

acetic acid ester prepared first by Willgerodt under the name acetyl-oxy-isobuttersäure-trichloride. [Later by Aldrich under the name monoacetyl trichlorotertiary-butyl-alcohol (chloretone acetic ester).]

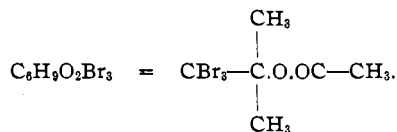
The following esters of chloretone were prepared by Wolffenstein: Propionic ester (yellow oil); isovaleric ester (oil); bromoisovaleric ester (oil); monochloroacetic ester (cryst.); trichloroacetic ester (cryst.); diethyl glycine ester (oil); dimethyl glycine ester (oil); piperidine acetyl ester (cryst.); allophanic ester (cryst.); acid malonic ester (cryst.); dibromocinnamic ester (cryst.); neutral malonic ester (cryst.).

#### Summary.

The acetic ester of tribromotertiary-butyl-alcohol is most conveniently prepared through the interaction of acetyl chloride or bromide and the alcohol, or by means of acetic anhydride and anhydrous sodium acetate, in the usual way.

Prepared by either of these processes and recrystallized from alcohol, the purified substance melts at 43-44° (uncorr.).

Bromine determinations (Carius) gave results sufficiently near to characterize the compound as brometone acetic ester with the formula



The compound is extremely soluble in the organic solvents, practically insoluble in water. It is not readily saponified by boiling with water or acidulated water and when saponified the alcohol is decomposed still further. Although saponification takes place slowly by boiling with water or water and acid, it takes place very quickly when heated with an excess of moderately concentrated nitric acid. Like chloretone and brometone, though not quite so readily, the ester is volatile in the air and especially with steam. The pharmacological action is similar to that of chloretone and brometone although, presumably on account of its greater insolubility in water, its effects are less rapid and marked.

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[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

### STUDIES IN ESTERIFICATION. VII.

#### THE ESTERIFICATION OF *o*-, *m*- AND *p*-TOLUIC ACIDS BY ETHYL MERCAPTAN.

By J. H. SACHS AND E. EMMET REID.  
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#### Historical.

As early as 1862 Berthelot and Pean de St. Gilles<sup>1</sup> began the investigation of the general problem of esterification. They studied the limit of

<sup>1</sup> *Ann. chim. phys.*, [3] 65, 385 (1862); 66, 5 (1862); 68, 225 (1863).

esterification for different temperatures. In 1878 Menschutkin<sup>1</sup> took up the problem and by using different alcohols with acetic acid first showed the effect of composition and isomerism on the rate and limit of esterification. Goldschmidt<sup>2</sup>, in 1895, first studied the effect of differences of constitution in isomeric acids upon ester formation. He studied the esterification of *o*-, *m*- and *p*-substituted benzoic acids with ethyl alcohol, using hydrochloric acid as catalyzer. By using a large excess of alcohol in which the hydrochloric acid was dissolved, he was able to use for the calculation of his results the equation for a monomolecular reaction:

$$K = (1/t) \log a/a - x$$

For the toluic acids he got the following constants:

<i>o</i> -Toluic.....	0.011
<i>m</i> -Toluic.....	0.0470
<i>p</i> -Toluic.....	0.0241

The same general relation was noted for other substituted benzoic acids.

About the same time Petersen<sup>3</sup> observed that *p*-toluic acid forms ester much more readily than does the ortho acid.

From 1894 to 1897 Victor Meyer<sup>4</sup> and his co-workers, investigating the problem of steric hindrance, threw much light on the effect of isomerism upon esterification. Working with ethyl and methyl alcohols with ortho, meta and para substituted benzoic acids, they showed that the toluic acids were esterified in the following order: Meta, para and ortho. The same held good for other monosubstituted benzoic acids.

Kellas<sup>5</sup> extended the work of Victor Meyer and found practically the same results. He also studied the rate of saponification of esters of the substituted benzoic acids by caustic potash. In the case of the esters of the toluic acids the results are so close together that no general relation can be gotten from them.

Recently McCombie and Scarborough<sup>6</sup> in studying the rate of saponification of esters of substituted benzoic acids by hydrochloric acid, found the following constants:

	<i>o</i> .	<i>m</i> .	<i>p</i> .
Toluic.....	0.00134	0.00405	0.00275
Chlorobenzoic.....	0.0158	0.0485	0.0298
Bromobenzoic.....	0.0118	0.0445	0.0234

Thus we see that the saponification relation is the same as that of esterification.

<sup>1</sup> *Ann.*, **195**, 334 (1878).

<sup>2</sup> *Ber.*, **18**, 3218 (1895).

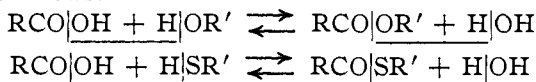
<sup>3</sup> *Z. physik. Chem.*, **16**, 403 (1895).

<sup>4</sup> *Ber.*, **27**, 510, 3146 (1894); **28**, 1254, 2773, 3197 (1895); *Z. physik. Chem.*, **24**, 219 (1897).

<sup>5</sup> *Z. physik. Chem.*, **24**, 221 (1897).

<sup>6</sup> *J. Chem. Soc.*, **107**, 156 (1915).

Reid<sup>1</sup> in studying the mechanism of the reaction in esterification showed that mercaptans esterify acids just as do alcohols. However, instead of getting esters of the general formula  $\text{RCOOR}'$ , he got the thiol esters of the general formula  $\text{RCOSR}'$ . This shows that esterification probably takes place as follows:



The present work was taken up therefore with the idea of finding whether or not the above relations hold when the toluic acids are esterified with ethyl mercaptan.

### Materials.

**Acids.**—The *o*- and *m*-toluic acids were a well-known firm's best grade. The *p*-toluic acid was made from *p*-tolyl nitrile which, in turn, was made from *p*-toluidine by the Sandmeyer reaction. This acid was purified by boiling with animal charcoal and then twice recrystallizing from boiling water, m. p.  $177^{\circ}$ .

**Mercaptan.**—The ethyl mercaptan was made by Reid for use in the above-mentioned work. It had been freed from sulfide, dried, and twice distilled, only the best fraction being used for the work.

The thiol esters were made by alkylating the thiol toluic acids which were prepared according to the directions of Kym<sup>2</sup> for thiolbenzoic acid.

***o*-Thiol Toluic Acid.**—To 80 g. of 85% caustic potash dissolved in 600 cc. of 95% alcohol and saturated with hydrogen sulfide, there was added, with cooling, 70 g. of *o*-toluyl chloride. The potassium salt of the *o*-thiol acid separated at once as a pasty brown mass. This was dried on the water bath, taken up with water and the solution shaken with ether in order to remove any ethyl toluate that might have been present. On acidifying the water solution of the potassium salt with hydrochloric acid, the acid separated as a red oil. This was taken up with ether, the ethereal solution dried over calcium chloride and, after distilling off the ether, the ester was twice distilled *in vacuo*. The yield was 26 g.; b. p.  $133^{0.36}$ ; d.  $1.1451_{25}^{25}$ . Weighed portions of the acid were dissolved in alcohol and titrated with 0.0905 *N* barium hydroxide.

I. 0.1559 g. acid required 11.32 cc. alkali; corresponding to M. W. 152.18.

II. 0.1418 g. acid required 10.62 cc. alkali; corresponding to M. W. 152.71.

Calculated, M. W. 152.12.

***p*-Thiol Toluic Acid.**—This was made in exactly the same way as the preceding. The acid separated as a red oil which on cooling, solidified. The yield was 48 g. from 70 g. of *p*-toluyl chloride. B. p.  $131^{0.15}$ . M. p. after recrystallizing from alcohol  $43.5\text{--}44^{\circ}$ . This was also titrated with the standard alkali.

<sup>1</sup> *Am. Chem. J.*, **43**, 489 (1910).

<sup>2</sup> *Ber.*, **32**, 3533 (1899).

I. 0.1409 g. acid required 10.30 cc. alkali; corresponding to M. W. 152.64.

II. 0.1981 g. acid required 14.44 cc. alkali; corresponding to M. W. 152.38.

The *m*-thiol toluic acid and its ethyl ester could not be made on account of the scarcity of *m*-xylene and *m*-toluidine.

**Ethyl *o*-Thiol Toluate.**—This was made by Wheeler's method for ethyl thiol benzoate, from potassium *o*-thiol toluate and ethyl bromide. The yield was 25 g. from 30 g. of the acid and 35 g. of ethyl bromide. B. p. 133<sup>0.15</sup>. D. 1.0513<sup>25</sup>/<sub>25</sub>. The ester has a clear yellow color which has remained unchanged after standing five months.

**Ethyl *p*-Thiol Toluate.**—This was made exactly as was the ortho ester. From 25 g. of the acid and 30 g. of ethyl bromide 23 g. of the ester were obtained. B. p. 150<sup>0.18</sup>. D. 1.0708<sup>25</sup>/<sub>25</sub>. This ester has also remained unchanged on five months' standing.

All of these acids and esters are insoluble in water, but dissolve readily in alcohol and ether. They are very resistant to oxidation by nitric acid, for after heating them five hours in a Carius tube with fuming nitric acid at 250°, they were not burned up.

The authors have been working for some time upon a new method for the determination of sulfur in organic compounds. The analysis of these acids and esters will appear in a later paper upon this method.

**Water.**—Conductivity water was used.

#### Heating.

The furnace used was that described by Pratt and Reid,<sup>2</sup> electrically controlled and heated, it maintained the desired temperature for weeks with a variation of  $\pm 2^\circ$ .

#### Standard Solution.

The standard hydrochloric acid and barium hydroxide were kept in large stock bottles from which they were run through siphons fitted with stopcocks into their respective burets. The tops of the acid bottle and buret were protected from the air by tubes containing acid of the same strength as the standard solution. The barium hydroxide system was protected by soda lime tubes. Both solutions were approximately 0.1 *N* and were frequently standardized.

#### Procedure.

Hard glass tubes about 6 by 70 mm. outside, closed at one end, were cleaned by boiling one day in dilute hydrochloric acid, 4 hours in distilled water and then thoroughly dried in an air bath at 150°.

**Acid Series.**—Each tube was weighed, partly filled with the acid, drawn out to a narrow neck and weighed again. The mercaptan was then added and after cooling in ice and salt, the tubes were sealed. The tube and tip were then weighed.

<sup>1</sup> *Am. Chem. J.*, 24, 69 (1900).

<sup>2</sup> *THIS JOURNAL*, 37, 1934 (1915).

**Ester Series.**—The procedure was the same as for the acid series, using ester instead of acid, and water instead of mercaptan.

These tubes were then placed in the furnace and heated to 198–202° for different periods of time. On taking the tubes from the furnace they were allowed to cool, scored with a file and broken over a short necked funnel into 120 cc. Erlenmeyer flasks. The funnel was rinsed with 25 cc. of ethyl alcohol, which had been distilled from caustic potash, which dissolved the reaction mixture. The mercaptan which had not reacted, was blown off by bubbling for 15 minutes through the solution, kept at 50°, a current of carbon dioxide-free air. The amount of toluic acid present was then determined by titration with the standard baryta water, using phenolphthalein as indicator. Uniformity of results was gotten by standardizing the baryta with alcoholic solutions of the toluic acids used.

#### Experimental.

The chief object of the work was to measure the limits of esterification, but the rates also are of interest. The velocities of esterification are calculated by the formula for bimolecular reactions:<sup>1</sup>

$$(1) \quad K = \frac{2.3025}{(A - B)T} \log \frac{(A - x)B}{(B - x)A}$$

in which A and B are the active masses of the two substances that react,  $x$  the amount of each transformed and T the time. As this equation holds even approximately for balanced reactions only when the reaction is proceeding with an appreciable velocity, that is, before the limit is nearly reached, it was applied to only the one-, two- and four-day series.

The limits of esterification are gotten by the usual reasoning in consideration of reversible reactions.<sup>2</sup> In this case the amount of ester formed in unit time being equal to (Acid  $\times$  Mercaptan) K and the amount of ester decomposed at the same time being equal to (Ester  $\times$  Water) K', at equilibrium these velocities being equal, we have

$$(2) \quad \frac{(\text{Acid} \times \text{Mercaptan})}{(\text{Ester} \times \text{Water})} = \frac{K'}{K} = r.$$

For equal concentrations of acid and mercaptan at equilibrium,

$$\frac{\text{Amount of mixture unesterified}}{\text{Amount of mixture esterified}} = \frac{\sqrt{K'}}{\sqrt{K}} = \frac{\sqrt{r}}{1}$$

or, the percentage of a mixture of equivalent amounts, esterified at limit =  $100/\sqrt{r} + 1$ .

In the following tables are given the results of the *o*-, *m*-, and *p*-toluic acids with ethyl mercaptan and the results of the *o*-, and *p*-ethyl ester with water.

<sup>1</sup> Reid, *Am. Chem. J.*, **24**, 398 (1900).

<sup>2</sup> Reid, *Ibid.*, **43**, 499 (1910); Bonz, *Zeit. physik. Chem.*, **2**, 865 (1888).

In tabulating the results, the data are thus arranged.

- a*, Acid or ester in grams.  
*b*, Millimols of acid or ester.  
*c*, Mercaptan or water in grams.  
*d*, Millimols of mercaptan or water.  
*e*, Cubic centimeters of standard alkali required for titration.  
*f*, Millimols of acid present, calculated from *e*.  
*g*, Millimols of mercaptan remaining (acid series).  
*h*, Millimols of ester remaining (ester series).  
*k*, Millimols of water remaining (ester series).  
*m*, Millimols of ester, equals water (acid series).  
 $\%$ , Percentage of esterification, calculated by the above formula.  
*x*, The same as *m* in acid series and *f* in ester series.  
*K*, The velocity constant of the reaction.

In the acid series the amount of ester = water, (*m*) is found by subtracting the acid remaining (*f*) from the original amount (*b*). The concentration of ester (*m*) equals the concentration of water. The millimols of mercaptan remaining, as given in (*g*), are obtained by subtracting the amount of ester (*m*) from (*d*), the amount of mercaptan originally present.

In the ester series, the amount of ester remaining (*h*) is found by subtracting the acid present from (*b*), the original amount of ester. The water remaining (*h*) is obtained by subtracting the acid present (*f*) from (*d*), the original amount of water.

The percentage esterification ( $\%$ ) and the velocity constant of the reaction (*K*) are obtained by calculation from the equations above discussed. In Series I all the data are tabulated, but in the tables that follow only the most essential are given. Some of the results which are out of harmony with others of same series are bracketed and are not included in the averages.

The work was undertaken as a study of the limits rather than the reaction velocities. Hence close temperature regulation and other precautions required for obtaining concordant values of *K* were not regarded. The values of *K* are only approximate and little stress is put on them.

### Results.

#### SERIES I.—24 HOURS AT 200°.



<i>a</i>	0.0669	0.0935	0.0817	0.0774	0.0778	0.0910
<i>b</i>	0.4919	0.6875	0.6007	0.5691	0.5722	0.6691
<i>c</i>	0.1242	0.1206	0.1605	0.0941	0.1680	0.1095
<i>d</i>	2.001	1.9428	2.586	1.515	2.707	1.765
<i>e</i>	5.32	7.21	6.48	5.98	6.21	7.09
<i>f</i>	0.4816	0.6529	5.846	5.412	0.5625	6.419
<i>g</i>	1.991	1.9082	2.570	1.487	2.697	1.738

$m$	0.0103	0.0346	0.0161	0.0279	0.0097	0.0272
$\sqrt{r}$	95.07	32.26	76.13	32.15	127.9	38.83
%	1.04	3.01	1.30	3.02	0.78	2.51
K	0.0110	0.0267	0.0101	0.0338	0.00637	0.0235

Mean K, 0.0186.

Mean, 1.94%.

	<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COOH + C <sub>2</sub> H <sub>5</sub> SH.				<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COOH + C <sub>2</sub> H <sub>5</sub> SH.				
<i>a</i>	0.1104	0.1324	0.1412	0.1609	0.0468	0.0420	0.0410	0.0507	0.0479
<i>b</i>	0.8118	0.9735	1.0375	1.183	0.3441	0.3088	0.3015	0.3728	0.3522
<i>c</i>	0.1690	0.1705	0.1238	0.1091	0.2641	0.1813	0.1621	0.1271	0.0939
<i>d</i>	2.723	2.747	1.995	1.758	4.255	2.921	2.612	2.048	1.513
<i>e</i>	8.00	8.72	10.24	11.92	3.48	3.11	3.04	3.85	3.58
<i>f</i>	0.7240	0.7882	0.9267	1.079	0.3150	0.2815	0.2751	0.3484	0.3240
<i>g</i>	2.635	2.5616	1.884	1.654	4.230	2.894	2.586	2.024	1.485
<i>m</i>	0.0878	0.1854	0.1108	0.1040	0.0291	0.0273	0.0264	0.0244	0.0282
$\sqrt{r}$	15.73	7.66	11.93	12.85	39.67	33.06	31.95	34.42	24.60
%	5.98	(11.55)	7.73	7.22	2.46	2.94	3.04	2.83	3.91
K	0.0428	0.0697	0.0579	0.0541	0.0207	0.0316	0.0354	0.0331	0.0558

Mean K, 0.0516. Mean, 6.98%.

Mean K, 0.0353. Mean, 3.03%.

*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COSC<sub>2</sub>H<sub>5</sub> + H<sub>2</sub>O.

<i>a</i>	0.2846	0.2734	0.2601	0.2820	0.2875	0.2722
<i>b</i>	1.5807	1.5184	1.4447	1.5662	1.5968	1.5180
<i>c</i>	0.2891	0.2104	0.2003	0.1634	0.1357	0.1398
<i>d</i>	16.061	11.688	11.128	9.078	7.539	7.767
<i>e</i>	2.60	2.70	2.01	1.44	1.92	2.66
<i>f</i>	0.2353	0.2444	0.1819	0.1303	0.1738	0.2407
<i>h</i>	1.3454	1.2740	1.2628	1.4359	1.4230	1.2711
<i>k</i>	15.826	11.446	10.946	8.948	7.365	7.526
$\sqrt{r}$	0.0510	0.0640	0.0489	0.0364	0.0537	0.0778
%	95.18	93.98	95.32	96.50	94.90	(92.80)
K	0.0102	0.0153	0.0125	0.0126	0.0154	(0.0229)

Mean K, 0.0132.

Mean, 95.17%.

*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COSC<sub>2</sub>H<sub>5</sub> + H<sub>2</sub>O.

<i>a</i>	0.2947	0.2551	0.2487	0.2682	0.2544	0.2663
<i>b</i>	1.6367	1.4168	1.3813	1.4897	1.4129	1.4790
<i>c</i>	0.1411	0.1747	0.1307	0.1862	0.1594	0.1844
<i>d</i>	7.8390	9.7055	7.2610	10.3440	8.8555	10.2440
<i>e</i>	8.55	5.95	3.86	5.95	8.08	8.14
<i>f</i>	0.7738	0.5385	0.3493	0.5385	0.7312	0.7367
<i>h</i>	0.8629	0.8783	1.0320	0.9512	0.6817	0.7423
<i>k</i>	7.0652	9.1670	6.9117	9.8055	8.1243	9.5073
$\sqrt{r}$	0.3134	0.1898	0.1308	0.1763	0.3106	0.2774
%	76.17	84.05	88.40	85.10	76.30	78.25
K	0.0860	0.0512	0.0409	0.0446	0.0864	0.0712

Mean K, 0.0634.

Mean, 81.21%.

## SERIES II.—48 HOURS AT 200°.



<i>b</i>	1.0405	1.089	0.9500	0.7522	0.7647
<i>d</i>	3.0285	3.5804	3.9108	1.281	3.2760
<i>f</i>	0.9957	1.0300	0.8960	0.7023	0.7321
$\sqrt{r}$	35.91	32.28	34.43	18.60	47.27
%	2.71	3.00	2.83	(5.10)	2.08
K	0.00736	0.00819	0.00742	(0.0280)	0.00451

Mean K, 0.00687. Mean, 2.65%.



<i>b</i>	1.5883	1.0118	1.1831	0.9721	0.4059	0.6559	0.4956	0.5780
<i>d</i>	1.9578	2.3623	2.1544	1.3954	2.8875	5.2788	2.5507	2.8715
<i>f</i>	1.4426	0.8823	1.0208	0.8751	0.3701	0.5819	0.4317	0.5294
$\sqrt{r}$	11.10	10.84	8.79	10.99	28.70	23.51	16.22	25.16
%	8.26	8.63	10.23	8.34	3.37	4.08	5.81	3.82
K	0.0249	0.0298	0.0343	0.0302	0.0164	0.0114	0.0266	0.0153

Mean K, 0.0298. Mean, 8.81%. Mean K, 0.0174. Mean, 4.27%.



<i>b</i>	1.3684	1.5545	1.5507	1.6034	1.6451
<i>d</i>	8.4778	16.061	11.406	12.917	14.067
<i>f</i>	0.1376	0.2742	0.3493	0.3321	0.2471
$\sqrt{r}$	0.0429	0.0610	0.0958	0.0830	0.0562
%	95.9	94.2	91.3	92.4	94.7
K	0.00627	0.00608	0.0113	0.00890	0.00585

Mean K, 0.00768. Mean, 93.7%.



<i>b</i>	1.5579	1.4518	1.4796	1.5723	1.5401
<i>d</i>	15.357	15.723	13.844	16.245	12.111
<i>f</i>	0.6598	0.9575	1.0605	1.0263	0.6552
$\sqrt{r}$	0.182	0.354	0.458	0.356	0.206
%	84.6	73.9	68.6	73.8	83.3
K	0.0185	0.0357	0.0507	0.0341	0.0233

Mean K, 0.0325. Mean, 76.8%.

## SERIES III.—4 DAYS AT 200°.



<i>b</i>	1.2442	1.1589	1.0294	1.2162	0.7397
<i>d</i>	2.7746	2.9681	2.1431	3.5562	1.9852
<i>f</i>	1.1421	1.0291	0.9068	1.0923	0.6661
$\sqrt{r}$	17.13	13.17	11.04	15.63	15.33
%	5.52	7.06	(8.32)	6.02	6.12
K	0.0079	0.0102	0.0152	0.0077	0.0125

Mean K, 0.0107. Mean, 6.18%.



<i>b</i>	1.6618	1.2455	1.6602	1.4220	0.5721	0.6265	0.7140	0.8029	0.9552
<i>d</i>	2.1555	2.6588	2.7925	2.5879	2.8036	3.1502	2.7022	4.0132	3.8060
<i>f</i>	1.4281	1.0326	1.4200	1.2064	0.4480	0.4928	0.5883	0.3992	0.7593
$\sqrt{r}$	7.10	7.46	7.93	7.85	8.83	9.54	9.80	3.06	8.45
%	12.35	11.83	11.20	11.30	10.18	9.53	9.25	(24.63)	10.58
K	0.0196	0.0194	0.0146	0.0166	0.0223	0.0167	0.0183	(0.0504)	0.0155

Mean K, 0.0175. Mean, 11.67%. Mean K, 0.0182. Mean, 9.88%.



$o\text{-CH}_3\text{C}_6\text{H}_4\text{COSC}_2\text{H}_5 + \text{H}_2\text{O}.$					$p\text{-CH}_3\text{C}_6\text{H}_4\text{COSC}_2\text{H}_5 + \text{H}_2\text{O}.$					
<i>b</i>	1.3612	1.7145	1.5451	1.4917	1.6890	1.3074	1.6140	1.5117	1.5423	1.4168
<i>d</i>	3.0667	5.2777	4.7000	4.9890	5.8389	5.6442	6.2833	4.3445	4.5112	3.2834
<i>f</i>	0.9430	1.0507	0.6943	0.7521	1.1267	1.2380	1.5159	1.3982	1.4272	1.3104
$\sqrt{r}$	1.00	0.627	0.376	0.425	0.690	2.24	2.22	2.45	2.40	2.86
%	50.0	61.4	72.6	70.2	59.2	30.86	31.06	28.98	29.41	25.90
K	0.1180	0.0507	0.0345	0.0383	0.0535	0.1551	0.1348	0.1940	0.1866	0.2779
Mean K,	0.0590. Mean, 62.7%.					0.1897. Mean, 29.24%.				

## SERIES IV.—8 DAYS AT 200°.

$o\text{-CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{C}_2\text{H}_5\text{SH}.$					
<i>b</i>	1.0176	1.2029	1.0537	0.9397	0.9191
<i>a</i>	1.1893	1.4180	2.0722	1.8208	1.2246
<i>f</i>	0.9168	1.0543	0.8887	0.8018	0.8127
$\sqrt{r}$	9.445	7.785	7.891	8.424	8.959
%	9.57	11.38	11.25	10.61	10.04
Mean,	10.57%.				

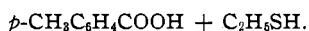
$m\text{-CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{C}_2\text{H}_5\text{SH}.$					$p\text{-CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{C}_2\text{H}_5\text{SH}.$					
<i>b</i>	1.1243	1.3382	1.1676	1.0492	1.2360	0.5647	0.5471	0.5713	0.5875	0.5971
<i>d</i>	0.7525	1.4760	1.2375	1.6388	1.9062	1.3600	1.5839	1.9915	2.0335	0.9877
<i>f</i>	1.0235	1.1655	1.0199	1.8932	1.0524	0.4606	0.4335	0.4344	0.4543	0.5059
$\sqrt{r}$	8.102	7.220	7.138	7.307	7.334	7.307	7.028	6.560	6.976	7.384
%	(10.98)	12.17	12.29	12.04	12.00	12.04	12.45	(13.24)	12.53	11.93
Mean,	12.12%.					12.24%.				

$o\text{-CH}_3\text{C}_6\text{H}_4\text{COSC}_2\text{H}_5 + \text{H}_2\text{O}.$					$p\text{-CH}_3\text{C}_6\text{H}_4\text{COSC}_2\text{H}_5 + \text{H}_2\text{O}.$					
<i>b</i>	1.3746	1.5518	1.3523	1.2130	1.2757	1.2119	1.2702	1.2930	1.3956	
<i>d</i>	3.9278	2.5445	3.2222	2.7111	4.8833	2.3777	3.3277	2.6777	3.0222	
<i>f</i>	1.0715	1.0606	1.1385	0.9104	1.1982	1.1095	1.1837	1.1873	1.2977	
$\sqrt{r}$	1.151	1.242	1.666	1.233	2.242	3.080	2.751	2.991	3.158	
%	46.49	44.60	37.51	44.78	(30.85)	24.52	26.67	25.06	24.05	
Mean,	43.34%.					25.07%.				

## SERIES V.—16 DAYS AT 200°.

$o\text{-CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{C}_2\text{H}_5\text{SH}.$						
<i>b</i>	0.7184	0.7728	0.6897	0.5728	0.8302	1.0022
<i>d</i>	0.7300	0.7525	0.6832	0.6445	0.8669	0.8782
<i>f</i>	0.6176	0.6645	0.5860	0.4932	0.7159	0.8709
$\sqrt{r}$	6.186	6.041	5.620	5.916	6.424	6.143
%	13.92	14.20	(15.11)	14.46	13.47	14.00
Mean,	14.01%.					

$m\text{-CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{C}_2\text{H}_5\text{SH}.$						
<i>b</i>	1.0044	0.7772	0.7309	0.7169	0.7103	0.8287
<i>d</i>	0.6752	0.5044	0.6494	0.6993	0.7686	0.8057
<i>f</i>	0.8926	0.6987	0.6401	0.6212	0.6113	0.7213
$\sqrt{r}$	6.343	6.950	6.587	6.398	6.588	6.608
%	13.62	(12.58)	13.18	13.52	13.18	13.14
Mean,	13.33%.					



<i>b</i>	0.6022	0.3434	0.3794	0.5235	0.5324	0.5662
<i>d</i>	0.5898	0.7992	0.7428	0.6188	0.2868	0.3158
<i>f</i>	0.5157	0.2750	0.3092	0.4481	0.4806	0.5049
$\sqrt{r}$	5.890	6.341	6.496	6.544	6.487	6.561
%	(14.51)	13.62	13.34	13.26	13.36	13.23

Mean, 13.36%.



<i>b</i>	1.4745	1.2757	1.4268	1.6301	1.3563	1.4075
<i>d</i>	2.3000	1.8944	2.3945	1.7722	2.2778	1.9722
<i>f</i>	1.2532	1.0683	1.2117	1.3153	1.1657	1.1783
$\sqrt{r}$	2.838	2.581	2.402	3.468	2.532	2.773
%	26.05	27.92	29.40	22.38	28.31	26.50

Mean, 26.41%.



<i>b</i>	1.3518	1.4751	1.5912	1.4601	1.5817
<i>d</i>	2.0222	3.6890	4.1222	4.0666	2.9278
<i>f</i>	1.2261	1.3785	1.4857	1.3703	1.4623
$\sqrt{r}$	4.352	2.918	2.820	2.785	3.496
%	18.68	25.52	26.18	26.42	22.24

Mean, 23.81%.

#### SUMMARY OF RESULTS.

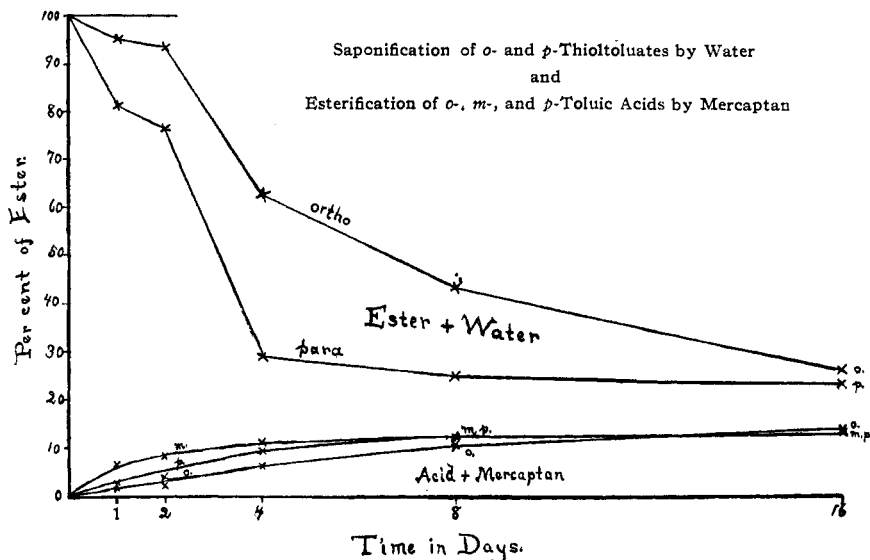
Time.	Acid series.						Ester series.			
	o.		m.		p.		o.		p.	
	%.	K.	%.	K.	%.	K.	%.	K.	%.	K.
1 day.....	1.94	0.0186	6.98	0.0516	3.03	0.0353	95.17	0.0132	81.21	0.063
2 days....	2.65	0.0069	8.81	0.0298	4.27	0.0174	93.7	0.0077	76.8	0.0325
4 days....	6.18	0.0107	11.67	0.0175	9.88	0.0182	62.7	0.0590	29.24	0.1897
8 days....	10.57	.....	12.12	.....	12.24	.....	43.34	.....	25.07	.....
16 days....	14.01	.....	13.33	.....	13.36	.....	26.42	.....	23.81	.....

#### Discussion of Results.

On examination of the foregoing results, it is seen that very concordant results are obtained in the acid series, while those from the ester series show large variations. Then, too, the same limit is not reached in the ester series that is reached in the acid series. The cause of these discrepancies lies, no doubt, in the fact that in the acid-mercaptan series the reaction mixture forms a homogeneous liquid at 200°; in the ester-water series, at that temperature, the oily ester and the water remain separated in two layers, thus leaving a comparative small surface of contact at which the reaction takes place.

On the whole, the results for the one and two days' series are rather unsatisfactory, looking at the curves plotted for the progress of the reaction, one sees at once that the reaction seems to lag at two days. As this lag is observed in all five cases it seems probable that the temperature, at which the two days' series was run, was low, due, doubtless, to faulty

regulation of the furnace. A few degrees, at the temperature at which these experiments were carried out, would make quite a large difference in the short periods of time.



The results for the four, eight and sixteen days' series are very good in the acid series. Another series was run for the eight-day period using larger tubes and smaller amounts of water; furnace trouble developed here and the results proved so unsatisfactory that they are not included. In the ester series there seems to be some relation between the amount of water used and the amount of ester remaining. As a rule, the smaller the amount of water used the more ester, relatively, was decomposed. This is opposite to what one would naturally expect.

A study of the results of the rates and limits of the esterification of the three acids is very interesting; one is struck at once by the very large velocity in the case of the meta acid and the small velocity in the case of the ortho acid. The meta acid proceeds over half way to its limit in the first day while the para goes to about one-fourth and the ortho, to about one-seventh their respective limits in the same time. Thus these results agree very well with those obtained by the workers cited in the first part of this paper. It seems that the limits in all their cases are about the same (14%), for there is a very small increase in the results of the sixteen days' series over those gotten at eight days. In the acid-mercaptan series, especially for the longer times, the relative amounts of acid and mercaptan used have no appreciable influence on the limit of the reaction.

In all the experiments run over two days there was a slight amount of

decomposition. This was shown by the presence of hydrogen sulfide which was detected by the lead acetate paper test.

#### Conclusion.

- I. Mercaptans esterify acids just as do alcohols.
- II. Mercaptans show the same relations between velocities and limits of esterification of the toluic acids as do alcohols.
- III. The limits in the case of ethyl mercaptan are much lower than in the case of ethyl alcohol.
- IV. The limit in the acid-mercaptan series is independent of the proportions of the reacting substances.
- V. *o*-, *m*- and *p*-Toluic acids reach nearly the same limits of esterification when esterified with ethyl mercaptan.

BALTIMORE, MD.

[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

### STUDIES IN ESTERIFICATION. VIII.

#### THE ESTERIFICATION OF BENZOIC ACID BY ISOMERIC BUTYL MERCAPTANS.

BY J. W. KIMBALL AND E. EMMET REID.

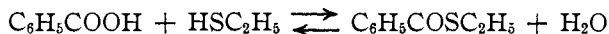
Received September 27, 1916.

#### Historical.

The influence of isomerism on the rates and limits of esterification of alcohols has been carefully studied by Menschutkin,<sup>1</sup> who found that the limits for primary alcohols, whether normal or iso-, are practically the same, while those for secondary alcohols are much lower. The limits for tertiary alcohols, he found to be still lower, but the results in this case are not the real limits since a part of the alcohol reacted in another way, decomposing into the unsaturated hydrocarbon and water.

With acetic acid Menschutkin found the following limits for the isomeric butyl alcohols: Normal 67.30%, iso- 67.38%, secondary 59.28%, tertiary 7.10%. The limits are reached in 120 hours at 154°.

Reid,<sup>2</sup> studying the mechanism of the reaction of esterification, employed mercaptans instead of alcohols and showed that the reaction



reaches a well-defined limit as in the case of the oxygen alcohols.

Pratt and Reid<sup>3</sup> then took up this work, using benzoic acid with methyl, ethyl and propyl mercaptans, and accurately determined the limits of these systems. These limits with mercaptans were found to be much lower

<sup>1</sup> *Ber.*, 11, 1507, 2117, 2148 (1878); *Liebig's Ann.*, 195, 334 (1879); 197, 193 (1879); *Ann. chim. phys.*, [5] 20, 289 (1880).

<sup>2</sup> *Am. Chem. J.*, 43, 489 (1910).

<sup>3</sup> *THIS JOURNAL*, 37, 1934 (1915).