Studies of Chemical Kinetics by Means of the Velocity of Sound. I. The Hydrolysis of Acetic Esters

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The velocity of sound is a function of the density and compressibility of fluids, and it is an important quantity in studying their physical properties. On the other hand, a chemical reaction in a solution causes a change in its compressibility because of the appearance and disappearance of molecular and ionic species. Therefore, the rate of chemical reactions can be determined by sound velocity measurements.

The ultrasonic velocity is one of a few physical quantities which can be determined with a very high degree of accuracy. One of the present authors[1] has determined the amount of ionic hydration and the critical micelle concentration of surfactants by means of a variable-path ultrasonic interferometer, the most accurate apparatus hitherto known for measuring the ultrasonic velocity. One disadvantage of this apparatus is, however, that it takes about one hour for one run of experiments in the velocity measurement. It is difficult, therefore, to trace thereby a rapid change in the sound velocity.

The sing-around method is a newly-develped technique in which the velocity is determined by the frequency measurement. Since the frequency can be determined quickly and precisely by means of the frequency counter, this method has the advantage over that of the interferometer when the velocity of sound varies with time.

In the present study, such chemical changes of a moderate rate as the hydrolysis of esters will be traced by means of the sing-around method.

Apparatus

The sing-around method, originally invented by Shepard and Knock,[2] has been developed recently by Greenspan and Tschieff.[3] The apparatus used in the present study was similar to that reported by the latter workers.

A schematic diagram of the circuit is given in Fig. 1. The principle of the operation of the circuit is as follows: The apparatus consists essentially of a pair of piezoelectric transducers, made of quartz crystals, mounted on both ends of a tube to form a sound path of a fixed length. An unmodulated pulse for starting the operation is generated by a pulse generator and fed to a sending transducer. The pulse received by a receiving transducer is then led to a high-gain pulse-shaping amplifier, and the amplified pulse retriggers the same pulse generator to emit the second pulse. By the repetition of this process, a train of repeated pulses is generated. When the path length is fixed, the frequency of the repeated pulses depends on the propagation velocity of the sound in the sample liquid and also on the circuit delays. The total time delay for a single cycle, τ, is given as:

$$\tau = 1/f = t_e + l/u \qquad (1)$$

where f is the frequency of the pulse repetition; t_e, the sum of electrical delays: u, the velocity of sound, and l, the path length.

The frequency was measured with a frequency counter. The time intervals of the gate for the frequency measurement were made as follows. First 5 Mc. continuous wave was generated by a temperature-controlled crystal oscillator, and then the frequency was lowered to 1 kc. by a multiplier circuit. The frequency of the 5 Mc. oscillator was monitored by the standard frequency of JJY. After it had been modified to the square wave, the 1 kc. wave

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[1] T. Yasunaga, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 87 (1951); T. Yasunaga and T. Sasaki, ibid., **72**, 89 (1951); T. Sasaki, T. Yasunaga and H. Fujiwara, ibid., **73**, 181 (1952).

[2] F. Shepard, Jr., U. S. Pat. 2333688 (1943); W. E. Knock, U. S. Pat. 2400309 (1946).

[3] M. Greenspan and C. E. Tschiegg, *J. Research Natl. Bur. Standards*, **59**, 249 (1957); *Rev. Sci. Instr.*, **28**, 897 (1957).

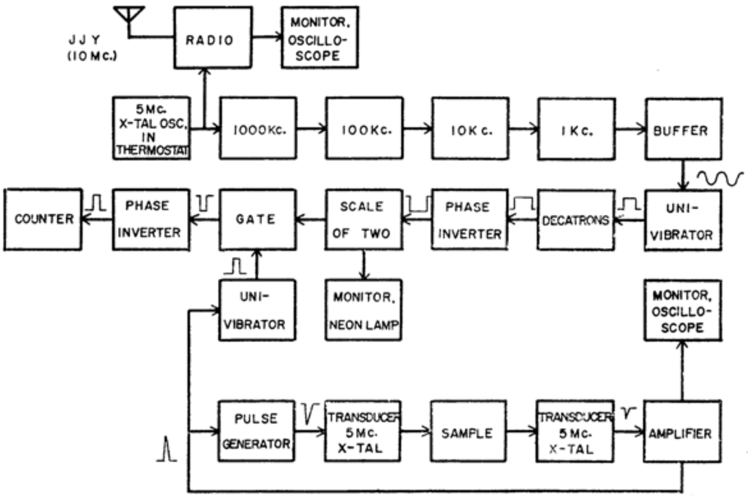

Fig. 1. Block diagram of sing-around velocimeter.

was fed to the decatron circuit to generate the 10 sec. intervals for the gate opening.

The repetition frequency was counted by the counter with six decatrons. The initiating pulse was generated by a blocking oscillator, using a pulse transformer with a ferrite core. The rise time of the pulse was less than 50 mμ sec., while the pulse width was about 200 mμ sec.

The cell shown in Fig. 2 was made of a pyrex tube, 16 mm. and 100 mm. in diameter and length respectively. The transducers, which had the 5 Mc. resonance frequency, were gold-plated x-cut crystals 20 mm. in diameter and 0.8 mm. thick. The grounding was made by thrusting the peripheries of the inner surfaces of transducers against brass rings on the ends of the glass tube. An epoxy resin was used to attach the transducers to the tube and also to protect the rings from the chemical attack.

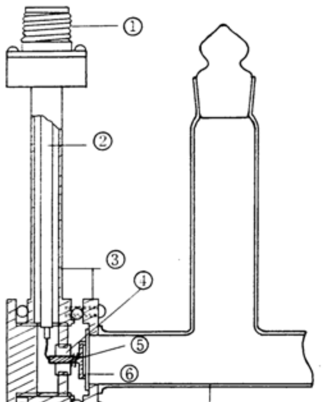

Fig. 2. Sectional diagram of one end of the cell, (1) connector, (2) coaxial cable, (3) brass, (4) polystyrene, (5) spring, (6) 5 Mc. quartz crystal, (7) neoprene O-ring, (8) pyrex tube.

The stability of the apparatus was examined by using water at 30±0.002°C for about thirty hours. The results given in Table I show that the sing-around velocimeter works steadily for a prolonged period with a high degree of accuracy. Since it requires only ten seconds to measure the sound velocity each time, slight and rapid changes in velocity in the solutions with respect to the reaction time can be traced continuously with a high degree of accuracy.

TABLE I. CHANGE IN THE REPETITION FREQUENCY IN WATER WITH TIME AT 30±0.002°C

Time, hr.	2	3	5	7	24	27	31
f, cycl./sec.	15766.5	15766.4	15766.6	15766.6	15766.6	15766.4	15766.6

Experimental

Both methyl and ethyl acetates were used in this study. In one flask, an aqueous solution of a reactant was prepared and in the other a hydrochloric acid solution was placed, separately. After thermal equilibrium was reached, the two solutions were mixed together in one of the flasks, and then the counting of the reaction time was started. Then the mixture was transferred into a measuring cell immersed in advance in the same thermostat, and the change in the repetition frequency with the reaction time was traced by the frequency counter. The concentration of acetic acid in the equilibrium mixture was determined by titration with dilute sodium hydroxide.

Chemically pure grade reagents were used without further purification.

Results and Discussion

In Figs. 3a and 3b, the pulse repetition frequencies during the reaction period are plotted against the reaction time. As may be seen from the figures, the frequency increases with time for ethyl acetate, while it decreases with time for methyl acetate.

These reactions can be expressed as follows:

$$CH_3COOR + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3COOH + ROH \tag{2}$$

and they are obviously bimolecular and reversible, although they can be treated as monomolecular in a dilute aqueous solution. The differential equation follows:

$$\mathrm{d}x/\mathrm{d}t = k_1(b-x)(w-x) - k_2x^2 \tag{3}$$

where b is the initial concentration of an ester; x, the decrease in concentration after time t; w, the concentration of water, and k_1 and k_2, the velocity constants of hydrolysis and esterification respectively. Writing $k_2/k_1 = K$, the equilibrium constant, where:

$$K = (b-x)(w-x)/x^2 \tag{4}$$

we can integrate Eq. 3 as:

$$\ln[\{A+(w+b)+2(K-1)x\}/\{A-(w+b)-2(K-1)x\}] = Ak_1t + \ln[\{A+(w+b)\}/\{A-(w+b)\}] \tag{5}$$

where

$$A = \sqrt{(w+b)^2 + 4(K-1)wb}$$

If it is assumed that the change in the sound velocity is proportional to that in the concentration, the following expression results for ethyl acetate:

$$X \propto (u-u_0) \tag{6}$$

where u_0 is the sound velocity at $t=0$. From Eq. 1, the difference in the sound velocities may be given as:

$$u-u_0 = l(f-f_0)/\{1-t_e(f+f_0)+ff_0t_e^2\} \tag{7}$$

where f_0 is the repetition frequency at $t=0$. For the present apparatus, t_e, f and l are $4\times10^{-8}\,\mathrm{sec}^{-1}$, 1.5×10^4 cycl./sec. and 10 cm. respectively, and the terms $t_e(f+f_0)$ and $ff_0t_e^2$ in Eq. 7 are both negligible in comparison with unity. The term $(u-u_0)$ is, therefore, proportional to $(f-f_0)$. Thus,

$$x = \alpha(f-f_0) \tag{8}$$

where α is a constant. Consequently, Eq. 5 reduces to:

$$\ln[\{A+(w+b)+2\alpha(K-1)(f-f_0)\}/\{A-(w+b)-2\alpha(K-1)(f-f_0)\}] = Ak_1t + \ln[\{A+(w+b)\}/\{A-(w+b)\}] \tag{9}$$

The left hand side of Eq. 9 is plotted against the reaction time in Fig. 4, and the value of

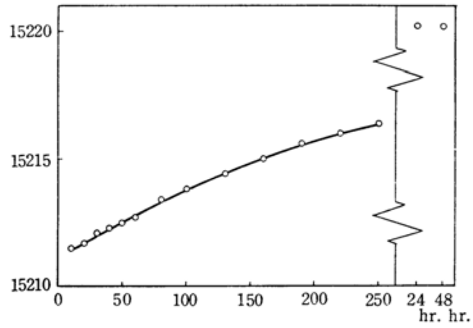

Fig. 3a. Change in velocity of sound with reaction time for ethyl acetate (25°C).

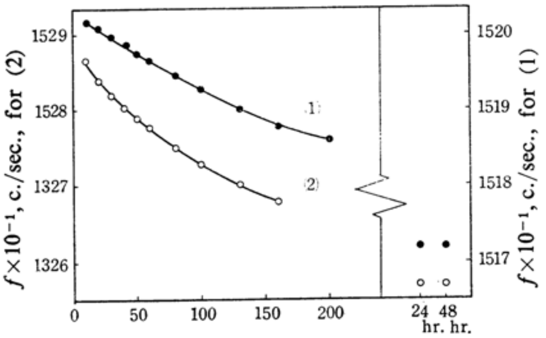

Fig. 3b. Change in velocity of sound with reaction time for methyl acetate, (1) 25°C, (2) 30°C.

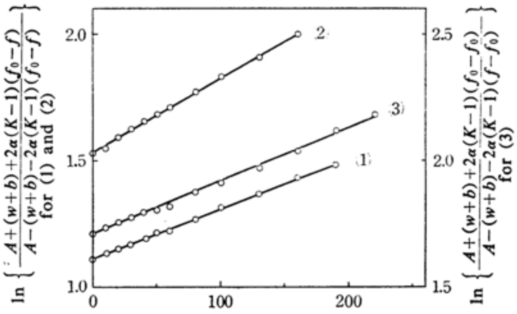

Fig. 4. The diagram of the hydrolysis of esters, (1) methyl acetate (25°C), (2) methyl acetate (30°C), (3) ethyl acetate (25°C).

f_0 is estimated by extrapolating f to $t=0$ in Figs. 3a and 3b. For methyl acetate the following equation holds instead of Eq. 8:

$$x=\alpha(f_0-f) \qquad (10)$$

The value of α can be obtained from Eq. 11:

$$x_\infty=\alpha(f_\infty-f_0) \text{ or } x_\infty=\alpha(f_0-f_\infty) \qquad (11)$$

where x_∞ and f_∞ are the concentration of products and the repetition frequency in the equilibrium state respectively. The measured points fall on a straight line for each one of the hydrolysis reactions studied in the present paper, as is shown in Fig. 4. The values of k_1 and k_2 obtained from the data given in Fig. 4 are listed in Table II, where those values reported by others are also included. As may be seen in the table, the values of the rate constant obtained in this study are in good agreement with those determined by other methods. The present results confirm that the sound velocity measurement by the sing-around method is applicable to the study of the chemical kinetics of such simple reactions as the hydrolysis of acetic esters. Further, it may also be expected that the present method can be extended to the study of faster reactions.

TABLE II. THE RATE CONSTANTS

Temp. °C	Initial concn. M	Concn. of HCl N	k_1 (M min.)$^{-1}$	k_2 (M min.)$^{-1}$
Methyl acetate				
25	0.595	0.547	6.23×10^{-5}	5.67×10^{-4}
30	0.595	0.547	12.2×10^{-5}	4.66×10^{-4}
24.3[4]	0.6857	0.5	6.23×10^{-5}	2.84×10^{-4}
Ethyl acetate				
25	0.490	0.565	8.84×10^{-5}	3.25×10^{-4}
25[5]	0.47	0.473	6.005×10^{-5}	2.25×10^{-4}
25[5]	0.47	0.660	8.603×10^{-5}	3.22×10^{-4}

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[4] B. O. Griffith, W. Cudmore and M. Lewis, *J. Chem. Soc.*, **109**, 67 (1916).

[5] H. S. Harned and R. Pfanstiel, *J. Am. Chem. Soc.*, **44**, 2193 (1922).