Two grams of substance were heated with concentrated KOH for four hours in a round bottom flask with a return condenser. Ammonia was given off. When cold it was acidified with concentrated hydrochloric acid, filtered, washed thoroughly with distilled water, dried in a steam oven, and then an attempt was made to recrystallize it from benzene. Only a very small portion would go into solution even in a large excess of the solvent. After drying, it was dissolved in alcohol and recrystallized twice. The product melted at 174–183° but was not nitrogen-free. A second attempt was made to saponify with KOH by prolonged treatment but the resulting compound was not free from nitrogen. All attempts to saponify the nitrile were unsuccessful.

Considerable work has been done to isolate the second product formed in the interaction of sodium benzyl cyanide with *p*-tolylcinnamic ester, but without satisfactory results. This problem will occupy our attention in the near future.

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[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

# STUDIES IN ESTERIFICATION. IX. THE ESTERIFICATION OF ACETIC AND PROPIONIC ACIDS BY METHYL, ETHYL, PROPYL, ISOBUTYL AND ISOAMYL MERCAPTANS.

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## Historical.

Ever since Berthelot and Pean de St. Gilles[2] so carefully investigated the formation of esters, the problem of esterification, with and without a catalyst, has been one of great interest to the chemist.

This was followed by the work of Menschutkin[3] in which the question of the influence of the structure of both the acid and of the alcohol was extensively studied.

Reid[4] in a study of the mechanism of esterification found that mercaptan esterifies benzoic acid and that a well-defined limit is reached.

This work was extended by Pratt and Reid[5] who studied the esterification of benzoic acid by various mercaptans, and further by Sachs and Reid[6] and Kimball and Reid[7] who took up the question of isomerism of the acids and of the mercaptans.

All of this work on mercaptans has gone to show that mercaptans esterify acids as do alcohols and that the relations between the limits reached are

[1] From dissertation of Edgar M. Faber.

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

[3] *Ber.*, **11**, 1510 (1878); *Ann. chim. phys.*, **23**, 58 (1881).

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

[5] THIS JOURNAL, **37**, 1934 (1915).

[6] *Ibid.*, **38**, 2746 (1916).

[7] *Ibid.*, **38**, 2757 (1916).

much the same with mercaptans as with alcohols, but up to the present only aromatic acids have been used with mercaptans.

The present investigation was undertaken to extend the work to the aliphatic acids. The esterification of acetic, propionic and butyric acids by methyl, ethyl, propyl, isobutyl and isoamyl mercaptans has been studied.

## Materials.

**Acids.**—The acetic acid used was prepared by cooling a pure glacial acetic acid to its freezing point and effecting crystallization by the introduction of an acetic acid crystal.

After pouring off the unsolidified portion the process was repeated until the acid, by titration with standard alkali, showed a high degree of purity.

The propionic acid was obtained by fractionating a standard commercial product.

**Mercaptans.**—The methyl and ethyl mercaptans used in this work were made by Reid. Both were freed from sulfides, dried and distilled, the best fractions only being used. The methyl mercaptan boiled at 6°, the ethyl at 35.5° to 36.1°.

The propyl, isobutyl and isoamyl mercaptans were standard commercial products.

**Ethyl Alcohol.**—To free the ethyl alcohol from carbonic and other acids which the commercial material usually contains it was distilled from caustic potash.

**Heating.**—The furnace employed was that constructed by Pratt and Reid, electrically controlled and heated, it maintained the temperature constant within 3°.

**Standard Solutions.**—The standard barium hydroxide was kept in a large stock bottle from which it was run through a siphon, fitted with a stopcock, into the buret. The tops of the bottle and buret were protected from the carbon dioxide of the air by soda-lime tubes.

For the standard hydrochloric acid solution a similar apparatus was used, except that the stock bottle and buret were protected by tubes containing acid of the same strength.

Both solutions were approximately 0.1 *N* and were standardized at intervals of two weeks.

## Method of Work.

Pyrex glass tubes about 6 × 75 mm., closed at one end, were washed with hot chromic acid, filled with a dilute solution of hydrochloric acid and allowed to stand in a boiling solution of the same for a period of six hours. They were then washed and boiled in distilled water for an hour, after which they were washed with distilled water and thoroughly dried in an air bath.

Each tube was weighed and, after introducing the acid by means of a capillary pipet controlled by a rubber exhaustion bulb, drawn out to a narrow neck and weighed again. The mercaptan was then added, the tube being placed in a mixture of ice and salt, and the tube sealed.

The tube and tip were then weighed. After this the tubes were placed in the furnace and heated to 197–203° for the desired length of time. When the furnace had cooled they were removed and analyzed. To do this the tube was scored with a file, the tip broken off and thrown into a 120 cc. Erlenmeyer flask. By means of a pipet, similar to the one used to introduce the acid, the content of the tube was transferred to the flask, the former washed out four times with alcohol (distilled from KOH) and the washings added to the main portion.

Sufficient alcohol was then added to the reaction mixture to bring the volume to 25 cc.

The mercaptan not entering into the reaction was eliminated by drawing carbon dioxide-free air through the solution, the flask containing the latter being immersed in water heated to 50°. Preliminary experiments with known amounts of acid and mercaptan showed that it is necessary to pass air through the solutions 15 minutes to remove methyl and ethyl mercaptans; 25 minutes for the propyl; 30 minutes for the isobutyl, and 45 minutes for the isoamyl. The amount of acid in the solution was then determined by titration with standard barium hydroxide solution using phenolphthalein as indicator.

## Experimental.

Since, according to the usual reasoning in the consideration of reversible reactions, the amount of ester formed in unit time is equal to (acid × mercaptan) K, and the amount of ester decomposed in the same time is equal to (water × ester) K′ (the expressions in parentheses represent concentrations), and since, at equilibrium, these opposing velocities are equal, we have:

$$\frac{[\text{acid}] \times [\text{mercaptan}]}{[\text{water}] \times [\text{ester}]} = \frac{K'}{K} = r^{1}$$

This is for the general case in which the amounts of acid and mercaptan are not equivalent. If the mass law holds, the value of $r$ will be the same whatever the relative concentrations of acid and mercaptan and we can use the value of $r$ found in one case to calculate the equilibrium in any other. The case that has been most frequently studied in esterification is the special case in which the initial concentrations are equal.

Since the two reacting substances are used up at the same rate and since equivalent amounts of the products are formed, the final concentrations of acid and mercaptan are equal, as are the concentrations of water and ester, and we may write

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[1] *Am. Chem. J.*, 43, 499 (1910); Bonz, *Z. Physik. Chem.*, 2, 865 (1888).

$$\frac{[\text{acid}] \times [\text{mercaptan}]}{[\text{ester}] \times [\text{water}]} = \frac{[\text{acid}]^2}{[\text{ester}]^2} = \frac{K'}{K} = r \quad \text{or} \quad \frac{[\text{acid}]}{[\text{ester}]} = \sqrt{r}.$$

If we consider the original amount of acid as 100% then at equilibrium when $x$% of the acid has reacted, the ester will be $x$% and the acid remaining, $100 - x$%. Then

$$\frac{100 - x}{x} = \sqrt{r} \quad \text{or} \quad x = \frac{100}{\sqrt{r} + 1}.$$

In this, $x$ is the percentage of an equivalent mixture which would have reacted when equilibrium has been reached. We may call $x$, the limit for equivalent quantities or, for general purposes, simply the esterification limit, understanding that it is calculated for equivalent concentrations from values of $r$ obtained working with other than equivalent concentrations. This is the percentage of esterification, or limit, that has been calculated in all of the articles of this series.

In tabulating the results, the data are arranged as follows:

*a*. Acid in grams weighed in.
*b*. Millimols of acid at start.
*c*. Mercaptan in grams weighed in.
*d*. Millimols of mercaptan at start.
*e*. Cubic centimeters of standard alkali required for titration.
*f*. Millimols of acid present at end calculated from *e*.
*g*. Millimols of mercaptan remaining, $d - m = g$.
*m*. Millimols of ester, equals water, $b - f = m$.
%. Percentage of esterification, or $x$, calculated by the above formula for equivalent quantities of mercaptan and acid.

The data are given in full in the first run but after that, to save space, the weights in g. of the acid and mercaptan, *a* and *c*, and the titration fig. *e*, are omitted.

## RESULTS.

Series I.—48 Hours at 200°.

$CH_3COOH + CH_3SH$.

| | | | | | | |
|---|---|---|---|---|---|---|
| *a*, Acid, g. | 0.0848 | 0.0872 | 0.1006 | 0.0909 | 0.1033 | 0.0924 |
| *b*, Acid, m. mols | 1.413 | 1.453 | 1.676 | 1.514 | 1.721 | 1.539 |
| *c*, Mercap., g. | 0.0869 | 0.0947 | 0.0622 | 0.0899 | 0.0527 | 0.0922 |
| *d*, Mercap., m. mols | 1.807 | 1.969 | 1.293 | 1.869 | 1.096 | 1.917 |
| *e*, $Ba(OH)_2$, cc. | 12.60 | 12.83 | 15.67 | 13.54 | 16.31 | 13.84 |
| *f*, Acid left | 1.159 | 1.180 | 1.442 | 1.246 | 1.500 | 1.273 |
| *g*, Mercap. left | 1.553 | 1.696 | 1.059 | 1.600 | 0.875 | 1.651 |
| *m*, Ester = water | 0.2535 | 0.2724 | 0.2344 | 0.2687 | 0.2204 | 0.2661 |
| $\sqrt{r}$ | 5.29 | 5.19 | 5.26 | 5.25 | 5.19 | 5.44 |
| % | 15.89 | 16.15 | 15.96 | 16.00 | 16.13 | 15.51 |

Mean, 15.94%

### $CH_3COOH + C_2H_5SH$.

| | | | | | | |
|---|---|---|---|---|---|---|
| *b*, Acid in m. mols. | 2.417 | 2.192 | 1.684 | 2.132 | 2.116 | 2.094 |
| *d*, Mercap., m. mols. | 3.147 | 3.062 | 2.040 | 2.780 | 3.046 | 2.568 |
| *f*, Acid left | 2.075 | 1.877 | 1.451 | 1.826 | 1.791 | 1.811 |
| *g* | 2.805 | 2.747 | 1.807 | 2.474 | 2.721 | 2.285 |
| *m*, Mercap. left | 0.3425 | 0.3153 | 0.2329 | 0.3066 | 0.3248 | 0.2833 |
| $\sqrt{r}$ | 7.04 | 7.20 | 6.95 | 6.93 | 6.79 | 7.17 |
| % | 12.43 | 12.20 | 12.57 | 12.61 | 12.82 | 12.23 |

Mean, 12.48%

### $CH_3COOH + C_3H_7SH$.

| | | | | | | |
|---|---|---|---|---|---|---|
| *b* | 1.453 | 1.444 | 1.944 | 1.658 | 1.609 | 1.404 |
| *d* | 1.505 | 1.379 | 1.328 | 1.429 | 1.426 | 1.514 |
| *f* | 1.272 | 1.284 | 1.757 | 1.472 | 1.430 | 1.227 |
| *g* | 1.325 | 1.219 | 1.141 | 1.243 | 1.247 | 1.337 |
| *m* | 0.1804 | 0.1601 | 0.1870 | 0.1656 | 0.1797 | 0.1772 |
| $\sqrt{r}$ | 7.19 | 7.81 | 7.57 | 7.29 | 7.42 | 7.22 |
| % | 12.20 | 11.35 | 11.66 | 12.06 | 11.86 | 12.10 |

Mean, 11.87%

### $CH_3COOH + (CH_3)_2CHCH_2SH$.

| | | | | | |
|---|---|---|---|---|---|
| *b* | 2.107 | 1.926 | 1.784 | 1.951 | 1.996 |
| *d* | 1.757 | 1.755 | 1.709 | 1.551 | 1.750 |
| *f* | 1.874 | 1.702 | 1.579 | 1.741 | 1.775 |
| *g* | 1.524 | 1.531 | 1.504 | 1.340 | 1.529 |
| *m* | 0.2335 | 0.2239 | 0.2056 | 0.2103 | 0.2211 |
| $\sqrt{r}$ | 7.23 | 7.20 | 7.49 | 7.26 | 7.45 |
| % | 12.14 | 12.18 | 11.77 | 12.10 | 11.83 |

Mean, 12.00%

### Series II.—96 Hours at 200°.

### $CH_3COOH + CH_3SH$.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *b* | 1.094 | 1.264 | 1.494 | 1.644 | 1.791 | 2.537 | 2.342 |
| *d* | 4.847 | 2.073 | 3.019 | 2.356 | 2.086 | 3.200 | 3.080 |
| *f* | 0.759 | 1.004 | 1.141 | 1.320 | 1.468 | 2.084 | 1.904 |
| *g* | 4.512 | 1.812 | 2.666 | 2.032 | 1.763 | 2.747 | 2.642 |
| *m* | 0.3355 | 0.2608 | 0.3536 | 0.3241 | 0.3226 | 0.4535 | 0.4380 |
| $\sqrt{r}$ | 5.51 | 5.35 | 4.93 | 5.05 | 4.98 | 5.27 | 5.12 |
| % | 15.38 | 15.74 | 16.86 | 16.52 | 16.70 | 15.96 | 16.34 |

Mean, 16.21%

### $CH_3COOH + C_2H_5SH$.

| | | | | | |
|---|---|---|---|---|---|
| *b* | 1.781 | 2.417 | 2.171 | 2.204 | 2.001 |
| *d* | 1.478 | 1.832 | 1.600 | 1.832 | 1.901 |
| *f* | 1.571 | 2.142 | 1.926 | 1.941 | 1.751 |
| *g* | 1.268 | 1.557 | 1.355 | 1.569 | 1.651 |
| *m* | 0.2100 | 0.2752 | 0.2448 | 0.2629 | 0.2500 |
| $\sqrt{r}$ | 6.72 | 6.63 | 6.60 | 6.63 | 6.80 |
| % | 12.95 | 13.10 | 13.15 | 13.10 | 12.81 |

Mean, 13.02%

### $CH_3COOH + C_3H_7SH$.

| | | | | | | |
|---|---|---|---|---|---|---|
| *b* | 2.382 | 2.091 | 2.364 | 2.216 | 2.167 | 2.127 |
| *d* | 1.608 | 1.667 | 1.751 | 1.848 | 1.943 | 2.116 |
| *f* | 2.129 | 1.862 | 2.104 | 1.960 | 1.907 | 1.859 |
| *g* | 1.354 | 1.438 | 1.491 | 1.592 | 1.682 | 1.848 |
| *m* | 0.2536 | 0.2288 | 0.2600 | 0.2562 | 0.2603 | 0.2682 |
| $\sqrt{r}$ | 6.69 | 7.15 | 6.81 | 6.89 | 6.88 | 6.89 |
| % | 12.90 | (12.27) | 12.80 | 12.67 | 12.70 | 12.67 |

Mean, 12.75%

### $CH_3COOH + (CH_3)_2CHCH_2SH$.

| | | | | | |
|---|---|---|---|---|---|
| *b* | 1.892 | 1.848 | 2.036 | 1.861 | 2.112 |
| *d* | 1.475 | 1.500 | 1.348 | 1.401 | 1.371 |
| *f* | 1.702 | 1.650 | 1.834 | 1.665 | 1.905 |
| *g* | 1.285 | 1.303 | 1.146 | 1.205 | 1.163 |
| *m* | 0.1906 | 0.1971 | 0.2017 | 0.1957 | 0.2077 |
| $\sqrt{r}$ | 7.75 | 7.43 | 7.18 | 7.23 | 7.16 |
| % | (11.42) | 11.85 | 12.21 | 12.14 | 12.24 |

Mean, 12.11%

### $CH_3COOH + (CH_3)_2CHCH_2CH_2SH$.

| | | | | | |
|---|---|---|---|---|---|
| *b* | 2.141 | 1.902 | 2.229 | 2.162 | 1.832 |
| *d* | 1.094 | 1.048 | 1.001 | 1.128 | 0.984 |
| *f* | 1.711 | 1.518 | 1.853 | 1.755 | 1.453 |
| *g* | 0.6647 | 0.6641 | 0.6256 | 0.7208 | 0.6055 |
| *m* | 0.4297 | 0.3842 | 0.3757 | 0.4072 | 0.3794 |
| $\sqrt{r}$ | 7.84 | 8.26 | 9.06 | 8.73 | 7.81 |
| % | 11.30 | 10.8 | 9.94 | 10.28 | 11.34 |

Mean, 10.73%

### $CH_3COOH + CH_3SH$—192 Hours at 200°.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *b* | 1.608 | 1.566 | 1.518 | 1.474 | 1.448 | 1.796 | 1.743 | 1.218 |
| *d* | 1.773 | 2.102 | 2.200 | 1.840 | 2.484 | 1.505 | 1.825 | 1.561 |
| *f* | 1.329 | 1.273 | 1.225 | 1.201 | 1.143 | 1.398 | 1.446 | 1.002 |
| *g* | 1.495 | 1.809 | 1.907 | 1.567 | 2.179 | 1.108 | 1.529 | 1.346 |
| *m* | 0.2783 | 0.2927 | 0.2923 | 0.2729 | 0.3051 | 0.3975 | 0.2964 | 0.2150 |
| $\sqrt{r}$ | 5.12 | 5.18 | 5.23 | 5.02 | 5.17 | (3.12) | 5.01 | 5.40 |
| % | 16.33 | 16.17 | 16.05 | 16.59 | 16.2 | (24.23) | 16.62 | 15.62 |

Mean, 16.23%

### Series III.—45 Hours at 200°.

### $CH_3CH_2COOH + CH_3SH$.

| | | | | | | |
|---|---|---|---|---|---|---|
| *b* | 1.573 | 1.477 | 1.715 | 1.483 | 1.550 | 1.611 |
| *d* | 1.661 | 1.928 | 2.212 | 2.655 | 2.990 | 2.389 |
| *f* | 1.335 | 1.224 | 1.420 | 1.188 | 1.223 | 1.313 |
| *g* | 1.423 | 1.674 | 1.918 | 2.361 | 2.663 | 2.091 |
| *m* | 0.2386 | 0.2536 | 0.2947 | 0.2944 | 0.3275 | 0.2978 |
| $\sqrt{r}$ | 5.77 | 5.64 | 5.60 | 5.68 | 5.51 | 5.56 |
| % | 14.76 | 15.05 | 15.15 | 14.95 | 15.72 | 15.23 |

Mean, 15.14%

### $CH_3CH_2COOH + C_2H_5SH$.

| | | | | | | |
|---|---|---|---|---|---|---|
| *b* | 1.507 | 1.472 | 1.349 | 1.373 | 1.508 | 1.402 |
| *d* | 2.553 | 2.908 | 2.724 | 2.602 | 2.922 | 2.753 |
| *f* | 1.287 | 1.246 | 1.146 | 1.168 | 1.278 | 1.207 |
| *g* | 2.334 | 2.681 | 2.521 | 2.397 | 2.692 | 2.559 |
| *m* | 0.2195 | 0.2263 | 0.2030 | 0.2049 | 0.2302 | 0.1942 |
| $\sqrt{r}$ | 7.89 | 8.07 | 8.37 | 8.16 | 8.05 | 9.05 |
| % | 11.24 | 11.02 | 10.67 | 10.91 | 11.04 | (9.94) |

Mean, 10.97%

### $CH_3CH_2COOH + C_3H_7SH$.

| | | | | | | |
|---|---|---|---|---|---|---|
| *b* | 1.508 | 1.402 | 1.295 | 1.258 | 1.323 | 1.287 |
| *d* | 1.644 | 1.355 | 1.309 | 1.220 | 1.291 | 1.288 |
| *f* | 1.361 | 1.262 | 1.156 | 1.123 | 1.191 | 1.152 |
| *g* | 1.497 | 1.216 | 1.171 | 1.085 | 1.158 | 1.153 |
| *m* | 0.1471 | 0.1396 | 0.1387 | 0.1356 | 0.1328 | 0.1353 |
| $\sqrt{r}$ | 9.7 | 8.87 | 8.39 | 8.32 | 8.84 | 8.51 |
| % | (9.34) | 10.00 | 10.65 | 10.72 | 10.16 | 10.51 |

Mean, 10.41%

### $CH_3CH_2COOH + (CH_3)_2CHCH_2SH$—48 Hours at 200°.

| | | | | | |
|---|---|---|---|---|---|
| *b* | 1.815 | 1.747 | 1.653 | 1.858 | 1.714 |
| *d* | 1.700 | 1.753 | 1.728 | 1.773 | 1.689 |
| *f* | 1.630 | 1.554 | 1.469 | 1.669 | 1.537 |
| *g* | 1.515 | 1.560 | 1.545 | 1.584 | 1.513 |
| *m* | 0.1853 | 0.1929 | 0.1836 | 0.1886 | 0.1767 |
| $\sqrt{r}$ | 8.48 | 8.07 | 8.20 | 8.62 | 8.63 |
| % | 10.55 | 11.02 | 10.86 | 10.40 | 10.39 |

Mean, 10.64%

## Series IV.—96 Hours at 200°.

### $CH_3CH_2COOH + CH_3SH$.

| | | | | | | |
|---|---|---|---|---|---|---|
| *b* | 1.250 | 1.458 | 1.349 | 1.514 | 1.658 | 1.703 |
| *d* | 2.536 | 2.177 | 2.609 | 2.349 | 2.395 | 2.954 |
| *f* | 0.989 | 1.192 | 1.061 | 1.221 | 1.368 | 1.361 |
| *g* | 2.275 | 1.910 | 2.321 | 2.057 | 2.105 | 2.612 |
| *m* | 0.2617 | 0.2667 | 0.2877 | 0.2924 | 0.2898 | 0.3417 |
| $\sqrt{r}$ | 5.73 | 5.65 | 5.45 | 5.42 | 5.85 | 5.51 |
| % | 14.86 | 15.03 | 15.49 | 15.58 | (14.59) | 15.34 |

Mean, 15.26%

### $CH_3CH_2COOH + C_2H_5SH$.

| | | | | |
|---|---|---|---|---|
| *b* | 1.872 | 1.758 | 1.830 | 1.676 |
| *d* | 2.281 | 2.431 | 1.639 | 1.594 |
| *f* | 1.631 | 1.519 | 1.603 | 1.485 |
| *g* | 2.041 | 2.192 | 1.412 | 1.403 |
| *m* | 0.2406 | 0.2391 | 0.2268 | 0.1912 |
| $\sqrt{r}$ | 7.58 | 7.63 | 6.63 | 7.54 |
| % | 11.65 | 11.58 | (13.1) | 11.70 |

Mean, 11.64%

$CH_3CH_2COOH + C_3H_7SH$.

| | | | | | | |
|---|---|---|---|---|---|---|
| b | 1.700 | 1.826 | 1.766 | 1.642 | 1.791 | 1.777 |
| d | 1.786 | 1.841 | 1.794 | 1.751 | 1.828 | 1.765 |
| f | 1.503 | 1.624 | 1.574 | 1.448 | 1.580 | 1.579 |
| g | 1.589 | 1.640 | 1.602 | 1.556 | 1.618 | 1.568 |
| m | 0.1968 | 0.2017 | 0.1925 | 0.1944 | 0.2103 | 0.1977 |
| $\sqrt{r}$ | 7.85 | 8.09 | 8.24 | 7.72 | 7.60 | 7.95 |
| % | 11.29 | 11.00 | (10.81) | 11.40 | 11.60 | 11.16 |

Mean, 11.29%

$CH_3CH_2COOH + (CH_3)_2CHCH_2SH$.

| | | | | | |
|---|---|---|---|---|---|
| b | 1.308 | 1.474 | 1.916 | 1.615 | 1.607 |
| d | 1.408 | 1.433 | 1.292 | 1.445 | 1.475 |
| f | 1.163 | 1.339 | 1.757 | 1.440 | 1.434 |
| g | 1.262 | 1.298 | 1.133 | 1.270 | 1.303 |
| m | 0.1455 | 0.1354 | 0.1588 | 0.1751 | 0.1726 |
| $\sqrt{r}$ | 8.32 | 9.73 | 8.88 | 7.72 | 7.92 |
| % | 10.72 | (9.31) | 10.12 | 11.46 | 11,20 |

Mean, 10.87%

$CH_3CH_2COOH + (CH_3)_2CHCH_2CH_2SH$.

| | | | | | | |
|---|---|---|---|---|---|---|
| b | 1.492 | 1.349 | 1.558 | 1.696 | 1.727 | 1.423 |
| d | 1.185 | 1.175 | 1.148 | 1.102 | 1.163 | 0.981 |
| f | 1.151 | 1.008 | 1.217 | 1.375 | 1.395 | 1.138 |
| g | 0.8433 | 0.8339 | 0.8072 | 0.7812 | 0.8310 | 0.6958 |
| m | 0.3413 | 0.3411 | 0.3409 | 0.3209 | 0.3325 | 0.2853 |
| $\sqrt{r}$ | 9.12 | 8.49 | 9.19 | 10.21 | 10.23 | 9.86 |
| % | 9.88 | 10.52 | 9.80 | 8.92 | 8.90 | 9.20 |

Mean, 9.53%

SUMMARY OF RESULTS.

Acetic Acid with Mercaptans.

| Time. | Methyl. | Ethyl. | Propyl. | Isobutyl. | Isoamyl. |
|---|---|---|---|---|---|
| 48 Hours | 15.94 | 12.48 | 11.87 | 12.00 | ..... |
| 96 Hours | 16.21 | 13.02 | 12.75 | 12.11 | 10.73 |
| 192 Hours | 16.23 | ..... | ..... | ..... | ..... |
| Propionic Acid with Mercaptans. | | | | | |
| 48 Hours | 15.14 | 10.97 | 10.41 | 10.64 | ..... |
| 96 Hours | 15.26 | 11.64 | 11.29 | 10.87 | 9.53 |

## Discussion of Results.

From the foregoing results it is noticed that a good degree of concordance exists between the individual results in a table, considering the experimental errors involved in using mercaptans and the variations in proportions of active materials used.

Preliminary experiments conducted to ascertain the time necessary to reach the limit showed that 96 hours was sufficient. This is brought out in the small increase in the limit for acetic acid and methyl mercaptan at 192 hours, over that at 48 hours, they being, respectively, 16.23% and 16.21%.

Below is a comparison of the limits obtained using mercaptans with those found by Menschutkin with acetic acid and various alcohols in equimolecular quantities at 154°, and with the limits found by Pratt and Reid and Kimball and Reid for mercaptans with benzoic acid.

| | Alcohols with acetic acid.[1] | Mercaptans with | | |
|---|---|---|---|---|
| | | Acetic acid. | Propionic acid. | Benzoic acid. |
| Methyl | 69.52 | 16.21 | 15.62 | 18.7[2] |
| Ethyl | 66.57 | 13.02 | 11.64 | 14.7[2] |
| Propyl | 66.85 | 12.75 | 11.29 | 14.1[2] |
| Isobutyl | 67.38 | 12.11 | 10.87 | 13.63[3] |

As has been found in all the work with mercaptans the limits using mercaptans are much lower than those with alcohols. With both mercaptans and alcohols the limits are much higher for methyl than for any other.

With the alcohols, ethyl gives the lowest limit and then there is a slight rise with increase of molecular weight, but with mercaptans there is a continual lowering of the limit as we go up the series. The values quoted for mercaptans with benzoic acid show the same relations.

Then, too, it is seen that the limits reached with acetic acid are slightly higher than those with propionic. Menschutkin[4] found this same relation between the rates, when acetic and propionic acids were heated one hour with isobutyl alcohol by obtaining 44.4% for the former and 41.2% for the latter. In all of the tubes except those containing the methyl esters, slight decomposition was shown by the presence of hydrogen sulfide. Judging from the extent of discoloration of the lead acetate paper the amount of decomposition seemed to increase with rise in molecular weight.

## Conclusions.

1. The limits of esterification of acetic and propionic acids with methyl, ethyl, propyl, isobutyl and isoamyl mercaptans have been determined at 200°.

2. The limits for propionic acid were found to be somewhat lower than those for acetic.

3. The limits obtained were found to be much lower than those for corresponding alcohols.

4. The proportions of reacting substances seemed to have but little influence on the limit.

5. The stability of the esters was found to decrease with increase in molecular weight.

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[1] *Ber.*, 11, 1510 (1878).

[2] THIS JOURNAL, **37**, 1947 (1915).

[3] *Ibid.*, **38**, 2766 (1916).

[4] *Ann. chim. phys.*, **23**, 58 (1881).