

XVI.—*The Rate of Saponification of Derivatives of Ethyl Benzoate.*

By HAMILTON MCCOMBIE and HAROLD ARCHIBALD SCARBOROUGH.

THE velocity of saponification by alkali hydroxides of the esters of fatty acids with such primary alcohols as ethyl alcohol and methyl alcohol has been studied very fully by many investigators. With few exceptions, however, none of these workers seems to have studied completely substituted methyl and ethyl benzoates. Meyer and Kellas (*Zeitsch. physikal. Chem.*, 1897, **24**, 221), in their historical research on substituted methyl benzoates, tabulate their results as the percentage of ester saponified in a given interval of time. As a consequence their figures depend on only one observation, except in such cases when the same ester has been examined twice. Even in those cases where these authors examined the behaviour of the same ester twice the results are not concordant. Thus in one experiment the ratios of the quantities of methyl *o*-toluate and methyl benzoate saponified in the same time was found to be 0.08, whilst in a second experiment the ratio was 0.33. This lack of concordance is to be found in every case in which a direct comparison is possible, but in some cases the difference might be due to a very small experimental error.

In these circumstances it was thought desirable to examine the velocity of saponification of the methyl and ethyl esters of the substituted benzoic acids in as complete a manner as possible, examining the reaction over a range of 60—70 per cent., except in such exceptional cases as ethyl *o*-toluate, where the rate of saponification is very slow.

EXPERIMENTAL.

The saponifications were carried out in ethyl-alcoholic solution in the manner described by the authors for phenyl benzoate (T., 1914, **105**, 1304).

Liquid esters were distilled twice under diminished pressure; solid esters were recrystallised until a constant melting point was obtained.

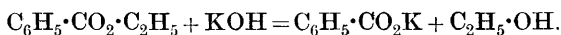
The alcohol was dried over lime for four or five days, and was then distilled over lime. This treatment was repeated twice. In preparing the alcoholic potassium hydroxide it was found best rapidly to grind pure potassium hydroxide and add it to the alcohol. Very little heating was thus required, and the amount of carbonate present was found to be very small.

The reaction was followed at $30^{\circ} \pm 0.05^{\circ}$. The indicator employed

was phenolphthalein. In the reaction-mixture at the commencement there were present 1.25—2 molecular proportions of potassium hydroxide and 1 molecular proportion of the ester.

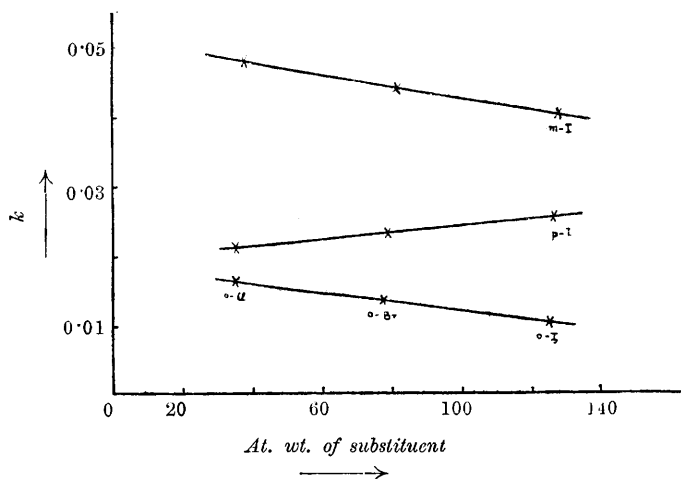
Discussion of the Results.

The reaction is bimolecular, and may be represented by the equation:



A consideration of the results given in tables I—XIII shows that:

(1) Halogen substituents show a marked increase in the velocity of saponification in comparison with the unsubstituted ester.



(2) The influence of the halogen is greatest in the meta-, and least in the ortho-position.

(3) In comparing the effects of the different halogen substituents it is found that chlorine has a greater influence than bromine, and bromine a greater influence than iodine. An exception to this is encountered in the case of the para-substituted derivatives, when this order is found to be reversed. This strange reversal has been found also in the case of the methyl esters, and, further, it was noticed by Meyer and Kellas (*loc. cit.*).

If curves are plotted (see figure) showing the relationship between the atomic weight of the halogen substituent and the velocities of saponification, these are found to be straight lines. Thus it is seen that the values of k for the bromo-substituted

esters are a mean between the values of k for the corresponding chloro- and iodo-substituted esters.

(4) The influence of the methyl group is in the opposite direction to that of the halogens.

TABLE I.

Ethyl Benzoate. B. p. $96.5^{\circ}/13$ mm.

$a = 0.5097 \cdot 10^{-3}$; $b = 0.3333 \cdot 10^{-3}$; $HCl = 0.02232N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
4	21.90	0.94	0.0210	0.00538
8	21.04	1.80	0.0402	0.00549
12	20.29	2.55	0.0569	0.00542
17	19.54	3.30	0.0737	0.00528
26	18.09	4.75	0.1060	0.00543
37	16.76	6.08	0.1375	0.00544
43	16.13	6.71	0.1497	0.00545

Mean of 12 determinations..... $k = 0.00543$

Amount of ester saponified in 43 hours is 44.9 per cent.

TABLE II.

Ethyl o-Toluate.

$a = 0.5303 \cdot 10^{-3}$; $b = 0.3333 \cdot 10^{-3}$; $HCl = 0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
6	21.76	0.37	0.0089	0.00143
12	21.44	0.69	0.0167	0.00138
20	21.05	1.08	0.0261	0.00132
31	20.54	1.59	0.0384	0.00129
44	19.90	2.23	0.0538	0.00133
51	19.60	2.53	0.0611	0.00133
69	18.87	3.26	0.0787	0.00133

Mean of 12 determinations..... $k = 0.00134$.

Amount of ester saponified in 69 hours is 23.6 per cent

TABLE III.

Ethyl m-Toluate.

$a = 0.5303 \cdot 10^{-3}$; $b = 0.3333 \cdot 10^{-3}$; $HCl = 0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
6-69	21.10-15.01	1.03-7.12	0.0248-0.173	0.00402 - 0.00414

Mean of 12 determinations..... $k = 0.00405$.

TABLE IV.

Ethyl p-Toluate.

$a=0.5303 \cdot 10^{-3}$; $b=0.3333 \cdot 10^{-3}$; $HCl=0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
6-69	21.4-16.65	0.73-5.48	0.0176-0.1323	0.00268 - 0.00288
Mean of 12 determinations.....				$k=0.00275$.

TABLE V.

Ethyl o-Chlorobenzoate. B. p. $122.5^\circ/15$ mm.

$a=0.5303 \cdot 10^{-3}$; $b=0.3333 \cdot 10^{-3}$; $HCl=0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
2.5	20.56	1.57	0.0379	0.0158
4.5	19.55	2.58	0.0623	0.0156
6.5	18.53	3.60	0.0870	0.0161
8.5	17.80	4.33	0.1045	0.0156
12	16.60	5.53	0.1335	0.0156
16	15.50	6.63	0.1600	0.0156
20	14.57	7.56	0.1826	0.0157

Mean of 12 determinations..... $k=0.0157$.

Amount of ester saponified in 20 hours is 54.8 per cent.

TABLE VI.

Ethyl m-Chlorobenzoate. B. p. $119^\circ/13$ mm.

$a=0.5303 \cdot 10^{-3}$; $b=0.3333 \cdot 10^{-3}$; $HCl=0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
2.5-20	18.03-10.37	4.10-11.76	0.0990-0.2840	0.0483 - 0.0492
Mean of 12 determinations.....				$k=0.0485$.

TABLE VII.

Ethyl p-Chlorobenzoate. B. p. $118^\circ/14$ mm.

$a=0.5303 \cdot 10^{-3}$; $b=0.3333 \cdot 10^{-3}$; $HCl=0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
2.5-20	20.05-13.5	2.08-8.63	0.0502-0.2083	0.0204 - 0.0215
Mean of 12 determinations.....				$k=0.0208$

TABLE VIII.

Ethyl o-Bromobenzoate. B. p. 132°/13 mm. $a=0.5303 \cdot 10^{-3}$; $b=0.3333 \cdot 10^{-3}$; $\text{HCl}=0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
2.5	20.87	1.26	0.0303	0.0124
4.5	20.05	2.08	0.0502	0.0119
6.5	19.34	2.79	0.0673	0.0117
8.5	18.73	3.40	0.0821	0.0114
12	17.60	4.53	0.1093	0.0117
16	16.56	5.57	0.1345	0.0118
20	15.80	6.33	0.1530	0.0116

Mean of 12 determinations..... $k=0.0118$.

Amount of ester saponified in 20 hours is 45.9 per cent.

TABLE IX.

Ethyl m-Bromobenzoate. B. p. 133°/15 mm. $a=0.5303 \cdot 10^{-3}$; $b=0.3333 \cdot 10^{-3}$; $\text{HCl}=0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
2.5-20	18.27-10.64	3.86-11.49	0.0932-0.2775	0.0442 - 0.0455

Mean of 12 determinations..... $k=0.0445$.

TABLE X.

Ethyl p-Bromobenzoate. B. p. 131°/13 mm. $a=0.5303 \cdot 10^{-3}$; $b=0.3333 \cdot 10^{-3}$; $\text{HCl}=0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
2.5-20	19.83-13.00	2.30-9.13	0.0555-0.2205	0.0321 - 0.0241

Mean of 12 determinations..... $k=0.0234$.

TABLE XI.

Ethyl o-Iodobenzoate. B. p. 148°/15 mm. $a=0.5303 \cdot 10^{-3}$; $b=0.3333 \cdot 10^{-3}$; $\text{HCl}=0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
2.5	21.20	0.93	0.0225	0.00895
4.5	20.54	1.59	0.0384	0.00889
6.5	19.91	2.22	0.0533	0.00886
8.5	19.37	2.76	0.0669	0.00887
12	18.49	3.64	0.0879	0.00800
16	17.61	4.52	0.1091	0.00878
20	16.83	5.30	0.1280	0.00882

Mean of 12 determinations..... $k=0.00884$.

Amount of ester saponified in 20 hours is 38.4 per cent.

TABLE XII.

Ethyl m-Iodobenzoate. B. p. 150.5°/15 mm.

$a = 0.5303 \cdot 10^{-3}$; $b = 0.3333 \cdot 10^{-3}$; $\text{HCl} = 0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
2.5-20	18.55-10.93	3.58-11.2	0.0865-0.2703	0.0403 - 0.0414
Mean of 12 determinations.....				$k = 0.0408$.

TABLE XIII.

Ethyl p-Iodobenzoate. B. p. 153.5°/14 mm.

$a = 0.5303 \cdot 10^{-3}$; $b = 0.3333 \cdot 10^{-3}$; $\text{HCl} = 0.02415N$.

t (hours).	Titre.	Acid used.	$X \cdot 10^3$.	k .
2.5-20	19.63-12.60	2.5-9.53	0.0604-0.2301	0.0251 - 0.0267
Mean of 12 determinations.....				$k = 0.0258$.

The influences of several other groups were examined roughly, and it was found that the amino-, the methoxy-, and the hydroxy-groups produced marked retardation, whilst the nitro-group had an enormous accelerative influence on the course of the reaction.

The influence of water on the velocity of saponification of ethyl benzoate has also been studied. Attention was drawn to a consideration of this influence by the fact that for ethyl benzoate and potassium hydroxide at 14.4° in aqueous solution $k = 0.83$, whilst in absolute ethyl-alcoholic solution $k = 0.00543$.

The general method of experiment was similar to that described in the investigation of the influence of substituents. The results are shown in table XIV.

TABLE XIV.

Alcohol. Per cent.	Number of observations.	Range.	k .
100	12	44.9	0.00543
96.7	12	86.7	0.02550
93.3	12	79.3	0.04085
90.0	12	85.9	0.05440
83.33	12	76.4	0.0810
73.33	12	83.5	0.108
60.00	12	89.2	0.148

At this stage of the proceedings it seems to the authors impossible to give a satisfactory explanation of this phenomenon, but it is their intention to investigate this reaction in the case of fatty and aromatic esters with a view to ascertain if any generalisation can be reached.

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CHEMICAL DEPARTMENT,
UNIVERSITY OF BIRMINGHAM.

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