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.

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Historical.

The influence of isomerism on the rates and limits of esterification of alcohols has been carefully studied by Menschutkin,[1] 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,[2] studying the mechanism of the reaction of esterification, employed mercaptans instead of alcohols and showed that the reaction

$$C_6H_5COOH + HSC_2H_5 \rightleftarrows C_6H_5COSC_2H_5 + H_2O$$

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

Pratt and Reid[3] 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

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

[2] *Am. Chem. J.*, 43, 489 (1910).

[3] THIS JOURNAL, 37, 1934 (1915).

than those found by Berthelot and St. Gilles[1] and by Menschutkin[2] with alcohols, but the relations between the limits in the two series are much the same.

As pointed out by Pratt and Reid, it is much more difficult to get concordant results with mercaptans than with alcohols, since the mercaptans must be eliminated before titration of the unesterified acid. The use, in individual experiments, of varying amounts of mercaptan and acid, instead of the identical and equivalent amounts of alcohol and acid such as have commonly been used, also increases the difficulty.

Materials.

Benzoic Acid.—The benzoic acid used was a well-known firm's best grade.

Mercaptans.—The normal mercaptan[3] was prepared from normal butyl bromide and potassium hydrosulfide. The mercaptan obtained was dried over calcium chloride, fractionated several times and the fraction boiling 97–98° used in the work.

The isobutyl mercaptan used was a standard commercial product.

The secondary butyl mercaptan[4] was prepared from secondary butyl bromide and potassium hydrosulfide. The mercaptan was dried over calcium chloride, fractionated several times, and the fraction boiling 83–84° used.

An effort was made to prepare the tertiary mercaptan according to the method of Dobbin,[5] except that tertiary butyl bromide was used instead of the iodide, but only traces of the desired mercaptan were obtained. On account of the difficulties involved, this preparation was abandoned.

Normal, Iso-, Secondary and Tertiary Butyl Thiolbenzoates.—The thiol esters were made by alkylating thiolbenzoic acid, prepared according to Kym's[6] directions. The acid was, however, purified by dissolving the potassium salt in water, filtering and liberating the acid with hydrochloric acid. After settling, the oily acid was separated and the aqueous solution extracted with ether. On evaporation of the ether the acid was ready for use. The potassium salt of the purified thiolbenzoic acid was treated, according to the general directions of Wheeler,[7] for the ethyl ester, with the butyl bromide of which the ester was desired. The esters so obtained were carefully fractionated in a partial vacuum. The boiling points and densities of these butyl thiolbenzoates are given in the following table:

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

[2] *Ber.*, 10, 1728 (1877); 11, 1507 (1878).

[3] Grabowsky and Saytzeff, Liebig's *Ann.*, 171, 251 (1874).

[4] Reyman, *Ber.*, 7, 1287 (1874).

[5] *J. Chem. Soc.*, 57, 640 (1890).

[6] *Ber.*, 32, 3533 (1899).

[7] *Am. Chem. J.*, 24, 69 (1900).

Normal	160° at 23 mm.	1.0514 25/25
Iso-	150° at 20 mm.	1.0457 25/25
Secondary	151° at 23 mm.	1.0488 25/25
Tertiary	110° at 28 mm.	1.0468 25/25

The normal and iso- esters were reddish in color when first prepared but, on standing for several months, the color faded to a light pink. The secondary ester faded from yellow to nearly colorless while the tertiary faded from a very light yellow to colorless. It seems probable that the color is due to some slight impurity.

Water.—Conductivity water was used.

Apparatus and Procedure.

The same furnace and the same standard solutions were used as in the work of Sachs and Reid in the preceding article. The preparation, filling, heating, and opening of the tubes and the analysis of the reaction products were also the same, except that a longer time was allowed for blowing off the mercaptan remaining. Preliminary experiments with known amounts of benzoic acid and mercaptan showed that it is necessary to pass air through the solutions 25 minutes to remove normal butyl mercaptan, 20 minutes for the iso-, and 15 minutes for the secondary.

The temperature of the heating was 200°.

Experimental.

In the first experiments, those given in Tables A to E, the tubes used had an internal diameter of about 4.5 mm. and the rates of esterification in them seem to have been quite different from those in the smaller tubes (3.5 mm. inside diameter) used later, as will be seen from the tables that follow, though Berthelot and St. Gilles[1] state that it is permissible to vary the volume of the unfilled portion considerably without modifying sensibly either the rate or the limit of the reaction.

In their work alcohols and acetic acid were used which do not differ greatly in volatility, but in the present work there is much difference in volatility between benzoic acid and the butyl mercaptans.

In the earlier experiments it was found in the ester-water series that an excess of ester over water gave place to some decomposition which yielded acid, since the results gave too low values for the limit. Samples of esters heated alone in the ordinary tubes to 200° for several days gave considerable acid, showing that the ester-water results could not be relied upon, at least in the case of an excess of ester over water.

Later experiments using an excess of water were run in the smaller tubes and here results were not satisfactory, since equilibrium was not reached in the time allowed, due to the nonmiscibility of ester and water and to the small surface of contact.

Tubes containing acid and mercaptan and others containing ester and

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[1] *Ann. chim. phys.*, [3] **66**, 50 (1862).

water in about the usual amounts were heated to 200° in a sulfuric acid bath so that the conditions obtaining in the tubes at that temperature could be observed. It was found that, while the acid and mercaptan formed a perfectly homogeneous solution at that temperature, the ester and water still remained in two distinct layers and showed no tendency to mix, separating rapidly after being shaken together. This undoubtedly shows why the esterification proceeds regularly and comparatively rapidly from the acid-mercaptan end, while the mixtures of esters and water are slow to react and yield irregular results.

The results are tabulated according to the plan adopted by Pratt and Reid and used by Sachs and Reid in the preceding article, to which reference must be made for the meaning of the terms and the methods of calculation. To save space, the weights are omitted and the substances are given only in millimols, *b* and *d* being the amounts put in and *f*, *g*, and *m* or *f*, *h*, and *k*, the amounts present at the end. The percentage of esterification, calculated for equivalent quantities, is given in the line marked %.

Some results which are out of harmony with others of the same series are bracketed and are not used in making the averages. All completed experiments, except a few preliminary ones and three from ester-water end, which were cut out to make the tables fit better, are given.

TABLE A.—24 HOURS AT 200°.

	C_6H_5COOH + *n*-C_4H_9SH.			C_6H_5COOH + *iso*-C_4H_9SH.			C_6H_5COOH + *sec*.-C_4H_9SH.		
b	1.6837	1.8623	1.9262	1.9549	2.4359	1.8443	1.8074	1.7009	1.9836
d	1.1061	1.0783	0.8043	0.8798	1.4866	0.8997	0.9885	1.1150	0.8198
f	1.5210	1.6761	1.7560	1.8185	2.2775	1.7242	1.6961	1.5773	1.8739
g	0.9434	0.8921	0.6341	0.7434	1.3282	0.7796	0.8772	0.9914	0.7101
m	0.1627	0.1862	0.1702	0.1364	0.1584	0.1201	0.1113	0.1236	0.1097
$\sqrt{r}$	7.3624	6.5672	7.8050	8.5305	10.980	9.6536	10.949	10.109	10.515
%	11.96	(13.31)	11.36	10.49	8.55	9.39	8.37	9.00	8.68
		Average,	11.66%		Average,	9.48%		Average,	8.68%

TABLE B.—48 HOURS AT 200°.

	C_6H_5COOH + *n*-C_4H_9SH.			C_6H_5COOH + *iso*-C_4H_9SH.			C_6H_5COOH + *sec*.-C_4H_9SH.			
b	1.0160	1.2356	1.3576	1.5494	1.1651	0.8882	1.2413	1.0242	1.0373	0.9855
d	1.4034	1.5321	1.8305	1.2902	0.8687	1.3113	1.1271	1.5676	1.2514	0.9485
f	0.8562	1.0521	1.1528	1.3605	1.0494	0.7546	1.1310	0.9143	0.9387	0.8127
g	1.2436	1.3486	1.6257	1.1013	0.7630	1.1777	1.0168	1.4577	1.1528	0.8657
m	0.1598	0.1835	0.2048	0.1889	0.1157	0.1336	0.1103	0.1099	0.0986	0.0828
$\sqrt{r}$	6.4573	6.4956	6.6844	6.4799	7.6826	7.0553	9.7322	10.666	10.550	10.130
%	13.41	13.34	13.02	13.37	11.52	12.42	9.32	8.57	8.66	8.98
		Average,	13.26%			12.44%			Average,	8.88%

TABLE C.—4 DAYS AT 200°.

	C_6H_5COOH + *n*-C_4H_9SH.			C_6H_5COOH + *iso*-C_4H_9SH.			C_6H_5COOH + *sec*.-C_4H_9SH.			
b	1.4601	1.0381	1.2093	1.2609	1.0971	0.9914	1.0496	0.9488	1.2437	0.8611
d	1.6608	1.3812	0.8398	1.5055	1.3950	1.7118	1.2104	1.6153	1.0351	1.4700
f	1.2707	0.8834	1.0811	1.0839	0.9605	0.8399	0.9542	0.8526	1.1555	0.7691
g	1.4714	1.2265	0.7116	1.3285	1.2224	1.5603	1.1150	1.5191	0.9469	1.3780
m	0.1894	0.1547	0.1282	0.1770	0.1366	0.1515	0.0954	0.0962	0.0882	0.0920
$\sqrt{r}$	7.2240	6.7440	6.8479	6.7793	7.9325	7.5562	10.811	11.830	11.860	11.203
%	12.19	12.91	12.76	12.85	11.20	11.69	8.47	(7.79)	(7.78)	8.20
		Average,	12.62%		Average,	11.91%			Average,	8.33%

TABLE D.—8 DAYS AT 200°.

	C_6H_5COOH + *n*-C_4H_9SH.					*n*-$C_6H_5COSC_4H_9$ + H_2O.				
b	1.7960	1.9123	2.0197	2.1114	1.8779	1.5692	1.5712	1.8220	1.3297	1.7535
d	1.9880	1.5498	1.2603	1.6785	1.2625	2.2480	1.7651	1.6763	0.8992	1.1878
f	1.5709	1.6952	1.8140	1.8784	1.6770	1.4848	1.4249	1.5238	0.8979	1.1764
g	1.7629	1.3327	1.0546	1.4455	1.0616	0.0844	0.1463	0.2982	0.4318	0.5771
m	0.2251	0.2172	0.2057	0.2330	0.2009	0.7632	0.3402	0.1525	0.0013	0.0114
$\sqrt{r}$	7.3930	6.9234	6.7242	7.0722	6.6420	5.8534	6.3860	7.1431	......	14.504
%	(11.91)	12.62	12.95	12.39	13.09	14.59	13.54	(12.28)	......	(8.12)
				Average,	12.76%				Average,	14.06%

	C_6H_5COOH + *iso*-C_4H_9SH.					*iso*-$C_6H_5COSC_4H_9$ + H_2O.				
b	2.3867	2.0590	2.4883	2.3515	2.0180	1.5548	1.4919	1.6124	1.7711	1.6887
d	1.5177	1.5365	1.5698	1.4189	1.6807	0.9769	1.2878	0.9214	0.9936	0.7882
f	2.1478	1.8321	2.2185	2.1106	1.7732	1.0594	1.1972	0.9288	1.0113	0.8018
g	1.2788	1.3096	1.3000	1.1780	1.4359	0.4954	0.2947	0.6836	0.7598	0.8869
m	0.2389	0.2269	0.2698	0.2409	0.2448	......	0.0906	......	......	......
$\sqrt{r}$	6.9368	6.8268	6.2971	6.5454	6.5183	......	7.3326	......	......	......
%	12.60	12.78	13.73	13.25	13.30	.....	(12.00)	......	......	......
				Average,	13.15%					

	C_6H_5COOH + *sec*.-C_4H_9SH.					*sec*.-$C_6H_5COSC_4H_9$ + H_2O.				
b	1.9484	2.0549	2.2958	2.1417	2.0754	1.4806	2.0517	1.6923	1.4631	1.7123
d	1.6475	1.4089	1.6075	1.7562	1.3945	1.3100	2.7032	1.4376	1.2876	1.9705
f	1.8095	1.9147	2.1287	1.9709	1.9365	1.2136	1.9455	1.3723	1.2208	1.5873
g	1.5086	1.2687	1.4404	1.5854	1.2556	0.2670	0.1062	0.3200	0.2423	0.1250
m	0.1389	0.1402	0.1671	0.1708	0.1389	0.0964	0.7577	0.0653	0.0670	0.3832
$\sqrt{r}$	11.90	11.12	10.479	10.343	11.226	7.5645	6.8585	9.4950	9.5818	7.2524
%	7.76	8.25	8.71	8.82	8.18	(11.67)	12.72	(9.75)	(9.45)	12.12
				Average,	8.34%				Average,	12.42%

	tert.-$C_6H_5COSC_4H_9$ + H_2O.				
b	1.6320	1.3179	1.3951	1.2113	1.3014
d	1.3599	2.2425	2.0871	1.6375	1.5375
f	0.7238	0.8118	0.8372	0.7755	0.6857
h	0.9082	0.5061	0.5579	0.4358	0.6157
k	0.6361	1.4307	1.24	0.8620	0.8518
$\sqrt{r}$	0.9501	0.9542	1.0025	1.2653	0.9499
%	51.28	51.17	49.94	44.14	51.28
				Average,	49.56%

TABLE E.—12 DAYS AT 200°.

C_6H_5COOH + *n*-C_4H_9SH.

b	1.9435	1.9820	1.8886	2.1827	2.4236
d	1.4300	1.5864	1.8494	1.6663	1.0528
f	1.7175	1.7508	1.6481	1.9374	2.1933
g	1.2040	1.3552	1.6089	1.4210	0.8225
m	0.2260	0.2312	0.2405	0.2453	0.2303
$\sqrt{r}$	6.3658	6.6624	6.7705	6.7640	5.8321
%	13.58	13.05	12.87	12.88	14.64
				Average,	13.40%

n-$C_6H_5COSC_4H_9 + H_2O$.

b	1.7139	1.6686	1.5455	1.8926	1.6181	1.8308
d	1.4099	1.2267	1.2822	1.9872	1.7207	2.1537
f	1.3345	1.1913	1.2030	1.6625	1.4264	1.6616
h	0.3794	0.4773	0.3425	0.2301	0.1917	0.1692
k	0.0754	0.0354	0.0792	0.3247	0.2943	0.4921
$\sqrt{r}$	7.8913	9.1513	7.2983	6.0823	6.0055	5.7585
%	(11.25)	(9.76)	(12.33)	14.12	14.27	14.79
					Average,	14.39%

	C_6H_5COOH + *iso*-C_4H_9SH.					*iso*-$C_6H_5COSC_4H_9 + H_2O$.				
b	2.3318	1.9484	2.1204	2.1991	2.0623	1.7721	2.0594	1.5486	1.5625	1.6675
d	1.7772	1.6519	1.6830	1.6231	1.6619	1.3932	2.0149	2.1592	2.4257	2.1925
f	2.0545	1.6977	1.8527	1.9320	1.8076	1.3264	1.7680	1.4300	1.4625	1.5310
g	1.4999	1.4012	1.4153	1.3560	1.4072	0.4457	0.2914	0.1186	0.1000	0.1365
m	0.2773	0.2507	0.2677	0.2671	0.2547	0.0668	0.2469	0.7292	0.9632	0.6615
$\sqrt{r}$	6.3304	6.1519	6.0464	6.0570	6.2617	7.688	6.5887	4.8646	4.7122	5.0941
%	13.64	13.92	14.19	14.17	13.77	(11.51)	(13.18)	17.05	17.51	16.41
				Average,	13.94%				Average,	16.99%

	C_6H_5COOH + *sec.*-C_4H_9SH.					*sec.*-$C_6H_5COSC_4H_9 + H_2O$.				
b	1.5256	2.0172	2.0500	1.3191	1.5289	1.6392	1.4986	1.4718	1.6011	1.8272
d	1.5765	1.3579	2.0202	1.8427	2.0579	1.8928	2.0815	2.0149	1.5320	1.8206
f	1.3931	1.8626	1.8743	1.1850	1.3877	1.5220	1.4165	1.3922	1.4057	1.6337
g	1.4440	1.2033	1.8445	1.7086	1.9167	0.1172	0.0821	0.0796	0.1954	0.1935
m	0.1325	0.1546	0.1757	0.1341	0.1412	0.3708	0.6650	0.6227	0.1263	0.1869
$\sqrt{r}$	10.704	9.6838	10.582	10.603	11.550	7.3009	6.0623	6.2533	8.9480	8.5906
%	8.54	9.36	8.63	8.62	7.97	12.05	14.16	13.78	(10.05)	(10.43)
				Average,	8.62%				Average,	13.33%

tert.-$C_6H_5COSC_4H_9 + H_2O$.

b	1.4301	1.4445	1.4214	1.3189	1.4348
d	1.8595	1.8262	1.7596	1.4321	1.4709
f	0.8209	0.8317	0.8272	0.7200	0.7371
h	0.6092	0.6128	0.5942	0.5989	0.6977
k	1.0386	0.9945	0.9324	0.7121	0.7338
$\sqrt{r}$	1.0321	1.0654	1.1113	1.1025	1.0302
%	49.21	48.42	47.56	47.56	49.37
				Average,	48.38%

TABLE F.—24 HOURS AT 200°.

$C_6H_5COOH + n\text{-}C_4H_9SH$.

b	1.3806	1.5731	1.5420	1.3601	1.5707
d	1.3745	1.4810	1.6220	1.4999	1.3967
f	1.2915	1.4491	1.4049	1.2482	1.4572
g	1.2854	1.3570	1.4849	1.3880	1.2832
m	0.0891	0.1240	0.1371	0.1119	0.1135
$\sqrt{r}$	14.461	11.309	10.535	11.763	12.076
%	(6.47)	8.12	8.67	7.84	7.65
				Average,	8.08%

$C_6H_5COOH + iso\text{-}C_4H_9SH$.

b	1.7222	1.6403	1.7943	1.9902	1.9402
d	1.2780	1.2203	1.2092	1.2081	1.2414
f	1.6220	1.5256	1.6634	1.8543	1.8292
g	1.1778	1.1056	1.0783	1.0722	1.1303
m	0.1002	0.1147	0.1309	0.1359	0.1111
$\sqrt{r}$	13.794	11.322	10.231	10.375	12.942
%	(6.76)	8.12	8.90	8.79	(7.17)
				Average,	8.60%

$C_6H_5COOH + sec.\text{-}C_4H_9SH$.

b	1.4248	1.8132	1.8492	1.9959
d	1.3424	1.6796	1.6142	1.4810
f	1.3698	1.7129	1.7607	1.9093
g	1.2874	1.5793	1.5257	1.3944
m	0.0550	0.1003	0.0885	0.0866
$\sqrt{r}$	24.145	16.399	18.520	18.841
%	(3.98)	5.75	5.12	5.04
			Average,	5.30%

TABLE G.—48 HOURS AT 200°.

$C_6H_5COOH + n\text{-}C_4H_9SH$.

b	1.5084	1.5723	1.6370	1.5903	1.7435
d	1.6574	1.3912	1.4422	1.3490	1.2259
f	1.3644	1.3914	1.4464	1.4130	1.5751
g	1.5134	1.2103	1.2516	1.1717	1.0575
m	0.1440	0.1809	0.1906	0.1773	0.1684
$\sqrt{r}$	9.9790	7.1737	7.0592	7.2571	7.6640
%	(9.12)	12.23	12.41	12.11	(11.54)
				Average,	12.25%

$C_6H_5COOH + iso\text{-}C_4H_9SH$.

b	1.9525	2.2122	1.8042	1.6895
d	1.1349	1.1216	1.0218	0.5580
f	1.7976	2.0092	1.6346	1.5851
g	0.9800	0.9186	0.8522	0.4536
m	0.1549	0.2030	0.1696	0.1044
$\sqrt{r}$	8.5700	6.6923	6.9586	8.1222
%	(10.45)	13.00	12.56	(10.97)
			Average,	12.78%

$C_6H_5COOH + sec.\text{-}C_4H_9SH$.

b	1.6354	1.8058	2.1303	1.7739	2.0401
d	1.2459	1.2869	1.6009	1.4866	1.5043
f	1.5535	1.7003	1.9858	1.6499	1.9165
g	1.1640	1.1814	1.4564	1.3626	1.3807
m	0.0819	0.1055	0.1445	0.1240	0.1236
$\sqrt{r}$	16.419	13.434	11.778	12.092	13.149
%	(5.74)	6.93	7.83	7.64	7.07
				Average,	7.37%

TABLE H.—4 DAYS AT 200°.

	$C_6H_5COOH + n\text{-}C_4H_9SH$.					$C_6H_5COOH + iso\text{-}C_4H_9SH$.				
b	1.5502	1.7820	1.7845	1.9271	1.8451	1.6591	1.7730	1.9730	1.8976	1.9041
d	1.1416	1.2814	1.2081	1.1039	1.3091	1.3690	1.4700	1.4345	1.4189	1.4866
f	1.3779	1.5698	1.5869	1.7220	1.6391	1.4617	1.5535	1.7418	1.6850	1.6814
g	0.9693	1.0692	1.0105	0.8988	1.1031	1.1716	1.2505	1.2033	1.2063	1.2639
m	0.1723	0.2122	0.1976	0.2051	0.2060	0.1974	0.2195	0.2312	0.2126	0.2227
$\sqrt{r}$	6.7070	6.1049	6.4087	6.0655	6.5274	6.6293	6.3466	6.2616	6.7061	6.5427
%	12.98	14.07	13.50	14.15	13.28	13.11	13.61	13.77	12.98	13.26
				Average,	13.75%				Average,	13.38%

	$C_6H_5COOH + sec.\text{-}C_4H_9SH$.				
b	1.7444	1.8206	1.7460	2.0770	1.8394
d	1.4777	1.3690	1.3346	1.3967	1.3623
f	1.6166	1.6913	1.6175	1.9327	1.7147
g	1.3499	1.2397	1.2061	1.2524	1.2376
m	0.1278	0.1293	0.1285	0.1443	0.1247
$\sqrt{r}$	11.559	11.208	10.870	10.782	11.692
%	7.96	8.20	8.42	8.49	7.89
				Average,	8.19%

TABLE I.—8 DAYS AT 200°.

	$C_6H_5COOH + n\text{-}C_4H_9SH$.					$C_6H_5COOH + iso\text{-}C_4H_9SH$.				
b	1.6870	1.9836	1.9623	2.0705	1.8025	1.8083	2.1311	1.9222	1.8869	2.1393
d	0.9874	1.2281	1.1072	1.0872	1.0750	1.4688	1.3834	1.3823	1.2913	1.4411
f	1.5094	1.7580	1.7445	1.8534	1.6085	1.5977	1.8976	1.7021	1.6751	1.8994
g	0.8098	1.0025	0.8894	0.8701	0.8810	1.2582	1.1499	1.1622	1.0795	1.2012
m	0.1776	0.2256	0.2178	0.2171	0.1940	0.2106	0.2335	0.2201	0.2118	0.2399
$\sqrt{r}$	6.2252	5.8846	5.7161	5.8496	6.1326	6.7288	6.3233	6.3901	6.3488	6.2963
%	13.84	14.52	14.89	14.60	14.02	(12.94)	13.66	13.53	13.61	13.71
				Average,	14.37%				Average,	13.50%

	$C_6H_5COOH + sec.\text{-}C_4H_9SH$.				
b	2.0860	1.8001	1.9197	1.9525	2.0639
d	1.3268	1.4034	1.2348	1.3479	1.5898
f	1.9417	1.6634	1.7832	1.7607	1.9093
g	1.1825	1.2667	1.0983	1.1561	1.4352
m	0.1443	0.1367	0.1365	0.1918	0.1546
$\sqrt{r}$	10.493	10.619	10.252	7.4386	10.707
%	8.70	8.61	8.89	(11.85)	8.54
				Average,	8.70%

TABLE J.—12 DAYS AT 200°.

	$C_6H_5COOH + n\text{-}C_4H_9SH$.					$n\text{-}C_6H_5COSC_4H_9 + H_2O$.				
b	1.6231	1.6075	1.5944	1.2994	1.5117	1.5239	1.6026	1.5594	1.4425	1.4028
d	1.7773	1.7429	1.5532	1.5931	1.5709	3.4525	2.2702	2.9197	2.3535	2.0427
f	1.3827	1.3628	1.3682	1.0920	1.2912	1.0459	1.2704	1.1953	1.1590	1.1047
g	1.5369	1.4982	1.3270	1.3857	1.3504	0.4780	0.3322	0.3641	0.2835	0.2981
m	0.2404	0.2447	0.2262	0.2074	0.2205	2.4066	0.9998	1.7244	1.1945	0.9380
$\sqrt{r}$	6.0630	5.8393	5.9568	5.9342	5.9887	0.9513	2.2045	1.5084	1.9925	2.0892
%	14.16	14.62	14.37	14.42	14.31	51.25	31.21	39.86	33.42	32.37

Average, 14.38%

	$C_6H_5COOH + iso\text{-}C_4H_9SH$.					$iso\text{-}C_6H_5COSC_4H_9 + H_2O$.				
b	2.0311	1.8541	1.3527	1.7288	1.7280	1.4821	1.5496	1.5923	1.6341	1.2957
d	1.7706	1.9559	1.6009	1.6031	1.3490	3.2805	3.6357	2.7143	3.5469	3.1417
f	1.7712	1.5928	1.1482	1.5095	1.5194	1.0069	0.9861	1.2433	1.1464	0.8140
g	1.5107	1.6946	1.3964	1.3838	1.1404	0.4752	0.5635	0.3490	0.4877	0.4817
m	0.2599	0.2613	0.2045	0.2193	0.2086	2.2736	2.6496	1.4710	2.4005	2.3277
$\sqrt{r}$	6.2913	6.2846	6.1919	6.5904	6.3133	0.9687	0.8108	1.7352	1.0596	0.7694
%	13.72	13.73	13.90	13.18	13.67	50.80	55.00	36.56	48.55	56.50

Average, 13.64%

	$C_6H_5COOH + sec.\text{-}C_4H_9SH$.					$sec.\text{-}C_6H_5COSC_4H_9 + H_2O$.		
b	1.3101	1.4871	1.5616	1.6010	1.7312	1.4811	1.5074	1.3261
d	1.5776	1.6785	1.6663	1.5665	1.7484	3.1917	4.0409	2.8475
f	1.1826	1.3492	1.4081	1.4579	1.5837	1.0468	0.9019	0.9272
g	1.4501	1.5406	1.5128	1.4234	1.6009	0.4343	0.6055	0.3989
m	0.1275	0.1379	0.1535	0.1431	0.1475	2.1449	3.1390	1.9203
$\sqrt{r}$	10.271	10.455	9.507	10.066	10.795	1.0850	0.6543	1.0594
%	8.87	8.73	9.51	9.04	8.48	47.96	60.40	48.50

Average, 8.92%

	$tert.\text{-}C_6H_5COSC_4H_9 + H_2O$.			
b	1.5115	1.7056	1.6454	1.4657
d	3.8411	3.1195	3.5191	3.6746
f	0.5687	0.6212	0.5976	0.5279
h	0.9428	1.0844	1.0478	0.9378
k	3.2724	2.4983	2.9215	3.1467
$\sqrt{r}$	0.3237	0.3774	0.3416	0.3074
%	75.5	72.6	74.5	76.5

Average, 74.8

TABLE K.—28 DAYS AT 200°.

	$tert.\text{-}C_6H_5COSC_4H_9 + H_2O$.				
b	1.3678	1.4121	1.6289	1.5223	1.3920
d	2.5311	2.7698	2.1259	1.9650	2.2647
f	0.3197	0.3107	0.4458	0.4053	0.3323
h	1.0481	1.1014	1.1831	1.1170	1.0597
k	2.2114	2.4591	1.6801	1.5597	1.9324
$\sqrt{r}$	0.2100	0.1888	0.3162	0.3070	0.2322
%	82.6	84.1	76.0	76.5	81.2

Summary of Results.

The averages of the results of Tables A and E are brought together in Table L. The figure for the iso- for 4 days is the highest in the run and not the average. The averages from tables F to J are in Table M, while the averages of all experiments with esters and water are grouped in Table N.

TABLE L.—FIRST SERIES.

Esterification of Benzoic Acid by the Butyl Mercaptans.

Time in days	1	2	4	8	12
From table	A	B	C	D	E
Normal	11.66	13.26	12.62	12.76	13.40
Iso-	9.48	12.44	12.85	13.15	13.94
Secondary	8.68	8.88	8.33	8.34	8.62

TABLE M.—SECOND SERIES.

Time in days	1	2	4	8	12
From table	F	G	H	I	J
Normal	8.08	12.25	13.75	14.37	14.38
Iso-	8.60	12.78	13.38	13.63	13.64
Secondary	5.30	7.37	8.19	8.70	8.93

TABLE N.

Ester Remaining when the Butyl Esters of Thiolbenzoic Acid are Heated with Water.

	First Series.		Second Series,	
Time in days	8	12	12	28
From table	D	E	J	K
Normal	14.06	14.39	32.37	..
Iso-	...	16.99	56.50	..
Secondary	12.42	13.33	48.50	..
Tertiary	49.56	48.38	74.8	76

The results of Table M are reproduced in the figure.

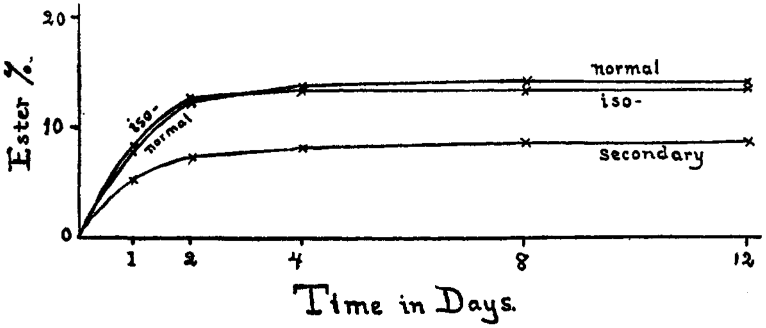

Figure.

Esterification of Benzoic Acid by Normal, Iso- and Secondary Butyl Mercaptans at 200°. Data from Table M.

Discussion of Results.

A comparison of the data of Tables L and M shows that, in the first series, with the larger tubes, the values for the one- and two day periods are much higher than the corresponding values in the second series, that is, esterification went on much more rapidly in the larger tubes. The limits for the iso- and secondary mercaptans are sensibly the same and are not greatly different for the normal. Whether it was the size of the tubes, giving a larger surface of contact and causing more rapid solution, or whether the difference in velocity of esterification is due to some peculiarity of the surface of the glass, or to some unsuspected cause, it is impossible to say. It is well known that the presence of traces of catalysts and other circumstances have enormous influence on reaction velocities without changing the limits of the reactions. The object of the present study was to find the limits, and the short period experiments were run only to get an idea of the rate of approach to the limits, so as to be sure that the limits had been reached. It is remarkable that the secondary mercaptan, in the first series, reached the limit in one day's time.

The first series is to be regarded as preliminary and much more confidence is felt in the results of the second series, since the accuracy of the work increased with experience. In Tables D and E of the first series the average divergence of individual results, except those bracketed, from the accepted mean is 0.34%, while, in the corresponding Tables I and J in the second series, it is 0.19% or just about half as great.

In Table N, first part, we find that the mixtures of the normal and secondary esters and water reached limits almost exactly agreeing with those obtained from the acid-mercaptan end. There is one result, 13.18, in Table E for the isobutyl ester, which is close to the accepted limit, but most of the values for this ester are higher than this. In the results from the second series, under J, we see that none of the mixtures came anywhere near the accepted limits.

The mixtures of tertiary butyl thiolbenzoate and water do not reach limits such as we would expect. It is more likely that this is a case of decomposition, possibly into butylene and acid, rather than of saponification in the ordinary way. This decomposition seems to have gone considerably further in the large tubes than in the small. Its amount appears to bear no relation to the time of heating, as there was rather less acid found in the tubes that had been heated 28 days than in those not heated so long.

It is seen that both the rates and the limits for the normal and isomercaptans are nearly the same, as has been found to be the case with the corresponding alcohols. Both of these are primary mercaptans, and the fact that one is a straight chain and the other a forked chain compound seems to make little difference. The secondary mercaptan, however, is seen to esterify slower and to reach a lower limit than the primary, as has been found to be the case with alcohols.

The stability of the esters, as was shown by the work of Pratt and Reid, decreases with increasing melocular weight and it was found that in nearly all the tubes there were at least traces of hydrogen sulfide after heating to 200°. The decomposition of the esters seems to take place more readily when little water is present and to give rise to the formation of an acid, since in tubes where there is an excess of ester over water the amount saponified as determined by titration goes below the limit.

It is also seen that the percentage saponification varies greatly with the relative amounts of water present, relatively less saponification taking place in cases with relatively large amounts of water. This is no doubt due to the immiscibility of the ester and water at the temperature employed.

Conclusions.

1. The rates and limits of esterification of benzoic acid by isomeric butyl mercaptans have been studied and the limits determined at 200°.
2. The rates and limits for normal and iso-mercaptans were found to be nearly the same, but those for the secondary mercaptan much lower.
3. The limits found were much lower than those for the corresponding alcohols.
4. The saponification of the esters was found to be very irregular and unreliable on account of the immiscibility of the ester and water and the decomposition of the esters.
5. The limits were found to be independent of the relative amounts of acid and mercaptan present.

BALTIMORE, MD.

ACTION OF THE GRIGNARD REAGENT ON CN COMPOUNDS. SYNTHESIS OF AMIDINES FROM CYANAMIDES.

BY ROGER ADAMS AND C. H. BEEBE.

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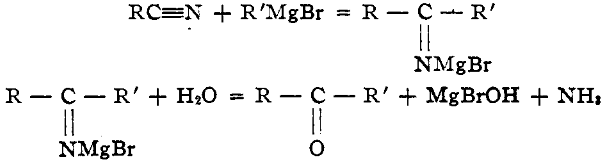
Although the reactions of the Grignard reagent with different types of carbonyl containing compounds have been carefully and exhaustively studied, the same cannot be said concerning the reactions of the Grignard reagent with organic substances containing the cyan radical —C≡N. Blaise[1] treated cyanogen and certain aliphatic and aromatic nitriles with alkyl and aryl magnesium halides, and found he obtained ketones according to the following equations:



$$RC\equiv N + R'MgBr = R - \underset{\underset{NMgBr}{\|}}{C} - R'$$

$$R - \underset{\underset{NMgBr}{\|}}{C} - R' + H_2O = R - \underset{\underset{O}{\|}}{C} - R' + MgBrOH + NH_3$$

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[1] *Compt. rend.*, 132, 38 (1901); 133, 1217 (1901).