

LXXVI.—*The Influence of the Hydroxyl and Alkoxy Groups on the Velocity of Saponification. Part I.*

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ALTHOUGH many investigations have been undertaken for the purpose of obtaining some insight into the influence of constitution on the velocity of ester formation under the influence of mineral acids, more especially in the case of the substituted benzoic and acetic acids (Menschutkin, Victor Meyer, Meyer and Sudborough, Goldschmidt, Kellas, Sudborough and Lloyd, Wegscheider, and others), comparatively little systematic work has been done on the rate of saponification of esters by alkalis as affected by constitution. In the case of esterification of acids in presence of hydrochloric acid, it was found that substitution diminishes, in every case, the velocity of esterification, and this influence is specially prominent in the case of the

ortho-substituted benzoic acids. In all such cases, it is apparently the mass, not the chemical nature of the substituent, that is of importance. The retarding influence of substitution, however, is observed not only in the case of the substituted benzoic acids, but also in the case of the substituted acetic acids (Sudborough and Lloyd, *Trans.*, 1898, **73**, 81; 1899, **75**, 467).

Whilst with regard to hydrolysis by hydrochloric acid the general rule applies that esters which are formed with difficulty under the influence of hydrochloric acid are also hydrolysed with difficulty (V. Meyer, *Ber.*, 1895, **28**, 1262; compare Kistiakowsky, *Zeit. physikal. Chem.*, 1898, **27**, 250), the same does not apply to saponification with alkali (compare Kellas, *Zeit. physikal. Chem.*, 1897, **24**, 243; van Dyken, *Rec. Trav. chim.*, 1895, **14**, 106). In this case, the effect of substitution varies with the nature of the substituent. Thus, whilst substitution of hydrogen by alkyl groups in acetic acid diminishes the velocity of saponification, replacement of hydrogen by halogens increases the velocity of saponification (Sudborough and Feilman, *Proc.*, 1897, **13**, 241). Although, in these cases, the velocity of saponification increases with the strength of the acid, other cases are known where this is not so; as, for example, in the case of the saponification of the esters of the substituted malonic acids (Hjelt, *Ber.*, 1896, **29**, 110; 1864, **31**, 1844). There are other factors, therefore, such as steric influences, affecting the velocity of saponification of an ester, and if the effect of different substituting groups be studied, it can easily happen that the steric influences may counterbalance or overbalance the influence of the particular substituting group on the strength of the acid. To determine in how far ease of saponification of an ester runs parallel with the strength of the acid from which it is formed, it will be necessary to eliminate the steric influences as far as possible, and to study the effect of introduction of some particular substituent on the strength of different acids and the rate of saponification of the esters derived from them.

As no measurements have yet been made of the effect of the hydroxyl group on the velocity of saponification of esters of the fatty series, we resolved to study this, as well as the effect of substituting the hydrogen of the hydroxyl group. The results of the first measurements in this direction are given in the present communication.

That the introduction of the hydroxyl group into an ester greatly increases the velocity of saponification is well known. One need only refer to the ready saponifiability of ethyl lactate as compared with that of ethyl propionate. The quantitative influence of this substitution has also been obtained indirectly in the case of the enolic form of ethyl acetoacetate (Goldschmidt, *Ber.*, 1900, **33**, 1150). As the velocity of saponification of the esters of lactic acid is too great to be

measurable, we chose for investigation the esters of mandelic acid, on which measurements can be made, although with difficulty. Measurements were carried out not only in aqueous solution (except in the case of ethyl phenylpropoxyacetate, which is too sparingly soluble), but also in 30 and 60 per cent. alcohol reckoned by weight. The temperature was 25° in all cases; for although the ready saponifiability of the esters made it advisable to work at a lower temperature, the sparing solubility of some of the esters rendered this course impossible.

In carrying out the measurements, 10 c.c. of the reaction mixture were run into excess of standard hydrochloric acid, and the excess of acid titrated with a solution of caustic soda. Since the velocity of the reaction is so great, an error in the determination of the time of mixing and of stopping the reaction becomes somewhat serious. We sought to diminish this as far as possible by noting the time occupied in mixing the solutions, as well as that required for the pipette to deliver, and the mean point of these intervals was taken as the time at which the reaction was started or stopped. The saponification constant was calculated by the usual formula for a reaction of the second order, $k = \frac{2 \cdot 302 \times 10}{T_{\infty} N t} \log \frac{T_t(T_0 - T_{\infty})}{T_0(T_t - T_{\infty})}$.

The values of the saponification constants in aqueous solution are as follows (see Tables 1—6):

Ester.	k .	Ester.	k .
Ethyl phenylacetate	12.4	Ethyl phenylmethoxyacetate... 23.3	
Methyl mandelate	157	Ethyl phenylethoxyacetate ... 15.7	
Ethyl mandelate	66	Ethyl phenylpropoxyacetate ... (13.3)	
Propyl mandelate	55		

In the case more especially of methyl mandelate, the velocity of saponification is so great that more than half the reaction had taken place during the first minute, so that only the second half—in the case of the stronger solutions only the last third—of the reaction could be measured. This fact introduces some uncertainty into the results, but it is evident from the agreement between the results of different experiments at different concentrations that the values obtained for the saponification constants are in any case fairly approximate.

The numbers in the foregoing table show at once the greatly accelerating influence which the hydroxyl group exercises on the velocity of saponification of ethyl phenylacetate, the saponification constant being increased to more than five times its previous value. With this we may compare the influence of the hydroxyl group on the affinity constants of the acids. Whereas the affinity constant of phenylacetic acid is 0.00502, that of mandelic acid is 0.0417, or about eight times as great.

On replacing the hydrogen of the hydroxyl group by an alkyl substituent, the velocity of saponification is greatly diminished, and the diminution increases with increase in the mass of the alkyl group. In the case of ethyl phenylpropoxyacetate, the saponification velocity could not be determined in aqueous solution on account of the sparing solubility of the ester. The number given in the foregoing table was calculated as follows: the saponification constant of ethyl phenylmethoxyacetate in 60 per cent. aqueous alcoholic solution was taken as being 7.97 (Table 17), and that for ethyl phenylpropoxyacetate, 4.77 (Table 19). Since the saponification constant of ethyl phenylmethoxyacetate in aqueous solution is 23.3, then, if the influence of the alcohol in the solution is the same on the saponification of the propoxy- as of the methoxy-ester, the saponification constant of the former in aqueous solution should be $\frac{4.77 \times 23.3}{7.97} = 13.9$. In the same

way, from the numbers for ethyl phenylethoxyacetate (Table 18), the value of the saponification constant was calculated to be 12.7. As the mean of the two numbers, 13.3 was taken; it can, however, be regarded only as approximate.

If we take this value for the saponification constant of ethyl phenylpropoxyacetate as approximately correct, we find that the effect of increase in the mass of the alkyl group is a regular one, the ratios between the constants for ethyl mandelate and for ethyl phenylmethoxyacetate, ethyl phenylethoxyacetate and ethyl phenylpropoxyacetate respectively being very nearly 2.8:1, 3.8:1, 4.8:1. The comparison between the velocities of saponification and the affinity constants of the acids from which they are derived cannot yet be made, but we hope soon to be in a position to do so.

The influence of substitution on saponification can also be readily seen by comparing the substituted esters with the esters of acetic acid. In the following table, the values of the saponification of methyl and propyl acetates have been calculated from the figures obtained by Reicher (*Annalen*, 1885, 228, 257), whilst that for ethyl acetate was determined by Messrs. Schmidt (*Ber.*, 1899, 32, 3396):

Ester.	<i>k</i> .	Ester.	<i>k</i> .
Methyl acetate	9.66	Methyl mandelate.....	157
Ethyl acetate	6.94	Ethyl mandelate	66
Propyl acetate	5.31	Propyl mandelate	55
		Ethyl phenylacetate	12.4

From this table, it is seen that the velocity constants of the mandelates are about 10 times, in the case of methyl mandelate about 16 times, as great as those for the corresponding acetates. This increase in the saponification constant is, of course, due to

two substitutions; firstly, to substitution of hydrogen by the phenyl group, which raises the saponification constant of the ethyl ester from 6.94 to 12.4, or by nearly 1.8 times; and secondly, to introduction of the hydroxyl group, which further increases the velocity constant 5.3 times. If, now, it is assumed that a given substitution always produces the same relative increase in the saponification constant of an ester, just as one finds it to do so approximately in the case of the affinity constants of acids (Wegscheider, *Monatsh.*, 1902, **23**, 289), one should be able to calculate the value of the saponification constants of methyl and propyl mandelates from the value of the constants for the corresponding acetates. In this way one obtains, for methyl mandelate, $9.66 \times 1.8 \times 5.3 = 92$ (instead of the experimentally determined value 157), and for propyl mandelate, $5.31 \times 1.8 \times 5.3 = 51$ (instead of the experimental value 55). From this it will be seen that whilst the saponification constants of the ethyl and propyl esters are equally affected by the substitutions, the methyl ester is affected to a much larger degree. As we do not possess the value of the saponification constant of methyl phenylacetate, it is not possible to say whether the abnormal influence of the substituent is found in both stages of the substitution between methyl acetate and mandelate, or only in one.

In the hydrolysis of esters under the influence of acids, it has been shown (compare Hemptinne, *Zeit. physikal. Chem.*, 1894, **13**, 389; Loewenherz, *ibid.*, **15**, 561) that the ratio of the hydrolysis constants of the methyl and ethyl and of the ethyl and propyl esters of the fatty acids is constant, no matter what the acid is. When one compares the saponification constants of the esters of acetic and mandelic acids, it is found that whilst the ratio of the constants for the ethyl and propyl esters is the same, namely, 6:5, there is no agreement between the ratios for the methyl and ethyl esters. Thus in the case of the acetates, the ratio of the constants is approximately 3:2, and in the case of the mandelates 4.8:2. Although it is not impossible that a portion of this deviation may be due to inaccuracy in the determination of the saponification constant of methyl mandelate, we do not think that the whole of the deviation can be thus accounted for.

It is somewhat remarkable that the ratios of constants for ethyl phenylmethoxyacetate and ethyl phenylethoxyacetate, and for ethyl phenylethoxyacetate and ethyl phenylpropoxyacetate, are very approximately 3:2 and 6:5. Whether this is merely a coincidence cannot yet be said. It must be remembered that the constant for the ethyl phenylpropoxyacetate has only been obtained indirectly.

On account of the ready saponifiability and the sparing solubility of some of the esters in water, measurements of the velocity of

saponification were also carried out in aqueous alcoholic solution. The results are given in the following table (see Tables 7—19):

	In 30 per cent. alcohol.	In 60 per cent. alcohol.
	<i>k</i> .	<i>k</i> .
Ethyl phenylacetate	8.6	(6)
Methyl mandelate	(109)	(84)
Ethyl mandelate	49.4	29.1
Propyl mandelate	39.5	22.7
Ethyl phenylmethoxyacetate.....	15.2	(8)
Ethyl phenylethoxyacetate	10.2	(6)
Ethyl phenylpropoxyacetate	—	(5)

In 30 per cent. aqueous alcoholic solutions, fairly concordant values of the saponification constant could be obtained, except in the case of methyl mandelate; but in 60 per cent. alcoholic solutions there was a considerably greater falling off in the constant as the reaction proceeded, and the values of the constants given are therefore all more or less approximate. This applies also to some extent to the constants given for ethyl and propyl mandelates (Table 16), although, as the falling off in the value of the constants was not so great, we have ventured to take the mean.

Certain other irregularities also were met with in the case of the saponification in alcoholic solution, but as it is proposed by one of us to continue the investigation of the saponification velocities in alcoholic solution, the discussion of these may be left over until further data have been obtained.

EXPERIMENTAL.

Methyl Mandelate.—By the action of methyl iodide on silver mandelate, Naquet and Louguinine (*Annalen*, 1866, 139, 299) obtained a product melting at 113—114°, whilst Breuer and Zincke (*Ber.*, 1880, 13, 636), using the same method, obtained a product melting at 47—48°. This method was also employed by Rupe (*Ber.*, 1895, 28, 259), who found the melting point to be 52°.

The process which we employed is based on the general method given by Fischer and Speier (*Ber.*, 1895, 28, 3254). Twenty grams of mandelic acid were mixed with 60 grams of pure methyl alcohol and 6 grams of concentrated sulphuric acid, and the mixture heated on the water-bath for 5 hours. Most of the alcohol was then distilled off and the residue poured into water. The solution was neutralised with sodium carbonate, the ester extracted with ether, and the ethereal solution dried over sodium sulphate. After evaporating off the ether, the residue was distilled under 30 mm. pressure, when a colourless oil passed over at a temperature of 153° and quickly solidified in the receiver. The yield was 17.5 grams. After crystallising from ligroin alone and from a mixture of ligroin and benzene, the melting point

of the ester was found to be 57° ; * it boiled at 250° with slight decomposition.

This method has also been used by Acree (*Ber.*, 1904, 37, 2767), who gives the melting point as 58° .

0.1887 gave 0.1030 H_2O and 0.4503 CO_2 . C = 65.1; H = 6.06.

0.1884 „ 0.1040 H_2O „ 0.4496 CO_2 . C = 65.0; H = 6.13.

$\text{C}_9\text{H}_{10}\text{O}_3$ requires C = 65.06; H = 6.07 per cent.

Ethyl Mandelate.—In preparing this ester, we employed Fischer and Speier's method, which had previously been used by McKenzie (*Trans.*, 1899, 75, 755). The latter gives the melting point as 37° , but we failed, even by repeated crystallisation from ligroin and from ethyl acetate and ligroin, to raise the melting point higher than 29° .

0.1712 gave 0.1072 H_2O and 0.4187 CO_2 . C = 66.7; H = 6.95.

$\text{C}_{10}\text{H}_{12}\text{O}_3$ requires C = 66.66; H = 6.66 per cent.

Propyl Mandelate.—Twenty grams of mandelic acid were mixed with 80 grams of propyl alcohol and 6 grams of concentrated sulphuric acid, and the mixture heated in an oil-bath at 110 — 115° for 7 hours. The product was then treated as in the preparation of methyl mandelate. A colourless oil was obtained which distilled at 145° under 12 mm. pressure, and solidified in needles on immersion in a freezing mixture. The ester melted at 14 — 15° and boiled, with partial decomposition, at 263° . The yield was 20 grams.

0.1976 gave 0.1328 H_2O and 0.4894 CO_2 . C = 67.5; H = 7.47.

$\text{C}_{11}\text{H}_{14}\text{O}_3$ requires C = 68.04; H = 7.28 per cent.

Ethyl Phenylchloroacetate.—In order to obtain the alkoxy derivatives of phenylacetic acid, it was first necessary to prepare ethyl phenylchloroacetate.

First method: Three hundred and fifty grams of ethyl mandelate were dissolved in a moderate volume of chloroform in a large flask, and 416 grams of phosphorus pentachloride added in small quantities from time to time. The mixture was then warmed on a water-bath at about 50° until no further action occurred. The excess of phosphorus pentachloride was destroyed by cautious addition of water, and the heavy oil which separated out was washed with water; it was then treated with sodium carbonate until slightly alkaline, and the ester then extracted with chloroform. The solution was dried over fused sodium sulphate and distilled under reduced pressure. Under 19 mm. pressure, a nearly

* When first prepared, the melting point was found to be 54° , but when this was again determined, after the lapse of about a year, the substance was found to melt at 57° .

colourless oil passed over at 142° . On analysis, it showed no trace of phosphorus.

0.2429 gave 0.1792 AgCl. Cl = 18.24.

0.2246 „ 0.1602 AgCl. Cl = 17.63.

$C_{10}H_{11}O_2Cl$ requires Cl = 17.85 per cent.

Second method: Fifteen grams of ethyl mandelate were treated with 42 grams of thionyl chloride, and the mixture was heated for 8 hours on the water-bath in a reflux apparatus. The excess of thionyl chloride was removed by warming on the water-bath, and the residue distilled under reduced pressure. A colourless oil was obtained which boiled at 143° under 25 mm. pressure, the yield being 14 grams.

0.2796 gave 0.2032 AgCl. Cl = 17.97 per cent.

0.3056 „ 0.2199 AgCl. Cl = 17.79 „

Preparation of the Alkoxy Esters.

The methyl ester of phenylmethoxyacetic acid was prepared by Meyer and Boner (*Annalen*, 1883, 220, 45) by acting on methyl phenylchloroacetate with sodium methoxide in methyl-alcoholic solution, and obtained as a pure product after two distillations. We endeavoured to utilise this method for the preparation of the alkoxy derivatives of ethyl mandelate, but although quite a number of experiments were carried out with sodium methoxide, ethoxide, and propoxide, we found it a matter of the greatest difficulty, and in some cases we were unable to obtain alkoxy esters quite free from chlorine. Even after thrice repeating the treatment with sodium ethoxide, a small quantity of the phenylchloroacetate appeared to have escaped decomposition. It was found impossible to effect a separation of the alkoxy ester from the chloro-ester by fractional distillation under reduced pressure, although this could be done by fractionation under atmospheric pressure. The process, however, was very troublesome and was accompanied by loss of ester, so that the above method of preparation was abandoned.

It may be mentioned that exactly similar results were obtained with ethyl phenylchloroacetate prepared by the action of thionyl chloride as from specimens obtained by the action of phosphorus pentachloride, so that the difficulty experienced in getting rid of all the chloro-compound could not have been due to chlorination in the benzene ring.

Although we did not investigate the matter further, it may be stated that replacement of chlorine by the alkoxy group took place with greater readiness in the case of sodium methoxide than in that of sodium ethoxide, and this, in turn, with greater ease than in the case of the propoxide. Since it is not at all improbable that the methyl

ester of phenylchloroacetic acid is more reactive than the ethyl ester, the success of the reaction in the preparation of methyl methoxymandelate by Meyer and Boner can be understood. We hope, however, to be able at a later date to undertake a quantitative study of the replacement of the chlorine by the alkoxy group in the above reaction.

Ethyl Phenylmethoxyacetate.—The above method having proved unsuccessful, we decided to prepare first the free phenylmethoxyacetic acid and to esterify this. For the preparation of the acid, the method of Meyer and Boner was followed. The small amount of chloro-ester which escaped conversion was converted into sodium mandelate by the action of caustic soda, and could thus be separated by crystallisation from the sodium salt of phenylmethoxyacetate.

Phenylmethoxyacetic acid was isolated by decomposing the sodium salt with sulphuric acid, and when purified by crystallisation from benzene and ligroin melted at 69° (McKenzie, *Trans.*, 1899, 75, 760).

Nine grams of pure phenylmethoxyacetic acid were boiled for 6 hours with 30 grams of absolute ethyl alcohol and 2 grams of strong sulphuric acid. After distilling off the alcohol and neutralising the residue with potassium carbonate, the ester was extracted with ether, when 7.5 grams of a colourless oil were obtained, boiling at 141° under 26 mm. pressure.

0.2014 gave 0.1325 H_2O and 0.5027 CO_2 . $\text{C} = 68.06$; $\text{H} = 7.31$.

$\text{C}_{11}\text{H}_{14}\text{O}_3$ requires $\text{C} = 68.04$; $\text{H} = 7.28$ per cent.

Ethyl Phenylethoxyacetate.—McKenzie (*loc. cit.*) has prepared ethyl *l*-phenylethoxyacetate by esterifying the free acid which he obtained by acting on *l*-mandelic acid with ethyl iodide and silver oxide. For the preparation of the inactive ester, the following method was employed. Thirty grams of ethyl phenylchloroacetate were boiled with 6 grams of sodium dissolved in 100 grams of ethyl alcohol for 12 hours. The resulting ethoxy-ester, which contained a slight admixture of the chloro-ester, was treated with caustic soda, whereby sodium phenylethoxyacetate was obtained as a mass of fine needles (compare Koerner and Radziszewski, *Zeit. Chemie*, 1868, 4, 143), whilst the sodium mandelate formed from the chloro-ester present remained in solution. The sodium salt was then decomposed by means of sulphuric acid, and in this way phenylethoxyacetic acid was obtained as a viscid, pale yellow oil, which could not be made to crystallise. An analysis of the silver salt gave $\text{Ag} = 37.39$ per cent., whereas the theory requires 37.35.

The acid was then esterified in exactly the same manner as phenylmethoxyacetic acid. Ethyl phenylethoxyacetate was obtained as a

colourless oil, which boils at 134° under 13 mm. pressure and at 255° under atmospheric pressure.

0.2018 gave 0.5090 CO_2 and 0.1392 H_2O . C = 68.8; H = 7.66.

0.2092 „ 0.5324 CO_2 „ 0.1437 H_2O . C = 69.4; H = 7.63.

$\text{C}_{12}\text{H}_{16}\text{O}_3$ requires C = 69.23; H = 7.69 per cent.

Ethyl Phenylpropoxyacetate.—Thirty grams of ethyl phenylchloroacetate were boiled for four hours with 120 grams of propyl alcohol in which 8 grams of sodium had been dissolved. After removing the salt which separated, the liquid was again boiled for five hours with a further quantity of sodium propoxide. After treating the extracted esters with caustic soda and evaporating to dryness, sodium phenylpropoxyacetate was obtained. From this ester, phenylpropoxyacetic acid was obtained by hydrolysing with sulphuric acid, and as it is sparingly soluble was freed from any mandelic acid present by washing thoroughly with water. The acid was then taken up with ether and the ethereal solution dried over sodium sulphate. Phenylpropoxyacetic acid was thus obtained as a light yellow oil, the yield being 14–15 grams. Analyses of the silver salt gave Ag = 35.55 and 35.87 per cent., whilst theory requires Ag = 35.85.

The ethyl ester of phenylpropoxyacetic acid was then prepared in a manner similar to that used for the esterification of the phenylmethoxy- and phenylethoxy-acids. It was obtained as a colourless oil which distilled over at 144° under 13 mm. pressure.

0.2006 gave 0.5107 CO_2 and 0.1462 H_2O . C = 69.4; H = 8.1.

0.2104 „ 0.5422 CO_2 „ 0.1515 H_2O . C = 70.3; H = 8.0.

$\text{C}_{13}\text{H}_{18}\text{O}_3$ requires C = 70.2; H = 8.15 per cent.

Velocity of Saponification. A. In Aqueous Solution.

TABLE I.—*Ethyl Phenylacetate.*

N/150 ester; *N*/150 NaOH.

(a) $k = 12.42$ [extreme values, 11.69 and 12.99].

(b) $k = 12.43$ [„ „ 11.96 „ 12.84].

General mean: $k = 12.42$.

TABLE II.—*Methyl Mandelate.*

First series:—*N*/30 ester; *N*/30 NaOH.

(a) $k = 157.1$ [extreme values, 151.9 and 164.7].

(b) $k = 155.5$ [„ „ 152.8 „ 161.2].

Second series:—*N*/60 ester; *N*/60 NaOH.

(a) $k = 160.1$ [extreme values, 153.8 and 165.9].

(b) $k = 156.8$ [„ „ 150.4 „ 160.9].

General mean: **157.4**.

TABLE III.—*Ethyl Mandelate.**First series*:—*N*/30 ester; *N*/30 NaOH.

- (a) $k=65.1$ [extreme values, 60.6 and 68.1].
 (b) $k=64.9$ [„ „ 61.8 „ 67.4].

Second series:—*N*/60 ester; *N*/60 NaOH.

- (a) $k=66.9$ [extreme values, 63.7 and 69.9].
 (b) $k=68.7$ [„ „ 63.1 „ 73.2].

General mean: $k=66.4$.TABLE IV.—*Propyl Mandelate.**N*/60 ester; *N*/60 NaOH.

- (a) $k=55.6$ [extreme values, 51.1 and 58.0].
 (b) $k=55.4$ [„ „ 52.4 „ 58.2].

General mean: $k=55.5$.TABLE V.—*Ethyl Phenylmethoxyacetate.**N*/60 ester; *N*/60 NaOH.

- (a) $k=23.4$ [extreme values, 22.7 and 24.0].
 (b) $k=23.3$ [„ „ 22.5 „ 23.8].

General mean: $k=23.3$.TABLE VI.—*Ethyl Phenylethoxyacetate.**N*/150 ester; *N*/150 NaOH.

- (a) $k=15.6$ [extreme values, 14.8 and 17.1].
 (b) $k=15.8$ [„ „ 15.0 „ 17.9].

General mean: $k=15.7$.B. *Saponification in Aqueous-alcoholic Solution.*I. *Solutions containing 30 per cent. of Alcohol.*TABLE VII.—*Ethyl Phenylacetate.**First series*:—*N*/40 ester; *N*/30 NaOH.

- (a) $k=8.62$ [extreme values, 8.24 and 9.10].
 (b) $k=8.53$ [„ „ 8.19 „ 8.97].

Second series:—*N*/60 ester; *N*/60 NaOH.

- (a) $k=8.67$ [extreme values, 8.43 and 9.02].
 (b) $k=8.63$ [„ „ 8.21 „ 9.01].
 (c) $k=8.60$ [„ „ 8.41 „ 8.75].

General mean: $k=8.61$.

TABLE VIII.—*Methyl Mandelate.* $N/30$ ester; $N/30$ NaOH; T =titre in c.c. of $N/115.1$ HCl.

Time.	T .	k .	Time.	T .	k .
0.0 mins.	19.26	—	0.0 mins.	19.26	—
1.22 „	6.04	108.6	1.22 „	6.04	109.0
2.30 „	3.84	106.3	2.22 „	4.01	104.7
3.72 „	2.75	98.9	3.72 „	2.79	97.9
5.22 „	2.18	92.6	5.22 „	2.22	91.8
7.22 „	1.72	87.8	7.22 „	1.76	86.3
9.22 „	1.48	83.4	9.22 „	1.51	80.2
12.22 „	1.26	73.7	12.22 „	1.26	74.7
17.22 „	0.98	69.3	17.22 „	0.99	69.7
24 hours	0.12	—	27.22 „	0.78	58.0
			24 hours	0.15	—

TABLE IX.—*Ethyl Mandelate.* $N/30$ ester; $N/30$ NaOH.

- (a) $k=49.5$ [extreme values, 47.6 and 51.1].
 (b) $k=48.6$ [„ „ 46.3 „ 49.9].
 (c) $k=50.0$ [„ „ 47.3 „ 51.9].

General mean : 49.4.

TABLE X.—*Propyl Mandelate.* $N/60$ ester; $N/60$ NaOH.

- (a) $k=39.5$ [extreme values, 35.1 and 42.4].
 (b) $k=39.5$ [„ „ 36.4 „ 41.9].

General mean : 39.5.

TABLE XI.—*Ethyl Phenylmethoxyacetate.**First series* :— $N/40$ ester; $N/30$ NaOH.

- (a) $k=15.0$ [extreme values, 14.3 and 15.5].
 (b) $k=15.2$ [„ „ 14.2 „ 15.9].

Second series :— $N/60$ ester; $N/60$ NaOH.

- (a) $k=15.2$ [extreme values, 14.5 and 15.8].
 (b) $k=15.5$ [„ „ 15.0 „ 15.7].

General mean : 15.2.

TABLE XII.—*Ethyl Phenylethoxyacetate.**First series* :—*N*/40 ester ; *N*/30 NaOH.(a) $k = 9.85$ [extreme values, 9.41 and 10.34].(b) $k = 9.95$ [, , 9.29 , 10.62].*Second series* :—*N*/60 ester ; *N*/60 NaOH.(a) $k = 10.44$ [extreme values, 9.95 and 10.93].(b) $k = 10.41$ [, , 9.82 , 10.87].

General mean : 10.2.

II. Solutions containing 60 per cent. of Alcohol.

TABLE XIII.—*Ethyl Phenylacetate.**N*/70 ester ; *N*/60 NaOH ; *T* = titre in c.c. of *N*/117.0 HCl.

Time.	<i>T</i> .	<i>k</i> .	Time.	<i>T</i> .	<i>k</i> .
0.0 mins.	9.81	—	0.0 mins.	9.81	—
1.24 „	9.27	6.45	1.23 „	9.27	6.52
2.74 „	8.85	5.45	2.73 „	8.88	5.31
4.24 „	8.54	4.84	4.23 „	8.55	4.84
6.24 „	8.11	4.64	6.23 „	8.14	4.59
8.24 „	7.63	4.84	8.23 „	7.73	4.58
11.24 „	7.17	4.60	11.23 „	7.21	4.80
14.24 „	6.69	4.64	15.23 „	6.63	4.48
19.24 „	6.08	4.57	21.23 „	5.94	4.33
24.24 „	5.67	4.35	28.23 „	5.37	4.29
32.24 „	5.10	4.21	36.23 „	4.83	4.24
40.24 „	4.53	4.34	44.23 „	4.41	4.20
50.24 „	4.09	4.26	54.23 „	4.02	4.11
60.24 „	3.72	4.20	24 hours	1.28	—
24 hours	1.25	—			

TABLE XIV.—*Methyl Mandelate.**N*/70 ester ; *N*/60 NaOH ; *T* = titre in c.c. of *N*/115.8 HCl.

Time.	<i>T</i> .	<i>k</i> .	Time.	<i>T</i> .	<i>k</i> .
0.0 mins.	9.86	—	0.0 mins.	9.86	—
1.23 „	5.80	83.6	1.23 „	5.82	82.5
2.23 „	4.67	75.5	2.23 „	4.69	74.3
3.73 „	3.89	66.0	3.73 „	3.94	63.9
5.73 „	3.32	58.0	5.73 „	3.34	56.8
7.73 „	2.96	53.3	7.73 „	3.01	51.4
10.73 „	2.66	46.8	10.73 „	2.68	45.8
13.73 „	2.46	42.6	13.73 „	2.46	42.1
18.73 „	2.21	38.9	18.73 „	2.21	38.2
24 hours	1.46	—	24 hours	1.43	—

TABLE XV.—*Ethyl Mandelate.**N*/70 ester ; *N*/60 NaOH.(a) $k = 29.6$ [extreme values, 27.5 and 31.4].(b) $k = 28.6$ [, , 25.4 , 31.3].

General mean : 29.1.

TABLE XVI.—*Propyl Mandelate.**N*/70 ester; *N*/60 NaOH; *T*=titre in c.c. of *N*/114·8 HCl.

Time.	<i>T</i> .	<i>k</i> .	Time.	<i>T</i> .	<i>k</i> .
0·0 mins.	9·75	—	0·0 mins.	9·75	—
1·75 „	7·29	27·0	1·75 „	7·29	26·9
3·75 „	5·92	24·8	3·75 „	5·92	24·7
5·75 „	5·04	24·0	5·75 „	5·03	24·0
8·75 „	4·16	23·6	8·75 „	4·17	23·3
11·75 „	3·62	22·9	11·75 „	3·60	23·0
16·75 „	3·07	21·7	16·75 „	3·04	22·0
21·75 „	2·69	21·2	21·75 „	2·65	21·7
29·75 „	2·33	20·3	29·75 „	2·31	20·4
39·75 „	2·09	18·8	39·75 „	2·04	19·5
24 hours	1·33	—	24 hours	1·31	—
Mean.....		22·7	Mean.....		22·8

General mean: 22·7.

TABLE XVII.—*Ethyl Phenylmethoxyacetate.**N*/70 ester; *N*/60 NaOH; *T*=titre in c.c. of *N*/117·0 HCl.

Time.	<i>T</i> .	<i>k</i> .	Time.	<i>T</i> .	<i>k</i> .
0·0 mins.	9·76	—	0·0 mins.	9·76	—
1·24 „	8·99	9·56	1·24 „	9·07	8·51
2·74 „	8·38	8·36	2·74 „	8·31	8·90
4·24 „	7·87	7·93	4·24 „	7·79	8·39
6·24 „	7·23	7·92	6·24 „	7·26	7·80
8·24 „	6·72	7·81	8·24 „	6·62	8·24
11·24 „	6·08	7·75	11·24 „	6·06	7·86
14·24 „	5·53	7·83	14·24 „	5·22	7·91
19·24 „	4·92	7·59	19·24 „	4·87	7·81
24·24 „	4·47	7·37	24·24 „	4·44	7·52
34·24 „	3·80	7·16	34·24 „	3·78	7·28
24 hours	1·25	—	24 hours	1·28	—

TABLE XVIII.—*Ethyl Phenylethoxyacetate.**N*/70 ester; *N*/60 NaOH; *T*=titre in c.c. of *N*/116·5 HCl.

Time.	<i>T</i> .	<i>k</i> .	Time.	<i>T</i> .	<i>k</i> .
0·0 mins.	9·80	—	0·0 mins.	9·80	—
1·24 „	9·05	9·06	1·24 „	9·03	9·33
3·24 „	8·41	6·95	3·24 „	8·40	7·01
5·24 „	7·87	6·40	5·24 „	7·91	6·25
8·24 „	7·25	5·90	8·24 „	7·31	5·71
11·24 „	6·73	5·65	11·24 „	6·67	5·79
15·24 „	6·17	5·43	15·24 „	6·18	5·40
19·24 „	5·64	5·44	19·24 „	5·74	5·21
25·24 „	5·11	5·23	25·24 „	5·13	5·19
31·24 „	4·69	5·08	31·24 „	4·66	5·15
39·24 „	4·20	5·06	39·24 „	4·27	4·89
49·24 „	3·71	5·08	49·24 „	3·79	4·88
24 hours	1·16	—	24 hours	1·16	—

TABLE XIX.—*Ethyl Phenylpropoxyacetate.**N*/70 ester ; *N*/60 NaOH ; *T*' = titre in c.c. of *N*/116·5 HCl.

Time.	<i>T</i> .	<i>k</i> .
0·0 mins.	9·82	—
1·24 „	9·28	6·41
3·24 „	8·76	5·12
9·24 „	7·47	4·74
17·24 „	6·39	4·51
24·24 „	5·67	4·34
38·24 „	4·72	4·18
56·24 „	3·91	4·13
24 hours	1·25	—

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