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On the Effect of Ultrasonic Waves on Aqueous Solutions of 2-Chloro-Ethanol

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The present investigation deals with the influence of ultrasonic waves on the rate of hydrolysis of 2-chloro-ethanol (ethylene chlorohydrin) in pure aqueous solution at practically constant temperature. The experiments have been performed mainly with ultrasonic waves of frequency 0.8 Mcps.

The acoustic power from the transducer has been calculated from the radiation pressure, which is measured with a radiometer. It is established that the reaction is promoted in the ultrasonic field and the velocity of the reaction has been found dependent on certain experimental variables (the acoustic power, the concentration of 2-chloroethanol, and the ultrasonic field, *i. e.* the experimental arrangement).

The rate constant has been expressed by the experimental variables in a joint interpolation formula.

When certain alkyl halides, *e.g.* $C_2H_4Cl_2$, $CHCl_3$, $CHBr_3$, CCl_4 *etc.* are subjected to intense ultrasonic waves in aqueous solution (saturated with air)[1] the action of the ultrasonic waves is revealed by a partial liberation of halide from the alkyl halides. This effect has not been considered as being due to the oxidizing properties acquired by water containing air, when exposed to ultrasonic irradiation [2,3], and should thus be the result of a specific action of the ultrasonic waves on the alkyl halides. However, information in the literature about the action of the ultrasonic waves is often of a qualitative character and in particular there is not sufficient information about the sonic field.

The alkyl halides mentioned above are more or less insoluble in water, which reduces the experimental possibilities. Experiments with soluble chloro compounds such as chloroethanoic acid and 2-chloro-ethanol, however, have shown that these compounds in pure aqueous solution also partly liberate chloride ions, when exposed to ultrasonic waves. However, it should be noted that

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2-chloro-ethanol, without the influence of ultrasonic waves, is hydrolyzed very slowly in pure aqueous solution and that the reaction follows 1'-order kinetics to high degrees of conversion [4]. The reaction in the ultrasonic field could be due to such a hydrolysis, which is somehow accelerated by the ultrasonic waves. The present investigation deals with the rate by which chloride ion is formed in pure aqueous solutions of 2-chloro-ethanol subjected to ultrasonic waves under different experimental conditions, and with the dependence of the rate constant on certain experimental variables.

EXPERIMENTAL

In the present investigation the ultrasonic waves were generated by a Siemens sonostat universal piezoelectric generator, which is able to produce ultrasonic waves of the frequencies 0.8 and 2.4 Mcps corresponding to the 1′ and 3′ harmonic mode of vibration and deliver acoustic powers from 2 to 50 watts from a quartz with a radiating surface of 10 cm^2. A cross-section of the experimental arrangement is illustrated in Fig. 1. Since the ultrasonic field plays an important role in the experiments, it is necessary to be careful, in particular when transferring the ultrasonic waves to the test-samples. This transfer is carried out as follows. The transducer (1) is inserted into the bottom of a water thermostat (2). A cylinder made up of two parts, which forms a container in connection with the transducer (3), is mounted on top of the transducer. The lower narrow part, which fits on to the transducer, consists of a short cylinder provided with a packing groove, which is secured with a bayonet socket and a packing ring without causing injury to the transducer. The upper wider part is screwed on to the lower part, the former being provided with windows to ensure lighting inside the container. Another cylinder (6) of inner diameter 45 mm and with double walls so that the cylinder can be cooled by conducting a flow of water between the walls, is inserted inside this outer container. This reaction cylinder may be closed below by some sort of membrane ("acoustic window"), *e. g.* 0.05 mm triacetate foil * (5), which is distended between the cylinder and a screwed cap, and then constitutes a reservoir for the samples. This inside silverplated reaction cylinder is kept in a fixed position vertical to the transducer by a ring (4), which also provides for a practically constant distance between the transducer and the liquid surface of the sample (7) in the cylinder. The distance between the transducer and the membrane is about 50 mm. When the ultrasonic waves are transmitted vertically from the transducer through the "acoustic window" into the sample in the reaction cylinder, the space between the transducer and the membrane and around the reaction cylinder is filled up by water carefully freed from dissolved air. It is convenient to use such water, since the ultrasonic waves otherwise liberate small air bubbles from the water, which rise below the membrane and have a scattering effect.

When the sample in the reaction cylinder and the water between the transducer and the membrane are influenced by the ultrasonic waves the temperature immediately rises due to absorption. It is therefore necessary to use automatic cooling to keep the temperature practically constant in the sample during the experiment. This has been done by conducting cooling water through the reaction cylinder when the temperature in the sample rises. The flow of cooling water is directed by means of a Cu-constantan thermocouple with the junctions placed in the sample and in the water thermostat, respectively, (8), combined with a photo relay and a magnet valve. During the experiments the temperature in the sample is recorded by the voltage of a thermo-couple with the junctions placed in the sample and in crushed ice (9), respectively, on a "Speedomax"-recorder Type G. It is thus possible to keep the temperature practically constant to $25.0° \pm 0.8°$ C; otherwise the temperature would rise about 10 degrees.

In an experiment the sample, usually 50 ml, is treated for a definite time in the reaction cylinder, observing, before and after the treatment, the absence of air bubbles below the membrane. After the treatment the constancy of the volume of sample is also observ-

* The foil has been demonstrated to be impermeable to chloride ions.

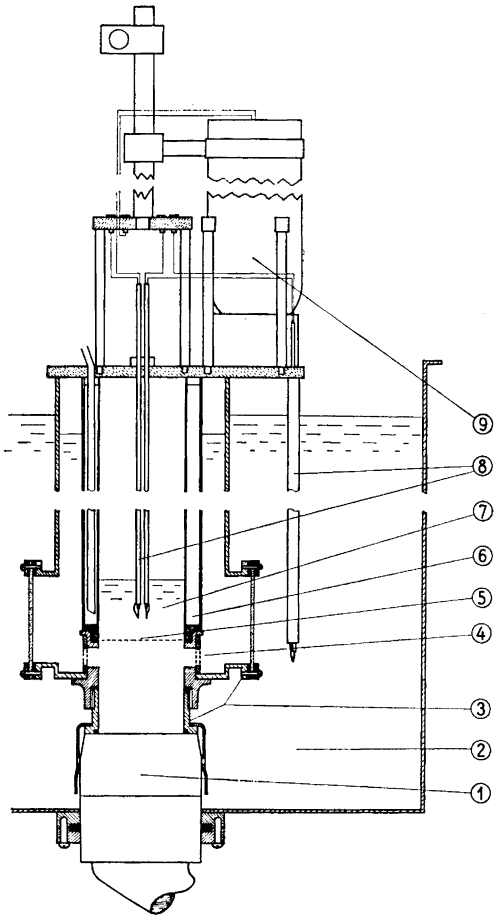

Fig. 1. Experimental arrangement in cross-section: 1, Transducer; 2, Water thermostat; 3, Outer container; 4, Distance-ring; 5, Membrane, "Acoustic window"; 6, Reaction cylinder; 7, Sample; 8, Thermo-couples; 9, Dewar flask for crushed ice.

ed to ensure that the sample has not been inadvertently diluted by water from the outer container, after which the chloride ions in a 20.0 ml sample are titrated with a 0.0028 N mercuric nitrate solution. Diphenylcarbazone is employed as indicator. This produces a red-purple color with excess of mercuric ions [5] in dilute acid solution. The color change during the end of the titration was followed by means of a Lange photoelectric colorimeter, which previously was adjusted against color-solutions for comparison prepared from the same quantities of reagents and an excess of 0.3 ml 0.0028 N mercuric nitrate. Since the initial solutions of 2-chloro-ethanol had a slight content of chloride ions, the data are corrected with regard to a blank value carried out with 20 ml solution. The blank values are about 0.4—3 ml 0.0028 N mercuric nitrate dependent on the concentration of 2-chloro-ethanol. The amounts of mercuric nitrate solution corresponding to the chloride ions formed during the experiments range from 1 to 40 ml 0.0028 N mercuric nitrate. In some of the long duration experiments the content of chloride ion was deter-

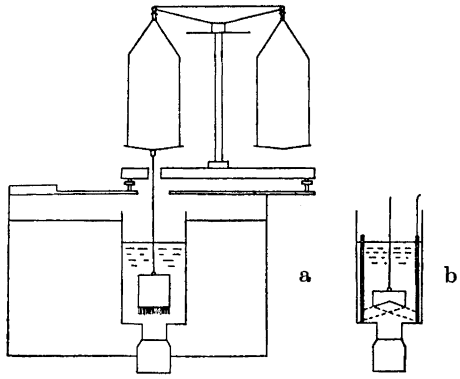

Fig. 2. Experimental arrangement for the measurement of the acoustic power.

mined by conductometric titration with 0.0028 N mercuric nitrate. The solutions of 2-chloro-ethanol were prepared from a fraction of 2-chloro-ethanol "Fluka" which distilled between 128.3° and 128.7°C at 753 mm Hg and had $n_D^{20} = 1.4422$. The boiling point of 2-chloro-ethanol is 128.6°C and $n_D^{20} = 1.4421$.

THE ACOUSTIC POWER FROM THE TRANSDUCER

When a beam of plane ultrasonic waves in a fluid encounters an obstacle, then the interaction of the obstacle with the plane wave motion results in a radiation pressure exerted upon the obstacle proportional to the mean energy density of the wave motion [6].

The power radiated in an ultrasonic field is closely related to the radiation pressure [7] and is usually determined by a measurement of the net force exerted on a proper "radiometer", which may be either a perfect reflector or a perfect absorber, placed in the path of the waves. For the present determinations of the total acoustic power emitted from the transducer two different radiometers have been used, one a nearly perfect absorbing nylon-brush, the other a nearly perfect reflecting hollow brass-radiometer. The experimental arrangement is shown in Fig. 2.

The brass-radiometer [8] which is provided with a conical turning out (135°) is filled with air. The air inside the radiometer ensures a practically complete reflection from the surface and the conical shape makes the radiometer self-centralizing and brings about a reflection parallel with the opposite surface. The reflected waves are absorbed in a cylinder of absorbing material to avoid standing waves acting back on the transducer (Fig. 2 b).

The radiometer is suspended below the pan of a balance in a thin nylon thread, and completely immersed in and surrounded by water freed from dissolved air, vertically above and as close as possible to the transducer. Air bubbles below the radiometer are carefully removed and the radiometer is tared. The resulting buoyancy when the ultrasonic waves interact with the

radiometer is finally counterbalanced with weights, q g. If the ultrasonic waves emitted from the transducer are assumed to be free plane waves in a lossless medium the alternating excess sound pressure p_e is related to the alternating particle velocity u by $p_e = u\varrho_o h_o$ and analogous $p_{e,rms} = u_{rms}\varrho_o h_o$ where ϱ_o is the static density of the medium, h_o the velocity of the waves and $\varrho_o h_o$ the characteristic impedance. The acoustic power W_P is

$$W_P = \frac{1}{T}\int_0^T up_e A\,dt = u_{rms}p_{e,rms}A = \frac{UPA}{2} = \frac{\varrho_o h_o U^2 A}{2} \text{ watts}$$

where T is the period, A the total area of the beam, and P and U are the respective amplitude values.

The radiation pressure Π is related to the particle velocity amplitude and the weights q g by

$$\Pi = \frac{\varrho_o U^2}{2} = q\ 9.81 \times 10^{-3} A^{-1} \text{ Newton m}^{-2}$$

With respect to the nylon-brush which is larger in section than the beam and as mentioned above acts as an absorber the counterbalanced weights q g corresponds thus, following the above expressions, with the acoustic power

$$W_P = \frac{\varrho_o U^2 h_o A}{2} = q\ 9.81 \times 10^{-3} h_o = 14.69\ q \text{ watts}$$

where the velocity of sound in water $h_o = 1\,497$ m sec^{-1} at 25°C.

In the case of the brass-radiometer, which is also larger in section than the beam and acts as a perfect reflector, the beam intersects the radiometer by an angle $\Theta = 22.5°$ and the acoustic power is then

$$W_P = \Pi\ h_o A = q\ 9.81 \times 10^{-3}\ h_o\ (2\cos^2\Theta)^{-1} = 8.61\ q \text{ watts}$$

Table 1. The acoustic power from the transducer at different primary voltages on the anode-transformer of the generator, as measured by a nylon-brush and a brass-radiometer.

V volt	0.8 Mcps				2.4 Mcps			
	Nylon-brush		Brass-radiometer		Nylon-brush		Brass-radiometer	
	q g	14.69 q watts	q g	8.61 q watts	q g	14.69 q watts	q g	8.61 q watts
50	0.15	2.2	0.26	2.2	0.12	1.8	0.20	1.7
75	0.36	5.3	0.60	5.2	0.34	5.0	0.44	3.8
100	0.61	9.0	1.05	9.0	0.51	7.5	0.80	6.9
125	1.04	15.3	1.75	15.0	0.83	12.2	1.30	11.2
150	1.44	21.2	2.63	22.6	1.23	18.1	2.00	17.2
175	2.01	29.5	3.65	31.4	1.73	25.4	2.85	24.5
200	2.69	39.5	4.93	42.4	2.27	33.3	3.80	32.7
225	3.30	48.5	6.35	54.7	2.81	41.3	4.70	40.5

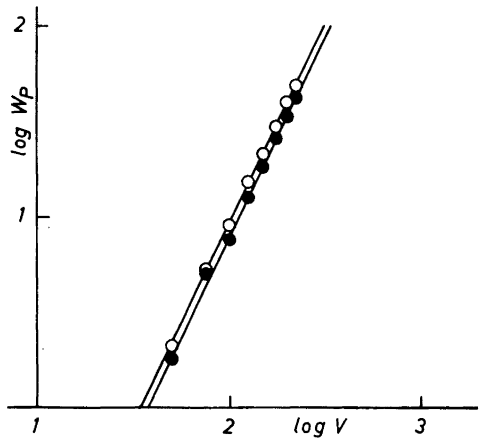

Fig. 3. A plot of log W_P against log V. W_P is the acoustic power as measured by the nylon-brush, V is the primary voltage on the anode-transformer of the generator. O, experiments performed at 0.8 Mcps; ●, experiments performed at 2.4 Mcps.

The results at different primary voltages on the anode transformer of the generator are shown in Table 1.

In Fig. 3 log W_P (as measured by the nylon-brush) is plotted against log V (primary voltage on the anode-transformer). From the figure it is inferred that approximately W_P = constant × V^2 in accordance with the expression for the acoustic power output from a piezoelectric quartz $W = V^2_{rms}/R_e$, where V_{rms} is the voltage applied to the quartz and R_e a motional resistance.

THE KINETIC OF THE REACTION IN THE ULTRASONIC FIELD

When 2-chloro-ethanol is hydrolyzed in dilute pure aqueous solution thus: $CH_2ClCH_2OH + HOH = CH_2OHCH_2OH + H^+ + Cl^-$, the reaction follows 1'-order kinetics, *i.e.* $-\frac{1}{c}\frac{dc}{dt} = k_1$, where $c = a-x$ is the concentration of 2-chloro-ethanol left at time t and a the initial concentration. When the reaction proceeds in the ultrasonic field the initial velocity $s = -\frac{dc}{dt}$ or $\frac{1}{c}s = -\frac{dc}{cdt}$ could be estimated from the experimental results.

1. The dependence on the acoustic power.

Experiments with samples of 0.05 litre at $\nu = 0.8$ Mcps and varying values of the acoustic power have shown that the initial velocity changes with the acoustic power.

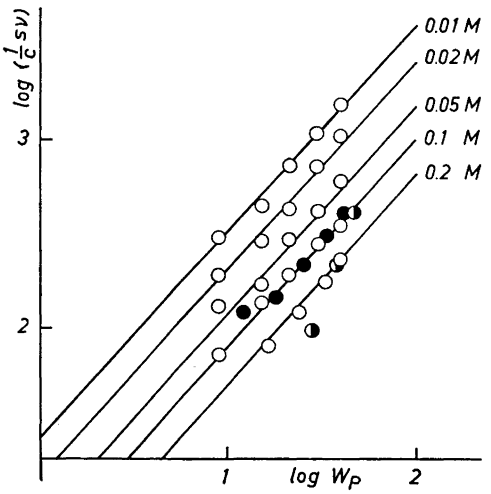

Fig. 4. A plot of $\log\left(\frac{1}{c}sv\right)$ against $\log W_P$. s is the initial velocity found in experiments with samples of 0.05 litre, c is the concentration of 2-chloro-ethanol, v the frequency and W_P the acoustic power. ○, experiments performed at 0.8 Mcps; ●, experiments with 0.1 M, and ◑ with 0.2 M, performed at 2.4 Mcps; 25°C.

In Fig. 4 for convenience $\log\left(\frac{1}{c}sv\right)$ is plotted against $\log W_P$. From the figure it could be inferred that $\frac{1}{c}sv = \text{constant} \times W_P^{1.1}$. In the figure are also indicated the results from experiments with 0.1 and 0.2 M solutions at $v = 2.4$ Mcps, whereof in all events the experiments with 0.1 M appear to follow the above relation fairly well. Similar experiments with a 0.01 M solution failed because the liberated amounts of chloride ion were too small for determining an initial velocity with any reasonable certainty.

2. The dependence on the concentration of 2-chloro-ethanol.

Experiments with samples of 0.05 litre at $v = 0.8$ Mcps, W_P kept constant and varying concentrations of 2-chloro-ethanol, have shown that the initial velocity also changes with the concentration. In Fig. 5 $\log\left(\frac{1}{c}sv\right)$ is plotted against $\log(10^2 c)$. From the figure it could be deduced that $\frac{1}{c}sv = \text{constant} \times c^{-0.62}$. By combining the results derived from Figs. 4 and 5 it could finally be inferred that the initial velocity in experiments with 0.05 litre sample, $v = 0.8$ Mcps, and the experimental conditions mentioned, follows the expression $s = 1.48\ v^{-1} W_P^{1.1} c^{0.38}$ mole litre^{-1} min^{-1}.

3. The dependence on the volume of sample.

Preliminary experiments with samples of 0.10 litre instead of 0.05 litre had shown that changes in the volume of sample had a marked effect on the initial velocity.

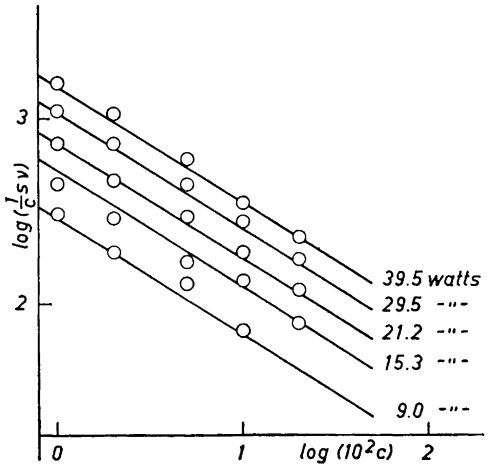

Fig. 5. A plot of $\log\left(\frac{1}{c}s\nu\right)$ against log (10^2c). Experiments with samples of 0.05 litre; $\nu = 0.8$ Mcps; 25°C.

Experiments with a 0.01 M solution of 2-chloro-ethanol at $\nu = 0.8$ Mcps, the acoustic power 43 watts and varying volume of sample have shown that this effect is closely connected with the dimension of the reaction cylinder (diameter 4.5 cm) and the ultrasonic field, *i.e.* the experimental arrangement.

In the present experimental arrangement the waves are radiated against the free liquid surface of the sample where the waves are almost completely reflected, which results in a field of standing waves. If we assume that the attenuation is small and the absorption coefficient nearly the same in the water below the membrane and in the sample, then we can say approximately that the acoustic energy absorbed in the sample is related to the part of the volume filled up by the ultrasonic waves, which is standing in the sample $\frac{V_1}{V_0 + V_1} = \frac{l_1}{l_0 + l_1}$, where l_0 is the distance from the surface of the transducer to the membrane in the reaction cylinder (about 5.0 cm), l_1 the height of sample in the reaction cylinder, and the radiating surface 10 cm^2.

When the absorbed acoustic energy finally is distributed in the sample, then the acoustic energy absorbed per unit volume of sample is related to $\frac{l_1}{(l_0 + l_1)V_s} = \frac{10^3}{(l_0 + l_1)A_R}$ where V_s litre is the volume of sample and A_R the area of the base of the reaction cylinder. In Fig. 6 $\log\left(\frac{1}{c}s\nu\right)$ is plotted against $\log\left(\frac{10^3}{(l_0 + l_1)A_R}\right)$. From this figure it could be inferred that $\frac{1}{c}s\nu = \text{constant} \times \left(\frac{10^3}{(l_0 + l_1)A_R}\right)^{2.0}$.

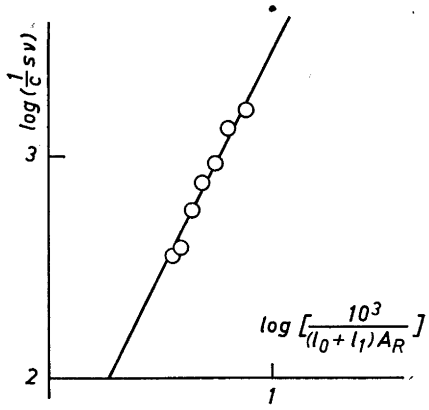

Fig. 6. A plot of $\log\left(\frac{1}{c}sv\right)$ against $\log\left(\frac{10^3}{(l_0+l_1)A_R}\right)$. Experiments with a 0.01 M solution of 2-chloro-ethanol and varying volume of sample; l_0 is the distance between the transducer and the "acoustic window", l_1 the height of sample in the reaction cylinder, A_R the area of the base of the reaction cylinder; $\nu = 0.8$ Mcps and the acoustic power $W_P = 43$ watts; 25°C.

By combination of this result with that previously obtained a joint interpolation formula could finally be deduced, thus

$$s = 2.48 \times 10^{-2}\left(\frac{10^3}{(l_0 + l_1)A_R}\right)^{2.0} W_P^{1.1}\nu^{-1}c^{0.38}$$

$= kc^{0.38}$ mole litre^{-1} min^{-1}, where $\nu = 0.8$ Mcps.

It is so established that

$$-\frac{d[CH_2ClCH_2OH]}{dt} = k[CH_2ClCH_2OH]^{0.38}$$

Table 2. Samples of 0.05 litre 0.01 M 2-chloro-ethanol subjected to ultrasonic waves of 0.8 Mcps and acoustic power 43 watts. 25°C. $t_{calc.} = \frac{1}{k_{graf.}} f(x)$; $k_{graf.} = 105 \times 10^{-6}$ and $k_{calc.} = 116 \times 10^{-6} \cdot (\text{mole/litre})^{0.62}\ \text{min}^{-1}$.

t min. obs.	x	$a - x$	$f(x)$	t min. calc.
60	0.00112	0.00888	0.00659	62.7
60	0.00115	0.00885	0.00677	64.5
60	0.00108	0.00892	0.00635	60.5
120	0.00214	0.00786	0.01287	122.6
120	0.00205	0.00795	0.01231	117.2
120	0.00203	0.00797	0.01218	116.0
120	0.00199	0.00801	0.01193	113.6
180	0.00277	0.00723	0.01691	161.0
180	0.00276	0.00724	0.01684	160.4
180	0.00282	0.00718	0.01723	164.1
240	0.00385	0.00615	0.02415	230.0
300	0.00483	0.00517	0.03116	296.8
360	0.00574	0.00426	0.03814	363.2

Table 3. The experimental values of the rate constant k found in experiments with samples of 0.05 litre and varying values of the acoustic power W_P and the concentration of 2-chloro-ethanol. 25°C. W_P^* is the acoustic power after a correction in the electric circuit of the generator.

0.8 Mcps. W_P^*	0.8 Mcps. W_P	0.2 M $k_{exp.}10^6$	0.1 M $k_{exp.}10^6$	0.05 M $k_{exp.}10^6$	0.02 M $k_{exp.}10^6$	0.01 M $k_{exp.}10^6$	$k_{calc.}10^6$	$k^*_{calc.}10^6$
43.0	39.5	106	104	118	117	108	105	—
33.0	29.5	83 *	82	85	79	78	76	86
24.0	21.2	55 *	56	58	52	52	53	61
16.6	15.3	38 *	41	32	32	30	37	41
10.1	9.0	—	21	24	22	21	21	—
2.4 Mcps. W_P^*	2.4 Mcps. W_P	0.2 M $k_{exp.}10^6$	0.1 M $k_{exp.}10^6$				$k_{calc.}10^6$	$k^*_{calc.}10^6$
47.2	41.3	68 *	45				37	43
37.6	33.3	36 *	35				29	33
28.2	25.4	17 *	25				22	24
20.2	18.1	—	14				15	—
14.3	12.2	—	12 *				—	11

which equation by integration gives

$$t = \frac{1}{k} f(x) = \frac{1}{k} \frac{1}{0.62} [(a)^{0.62} - (a-x)^{0.62}]$$

Table 2 gives the results from experiments with a 0.01 M solution of 2-chloro-ethanol, $\nu = 0.8$ Mcps, and the acoustic power 43 watts. From the table it appears that the reaction follows the above integrated form of the rate equation fairly well. For comparison of the rate of reaction in the ultrasonic field with that without ultrasonic waves a value of the rate constant at 25°C extrapolated from the data of Radulescu and Muresanu [9] should be stated $k_1 = 6 \times 10^{-8}$ min^{-1} and thus the rate of reaction is considerably increased

Table 4. The dependence of the rate constant k at 25°C on the volume of sample V_s in experiments with a 0.01 M solution of 2-chloro-ethanol at $\nu = 0.8$ Mcps and the acoustic power 43 watts. $l_0 = 5.0$ cm and $A_R = 15.9$ cm^2.

Sample V_s litre	Height of liquid column of sample l_1 cm	$\frac{10^3}{(l_0 + l_1) A_R}$ litre^{-1}	$k_{exp.}10^6$	$k_{calc.}10^6$
0.050	3.15	7.72	105	116
0.075	4.72	6.47	88	81
0.100	6.29	5.57	66	60
0.125	7.86	4.89	53	46
0.150	9.44	4.36	40	37
0.175	11.01	3.93	27	30
0.200	12.58	3.58	24	25

in the ultrasonic field. In Table 3 are the experimental values of the rate constant k found in experiments with 0.05 litre sample and with varying values of the acoustic power W_P and the concentration of 2-chloro-ethanol at $\nu = 0.8$ Mcps and extended up to 100 min.

For comparison the values calculated from

$$k = 2.48 \times 10^{-2} \left(\frac{10^3}{(l_0 \times l_1) A_R} \right)^{2.0} W_P^{1.1} \nu^{-1} \text{ (mole/litre)}^{0.62} \text{ min}^{-1}$$

are also given in Table 3.

It is remarkable that the experiments at 2.4 Mcps, which is indicated in Table 3, also look as if they comply with the expression for the rate constant at $\nu = 0.8$ Mcps, but this fact is for the present not sufficient to elucidate the dependence on frequency, the previously mentioned experiments with a 0.01 M solution also being taken into account.

In Table 4 are the experimental and calculated values of the rate constant k originating from experiments with a 0.01 M solution of 2-chloro-ethanol, $\nu = 0.8$ Mcps, $W_P = 43$ watts and varying volume of sample V_s extended up to 120 min.

From the results of the experiments it has been established that the ultrasonic waves promote the liberation of chloride ions from 2-chloro-ethanol in pure aqueous solution and that there is a connection between the rate of reaction in the ultrasonic field and the experimental conditions by which the experiments are performed, which in this instance means the acoustic energy dissipated per unit volume. When the chemical activation is connected with the acoustic energy dissipated in the sample, a subsequent investigation on the absorption coefficients of sound in solutions of 2-chloro-ethanol may possibly give important information, whether the activation is connected with the absorption and thus a relaxation mechanism alone or also other factors are of importance.

The experiments with varying volumes of sample have revealed a deficiency as to the present experimental arrangement. Because of the distance l_0 between the transducer and the "acoustic window" in the reaction cylinder only a part of the acoustic energy emitted has been available for the present purpose of activation in the sample, and thus l_0 has to be as small as possible.

When all the experiments are carried out with solutions containing air and with free access to the air, oxidation is to be expected in the samples exposed to the ultrasonic waves. This fact may have nothing to do with the liberation of chloride ions from the 2-chloro-ethanol, but it should be noted that aldehyde, possibly originating from 1,2-ethanediol (glycol), has been demonstrated in the samples, and may thus be regarded as a secondary phenomenon.

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REFERENCES

1. Kling, A. and Kling, R. *Compt. rend.* **223** (1946) 1131.
2. Kling, A. and Kling, R. *Ibid.* **223** (1946) 33.
3. Virtanen, A. and Ellfolk, N. *Acta Chem. Scand.* **4** (1950) 93.
4. Cowan, H., McCabe, C. and Warner, J. *J. Am. Chem. Soc.* **72** (1950) 1194.
5. Charlot, G. and Bézier, D. *Analyse Quantitative Minérale*, Masson et Cie, Paris 1955, p. 473.
6. Borgnis, F. *Revs. Modern Phys.* **25** (1953) 653.
7. Hueter, T. and Bolt, R. *Sonics*, Wiley and Sons, Inc., New York 1955, p. 41.
8. Oberst, H. and Rieckmann, P. *Amtsblatt der PTB, Braunschweig* **H.3** (1952) 106; **H.4** (1952) 143; Ref. Bergmann, L. *Der Ultraschall*, Hirzel Verlag, Stuttgart 1954, p. 216.
9. Radulescu, D. and Muresanu, P. *Bull. soc. sci. Cluj, Roumanie* **7** (1932) 129.

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