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THE VELOCITY OF SAPONIFICATION OF METHYL ACETATE BY SODIUM HYDROXIDE AT 25°

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As a part of a systematic study of catalysis in homogeneous solution carried out in this Laboratory[1] under the direction of Professor Julius Stieglitz, an exact measurement has been made of the rate of saponification of methyl acetate of about one hundredth molar concentration in aqueous sodium hydroxide solution at 25°.

Experimental Detail

Except for the case of the ester the preparation of materials, the method of measurement, the exclusion of carbon dioxide of the air from contact with reagents, etc., were the same as described elsewhere.[1]

Methyl acetate was prepared, first, by fractionation of Kahlbaum's best grade of ester, second, by the reaction of acetic anhydride and methyl alcohol and, third, by the reaction of acetic acid and methyl alcohol catalyzed by sulfuric acid as described by Wade[2] and purified by the method of Wade and Merriam.[3] All samples were neutral to azolitmin in water solution. No difference was found for the rate of reaction of the ester of these samples.

In this work and in part of the work of Wilson and Terry[4] a special apparatus was used to take the samples of the reaction mixture for analysis at noted times. The apparatus, which was developed jointly with Wilson, will now be described with the assistance of Fig. 1. The main parts are as follows: (1) the flask A which held the reaction mixture, (2) the valve tube B connecting A with the mercury pipet C from which mercury was discharged into A, producing simultaneously the discharge of an equal volume of the reaction mixture from e, the delivery tube of A, into the receiving bottle at M, (3) the reservoir E from which mercury was forced into C as it was needed, (4) the device H by means of which the delivery tube A could be freshly filled with solution just prior to the discharge of mercury from C, and (5) the coiled copper tube F through which water from the hydrant passed into E, thus supplying the pressure

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[1] See ref. 2 of Terry and Stieglitz, THIS JOURNAL, 49, 2216 (1927), for details of this study. The present paper is based on the thesis of Dr. Gooch, which was presented in 1916.

[2] Wade, *J. Chem. Soc.*, 87, 1656 (1905).

[3] Wade and Merriam, *ibid.*, 101, 2429 (1912).

[4] Wilson and Terry, THIS JOURNAL, 50, 1250 (1928).

which caused the flow of mercury from E whenever Stopcock 1 was opened. The apparatus was contained in a de Khotinsky thermostat, the water level of which is indicated by the horizontal broken line in the diagram.

Although much of the apparatus will be evident from the diagram, the following details and explanations are given to complete the very brief description of the apparatus which space permits. The glass to metal, glass to rubber and the glass to glass seals (at z and z′) were made with de Khotinsky cement. Each unit of the apparatus was equipped with a stopcock used only in filling it. These stopcocks are s and 2, 5, 6, 7 and 8.

The mercury pipet C, which was of 98-cc. capacity, had a small cap f with a two-millimeter hole through the top. The cap could be removed when it was necessary to clean C.

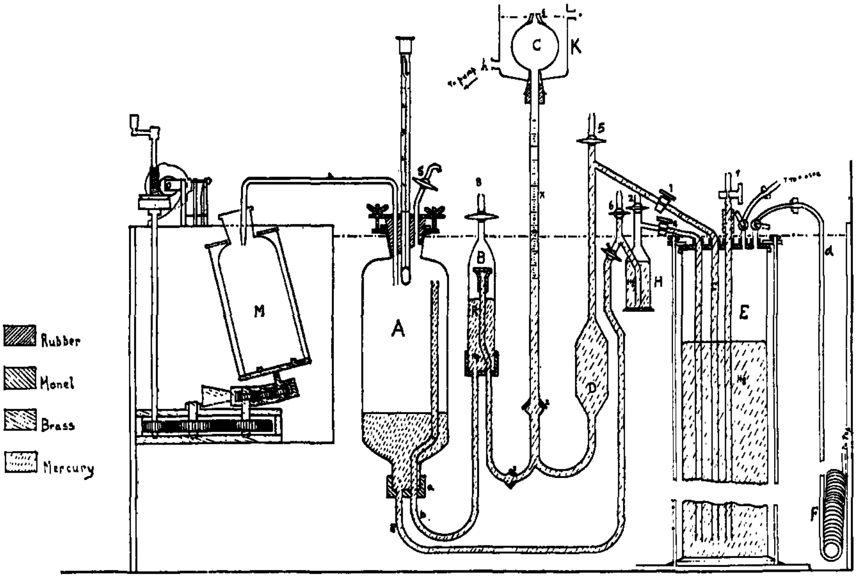

Fig. 1.

Before a bottle had been put in place at M, the operator stopped the exit of e with a finger and opened Stopcock 1. Mercury then flowed upward in C to fill it. Stopcock 1 was then closed and the hole at f was closed with a finger, the operator being careful to leave no air bubble in C. The tip of e was then released and prepared for the discharge of a sample from A in the manner used commonly for pipets. The operator removed his finger from f at the desired instant, thus permitting the entrance of air to C and the discharge of mercury from C through R into the water layer in the top of B. An equal quantity of mercury was simultaneously discharged into A. R was a monel metal cap carrying an adjustable annular slit so narrow that the momentum acquired by the falling mercury in C was expended in forcing the last portion through the aperture into water. With this device the mercury in C descended quietly to a position of rest at a nearly constant level in the graduated stem of C, and a reading was quickly made of the exact location of the meniscus in order to determine the exact volume discharged from A to M. The valve R was designed and made for us by Captain A. de Khotinsky, now of Pentwater, Michigan, who was associated with this Laboratory at the time this work was done.

When an experiment was begun the apparatus had already been filled with mercury to the levels shown in Fig. 1 except in the case of Flask A, which was empty. The lugs of the cover of A (see diagram) had been unscrewed and the stopper with its equipment of Beckmann thermometer, discharge tube e and air tube had been removed. After the reaction mixture had been prepared in A, the stopper, etc., was clamped in place, mercury was forced into A from E through C and B until all the air was displaced in A, the last bubbles under the stopper being forced out through stopcock s, which was then closed for the remainder of the experiment. The diagram shows the apparatus ready for the first discharge of a measured sample of the reaction mixture.

Constant temperature in C was maintained by means of the water jacket K through which water was pumped from the thermostat in which the main apparatus stood.

The bulb "D" was simply a trap to prevent grease from Stopcock 1 from being carried into C.

The chamber H contained a constant quantity of air under pressure imposed by opening Stopcock 4, thus connecting H with E. When Stopcock 4 was closed and 3 was opened the air compressed in H forced the required amount of mercury into A, thus causing fresh liquid to displace that already in the discharge tube, e. This operation was carried out just before taking a reaction mixture sample. H could be dispensed with when economy of material was not important.

The advantage of the above-described apparatus over that first used in this Laboratory[1] was that greater ease and speed of operation were possible with it. Only when it was necessary to remove samples every minute was more than one operator needed. Under these conditions two were required instead of three as with the older form.

Another apparatus that simplified work, this time of titration, was the mechanical shaker already referred to. This could be used as shown in Fig. 1 or to shake the samples during titration. The sample taken from the reaction mixture was always discharged into a measured amount of hydrochloric acid sufficient in quantity to more than neutralize the free base present. The titration of the excess acid, which was acetic acid because of double decomposition of hydrochloric acid with sodium acetate, required careful observation of the end-point, as the solutions were dilute. This was made tedious by the necessity of removing mist from the surface of the container, which was at 0° (see ref. 1 for these details).

Captain de Khotinsky, therefore, designed and made for us the shaker in question. It was controlled by a foot switch so that the operator had both hands free for the necessary manipulations. The efficiency of shakers of this type is evinced by the fact that they are still in use (1915–1928) at this Laboratory in cases where the titration samples are large and the observation of the end-point is difficult.

The construction of the shaker, shown at M of Fig. 1, is described briefly as follows. The titration bottle is supported on a circular base and held in place by two rods connected to a semicircular collar that easily slips into place around the neck of the bottle. This circular base is mounted at a slight angle to the horizontal on one end of a counterbalanced frame which is made to whirl by an intermittent electric clutch driven by a small motor (not shown in the diagram). The angle of the base is so adjusted to the height of the bottle that while the base of the bottle is moving in a circle, the opening in its neck does not change its position and thus permits the presence of the buret tip without contact with the neck of the bottle. Thus the frame and the bottle revolve about a perpendicular line (see dotted line at M of Fig. 1) while an equal counter rotation of the bottle itself, produced by a series of compensating gears, prevents the bottle from revolving about its own axis. The advantage of this is that the liquid is whirled within the bottle and not with the bottle. The clutch is made intermittent because a continuous whirling motion causes the liquid to form layers at the sides of the bottle without mixing with the solution which is being added.

We take pleasure in acknowledging here our indebtedness to Captain de Khotinsky for the design of the valve and shaker.

Results

Coefficients of the rate of the reaction were calculated by means of the following integrated form of the bimolecular reaction equation

$$k = [2.303/(t_2 - t_1)(B - E)] \log (B - X_1)(E - X_2)/(B - X_2)(E - X_1) \quad (1)$$

The initial concentration of ester and base are indicated by the letters B and E, respectively; the concentration of ester or base changed up to the time t is called X; K is the coefficient of the reaction.

In Table I are given the results of a representative experiment. The term $(b-x)$ is the composition of the solution with respect to base in terms of f, the normality of standard acid, which was 0.009917. Obviously $(b-x)f = (B-X)$ but the implied multiplication is not carried out since f would subsequently be canceled when $(B-X)$ is substituted in the above equation. The term $(b-e)$ is the composition of the solution at the end of the reaction in terms of f. Obviously $(E-X) = f[(b-x) - (b-e)] = f(e-x)$, e being the concentration of the ester in terms of f, and $(e-x)$ may be used in place of $(E-X)$ in Equation 1. The value of B given in the table was calculated from the dilution of the stock solution used to make the reaction mixture.

TABLE I

RESULTS OF A REPRESENTATIVE EXPERIMENT

Time	$(b - x)$	Temp., °C.	K (2.050 = t_1)	K (2.800 = t_1)	K (3.604 = t_1)
2.050	0.8552	24.967			
2.800	.8135	24.970			
3.604	.7756	24.976			
6.917	.6550	24.986	11.64	11.59	11.63
7.992	.6255	24.988	11.64	11.61	11.64
8.908	.6027	24.990	11.67	11.65	11.68
9.900	.5817	24.995	11.61	11.58	11.60
10.925	.5608	24.994	11.64	11.62	11.64
12.112	.5399	24.994	11.63	11.60	11.62
		Av.	11.641	11.614	11.639

$f = 0.009917$

$B = 0.0094$

$(b-e) = 0.2691$

Av. temperature 24.983°. $K_{25.00} = 11.64$.

In Table II is given a survey of experiments. In Part 1 are given the results for temperature close to 25.00° and in Part 2 are given results at temperatures near 25.20°. From the average of the two series at coefficient of 0.0087 per 0.01° change of temperature was obtained. By means of this all results (except those at 25.20°, Part 2) are corrected to 25.00°.

In Part 3 of the table are the results of experiments done under photographic dark room conditions as described elsewhere.[5] It will be seen that

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[5] Gooch, THIS JOURNAL, 49, 2257 (1927).

TABLE II

SUMMARY OF THE RESULTS OF THE FIRST SERIES OF EXPERIMENTS (1915)

B	E	Temp. (average), °C.	K	$K_{25.00}$
		Part 1		
0.01000	0.00792	24.979	11.674	11.690
.00994	.00726	24.983	11.631	11.644
.00994	.00789	24.980	11.604	11.621
.01009	.00763	24.980	11.650	11.667
.01009	.00728	25.000	11.677	11.696
.01009	.00749	24.975	11.688	11.710
.01009	.00778	24.974	11.709	11.731
.01009	.00785	24.970	11.689	11.714
.01010	.00785	24.962	11.647	11.684
.01010	.00779	24.994	11.669	11.674
.01010	.00788	24.989	11.610	11.619
.01010	.00760	24.975	11.652	11.674
.01011	.00753	24.988	11.654	11.664
.01011	.00803	24.988	11.664	11.674
.01011	.00815	24.990	11.632	11.644
			Av.	11.674
		Part 2		
0.01001	0.00810	25.190	11.799	
.01011	.00765	25.195	11.874	
.01011	.00788	25.178	11.829	
.01011	.00799	25.186	11.839	
	Part 3 (Experiments under dark room conditions)			
0.01010	0.00780	24.997	11.650	11.650
.01010	.00802	24.987	11.612	11.624
.01010	.00770	24.989	11.664	11.674
			Av.	11.649
		Part 4		
0.02003	0.01747	25.010	11.629	11.620
.02003	.01692	25.009	11.624	11.606
.02003	.01665	25.000	11.644	11.644
.02007	.01488	25.006	11.792	11.697
.02007	.01553	24.988	11.674	11.684
.02007	.01589	25.000	11.642	11.642
			Av.	11.649

as in the case of ethyl acetate diffuse daylight has no effect on the speed of the reaction.

In Part 4 are given the results of experiments with mixtures near to 0.02 molar with respect to sodium hydroxide and 0.016 with respect to ester. The difference between the first series of Part 1 and this series is slight and within the limits of experimental error.

Table III gives the results of experiments carried out one year later than the others. The results will be seen to be in good agreement with the earlier ones.

Table III

Summary of Results of the Second Series of Experiments (1916)

B	E	Temp. (average), °C.	K	$K_{25.00}$
		Part 1		
0.01003	0.00758	25.018	11.765	11.748
.01003	.00741	25.026	11.670	11.678
.01003	.00750	25.020	11.731	11.714
.01000	.00754	25.025	11.724	11.702
			Av.	11.710
		Part 2		
0.02012	0.01621	25.031	11.760	11.733
.02012	.01595	25.048	11.727	11.684
.02012	.01607	25.042	11.669	11.634
.01974	.01602	25.045	11.757	11.717
.01986	.01723	25.090	11.739	11.662
			Av.	11.686

The widest deviation of value of $K_{\text{obs.}}$ in a single experiment was 1.63%. The average deviation was 0.93%. The maximum deviation of the mean coefficient of each experiment from the average of all is 0.65%. The expected error in timing and measurements of samples was 0.75%. Therefore it may be stated that the value 11.67 has an error not greater than 1%.

Comparison of Results with the Work of Others.—Although various workers[6] have made measurements on the reaction under consideration, only one experiment, that of Walker,[7] is comparable with the present experiments. Professor Walker used the conductivity method. Although he felt uncertain of the first and last quarter of his experiment and his results varied as much as 3%, still his average coefficient was 11.7, differing from the value obtained in this work by only 0.3%.

Summary

Measurements are reported of the rate of saponification of methyl acetate at 0.008 and 0.016 molarity in aqueous solutions of sodium hydroxide of 0.01 and 0.02 molarity, respectively. The coefficient of the reaction for 25.00° was found to be 11.67 moles per minute with a possible error not greater than 1%. It was demonstrated that diffuse daylight has no effect upon the rate of the reaction.

[6] Reicher, *Ann.*, **228**, 278 (1885), experiments at 9.4°; Bugarsky, *Z. physik. Chem.*, **8**, 398 (1891), measurements at 19.4°; Volkmann, "Dissertation," Freiburg, i/Br, experiments at 0, 10, 20, 30, 40 and 50°.

[7] Walker, *Proc. Roy. Soc. London*, **78A**, 158 (1906).

Two special pieces of apparatus are described. One is a machine for the rapid measurement of samples of a solution without exposure of the latter to air. The other is a device for shaking a solution while it is being titrated.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF PRINCETON UNIVERSITY]

A NEW QUALITATIVE REAGENT FOR SODIUM

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It is generally acknowledged that the usual methods for detecting sodium in qualitative analysis are far from satisfactory. The flame test is much too sensitive in that it fails to show whether sodium is present as an essential constituent or whether it is present in traces as an accidental impurity, while the pyroantimonate test is not sufficiently sensitive in the presence of large amounts of potassium and in other respects is an unsatisfactory reagent.

The possibilities suggested by Streng's[1] discovery of a specific microscopical reagent for sodium have not been generally appreciated. This worker found that a solution containing properly adjusted quantities of uranyl acetate, magnesium acetate and acetic acid formed characteristic crystals of a sodium–magnesium uranyl triple acetate when added to solutions containing sodium ions. Streng also noted that certain other bivalent metals might be substituted for magnesium in this reaction and this observation suggested, in part, the present experimental work.

In 1923 Blanchetière[2] devised a magnesium–uranyl acetate reagent that could be used as a precipitant for sodium in ordinary analysis. Kolthoff[3] improved this reagent and tested its value for qualitative purposes. These results were confirmed by Crepaz.[4] Noyes and Bray[5] also showed the value of Blanchetière's magnesium–uranyl acetate reagent as a confirmatory test for sodium in systematic qualitative analysis. In 1927 Kolthoff[6] described a reagent of the same type in which zinc was substituted for magnesium and found that this was an even more sensitive reagent for sodium.

While the two reagents mentioned above are quite sensitive toward sodium, they possess the disadvantage of giving precipitates with potassium when moderate amounts of this ion are present in the solution tested,

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[1] A. Streng, *Z. wiss. Mikroskop.*, **3**, 129–130 (1886); *Chem. Zentr.*, **17**, 488 (1886).

[2] A. Blanchetière, *Bull. soc. chim.*, **33**, 807–818 (1923).

[3] I. M. Kolthoff, *Pharm. Weekblad*, **60**, 1251–1255 (1923).

[4] E. Crepaz, *Ann. chim. applicata*, **16**, 219–224 (1926).

[5] A. A. Noyes and W. C. Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Company, New York, **1927**, pp. 258 and 472.

[6] I. M. Kolthoff, *Z. anal. Chem.*, **70**, 397–400 (1927).