Kinetic Study of the Hydrolysis
of Cellulose Acetate in the pH Range of 2–10

KENNETH D. VOS, FLOYD O. BURRIS, JR., and ROBERT L. RILEY,
*General Atomic Division of General Dynamics Corporation, John Jay Hopkins
Laboratory for Pure and Applied Science, San Diego, California*

Synopsis

A kinetic study of the hydrolysis of 39.8 wt.-% acetyl cellulose acetate has been made
as a function of pH and temperature over the pH range of 2.2–10 and temperature range
of 23–95°C. The hydrolysis reaction was carried out on highly porous membranes under
quasihomogeneous conditions and the data have been treated as a pseudo-first-order reac-
tion in acetyl concentration. The reaction can be represented by the equation $k_1 =
k_{H^+} [H^+] + k_{OH^-} [OH^-] + k_{H_2O}$, and where $k_{H^+} = 5.24 \times 10^5 \exp \{ -16.4 \times 10^3/RT \}$,
$k_{OH^-} = 1.55 \times 10^4 \exp\{ -8.1 \times 10^3/RT \}$, and $k_{H_2O} = 4.25 \times 10^{-2} \exp\{ -11.5 \times 10^3/
RT \}$ (where the quantities in brackets are activities of the ions shown).

Introduction

Hydrolysis rate studies of esters have been made for many years. These
studies have not, in general, been concerned with the measurement of the
hydrolysis rate under near neutral conditions. The hydrolysis studies of
cellulose acetate are no exception to this statement. Although there are
several papers[1–4] concerned with the hydrolysis of cellulose acetate, these
studies have examined the reaction under rather extreme conditions of
pH. When the reaction is studied on fibers and films, as has sometimes
been done, the diffusion of the components into and out of the reaction site
may be rate determining. In these heterogeneous experiments the differ-
ence between the "amorphous" and "crystalline" regions has been studied.[5]

The hydrolysis study reported in this paper was made on cellulose acetate
under more nearly neutral pH conditions. The effect of pH and tempera-
ture on the reaction was examined over the pH range of 2.2–10 and the
temperature range of 23–95°C.

Experimental

Approximately 6.5 g. of Eastman E-398-3 cellulose acetate in the form
of reverse osmosis membranes[6] was placed in a series of flasks, each con-
taining one liter of buffered water preheated to the desired temperature.
The buffer solutions are listed in Table I. Each flask was placed in a
constant-temperature bath (±1°C.), and at designated intervals about
1.3 g. of membrane was removed. When the membrane samples were

TABLE I
Buffer Systems Used in Kinetic Studies of the Hydrolysis
of Cellulose Acetate Membranes

pH at room-temperature	Buffers
2.2	$0.40M$ citric acid, $0.075M$ Na_2HPO_4
3.0	$0.0659M$ citric acid, $0.0341M$ Na_2HPO_4
4.0	$0.0615M$ citric acid, $0.060M$ Na_2HPO_4
5.1	$0.0485M$ citric acid, $0.0735M$ Na_2HPO_4
6.0	$0.0378M$ citric acid, $0.088M$ Na_2HPO_4
7.0	$0.039M$ NaH_2PO_4, $0.0305M$ Na_2HPO_4
8.1	$0.375M$ H_3BO_3, $0.075M$ NaOH
9.0	$0.025M$ H_3BO_3, $0.011M$ $Na_2B_4O_7$
9.0	$0.238M$ $NaHCO_3$, $0.050M$ Na_2CO_3
9.9	$0.10M$ $NaHCO_3$, $0.10M$ Na_2CO_3

removed, a sample of the solution was taken to make a room-temperature check of the pH.

The acetyl content of the membrane was measured by the modified Eberstadt method as outlined by Genung and Mallatt.[7] The only modification of the method was a very thorough washing of the sample before drying and weighing. When this procedure was used on the control samples, which were run with each set of determinations, a value of 39.7 ±0.2 wt.-% acetyl was obtained; this was in good agreement with the stated acetyl content of the starting material. The final acetyl measurement of each run was, in general, approximately 34%. On some of the runs with the slowest rates, the final acetyl measurement was 36 or 37%.

Because one of the hydrolysis reaction products is acetic acid, the pH of the solutions tended to decrease during the experiments. The average change in the pH of the solutions from the beginning to the end of the experiment was ≤0.1 pH unit, with the pH 8 and 9 buffers showing the largest change. The maximum pH change observed in any of the experiments was 0.3 pH units.

Because of the change in the dissociation constants of the buffering agents and water with temperature, the pH of the solutions is temperature-dependent. The change in pH with temperature was measured on samples of each buffer solution by using a Beckman Zeromatic pH meter, and fiber junction Ag|AgCl and amber glass electrodes, the buffers given by Bates[8] being used to standardize the electrodes at each temperature. The resultant curves were used to correct the room-temperature pH values to the experimental temperatures. The estimated accuracy of the pH measurements is ±0.1 pH units.

Results and Discussion

In Figure 1 the results of a typical hydrolysis run are given as natural logarithm of weight-per cent acetyl versus time. The pH 6 run at 95°C.,
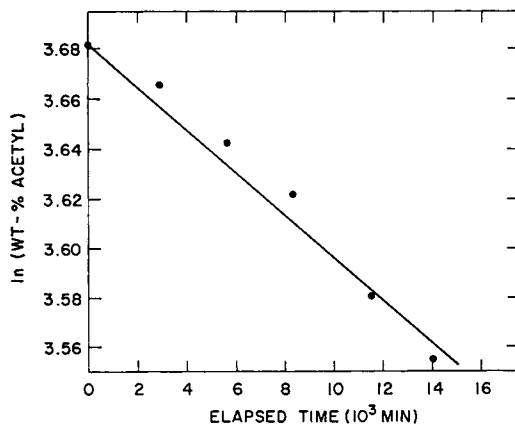
Fig. 1. pH 6 hydrolysis at 95°C.

shown in this figure, has been plotted as a first-order reaction in acetyl concentration.

The cellulose acetate used in these experiments was in the form of reverse osmosis membranes,[8] which are approximately 60% porous[9] with pores of less than 1 μ diameter.[10] The diffusion coefficient of water in Eastman E-398-3 cellulose acetate is 1.6×10^{-6} cm.^{2}/sec. at 25°C. and has an activation energy of 4.2 kcal./mole[9] (the diffusion coefficient of water in water is 2.4×10^{-5} cm.^{2}/sec. at 25°C.[11]). Since the greatest distance water must travel in the cellulose acetate is approximately 0.25 μ,[10] the water can be exchanged in only 4×10^{-4} sec. The diffusion coefficient of acetic acid, the product of the hydrolysis reaction, may be somewhat slower than that for water but is probably not a factor of 1000 slower (the diffusion coefficient of NaCl in this cellulose acetate is 1×10^{-9} cm.^{2}/sec. at 25°C.[9]). The water and the acetic acid, then, rapidly reach equilibrium with the bulk water. The reaction is thus considered to be quasihomogeneous; i.e., there are two phases present, but the reaction is not diffusion-limited.

The saponification of esters is, in general, a second-order reaction, dependent on the concentrations of the ester and water. In the systems used here, water activity was essentially constant throughout each run. These considerations and plots of the type given in Figure 1 have led us to treat the hydrolysis of cellulose acetate under these conditions as a pseudo-first-order reaction. The results obtained are listed in Table II. The uncertainties given in Table II are the standard deviations of the least-squares fit of the best straight line through the data.

The rate expression must, of course, be written to contain molar concentration units instead of the weight-per cent units of Figure 1. However, in the limited acetyl range studied here, while weight-per cent acetyl is not exactly proportional to moles acetyl per mole anhydroglucose units, it should be sufficiently near for our purposes. Since the data have been

TABLE II
Experimental Values of Hydrolysis Rate Constants

pH[a]	Temperature, °C.	k_1, sec.$^{-1}$
pH 2.2	91	$2.90(\pm0.18) \times 10^{-7}$
	81	$1.47(\pm0.10) \times 10^{-7}$
	74	$1.20(\pm0.15) \times 10^{-7}$
	50	$2.62(\pm0.22) \times 10^{-8}$
pH 3.0	95	$4.77(\pm0.16) \times 10^{-8}$
	83	$3.48(\pm0.15) \times 10^{-8}$
	71	$1.30(\pm0.09) \times 10^{-8}$
	51	$4.00(\pm0.36) \times 10^{-9}$
pH 4.0	95	$1.34(\pm0.14) \times 10^{-8}$
	83	$9.87(\pm3.45) \times 10^{-9}$
	72	$3.26(\pm0.89) \times 10^{-9}$
	52	$1.33(\pm0.09) \times 10^{-9}$
pH 5.1	95	$3.06(\pm0.18) \times 10^{-8}$
	83	$1.50(\pm0.72) \times 10^{-8}$
	71	$5.54(\pm1.07) \times 10^{-9}$
pH 6.0	95	$1.46(\pm0.09) \times 10^{-7}$
	95	$1.23(\pm0.06) \times 10^{-7}$
	83	$6.68(\pm0.89) \times 10^{-8}$
	72	$1.92(\pm0.14) \times 10^{-8}$
pH 7.0	91	$5.69(\pm0.36) \times 10^{-7}$
	83	$3.66(\pm0.42) \times 10^{-7}$
	83	$5.63(\pm0.22) \times 10^{-7}$
	73	$1.52(\pm0.12) \times 10^{-7}$
	51	$1.93(\pm0.46) \times 10^{-8}$
pH 8.1	95	$5.14(\pm0.11) \times 10^{-6}$
	95	$4.62(\pm0.39) \times 10^{-6}$
	83	$3.65(\pm0.22) \times 10^{-6}$
	73	$1.05(\pm0.11) \times 10^{-6}$
	51	$1.76(\pm0.49) \times 10^{-7}$
	23	$1.92(\pm0.45) \times 10^{-8}$
pH 9.0 (H_3BO_3 + $Na_2B_4O_2$)	94	$1.92(\pm0.17) \times 10^{-5}$
	90	$1.19(\pm0.11) \times 10^{-5}$
	82	$7.60(\pm0.76) \times 10^{-6}$
	71	$3.83(\pm0.38) \times 10^{-6}$
	63	$1.02(\pm0.04) \times 10^{-6}$
	51	$6.69(\pm0.81) \times 10^{-7}$
	23	$1.10(\pm0.13) \times 10^{-7}$
pH 9.0 (Na_2CO_3 + $NaHCO_3$)	85	$3.31(\pm0.13) \times 10^{-5}$
pH 9.9	68	$6.35(\pm0.62) \times 10^{-5}$
	23	$1.33(\pm0.17) \times 10^{-6}$

[a] Measured at room temperature.

treated as a pseudo-first-order reaction, the proportionality constant drops out of the kinetic expression.

The hydrolysis rate has been plotted in Figure 2 as a function of solution pH. The pH values given in Table I are the room-temperature values;
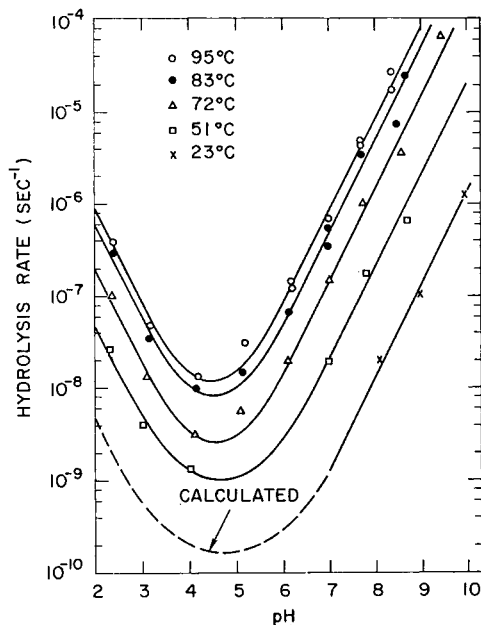
Fig. 2. Hydrolysis rate vs. pH.

the values shown in Figure 2 are these measured values corrected to the temperature of the experiment. The curves drawn through the data have been determined by using the procedure outlined by Garrett[12] and Laidler.[13] They treated the overall reaction rate constant k_1 as the sum of three terms,

$$k_1 = k_{H^+}[H^+] + k_{OH^-}[OH^-] + k_{H_2O} \qquad (1)$$

where k_{H^+} is the acid-catalyzed rate constant, k_{OH^-} is the base-catalyzed rate constant, and k_{H_2O} is the rate of the spontaneous reaction. The quantities in brackets are the activities of the ions shown. Under the low-pH condition, the concentration of hydroxyl ions was sufficiently low that the effect of $k_{OH^-}[OH^-]$ on k_1 was negligible and a value for k_{H^+}

TABLE III
Rate Constants for the Separate Hydrolysis Reactions

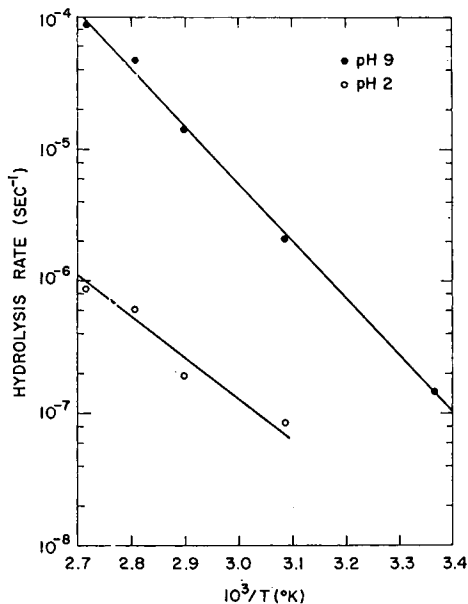| Temperature, °C.	k_{OH^-}, l./mole-sec.	k_{H^+}, l./mole-sec.	k_{H_2O}, sec.$^{-1}$	pH_{min}
95	1.90×10^{-1}	8.54×10^{-5}	6.40×10^{-9}	4.50
83	1.61×10^{-1}	6.25×10^{-5}	4.80×10^{-9}	4.55
72	8.13×10^{-2}	1.94×10^{-5}	1.55×10^{-9}	4.60
51	3.53×10^{-2}	4.60×10^{-6}	8.50×10^{-10}	4.65
23	1.43×10^{-2}	4.08×10^{-7} [a]	1.36×10^{-10} [a]	4.80[b]

[a] Calculated.
[b] Extrapolated.

Fig. 3. Hydrolysis rate vs. $1/T$ for pH 9 and pH 2.

could be calculated. Similarly, under the basic conditions, the catalytic effect of the hydrogen ion was so small that a value for k_{OH^-} could be calculated. The average values determined for k_{H^+} and k_{OH^-} from the low-pH and high-pH data, respectively, are given in Table III. By using these values for k_{H^+} and k_{OH^-} and eq. (1), k_{H_2O} was chosen to make the curves fit the pH 4 data. The k_{H_2O} rate constant data are given in Table III.

The reaction rate minimum will occur when the values of $k_{OH^-}[OH^-]$ and $k_{H^+}[H^+]$ are equal. Since $[H^+]$ and $[OH^-]$ are related through the ionic product of water, Kw, eq. (2) may be derived:[13]

$$[H^+]^2_{min} = (k_{OH^-})(Kw)/(k_{H^+}) \tag{2}$$

where $[H^+]_{min}$ is the hydrogen ion concentration at the reaction rate minimum. These data are also given in Table III. The solid curves in Figure 2 have been determined from eq. (1), using the constants in Table III, and give a reasonable fit to the data. (Some of the points in Figure 2 are interpolations between the nearest experimental temperatures of Table II.) Also shown in Figure 2 is a calculated curve for the hydrolysis rate at 23°C.

In Figure 3, log k_1 versus $1/T$ is given for the base-catalyzed and acid-catalyzed reactions. The values of k_1 are the extrapolated values determined from Figure 2 for pH 9 and pH 2, respectively. The activation energies determined in this way are 20.1 ± 0.5 and 16.4 ± 1.3 kcal./mole for the base- and acid-catalyzed reactions, respectively. This value for

the activation energy of the base-catalyzed reaction is not the activation energy for k_{OH^-} because it is obtained by examining data at constant $[H^+]$, not at constant $[OH^-]$. The data for the dissociation constant of water show that its heat of dissociation is about 12.0 kcal./mole,[14] so the activation energy for k_{OH^-} is only 8.1 kcal./mole. The calculated activation energy for k_{H_2O} is 11.5 ($\pm$1.7) kcal./mole. An adequate representation of the data is

$$k_{H^+} = 5.24 \times 10^5 \exp\left\{-16.4 \times 10^3/RT\right\}$$

$$k_{OH^-} = 1.55 \times 10^4 \exp\left\{-8.1 \times 10^3/RT\right\}$$

and

$$k_{H_2O} = 4.25 \times 10^{-2} \exp\left\{-11.5 \times 10^3/RT\right\}$$

where RT is in units of calories per mole.

The activation energy for the hydrolysis of cellulose acetate has been determined for both the base- and acid-catalyzed reactions under quite different experimental conditions. The base-catalyzed reaction has been studied under homogeneous conditions, and an activation energy of 11.7 kcal./mole has been determined.[3] The acid-catalyzed reaction has been measured under both homogeneous[1,15] and heterogeneous[16] conditions, and an activation energy of approximately 14.4 kcal./mole has been measured. In other studies, the concentrations of reactants were such that it was necessary to employ the second-order rate expression,[1,3] and the reactions were carried out at pH's less than 1[1,4] or greater than 12.[3] Considering these substantial differences in experimental conditions, the activation energies determined in the present work are in reasonable agreement with the other values. Timm and Hinshelwood[17] have presented data showing that a difference in activation energy between the acid- and base-catalyzed reactions is not uncommon in ester hydrolysis. The effect of salts was found to be important in the studies of hydrolysis under acid conditions conducted by Haward and White.[4] In the present work, several different buffers were used. The ionic strength range of the buffers was approximately 0.4–0.8M, and within this range no salt effect appears to be present. However, the effect of large changes in ionic strength was not examined.

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Résumé

Une étude cinétique de l'hydrolyse de l'acétate de cellulose à 39.8 % poids a été effectuée en fonction du pH et de la température dans un domaine de pH variant de 2.2 à 10 et dans un domaine de température de 23 à 95°C. La réaction d'hydrolyse a été effectuée sur des membranes hautement poreuses dans des conditions quasi-homogènes et les résultats ont été traités comme des réactions de premier ordre apparent en concentration en acétyle. La réaction peut être présentée par l'équation $k_1 = k_{H+}(H^+) + k_{OH-}(OH^-) + k_{H_2O}$ où $k_{H-} = 5.24 \times 10^5 \exp -16.4 \times 10^3/RT$, $k_{OH-} = 1.55 \times 10^4 \exp -8.1 \times 10^3/RT$, et $k_{H_2O} = 4.25 \times 10^{-2} \exp -11.5 \times 10^3/RT$ (où les quantités entre parenthèses expriment des activités des ions indiqués).

Zusammenfassung

Eine kinetische Untersuchung der Hydrolyse von Zelluloseacetat mit 39,8 Gewichts% Acetyl wurde als Funktion von pH und Temperatur im pH-Bereich von 2,2–10 und Temperaturbereich von 23–95°C ausgeführt. Die Hydrolysereaktion wurde an hochgradig porösen Membranen unter quasihomogenen Bedingungen durchgeführt und die Ergebnisse als eine Reaktion erster Ordnung in bezug auf die Acetylkonzentration behandelt. Die Reaktion kann durch die Gleichung $k_1 = k_{H+}[H^+] + k_{OH-}[OH^-] + k_{H_2O}$ dargestellt werden, wo $k_{H+} = 5{,}24 \cdot 10^5 \exp \{-16{,}4 \cdot 10^3/RT\}$, $k_{OH-} = 1{,}55 \cdot 10^4 \exp \{-8{,}1 \cdot 10^3/RT\}$ und $k_{H_2O} = 4{,}25 \cdot 10^{-2} \exp \{-11{,}5 \cdot 10^3/RT\}$ und die Grössen in eckigen Klammern die Aktivitäten der betreffenden Ionen sind.