1-phenyl-5-methyl-4-acetylpyrazole, which is capable of forming a hydrazone and azine derivatives.

3. Hydrazine and anilino-methylene-acetylacetone give an unreactive high-melting product, probably an azine.

LAWRENCE, KANSAS.

[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

STUDIES IN ESTERIFICATION. X. THE ESTERIFICATION OF BENZOIC AND THE TOLUIC ACIDS BY METHYL, ETHYL AND PROPYL ALCOHOLS.

BY RAYMOND FREAS[1] AND E. EMMET REID.

Historical.

Since the work of Berthelot and Pean de St. Gilles,[2] in 1862, esterification has been one of the most frequently studied reactions. It has been regarded as one of the best examples of a reversible reaction and has been commonly used to illustrate the mass law. However, calculation of the results obtained by these workers shows that they do not agree closely with the mass law. Their work was done almost exclusively with the acids of the aliphatic series. They obtained 64.8 and 66.5% as the limits when methyl and ethyl alcohols were heated with benzoic acid in equivalent quantities, while with acetic acid the corresponding limits were 67.5 and 66.5%. Since ethyl alcohol gives sensibly the same limits with the two acids, their low result with methyl alcohol and benzoic acid seems doubtful. In fact, in a study of the interdependence of limits by Reid[3] it was assumed that methyl and ethyl alcohols give the same limits with both acids. The first object of the present investigation was to obtain accurate values for the limits of benzoic and toluic acids with methyl, ethyl and propyl alcohols. The second object was to ascertain how closely the esterification of benzoic acid by these alcohols obeys the mass law then the proportions of acid and alcohol are varied, and the third object was to study the effect of isomerism as illustrated by the three toluic acids.

Materials.

Acids.—The benzoic, o- and m-toluic acids were the commercial C. P. products; the p-toluic acid was made by the Sandmeyer reaction. All were purified by boiling with animal charcoal, recrystallizing several times from boiling water (diluted alcohol for the toluic acids). They were then dried for one week in a vacuum desiccator.

Alcohols.—The alcohols used were the C. P. commercial products.

[1] From dissertation of Raymond Freas.

[2] *Ann. Chim. phys.*, [3] **65**, 385 (1862); 66, 5 (1862); **68**, 225 (1863).

[3] *Am. Chem. J.*, **45**, 479 (1911).

They were all refluxed with quicklime or metallic calcium until density determinations showed a water content of less than 0.04%.

Esters.—The esters were prepared by usual methods and carefully purified by washing, drying and distilling.

Standard Solutions.—Standard hydrochloric acid and barium hydroxide solutions were kept in large stock bottles directly connected to the buret and protected from the air by U-tubes containing similar solutions. The barium hydroxide solution was, in addition, protected by soda lime. The solutions were very nearly 0.1 N and the barium solution which was most subject to change was restandardized about twice a month with the acids used in that period of time.

Glass Tubes.—The tubing used was 6 mm. in diameter, of Pyrex hard glass. Small tubes of 70 mm. length were made. These were cleaned with chromic acid solution boiled several hours in dilute hydrochloric acid and then several hours each in two changes of distilled water. They were then thoroughly dried in an air oven at 150° and kept covered to protect from dust.

Furnace.—The furnace used was an electrically heated and controlled tube furnace, similar to that described by Pratt and Reid, but of better construction. It kept the desired temperature within ± 1°.

Procedure.

The tubes were weighed, partly filled with acid or ester, drawn out and weighed again. The alcohol or water was then introduced to fill the tubes about two-thirds full. The tubes were then sealed off and the filled tube and tip weighed. Numbers scratched on the tip and the tube identified these during weighing and at titration. The tubes were then heated from 2 to 8 days at 200°, and after cooling, opened and titrated. The contents of the tubes were nearly always liquid, which necessitated a different procedure from that used in former work done in this laboratory. The tubes were gently heated at the tip to drive from the tip any adherent liquid. They were then scored with a file and the tips broken off. The contents of the tube were then transferred to a flask by a capillary pipet, and the tube and pipet washed out four times thoroughly with alcohol that had been distilled from caustic potash. The contents of the flask were then diluted to 25 cc. with the same alcohol. The acid remaining was then titrated, using phenolphthalein as indicator. An alcohol correction of 0.05 cc. was deducted to correct for the apparent acidity as determined for the amount of alcohol present.

Experimental.

In this investigation the points of interest were the limits of esterification and the effect of varying concentration of the reagents on the limits.

The letters used in tabulating results are those usually found in text-book expressions of the mass law.

A — Weight of alcohol or water in grams.

B — Weight of acid or ester in grams.

p — Active mass of alcohol or water in millimoles.

q — Active mass of acid or ester in millimoles.

$alk.$ — Cc. of standard alkali required in titration.

x — Millimoles of reagents transformed when equilibrium is reached, which is equivalent to the amount of ester and water formed in the acid series, and the alcohol and acid formed in the ester series.

$p - x$ — Millimoles alcohol remaining (acid series) millimoles water remaining (ester series).

$q - x$ — Millimoles acid remaining (acid series) millimoles ester remaining (ester series).

r — The equilibrium constant.

$\%$ — Per cent. esterification calculated for formula given below.

In the acid series at equilibrium we get from the titration the concentration of acid remaining $q - x$, from which by subtraction we get x, the concentration of the ester and water formed, and from this value that of the alcohol remaining $p - x$. The equilibrium constant is then obtained.

$$\frac{[\text{Water}] \times [\text{Ester}]}{[\text{Alcohol}] \times [\text{Acid}]} = \frac{x^2}{(p - x)(q - x)} = r.$$

In the ester series at equilibrium, we get from the titration the concentration of acid and alcohol formed, x, which also, by subtraction from the original concentrations of water and ester, gives the concentrations of these untransformed. From these data we obtain our equilibrium constant

$$\frac{[\text{Water}] \times [\text{Ester}]}{[\text{Alcohol}] \times [\text{Acid}]} = \frac{(p - x)(q - x)}{x^2} = r.$$

To calculate the percentage of equivalent amounts esterified at equilibrium we use the formula given by Reid,[1] and more fully explained by Faber and Reid,[2]

$$\% = \frac{100}{\sqrt{r} + 1}.$$

The heating was continued either 96 or 192 hours, as it was found with methyl and ethyl alcohol and benzoic acid that after 48 hours' heating the percentages esterified at the limit in the acid series were about 2 or 3% less than in the ester series.

[1] *Am. Chem. J.*, **43,** 499 (1910).
[2] THIS JOURNAL, **39,** 1930 (1917).

Experimental Results.

SERIES I.—96 HOURS AT 200°.

$CH_3OH + C_6H_5COOH.$

Expt. No.	1.	2.	3.	4.	5.
p	2.885	3.621	4.936	7.826	7.158
q	4.787	3.844	2.923	4.168	3.735
p/q	0.60	0.94	1.69	1.83	1.92
x	2.426	2.602	2.464	3.620	3.620
$p - x$	0.4584	1.019	2.471	4.206	4.206
$q - x$	2.361	1.242	0.4585	0.5484	0.5484
r	2.332	2.312	2.315	2.383	2.332
$\%$	69.99	69.80	69.84	70.44	69.99

Mean, 70.02%

$H_2O + C_6H_5COOCH_3.$

Expt. No.	6.	7.	8.	9.	10.
p	1.871	2.194	2.731	4.918	5.528
q	4.962	4.402	4.013	4.895	4.475
p/q	0.38	0.50	0.68	1.00	1.24
x	0.7694	0.9014	0.9693	1.477	1.502
$p - x$	1.101	1.203	1.762	3.441	4.026
$q - x$	3.293	3.501	3.044	3.418	2.973
r	2.475	2.276	2.389	2.321	2.304
$\%$	70.55	69.48	70.49	69.89	69.73

Mean, 70.03%

$C_2H_5OH + C_6H_5COOH.$

Expt. No.	11.	12.	13.	14.	15.
p	2.645	3.238	4.223	4.295	4.178
q	4.194	3.274	4.096	3.353	2.734
p/q	0.63	0.99	1.03	1.28	1.53
x	2.105	2.162	2.760	2.468	2.134
$p - x$	0.5397	1.076	1.463	1.828	2.045
$q - x$	2.089	1.112	1.336	0.8849	0.6006
r	1.983	1.976	1.974	1.941	1.925
$\%$	66.48	66.40	66.38	65.99	65.82

Expt. No.	16.	17.	18.	19.	20.
p	2.986	3.755	4.023	4.013	3.968
q	5.125	3.121	3.286	3.249	3.014
p/q	0.58	1.20	1.22	1.23	1.32
x	2.431	2.244	2.381	2.358	2.239
$p - x$	0.5551	1.511	1.642	1.655	1.729
$q - x$	2.694	0.8772	0.9045	0.8918	0.7755
r	1.988	1.949	1.954	1.940	1.934
$\%$	66.53	66.09	66.15	65.99	65.91

Mean, 66.17%

SERIES I (*continued*).

$H_2O + C_6H_5COOC_2H_5$.

Expt. No.	21.	22.	23.	24.	25.
p..............	2.673	5.198	11.101	10.702	10.996
q..............	3.231	4.181	6.465	4.769	4.667
p/q..............	0.83	1.24	1.72	2.25	2.36
x..............	0.988	1.576	2.828	2.332	2.306
$p - x$..........	1.684	3.622	8.273	8.369	8.690
$q - x$..........	2.242	2.604	3.638	2.436	2.361
r..............	1.966	1.948	1.940	1.936	1.965
$\%$..............	66.28	66.08	65.99	65.94	66.27

Expt. No.	26.	27.	28.	29.	30
p..............	2.956	2.850	3.114	3.372	3.708
q..............	2.048	2.898	2.948	2.861	3.161
p/q..............	0.97	0.98	1.06	1.18	1.18
x..............	1.010	0.970	1.025	1.049	1.154
$p - x$..........	1.946	1.880	2.089	2.323	2.554
$q - x$..........	2.038	1.928	1.923	1.812	2.007
r..............	1.972	1.963	1.955	1.956	1.961
$\%$..............	66.35	66.25	66.16	66.17	66.23

Mean, 66.17%

$C_3H_7OH + C_6H_5COOH$.
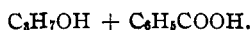
Expt. No.	31.	32.	33.	34.	35.
p..............	2.171	3.390	2.963	3.545	5.063
q..............	4.737	3.830	2.933	3.289	3.006
p/q..............	0.46	0.89	1.01	1.08	1.69
x..............	1.867	2.399	1.972	2.276	2.423
$p - x$.........:	0.3037	0.9906	0.9912	1.269	2.640
$q - x$.......;..	2.870	1.430	0.9610	1.013	0.5832
r..............	2.000	2.015	2.021	2.007	1.953
$\%$..............	65.89[a]	66.84	66.90	66.74	66.13[a]

Expt. No.	36.	37.	38	39.	40.
p..............	3.424	3.515	2.946	3.160	4.557
q..............	3.725	3.386	2.780	2.793	3.916
p/q..............	0.92	1.04	1.06	1.13	1.16
x..............	2.384	2.303	1.909	1.973	2.800
$p - x$..........	1.040	1.212	1.037	1.187	1.757
$q - x$..........	1.341	1.083	0.870	0.820	1.116
r..............	2.018	2.026	2.010	2.004	1.999
$\%$..............	66.87	66.95	66.78	66.71	66.58

Mean, 66.80%

[a] Not used in taking average.

SERIES II.—192 HOURS AT 200°.

$CH_3OH + o\text{-}CH_3C_6H_4COOH.$

Expt. No.	41.	42.	43.
p...............	6.818	7.008	7.992
q...............	3.028	2.846	2.671
p/q............	2.25	2.46	2.99
x...............	2.636	2.514	2.386
$p - x$..........	4.182	4.695	5.606
$q - x$..........	0.3915	0.3321	0.2853
r...............	2.061	2.013	1.886
$\%$...............	67.33	66.81	65.36^a

Mean,   67.06%

$C_2H_5OH + o\text{-}CH_3C_6H_4COOH.$
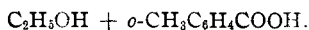
Expt. No.	44.	45.	46.	47.	48.
p...............	3.543	3.262	3.865	4.643	5.143
q...............	2.773	2.495	2.788	2.086	2.015
p/q............	1.28	1.31	1.39	2.22	2.57
x...............	2.055	1.862	2.094	1.773	1.748
$p - x$..........	1.488	1.399	1.771	2.870	3.395
$q - x$..........	0.718	0.6327	0.6933	0.3132	0.2664
r...............	1.988	1.979	1.890	1.870	1.839
$\%$...............	66.53	66.44	65.40	65.16	64.77

Mean,   65.66%

$C_3H_7OH + o\text{-}CH_3C_6H_4COOH.$
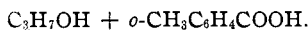
Expt. No.	49.	50.	51.	52.	53.
p...............	2.919	3.654	3.325	3.537	4.464
q...............	2.985	2.775	2.207	2.162	2.731
p/q............	0.98	1.32	1.51	1.64	1.64
x...............	1.977	2.097	1.743	1.745	2.201
$p - x$..........	0.9420	1.556	1.582	1.792	2.263
$q - x$..........	1.008	0.6777	0.4644	0.4167	0.5301
r...............	2.029	2.042	2.034	2.020	2.010
$\%$...............	66.99	67.13	67.04	66.89	66.77

Mean,   66.96%

SERIES III.—192 HOURS AT 200°.

$CH_3OH + m\text{-}CH_3C_6H_4COOH.$
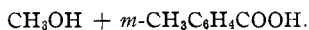
Expt. No.	54.	55.	56.	57.	58.
p...............	4.970	3.940	5.242	4.692	4.911
q...............	3.499	2.710	3.249	2.701	2.460
p/q............	1.42	1.45	1.61	1.74	2.00
x...............	2.742	2.131	2.630	2.251	2.101
$p - x$..........	2.228	1.809	2.619	2.441	2.810
$q - x$..........	0.7569	0.5796	0.6192	0.4500	0.3591
r...............	2.112	2.081	2.065	2.147	2.091
$\%$...............	67.86	67.54	67.37	68.23^a	67.65

Mean,   67.61%

^{a} Not included in average.

SERIES III (*continued*).

$C_2H_5OH + m\text{-}CH_3C_6H_4COOH.$
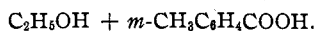
Expt. No.	59.	60.	61.	62.	63.
p	2.849	3.172	3.344	3.203	3.743
q	2.615	2.846	2.649	2.314	2.474
p/q	1.09	1.11	1.26	1.38	1.51
x	1.796	1.973	1.925	1.742	1.909
$p - x$	1.053	1.199	1.419	1.461	1.834
$q - x$	0.819	0.873	0.724	0.5715	0.5652
r	1.934	1.929	1.898	1.907	1.875
$\%$	65.91	65.86	65.50	65.60	65.22

Mean, 65.61%

$C_3H_7OH + m\text{-}CH_3C_6H_4COOH.$
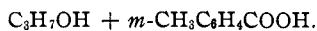
Expt. No.	64.	65.	66.	67.	68.
p	2.430	3.028	3.489	3.545	3.686
q	3.084	2.932	3.101	2.668	2.588
p/q	0.78	1.03	1.12	1.33	1.42
x	1.792	1.984	2.177	2.000	1.985
$p - x$	0.637	1.044	1.311	1.544	1.701
$q - x$	1.291	0.948	0.923	0.668	0.603
r	1.975	1.994	1.978	1.970	1.960
$\%$	66.39	66.30	66.43	66.33	66.21

Mean, 66.39%

SERIES IV.—192 HOURS AT 200°.

$CH_3OH + p\text{-}CH_3C_6H_4COOH.$
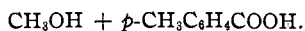
Expt. No.	69.	70.	71.	72.	73.
p	3.787	4.238	4.987	5.004	5.391
q	3.204	2.520	2.793	2.133	2.232
p/q	1.18	1.68	1.79	2.34	2.42
x	2.359	2.056	2.340	1.859	1.963
$p - x$	1.427	2.182	2.648	3.146	3.428
$q - x$	0.844	0.4644	0.4536	0.2745	0.2682
r	2.149	2.043	2.135	2.000	2.043
$\%$	68.25	67.13	68.10	66.67	67.14

Mean, 67.46%

$C_2H_5OH + p\text{-}CH_3C_6H_4COOH.$
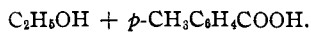
Expt. No.	74.	75.	76.	77.	78.
p	3.974	2.986	3.427	3.644	4.693
q	3.136	2.085	2.195	2.243	2.536
p/q	1.27	1.43	1.56	1.62	1.85
x	2.275	1.590	1.711	1.766	2.063
$p - x$	1.699	1.396	1.710	1.878	2.630
$q - x$	0.8613	0.4949	0.4842	0.4770	0.4734
r	1.882	1.913	1.877	1.866	1.849
$\%$	65.30	65.67	65.24	65.11	64.90

Mean, 65.24%

SERIES IV (continued).

$C_3H_7OH + p\text{-}CH_3C_6H_4COOH.$
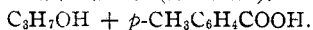
Expt. No.	79.	80.	81.	82.
p	2.569	2.889	2.953	3.921
q	2.579	2.685	2.255	2.427
p/q	1.00	1.08	1.31	1.61
x	1.709	1.841	1.679	1.927
$p - x$	0.859	1.047	1.275	1.825
$q - x$	0.869	0.843	0.5760	0.5004
r	1.978	1.960	1.959	2.017
%	66.42	66.21	66.21	66.85[a]

Mean, 66.28%

SUMMARY OF RESULTS.

Percentage Esterified at Equilibrium.

Alcohol.	Methyl.	Ethyl.	Propyl.
Benzoic acid	70.02	66.17	66.80
o-Toluic acid	67.06	65.66	66.96
m-Toluic acid	67.61	65.62	66.39
p-Toluic acid	67.46	65.24	66.28

Discussion.

The foregoing results furnish fairly concordant values for the equilibria of the various acids with corresponding alcohols. Since the experimental error is greater the further the ratio of alcohol to acid is from unity, to obtain the most reliable values for the limit only those experiments have ben considered in which the ratio of alcohol to acid was less than 1.5. The limits are tabulated below and are slightly different from the averages given above.

Alcohol.	Methyl.	Ethyl.	Propyl.
Benzoic acid	69.98	66.22	66.80
o-Toluic acid	67.07	66.12	66.72
m-Toluic acid	67.70	65.62	66.39
p-Toluic acid	68.17	65.36	66.28

For the purpose of showing the effect of varying ratio of alcohol to acid as influencing the equilibrium, the results have been arranged in the order of increasing proportions of alcohol.

BENZOIC ACID.

Methyl alcohol.		Ethyl alcohol.		Propyl alcohol.	
Ratio.	Limit.	Ratio.	Limit.	Ratio.	Limit.
..	...	0.58	66.53	0.46	65.89
..	ı ...	0.63	66.48	0.88	66.84
0.62	69.99	0.99	66.40	0.92	66.87
0.94	69.80	1.03	66.38	1.01	66.90
1.69	69.84	1.20	66.09	1.04	66.95
1.88	70.44	1.22	66.15	1.06	66.78
1.92	69.99	1.23	65.99	1.08	66.74
..	...	1.28	65.99	1.13	66.71
..	...	1.32	65.91	1.16	66.58
..	...	1.53	65.82	1.67	66.13

[a] Not included in average.

This effect was studied particularly with ethyl alcohol.

ETHYL ALCOHOL.

o-Toluic acid.		m-Toluic acid.		p-Toluic acid.	
Ratio.	Limit.	Ratio.	Limit.	Ratio.	Limit.
1.28	66.53	1.09	65.91	1.27	65.30
1.31	66.44	1.11	65.86	1.43	65.67
1.39	65.40	1.26	65.50	1.56	65.24
2.23	65.16	1.38	65.60	1.62	65.11
2.55	64.77	1.52	65.22	1.85	64.90

From the tables above it appears that there is a gradual drop in the limit with increase of the ratio of alcohol to acid. The drop is slight and not much beyond the unavoidable experimental error, but as the trend in nearly all cases is in the same direction, it seems to be real.

The results of Berthelot and St. Gilles[1] have been recalculated for comparison and are given below, the first two columns being their figures, the last two being their figures recalculated to our basis.

	Ratio.	% esterifi- cation.	r.	Limit.
Methyl alcohol and benzoic acid...............	1.0	64.8	1.841	64.80
	3.0	87.4	1.689	62.81
Ethyl alcohol and benzoic acid................	1.0	66.5	1.985	66.50
	2.0	83.1	1.870	66.15
	3.0	87.0	1.653	62.31
	4.0	89.3	1.549	60.77
Methyl alcohol and acetic acid................	0.20	19.3	2.568	71.97
	0.45	39.0	2.287	69.58
	0.50	42.9	2.131	68.06
	0.67	54.6	2.301	69.71
	1.00	66.5	1.985	66.50
Ethyl alcohol and acetic acid................	1.00	67.5	2.077	67.50
	1.50	75.9	1.796	64.24
	2.00	84.0	1.951	66.10

It appears from the results that the change of the limit of esterification is in the same general direction, although some of the individual determinations are out of line.

From the above it appears that for esterification, the mass law holds very nearly but not quite exactly. The gas law holds for perfect gases only, and correction terms must be inserted on account of the mutual attraction of the particles and also because the particles are not infinitely small. The mass law in its simplest form tacitly assumes that the four substances A, B, C and D have no influence whatever on each other except that the reaction $A + B \rightleftarrows C + D$ takes place. This assumption, though nearly correct, in some cases, can never be absolutely so. Sup-

[1] Ann. chim. phys., [3] 68, 275–279 (1862).

pose, for instance, that A and C are very soluble in each other, more so than the other pairs; that is to say, that A and C have an attraction for each other, which we may call physical, but it would have the effect of restraining the molecules of these two substances, so to speak, from taking part in the reactions as they otherwise would, and hence diminish their effective concentrations. While the mass law probably holds absolutely in ideal cases, in actual cases we expect only approximations such as we find with the gas law when actual cases are considered.

The effect of isomerism, in the acids, on the limit found with mercaptans and the three toluic acids was worked out by Sachs and Reid.[1] These authors found that the limit with ethyl mercaptan was practically the same with the o-, m-, and p-toluic acids. The results obtained above with alcohols, however, show a variation in the limit. With methyl alcohol the limit rises from ortho, meta to para, while with ethyl and propyl alcohols the reverse is true. This exceptional behavior of methyl is also observed in the high value of the limit with benzoic acid.

Conclusions.

1. Esterification limits have been found for benzoic and the three toluic acids with methyl, ethyl and propyl alcohols.

2. The limits found vary only slightly with change of ratio of active masses, that is, the mass law holds very nearly.

3. With the exception of methyl alcohol the esterification limit rises with increase of molecular weight of the alcohol.

4. With methyl alcohol and the toluic acids, toluic acid shows the highest limit, o-toluic acid the lowest.

5. The reverse is true of ethyl and propyl alcohols and the toluic acids.

6. These acids have been found to be esterified very slowly by alcohols even at $200°$, four days being required to reach the limit.

BALTIMORE, MD.

NEW BOOK.

Charles Anthony Goessmann. Published Jointly by the Corporation and the Associate Alumni of the Massachusetts Agricultural College; printed at the University Press, Cambridge, Mass., 1917.

A beautifully printed brochure from the Riverside Press at Cambridge, lies open before me. I see the impressive frontispiece—the portrait of Goessmann, in his prime. I look at the dignified features of one of the Big Four of the early Agricultural Chemists of the country, Johnson, Storer, Hilgard, Goessmann! Who of their successors will do more for agricultural science than they have done? Goessmann had a precious opportunity to prepare himself for brilliant work and he embraced it to the fullest extent. He was first a pupil of and for five years assistant to

[1] THIS JOURNAL, 38, 2746 (1916).