lower the potential gradient as a space charge effect, and thus the net current is reduced under light.

While the space charge effect due to negative ions may be anticipated in chlorine due to the high electron affinity of the gas, literature on the subject provides evidence of negative ions in other systems showing large negative Joshi effect. The presence of H$^-$ ions in a hydrogen beam due to a glow discharge has been confirmed by Tüxen (cf. Massey[14]). Besides H$^-$, the formation of H$_2$$^-$ ions is also inferred corresponding to an electron affinity of -2.4 e.v. In the case of mercury vapor, Arnot showed the conversion of Hg$^+$ into Hg$^-$ occurs following the capture of two electrons successively from the cathode (Massey[14]).

(14) H. S. W. Massey, "Negative Ions," Cambridge Physical Tracts, Cambridge, 1938, pp. 1-2, 26-27, 68

The third postulate of Joshi's theory that these negative ions build into a space charge which has the effect of quenching the discharge receives additional support in the recent experiment of Weissler and Mohr.[15] They found that the corona discharge in freon-12 and air mixture is suppressed by negative ions.

Grateful thanks are due to Prof. S. S. Joshi, University Professor of Physical Chemistry and Principal College of Science, Banaras, for his valuable advice and guidance; and to Prof. P. S. Gill, Chairman of the Physics Department, Aligarh, for facilities for carrying out a part of this work in his department.

(15) G. L. Weissler and E. I. Mohr, Phys. Rev., 72, 289 (1947).

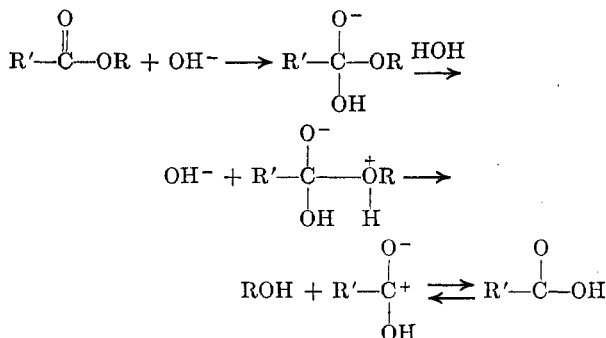# THE RATE OF SAPONIFICATION OF ACETATES OF UNSATURATED ALCOHOLS[1]

By R. Thomas Myers,[2] A. R. Collett and C. L. Lazzell

Chemistry Department, West Virginia University, Morgantown, West Virginia
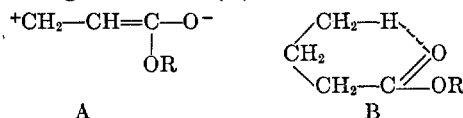
The following new esters were prepared and characterized: 3-methyl-1-pentyn-3-ol acetate and 3-methyl-1-penten-3-ol acetate. In addition 3-methyl-1-penten-3-ol was characterized. Using a conductometric method the rate of saponification of the following acetates with 0.01 N NaOH at 25° was determined: ethyl, n-propyl, allyl, s-butyl, 2-propyn-1-ol, 3-buten-2-ol, 3-butyn-2-ol, 3-methyl-1-pentyn-3-ol and 3-methyl-1-penten-3-ol. For each ester, runs of two kinds were made: ester and base of the same concentration, and ester of higher concentration than the base. Trials using base of higher concentration than ester gave unsatisfactory values for the velocity constants.

According to many investigators in this field the mechanism of the saponification of carboxylic esters is considered to be[3,4]

It is assumed that most of the energy of activation is involved in the fixation of the hydroxyl ion on the carbonyl carbon.[4] Therefore any group which increases the positive charge on the carbonyl carbon will accelerate the hydrolysis. An unsaturated carbon-to-carbon linkage near the carbonyl carbon in carboxylic esters always speeds the rate of hydrolysis compared to that of the saturated ester. For this and other reasons it has been assumed that an unsaturated group is electronegative with

(1) Adapted from a dissertation by R. Thomas Myers, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at West Virginia University.

(2) Chemistry Department, Colorado School of Mines, Golden, Colo.

(3) Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 82.

(4) Mumm, Ber., 72B, 1874 (1939).

respect to hydrogen.[5,6] Much of this work has been done with esters of unsaturated acids. In this case the interpretation of results has been obscured by electromeric shifts (A) and possible chelate ring structures (B).[7]

The following work was carried out to extend the information on ester saponification, and to supply some of the information necessary to determine the reason for the acceleration of the saponification of esters caused by unsaturation. No previous work has been reported on the rate of saponification of esters of acetylenic alcohols.

In order to compare and relate the effect of various structures, ten esters were used, of which six were prepared by the authors. The alcoholic components contained saturated, ethylenic and acetylenic linkages connected to primary, secondary and tertiary carbinol groups. The physical properties of the esters used are listed in Table I.

The saponifications were done with sodium hydroxide, using a conductometric method.[8] This was used for three reasons. The first was the ease of manipulation, since no samples need be taken for analysis. The second reason was that errors due

(5) Dippy, Chem. Rev., 25, 151 (1939).

(6) Olsson, Z. phys. Chem., 133, 233 (1928).

(7) Smith and McReynolds, J. Am. Chem. Soc., 61, 1963 (1939).

(8) Walker, Proc. Royal Soc. (London), 78A, 157 (1906).

Table I

Physical Properties of Compounds

Acetate of:	Boiling point, °C. (cor.)	Pressure, mm.	n^{25}D	d^{25}_4
I Ethanol	75.7–75.9	730	1.3701	0.8942
II n-Propyl alcohol	101.0 (const.)	742	1.3822	0.8833
III Allyl alcohol	102.9–03.7	736	1.4009	0.9222
IV 2-Propyn-1-ol	122.4–23.6	738	1.4151	0.9943
V s-Butyl alcohol	111.3–11.9	747	1.3863	0.8647
VI 3-Buten-2-ol	111.7 (const.)	727	1.4016	0.8939
VII 3-Butyn-2-ol	124.4–25.4	738	1.4112	0.9437
VIII 3-Methyl-3-pentanol	142.0–43.5	744	1.4070	0.8768
IX 3-Methyl-1-penten-3-ol	146.9	730	....	....
X 3-Methyl-1-pentyn-3-ol	151.4–52.4	739	1.4238	0.9256
Free alcohol:				
3-Methyl-1-penten-3-ol	114.0–16.6	735	1.4262	0.8334
	115.4–15.5	730	....	....

to evaporation were eliminated. Preliminary experiments showed that these errors were rather large, even for the higher-boiling esters. Lastly, the simplicity was greatly enhanced by the fact that the same ions were present in all cases.

$$\begin{matrix} & O \\ & \| \\ CH_3 & -C-OR + Na^+ + OH^- \longrightarrow \end{matrix}$$
$$CH_3COO^- + Na^+ + ROH$$

The fraction of material reacted at any time t was assumed to be $C_0 - C_t/C_0 - C_\infty$ where C is the conductivity. (In practice 1000/resistance was used instead of conductivity.) If we note that the concentration of base corresponding to this fraction is $b(C_0 - C_t)/(C_0 - C_\infty)$, the following formula is applicable when the initial concentration of reactants is the same

$$k = \frac{C_0 - C_\infty}{b(t_2 - t_1)} \frac{C_1 - C_2}{(C_2 - C_\infty)(C_1 - C_\infty)}$$

When the concentration of base and ester are not the same the following formula applies

$$k = \frac{2.303}{(a-b)(t_2-t_1)} \log$$
$$\frac{a(C_0 - C_\infty)/b - (C_0 - C_2)(C_1 - C_\infty)}{a(C_0 - C_\infty)/b - (C_0 - C_1)(C_2 - C_\infty)}$$
$$= \frac{2.303}{(a-b)(t_2-t_1)} \log Y$$

In these equations a is the concentration of ester

and b the concentration of base. The former was determined by weighing out a definite amount of ester and diluting with carbon-dioxide-free conductivity water in a volumetric flask, the latter by standardization against sulfamic acid. The conductivity water was prepared by redistilling water from alkaline permanganate, using a block-tin condenser. It will be noted that this method of preparing the ester solutions was a check on their purity. Impurities, either saponifiable or not, will cause unsatisfactory values for the rate constant.
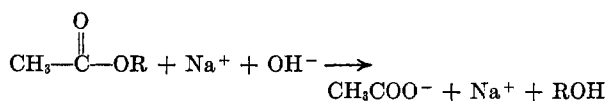
The concentration of ester was always equal to or greater than that of the base. Determinations using base stronger than ester did not give satisfactory results for the rate constant. Values of the constant from the first and last quarter were not used.

In order to illustrate the procedure, data for a typical run are included in Table II.

Table II

Saponification of 2-Propyn-1-ol Acetate

Initial Concentrations: ester 0.01200 N, base 0.0100 N.

R	$1000/R$ (C)	$C_0 - C$	$\frac{a(C_0 - C_\infty)}{-(C_0 - C)}$	$C - C_\infty$	$\log Y$	$t_2 - t_1$	k(l./mole-min.)
(726)	(1.377)		(1.064)	(0.887)	.....	...	..
920	1.087	0.290	0.774	0.597	.....	...	..
960	1.042	.335	.729	.552	0.00802	0.200	46.1
1000	1.000	.377	.687	.510	.00860	.217	45.6
1050	0.952	.425	.639	.462	.0015	.32	41.4
1100	.909	.468	.596	.419	.0122	.31	45.3
1150	.870	.507	.557	.380	.0130	.35	42.8
1200	.833	.544	.520	.343	.0146	.39	43.1
1250	.800	.577	.487	.310	.0155	.40	44.6
1300	.769	.608	.456	.279	.0173	.45	44.2
1350	.741	.636	.428	.251	.0184	.51	41.5
1400	.714	.663	.401	.224	.0211	.52	46.7
(2041)	(.490)	(.887)	(.177)	0	.....	...	..

The experimental results for all esters are summarized in Table III. The acetate of 3-methyl-3-pentanol is too insoluble to be determined with 0.01 N base. The units of the saponification constants are liters $\times$ mole^{-1} $\times$ min.$^{-1}$. The base is 0.01 N sodium hydroxide.

Table III

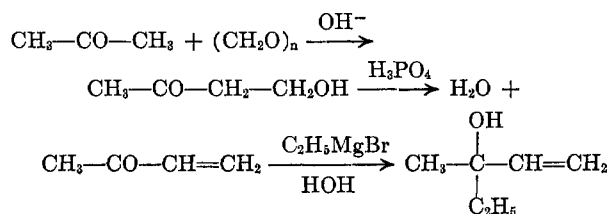Saponification Rate Constants for Esters at 25.0°

Acetate of:	Init. concn. of ester	Trial 1	Trial 2	Trial 3	Av. k
Ethanol	0.0100	6.69			
	.0200	6.62			6.66
2-Propyn-1-ol	.0100	43.7	43.9		
	.0120	44.1			43.9
Allyl alcohol	.0100	12.48	12.64		
	.0150	12.55			12.56
n-Propyl alcohol	.0100	5.85	5:90		
	.0200	5.76	5.75		5.82
3-Butyn-2-ol	.0100	22.1	21.9		
	.0150	21.9	21.6		21.9
3-Buten-2-ol	.0100	4.33	4.36	4.27	
	.0200	4.23	4.23		4.30
s-Butyl alcohol	.0100	1.039			
	.0200	1.023	1.046	1.063	1.043
3-Methyl-1-pentyn-3-ol	.0100	1.291	1.342		
	.0150	1.322			1.318
3-Methyl-1-penten-3-ol	.0100	0.24			0.24
3-Methyl-3-pentanol[9]	....	(0.025)			(0.025)

(9) Calculated from k at 20° (6), assuming the same temperature coefficient as for t-butyl acetate.

Experimental

Preparation of Esters.—I, II, III and V (Table I) were purchased from Eastman Kodak Company and redistilled before use. Esters IV, VI, VII, VIII, IX and X were prepared by the action of acetyl chloride on the alcohol in the presence of pyridine or dimethylaniline.

The alcohols were obtained as follows. 2-Propyn-1-ol and 3-methyl-1-pentyn-3-ol were purchased from Farchan Research Laboratories, Cleveland, Ohio. 3-Butyn-2-ol was supplied by the Electrochemicals Division, E. I. du Pont de Nemours and Co. 3-Buten-2-ol was prepared by a Grignard reaction with acrolein and methylmagnesium iodide. The yield was rather low. 3-Methyl-1-penten-3-ol was prepared by the reduction of the corresponding alkynol using coppered zinc dust.[10,11] Since this alcohol has not been sufficiently characterized in the literature, its physical properties are included in Table I. An attempt was made to prepare this alcohol by the following series of reactions[12]

$$CH_3\text{—}CO\text{—}CH_3 + (CH_2O)_n \xrightarrow{OH^-}$$

$$CH_3\text{—}CO\text{—}CH_2\text{—}CH_2OH \xrightarrow{H_3PO_4} H_2O +$$

$$CH_3\text{—}CO\text{—}CH=CH_2 \xrightarrow[HOH]{C_2H_5MgBr} CH_3\text{—}\underset{\underset{C_2H_5}{|}}{\overset{\overset{OH}{|}}{C}}\text{—}CH=CH_2$$

The result was a mixture of methyl n-butyl ketone and the alcohol, so the procedure was abandoned. The esterification of 3-methyl-1-penten-3-ol proved very difficult; the ester was never obtained free from combined chlorine. This was further evidenced by the unsatisfactory value obtained for the rate constant. 3-Methyl-3-pentanol was obtained from 3-methyl-1-pentyn-3-ol by the complete hydrogenation with Raney nickel catalyst.

Apparatus.—The conductance cell was constructed similarly to those of Jones and Bollinger,[13] except that only one opening for filling was provided. The conductivity bridge was assembled from Leeds and Northrup apparatus: audiofrequency oscillator, audiofrequency amplifier, shielded ratio box (with Wagner earthing device) and resistance box (non-inductively wound). As is usual in such measurements, the internal series capacitance of the cell, due both to geometry and polarization, was corrected for by a variable capacitor connected in parallel with the resistance box. It was estimated that the accuracy of any resistance reading was about 0.1%.

Saponification Technique.—From saturated aqueous C.P. sodium hydroxide, 0.0601 molar sodium hydroxide was prepared by diluting with conductivity water. This was standardized against sulfamic acid using phenolphthalein as indicator. A flask of the base was placed in the constant temperature bath. The latter was set at 25.0°, using a thermometer calibrated by the National Bureau of Standards. Ester solutions of a definite concentration were prepared by weighing out the requisite amount of ester in small thin-walled glass bulbs. Each bulb was placed in a volumetric flask and the necessary amount of conductivity water added to bring the solution to the mark. The flask was closed with a rubber stopper through which a glass rod extended almost to the bottom. The bulb was broken, the flask shaken until the ester dissolved and the flask then placed in the constant temperature bath. By means of a pipet 9.97 cc. of ester solution was delivered into the conductivity cell, and 1.99 cc. of sodium hydroxide solution added. Timing was started when one-half of the base was added.

The value of the conductivity at zero time was obtained by diluting the base with conductivity water to the desired

normality. The value of the conductance at infinite time (C_∞) was obtained from experimental measurements of a 0.01 N solution of sodium acetate. This method was satisfactory for those reactions which go to completion in a reasonable time.

Discussion

Inspection of the results in Table III shows that unsaturation speeds the rate of saponification in all cases. It also shows the following: (1) as regards branching in the alkyl group, the rate of saponification is in the order primary > secondary > tertiary, (2) the ethynyl group changes the rate more than the vinyl group (as compared to the ethyl group), (3) the relative amount of this change is in the order tertiary > secondary > primary.

Models of these ester molecules made with Fisher–Hirshfelder–Taylor atom models show that replacing an ethyl group by a vinyl group, and that in turn by an ethynyl group, causes a decrease in the purely steric blocking of the carbonyl carbon. The relative decrease in steric hindrance of the carbonyl carbon caused by exchanging ethyl for vinyl is greatest in tertiary, less in secondary and least in primary esters. The same is true for the exchange of vinyl for ethynyl. This indicates that the increase in rate of saponification in passing from propyl to allyl to 2-propyn-1-ol acetate may be due to steric factors, and not to changes in energy of activation. This is true in increasing amount in the other two series of secondary and tertiary esters. This is corroborated by data for allyl and n-propyl acetate. Olsson has found that the energy of activation for the saponification of allyl acetate is greater than that of propyl acetate, even though the former hydrolyzes more rapidly.[6] This increase in the energy of activation contradicts the supposed electron-attracting powers of the carbon-to-carbon unsaturated bonds, and could be explained by chelate structures C and D of the type postulated by Smith and McReynolds[7] and by Dippy.[5]

C   D
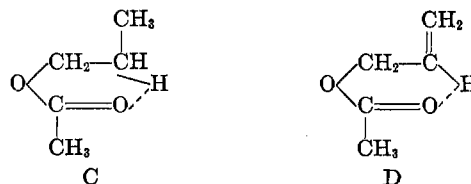
Since the ethylenic hydrogen is more labile, it seems probable that it would form a more stable hydrogen bond than the alkyl hydrogen, stabilizing D more than C. This stabilization would raise the activation energy for the hydrolysis. The increased rate of hydrolysis is then due to an increase in the probability of reactive collisions.

Models show that the lone acetylenic hydrogen of 2-propyn-1-ol acetate cannot approach the carbonyl oxygen, thus barring the chelate ring structure. Therefore if the ethynyl group is actually electronegative compared to the ethyl group, then the activation energy of 2-propyn-1-ol acetate should be significantly lower than for ethyl and allyl acetate.

(10) Rupe and Vonaesch, Ann., **442**, 81 (1925).

(11) Strauss, Ber., **26**, 284 (1893); ibid., **342**, 190, 238 (1905).

(12) White and Haward, C. A., **37**, 1989 (1943); J. Chem. Soc., 2531 (1943).

(13) Jones and Bollinger, J. Am. Chem. Soc., **53**, 411 (1931).