetic acid reduces the etherification constant to about 1/300th of its original value; in the

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benzoic series, on the other hand, we find that the introduction of two bromine atoms in place of two hydrogen atoms in ortho-positions with respect to the carboxylic groups renders the acid incapable of forming etheric salts. At present, we do not understand why the two atoms in the ortho-positions have an influence so much greater than that of three atoms attached to the carbon atom to which the carboxylic group is directly united; the explanation may perhaps be found in the stereochemistry of the benzene molecule.

Hydrolysis of the Etheric Salts of Substituted Acetic Acids.—V. Meyer (*Ber.*, 1895, **28**, 1263) has shown that the etheric salts of diortho-substituted benzoic acids are much more difficult to hydrolyse than their isomerides, and Kellas (*loc. cit.*) has shown the same for the etheric salts of ortho-substituted acids. In the latter series, however, it is not always the salt most difficult to form which is most difficult to hydrolyse (compare Wegscheider, *Ber.*, 1895, **28**, 2536). The velocity of hydrolysis of various etheric salts of fatty acids has been determined by Reicher (*Annalen*, 1885, **228**, 257), Hemptinne (*Zeit. physikal. Chem.*, 1894, **13**, 562), Löwenherz (*ibid.*, 1894, **15**, 389), and others, and it is shown that when the hydrolysis is brought about by an acid the results differ from those obtained when an alkali is employed.

As already stated, the recent work of Kistiakowsky shows that the velocity constant of hydrolysis of an etheric salt, $R{\cdot}COOC_2H_5$, by a solution of hydrogen chloride in a mixture of water and alcohol is identical with the etherification constant of the acid $R{\cdot}COOH$ when an aqueous alcoholic solution of hydrogen chloride of exactly the same concentration is employed. Our results indicate that the latter constant is independent of the strength of the acid, and depends on the constitution or the stereochemistry of the acid molecule. It would necessarily follow that the velocity of hydrolysis is independent of the strength of the organic acid when hydrochloric acid is employed as the hydrolysing agent. That the same remark does not hold good when an alkaline hydrolysing agent is used, is proved by experiments made by Feilmann in conjunction with one of us on the hydrolysis of the etheric salts of substituted acetic acids by the aid of alcoholic potash (Proc., 1897, **13**, 241). The results obtained indicate that, of the ethylic salts of methylacetic acids, ethylic acetate is most readily hydrolysed, then follow ethylic propionate, isobutyrate, and trimethylacetate; in other words, in this series the etheric salts which are formed least readily are those which are hydrolysed by sodium hydroxide with the greatest difficulty. The results we obtained with the ethers of halogen acetic acids were quite different. When a N/5 solution of ethylic chloracetate, dichloracetate, trichloracetate, monobromacetate, or tribromacetate in rectified spirit was mixed with an equal volume

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of N/5 sodium hydroxide, dissolved in rectified spirit, and after some time, the mixture was titrated with N/5 oxalic acid, using phenolphthalein as an indicator, it was found that, in each case, practically the whole of the alkali had disappeared in 10 minutes. The solutions were tested for chloride or bromide, but none was found, thus indicating that the alkali had been employed in hydrolysing the etheric salt. When the N/5 solution of the etheric salt was mixed with twice its volume of the N/5 alkali, and the mixture titrated at the end of 10 minutes, it was found in each case that the amount of alkali used was practically the amount required to hydrolyse the salt; if, instead of being titrated at the end of ten minutes, the mixture was allowed to remain for 1—2 days at the ordinary temperature, then a considerable amount of chloride or bromide was found in the solution, indicating that the excess of alkali had been more or less used up in decomposing the halogen acetic acids.

The only way in which we can account for this ready hydrolysis of the etheric salts of halogen acetic acids is by taking into account the strength of the acids. According to Ostwald's determinations of their electrical conductivities, they are all remarkably strong acids when compared with acetic acid or the fatty acids generally, and this we are forced to consider is the reason why their etheric salts are so readily hydrolysed by alkalis. This consideration may account for the differences previously observed in the hydrolysis of etheric salts with hydrochloric acid and with alkalis. When hydrochloric acid is employed, the hydrolysis will depend mainly on the stereochemistry of the salt molecule (that is, both of the acid and alcohol portion), and not on the strength of the acid, but when an alkali is employed the strength of the organic acid becomes an important factor, and in certain cases, for example, in the etheric salts of halogen fatty acids becomes the main factor, more or less completely masking the influence of the stereochemistry of the molecule.

UNIVERSITY COLLEGE,
NOTTINGHAM.