

THE CHEMICAL EFFECTS OF PRESSURE 60-0098

PART 6.—THE ELECTRICAL CONDUCTIVITY OF SEVERAL LIQUIDS AT HIGH SHOCK PRESSURES

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This paper reports some measurements of the electrical conductivities of liquids compressed by explosive shock waves. Water, methyl alcohol, acetic acid, propionic acid and a 1 : 1 mixture of water and ethyl alcohol all became good conductors ($\kappa > 10^{-2} \Omega^{-1} \text{cm}^{-1}$) at shock pressures of about 100,000 atm. But ethyl alcohol, acetone and glycerol remained poor conductors under the same conditions. It is likely that the high conductivities of the first group of liquids arose from enhancement of their self-ionization.

The shock conductivity of water was found to be increased by the reflection of a shock wave or by the head-on collision of two equal shocks.

In the last paper of this series¹ we described some measurements of the electrical conductivity of water in the pressure range 33,000 to 127,000 atm. We produced the pressures by detonating charges of high explosive in contact with the water. The explosions drove strong shock waves into the water, compressing it very quickly to high densities and temperatures. We found that the shocked water was a good electrical conductor and we concluded that the conductivity arose from extensive ionization of the water to H_3O^+ and HO^- ions. It appears that the ionic product of water may have increased by a factor as great as 10^{12} under our most extreme conditions.

We have now extended these measurements to some other liquids which can also ionize by autoprotolysis:



$$K_{\text{auto}} = [\text{ROH}_2^+][\text{RO}^-]$$

The following is a list of the liquids studied, together with their autoprotolysis constants where they are known.

TABLE 1

liquid	K_{auto} /mole l^{-1} at 25°C and at 1 atm
water	1.0×10^{-14}
methyl alcohol	2×10^{-17}
ethyl alcohol	8×10^{-20}
acetic acid	3×10^{-13}
1 : 1 (vol.) water/ethyl alcohol	(<i>ca.</i> 10^{-17})*
propionic acid	—
glycerol	—
acetone	—

* estimated from the values of K_{auto} for water and ethyl alcohol.

We have also tried to increase the pressure range for water by reflecting secondary shock waves back into the incident waves, and by causing the head-on collision of pairs of shock waves.

EXPERIMENTAL

PRODUCTION OF SHOCK WAVES

We used three methods to generate the shock pressures.

(a) SINGLE SHOCK WAVES.—This method was described in our earlier paper¹ and there is no need to discuss it in detail here. Briefly, we placed the liquid in a polyethylene tube fitted over the top of a cylindrical stick of 65/35 RDX/TNT and then detonated the explosive from the bottom. A detonation wave of about 250,000 atm pressure travelled up the charge and, at the top, drove a nearly planar shock wave into the liquid. A fast oscillograph recorded the change in conductance as the shock wave passed between a pair of thin foil electrodes mounted perpendicularly to the shock front (fig. 1a).

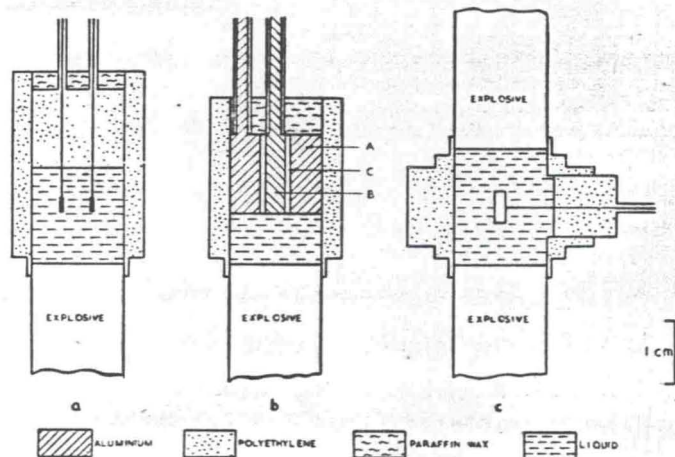


FIG. 1.—Electrodes used to measure conductivities in (a) single shock waves, (b) reflected waves, (c) colliding waves.

The full experimental details were given in part 5 of this series.¹

(b) REFLECTED SHOCK WAVES.—In this method the shock wave was launched in the same way as in (a) but the electrodes, instead of being designed to offer the least resistance to the shock wave, were deliberately arranged to reflect a secondary shock back into the tail of the oncoming wave. It is known that the normal reflection of a shock wave at a rigid surface produces an instantaneous pressure which is more than twice that of the incident wave.^{2, 3} But, of course, no material is completely rigid and the actual pressure reached in the reflected wave depends on the relative shock impedances of the liquid and the reflecting substance. Walsh and Rice⁴ have made some direct measurements of the pressure of shock waves reflected into water from plates of 24ST aluminium and found that the intensification is roughly two-fold. We have tried to make use of this effect to extend our pressure range.

The arrangement is shown in fig. 1b. It consisted of two coaxial cylinders A and B, of gold-plated aluminium, separated by a Teflon sleeve C. The bottom ends of the cylinders acted both as reflecting surfaces and as the electrodes. The cell constant, measured with the electrodes mounted in the polyethylene tube, was usually about 1.5 cm^{-1} .

(c) COLLIDING SHOCK WAVES.—The head-on collision of two equal shock waves is mathematically similar to the total reflection of a single shock from a perfectly rigid wall. The pressure is therefore higher than it is for reflection at a real non-rigid surface of the kind used in method (b).

The pressure in the plane of collision can be found by introducing into each incident shock a "reflected" shock of sufficient intensity to reduce the flow velocity to zero. Rice and Walsh⁵ have worked out the relationships between the flow velocity and pressure for incident and reflected shock waves in water, and from their results we find, for instance, that the head-on collision of two plane shock waves of 100,000 atm pressure will produce

a pressure of about 340,000 atm. This is a considerable gain over the pressure doubling which occurs in reflection at an aluminium surface.

Fig. 2 shows the arrangement which we used to generate two converging shock waves. The shocks were launched by the main cylindrical charges A and B, which were fired simultaneously from a semi-circular bridge of high explosive C, detonated at the mid-point of its circumference.⁶ We found that with this arrangement the shocks could be synchronized to within 0.2 μ sec, corresponding to an uncertainty of about 1 mm in the position of their collision.

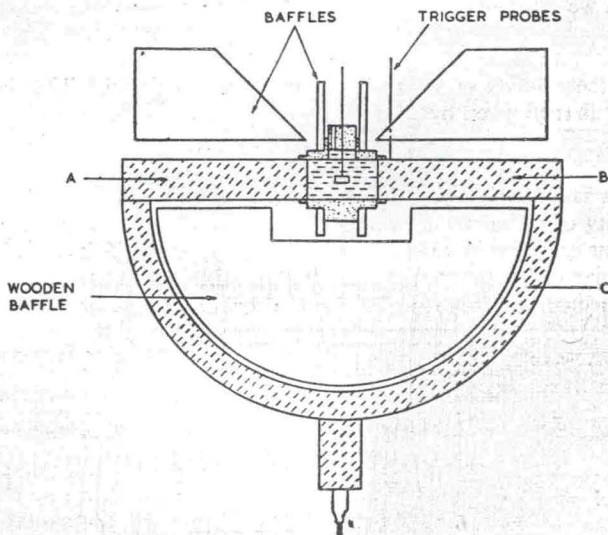


FIG. 2.—The arrangement used to produce the head-on collision of two shock waves.

The electrodes were rectangular plates of gold-plated brass (5 mm long \times 2 mm wide \times 0.2 mm thick), mounted parallel to the path of the shock waves and centrally between the explosive charges (fig. 1c). The external connections to the electrodes were heavily insulated and were shielded by baffles from the air shocks produced by the explosion.

MATERIALS

The liquids were purified chemically, and distilled. Their conductivities in $\Omega^{-1} \text{cm}^{-1}$ at 25°C and 1 atm were: water, 5.0×10^{-7} ; methyl alcohol, 4×10^{-7} ; ethyl alcohol, 3.5×10^{-8} ; acetic acid, 2.2×10^{-8} ; propionic acid, $< 10^{-9}$; glycerol, *ca.* 10^{-6} ; acetone, 8×10^{-8} .

The main explosive charges were cylinders of cast 65/35 RDX/TNT, similar to the ones used in our earlier work. This explosive is quite soluble in some of the organic liquids but we find that we could prevent it from dissolving by coating it with a very thin film of paraffin wax. The semi-circular charges used in method (c) were made of cast 60/40 RDX/TNT.

PROCEDURE

The measurements were made by an oscillographic method which we have already described in some detail.¹ We modified the original arrangement slightly by using a motor-driven rotary switch to synchronize the events before the explosion. This ensured that the detonator was fired no later than 0.02 sec after the e.m.f. had been applied to the conductance cell.

Some of the reflected and colliding shocks produced rather high conductivities and in these cases we reduced the load resistance from 10 Ω to 1 Ω and made the connections in the RC circuit as short as possible, to minimize their inductance. We also measured, and allowed for, the internal resistance of the condenser to microsecond pulses.

RESULTS

SHOCK VELOCITIES AND PRESSURES

Of the eight liquids studied, five gave well-defined current pulses when the shock waves reached the electrodes. In each experiment the position of the current pulse on the oscillograph trace provided a measure of the time t which the shock had taken to travel the distance d between the explosive and the electrodes. By varying this distance in different experiments we obtained a family of d, t points which we fitted to the empirical relation: ¹

$$d = U_s t + A[1 - \exp(-\alpha t)], \quad (1)$$

where U_s is the velocity of sound in the unperturbed liquid. The shock velocity at any time t is then given by

$$U = U_s + A\alpha \exp(-\alpha t). \quad (2)$$

This formula satisfies the condition that the shock velocity must ultimately decay to the velocity of sound as the wave travels away from the explosive.

Our results are given in table 2, where $U_{t=0}$ ($= U_s + \alpha A$) is the calculated velocity at the explosive/liquid interface. The pressure $P_{t=0}$ at that point can be worked out from the shock impedance of the liquid, defined as the product of its normal

TABLE 2.—CONDITIONS * IN SHOCK WAVES LAUNCHED BY 65/35 RDX/TNT

liquid	number of t, d points	U_s (mm/ μ sec)	A (mm)	α (μ sec ⁻¹)	initial conditions	
					$U_{t=0}$ (mm/ μ sec)	$P_{t=0}$ (atm)
water	22	1.51	19	0.241	6.1 ± 0.07 †	161,000
methyl alcohol	8	1.09	19	0.319	7.1 ± 0.15	152,000
acetic acid	6	1.10	19	0.296	6.7 ± 0.15	175,000
propionic acid	4	1.16	30	0.168	6.2 ± 0.06	162,000
1:1 (vol.) water/ethyl alcohol	6	1.42	20	0.285	7.1 ± 0.20	168,000

* These conditions apply only to the particular geometry of our experiments.

† The figures after the \pm signs are the statistical "mean square errors".⁷ The actual errors may be greater.

density and the initial shock velocity $U_{t=0}$, together with the corresponding detonation impedance of the explosive.⁸ The calculated values of $P_{t=0}$ are listed in the last column of table 2 and are probably correct to within 5,000 atm. The pressures at later times can be found for water and methyl alcohol from the U, P data of Walsh and Rice,⁴ but they are not known for the other liquids.

CONDUCTIVITIES

The methods (a) and (b) gave single current pulses similar to those described in part 5 of this series.¹ The shock conductivities were derived from the pulse amplitudes in the same way as before.

However, the colliding shock waves in method (c) usually produced two fairly distinct pulses. Fig. 3 reproduces an oscillograph trace given by the interaction of two shocks in water. It was obtained with the electrode arrangement shown in fig. 1c, the mid-point of the electrodes being 7.8 mm from the two explosive charges. The interval between the launching of the shocks at t_0 and the beginning of the first pulse at t_1 was about 0.8 μ sec, which is roughly the time required for the shock waves to travel the distance of 5.3 mm between the explosives and the leading edges of the electrodes (eqn. (1) gives 0.95 μ sec). Moreover, the interval between t_1 and the appearance of the second pulse at t_3 was 0.5 μ sec, and this is close to the time needed for the waves to move from the edges to the centre of the

electrodes (eqn. (1) gives $0.51 \mu\text{sec}$). It seems clear therefore that the first pulse was caused by the arrival of the shocks at the edges of the electrodes and the second by the collision of the shocks in the centre. The presence of the step in the first pulse in fig. 3, at t_2 , probably means that one wave reached the electrodes

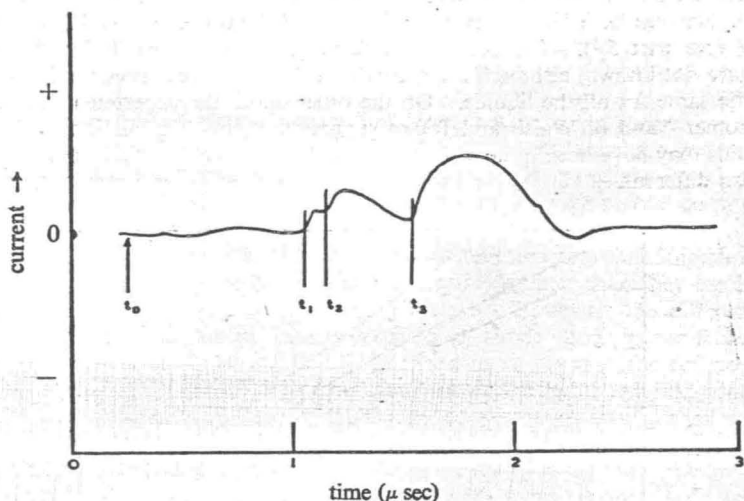


FIG. 3.—An oscillogram showing the change in conductivity of water during the collision of two shocks.

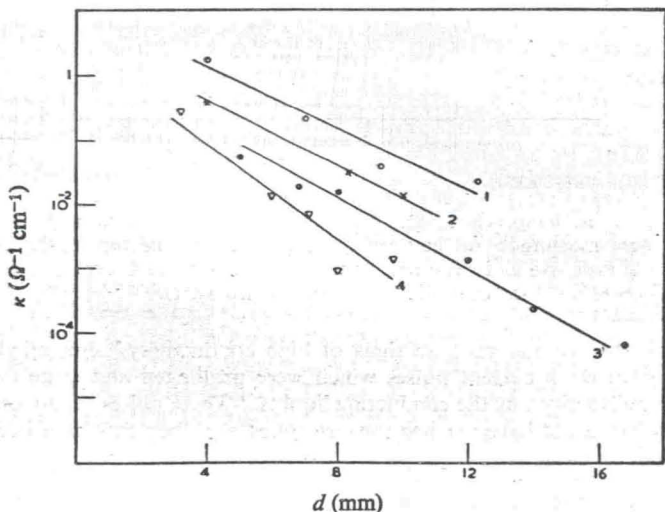


FIG. 4.—The conductivities of various liquids compressed by single shock waves (method (a)). The liquids are: 1, acetic acid; 2, propionic acid; 3, 1:1 (vol.) water/ethyl alcohol; 4, methyl alcohol. The distances d were measured between the top of the explosive charge and the top of the electrodes.¹ The initial temperatures and pressures were about 30°C and 1 atm.

slightly before the other, but the differences in their times of arrival was quite small (about $0.1 \mu\text{sec}$). We calculated the conductivity in the region of shock interaction from the height of the second pulse, assuming the effective thickness of the compressed region to be 2 mm (as suggested by the duration of the pulse).

The results are shown in fig. 4 and 5, where the conductivities are plotted against the distance between the explosive and the electrodes. The conductivity always decreased as this distance increased, because the shock waves became attenuated by heat losses and release waves: for instant, the conditions behind a shock which had travelled 3 mm into water were: $P = 127,000$ atm, $T = 1045^\circ\text{K}$, $V = 0.58$ cm^3 g^{-1} , whereas at 17 mm they were: $P = 33,000$ atm, $T = 431^\circ\text{K}$, $V = 0.71$ cm^3 g^{-1} (see part 5¹). The corresponding values of P , T and V for the other liquids are not known, although it appears that the initial pressures (table 2) were much the same for all the liquids. On the other hand, the experiments of Schall and Thomer⁹ and of Walsh and Rice⁴ suggest that the compressions V_P/V_0 of the liquids may have been quite different and it is probable that their temperatures were also different.

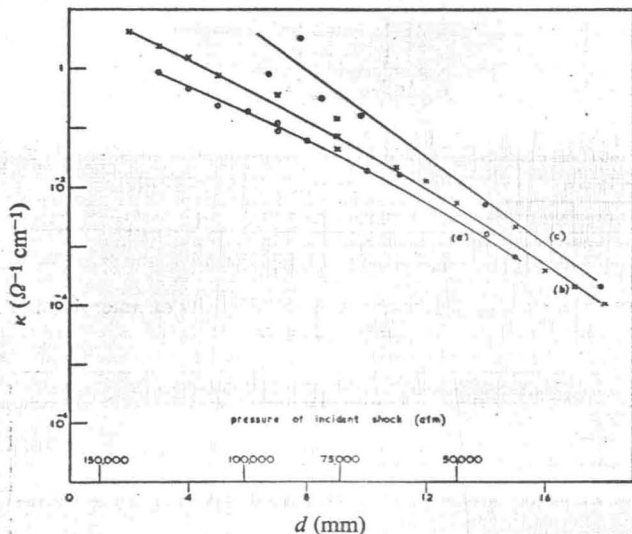


FIG. 5.—The conductivity of water in (a) single shocks, (b) reflected shocks, (c) colliding shocks. The initial temperatures and pressures were about 30°C and 1 atm. The distances d were measured: (a) between the explosive and the top of the electrodes, (b) between the explosive and the electrode faces, (c) between each explosive charge and the centre of the electrodes (see fig. 1).

Glycerol and acetone gave no signs of high conductivity. But ethyl alcohol sometimes gave weak current pulses which were prolonged and quite unlike the usual sharp pulses given by the conducting liquids. These pulses began long before the shock waves could have reached the electrodes, and they may have been due to photoconduction caused by the explosive flash.

DISCUSSION

In part 5¹ we ascribed the high shock conductivity of water to a very large increase in its self-ionization constant K_{auto} , brought about by the high pressure and temperature behind the shock front. It is likely that the same explanation applies to the other liquids which showed high conductivities in the present experiments. It is significant that their conductivities, at any particular distance from the explosive, decreased in the order:

acetic acid > water > propionic acid > 1 : 1 (vol.) water/ethyl alcohol

> methyl alcohol

which is roughly the order of their autoprotolysis constants under normal conditions (table 1).

The shock conductivities of ethyl alcohol, acetone and glycerol were less than we could measure (i.e. $<ca. 10^{-4} \Omega^{-1} \text{cm}^{-1}$). Examining the possible reasons for this, we observe first that the autoprotolysis constant of ethyl alcohol is considerably lower than those of the other liquids in table 1 and this probably explains its failure to conduct. Acetone can only undergo autoprotolysis in its enolic form, whose concentration is extremely small¹⁰ and whose autoprotolysis constant is unknown: it is not surprising that its resistance remained high. The autoprotolysis constant of glycerol is also unknown, but its acidic ionization constant in water is very low.¹¹ Moreover, glycerol has a high viscosity which increases steeply with increasing pressure,¹² causing a corresponding decrease in the mobility of dissolved ions.¹³ This factor may contribute to the high resistance of glycerol in shock compression.

Turning now to the behaviour of water in reflected and colliding shocks, we see from fig. 5 that the conductivities are certainly greater than they are in single shocks at the same distance from the explosive. However, the differences are unexpectedly small. An increase in intensity of single shock waves from 50,000 atm to 100,000 atm causes an 80-fold increase in κ , whereas the reflection of a 50,000 atm wave by the arrangement shown in fig. 1*b* (which should produce an instantaneous pressure of about 100,000 atm) causes only a twofold increase in κ , and the collision of two 50,000 atm waves by the method shown in fig. 1*c* (which should raise the pressure to about 160,000 atm) causes only a fivefold increase in κ . These results are surprising, but they can be explained in two kinds of ways.

The first possibility is that the conductivity of water in reflected and colliding shocks is, in fact, less than it is in a single shock of the same total pressure. This may well be so, because the temperature is lower in multiple shocks than in a single shock of the same intensity. The lower temperature probably reduces the mobilities of the ions and lowers the value of K_{auto} . In addition it favours the partial freezing of water which Altshuler, Bakanov and Trunin observed in single shock waves at pressures above 130,000 atm.¹⁴

The second possibility is that we failed to produce the pressures we imagined. There could be several reasons for this. First, the calculated pressures are for normal reflections and head-on collisions of *plane* shock waves, whereas some photographs taken by Dr. A. H. Ewald show that the shock fronts in our experiments are actually spherical, with radii of about 30 mm. This means that at points away from the principal axis, the interactions must have been oblique and the pressures less than those for normal incidence. Secondly, the main charges shown in fig. 2 were detonated at points on their circumference instead of on their axes, and this must have increased the obliqueness of the collisions. Thirdly, it is possible that the conductivities measured by the arrangement shown in fig. 1*b* relate to conditions in front of the Teflon rather than in front of the aluminium, because the principal electrical path was through a thin layer of water near the surface of the Teflon. We have measured the shock impedance of Teflon and found it to be only about half that of aluminium, so that the reflected pressure at a water/Teflon interface will certainly not be twice the incident pressure, as it is at a water/aluminium boundary. Finally, Finkelstein¹⁵ has calculated that the reflection or collision of strong shocks in water causes a "spiking" of the interaction wave, and that although the excess pressure is high its duration is short. It might even be less than the response time of our measuring circuits (*ca.* 0.15 μsec) although this seems unlikely.

At present we are unable to decide which of these factors was the main cause of the unexpectedly low conductivities.

We are grateful to Dr. G. P. Cachia for his advice on methods of producing simultaneous detonations.

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