Reaction of Diallylsilanes and Polymercaptans.—Compounds XIII and XIV, which are viscous oils, were prepared by reaction of ethylene bis-thioglycolate with diallyldimethylsilane and 1,3-diallyltetramethyldisiloxane, respectively.

Acknowledgment.—The author wishes to acknowledge the helpful suggestions given by Dr. B. W. Nordlander and Dr. R. W. Burnett and to thank Dr. E. W. Balis, Mr. L. B. Bronk, Miss M. Caldwell and Mr. C. Weeks for analytical data, and Dr. F. J. Norton for mass spectrum data.

Summary

1. The addition reaction of mercaptans to alkenyl silanes has been studied.
2. Thio ethers, thia acids and thia esters have been prepared by the reaction of mercaptans, thioglycolic acid and its esters with alkenyl silanes.
3. Dimercaptans and dialkenylsilanes react to form viscous oils.
4. The presence of sulfur in the delta position with respect to the silicon does not appear to affect the stability of the carbon–silicon bond toward acids or bases.
5. Diallyldimethylsilane, allylpentamethyldisiloxane and 1,3-diallyltetramethyldisiloxane have been prepared and characterized.

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[FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Gaseous Detonations. I. Stationary Waves in Hydrogen–Oxygen Mixtures[1]

BY DONALD J. BERETS, EDWARD F. GREENE AND G. B. KISTIAKOWSKY

The existence of gaseous detonation waves was recognized nearly seventy years ago and since then a great deal of experimental and theoretical work has been done on this subject. The phenomena involved in their initiation appear to be extremely complicated according to experimental evidence and they have not received much theoretical attention. On the other hand, a successful theory of stationary detonation waves does exist, which treats them from a hydrothermodynamic point of view, disregarding finer kinetic and chemical details. This so-called Chapman–Jouguet[1a] theory interprets detonation waves as shock waves in which the continuing degradation of shock energy into heat is balanced by the release of energy by the spontaneous chemical reactions of the explosive substance. Detonation waves, therefore, can possess stationary character. Specifically, the theory assumes that the chemical reactions reach the state of chemical equilibrium. The energy set free in the spontaneous reaction is quantitatively utilized for the propagation of the shock wave in accordance with the Rankine–Hugoniot equations.[2]

Analyzing the implications of this theory from the point of view of finite chemical reaction rates, v. Neumann[3] showed that the front of a detonation wave must be a mechanical shock in the unreacted material. Chemical reactions are initiated by the compression and heating due to the shock. There follows in the wave a layer of incompletely reacted material in which, normally, pressure drops and temperature rises. This layer has a stationary pressure profile even though energy is constantly drained from it, because of the energy evolution in the chemical reaction. With the completion of the reaction the stationary profile of the wave ends because the supply of useful energy is exhausted. What follows is a rarefaction wave, whose pressure profile changes with time as the wave progresses through the medium. To maintain a stationary character of the detonation wave, the rarefaction must not be able to overtake it. This defines the value of the detonation velocity as the sum of the acoustic and material ("particle") velocities in the plane in which the reaction is completed. This plane will be called the Chapman–Jouguet plane. The theory does not forbid further chemical changes to take place in the rarefaction wave, following pressure and temperature changes, but their occurrence has no effect on the detonation wave because, looked at from this region, the detonation front propagates with supersonic velocity.

A critical experimental test of the quantitative applicability of the Chapman–Jouguet theory was carried out by Lewis and Friauf.[4] They compared its predictions with the experimentally determined detonation velocities in hydrogen–oxygen mixtures, to some of which nitrogen, helium or argon were added. The theory agreed quite well with experiments for mixtures in which hydrogen and oxygen concentrations were not too low provided it was assumed that in the Chapman–Jouguet plane the reaction reached the state of thermodynamic equilibrium, rather than completion. The "complete reaction" of v. Neumann must therefore be interpreted as equilibrium. This is not surprising because no net work can be gained from subsequent chemical changes, accompanying pressure and tempera-

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[1] The research reported in this document was made possible by funds extended Harvard University under O. N. R. Contract N5ori-76 T. O. XIX NR-053-094.

[1a] Chapman, *Phil. Mag.*, **47**, 90 (1899); Jouguet, *J. de math.*, 347 (1905); 6, (1906).

[2] Rankine, *Phil. Trans.*, **160**, 277 (1870); Hugoniot, *J. l'ecole polytech.*, **57**, 3 (1887); **58**, 1 (1889).

[3] v. Neumann, O. S. R. D. Report No. 549 (1942).

[4] Lewis and Friauf, THIS JOURNAL, **52**, 3905 (1930); references there to earlier calculations.

ture decrease. Hence their occurrence does not support the detonation wave any more than pressure and temperature changes of a non-reactive material.

One of several possibilities may account for the discrepancies observed by Lewis and Friauf in certain mixtures: (1) the thermodynamic data used by them have since been shown to be inexact; (2) the experimental detonation velocities were obtained in tubes of small diameter and energy losses to the walls may have caused the low observed velocities, as suggested by Lewis and Friauf; (3) some of the reaction energy may not be available for the propagation of the detonation wave, making the Chapman–Jouguet theory a limiting case only; (4) this theory may be altogether inapplicable.

The present paper is concerned with the limits of validity of the Chapman–Jouguet theory and with the causes of deviations from it.

Experimental Details

The data herein reported are velocities of essentially plane detonation waves in cylindrical pipes. They were measured electronically by the use of miniature piezoelectric gages.

Velocity measurements were carried out in two stainless steel pipes of 1.2- and 10-cm. diameter, respectively. The flanged pipes were made in two sections, bolted together, with a thin cellophane diaphragm clamped between the flanges. The ends of the pipes were closed by flat plates bolted to the flanges. To ensure air-tight connections, grooves were machined in the flanges, into which fitted rubber "O" rings. All other connections were welded air tight. The first "initiator" section was 50 cm. long and was normally filled with readily detonable acetylene–oxygen mixtures, which were ignited by a powerful spark in a spark plug screwed centrally into the end-plate. The other, "experimental," section, 120 cm. long, was filled with the gas mixture to be examined. The initial spark ignition of the acetylene–oxygen mixtures was found to change into a detonation within a distance of a few centimeters. The experimental mixtures were detonated, therefore, by a nearly plane detonation wave striking them through the rupturing cellophane diaphragm. This technique[5] eliminated the long run-up distances required to produce detonation waves from flames in less readily detonable mixtures.

Wave velocities were measured by recording the signal from small tourmaline piezo gages set into the walls of the pipes at 5- and 10-cm. intervals beginning with a gage in front of the cellophane diaphragm. The signals were amplified and recorded photographically as pips on a special cathode ray oscilloscope with a single sweep writing twenty-two lines of 550 microseconds total duration.[6] The sweep was blanked every five microseconds by a precision oscillator, enabling time differences between signals to be evaluated to about 0.2 microsecond. The absolute accuracy of time measurements was at least 0.1%. Detonation velocities were calculated from the time differences between the pips and measured distances between the centers of the gages.

The construction of the piezo gages, which were screwed into the walls of the pipe flush with its inner surface, is shown in Fig. 1. It is a compromise between providing the maximum protection to the crystal from the destructive effects of the detonation waves, producing a sharp signal with least delay and eliminating spurious signals.

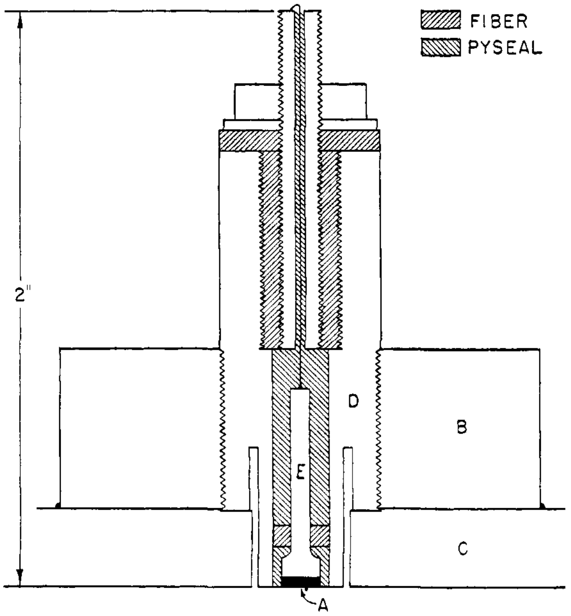

Fig. 1.—Tourmaline piezoelectric gage: A, tourmaline crystal; B, steel block welded to pipe wall (C); D, brass body of gage; E, brass pin.

The troublesome response of gages to advance pressure waves transmitted by the walls of the pipes was reduced by a narrow air gap between the gage proper and the walls of the pipe. The tourmaline crystals with silvered faces[7] were 3 mm. in diameter and 0.5 mm. thick; they were soldered to the supporting brass pin and to the protective front brass shim. These gages gave signals of about a tenth of a volt for waves of average detonation strength. The first signal from each gage was followed by numerous other, usually weaker, signals. They were presumably due to shock reflections within the body of the gage, since their character differed from one gage to another. This led to a frightful hash on the CRO records when several gages were placed in parallel. It was minimized by feeding the signals from each gage to the cathode of a 6H6 diode shunted by 0.5 M ohm with 50 K ohm as the plate resistance. This separate circuit for each gage had the effect of blocking weaker signals, following rapidly on the first one, and leaving only the latter for amplification by a common amplifier.

The amplifier employed two stages of contact biased 6AC7 pentodes, followed by a 6AG7 which had a higher supply voltage to reduce saturation by strong signals. Maximum gain was 10,000, falling off to half this at 300 Kc. The piezo gage nearest to the point of initiation was used as the trigger for the sweep. Directly on the gage was mounted a small two-stage preamplifier using a 6J6, which was coupled to two contact biased 6AC7 pentode stages, whose output fired the trigger thyratron in the CRO circuit. All these circuits were carefully shielded to avoid interference by the initiating spark, which was produced by the discharge of a 1-microfarad condenser charged to 12,000 volts, this circuit being shielded also.

The gas mixtures investigated were made from commercial high pressure cylinder gases, dried by passing through a Drierite column but not otherwise purified or analyzed. According to the manufacturers, the purity of the gases was as follows: hydrogen 99.6% plus, with oxygen the impurity; oxygen 99.5% plus, with nitrogen the chief impurity; helium and argon both better than 99% pure. The gases were mixed in twelve-liter flasks by magnetically operated stirrers. Partial gas pressures were measured to 0.5 mm. In the composition data given

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(5) *Cf.* Wendlandt, *Z. physik. Chem.*, **116**, 227 (1925).

(6) Constructed by the Atomic Instrument Company. We are much indebted to the Rand Project, Douglas Aircraft Company, for lending us this instrument.

(7) Made by Cambridge Thermionic Corporation.

below the oxygen in hydrogen was counted as oxygen but all other gases were taken as 100% pure since the corrections made no significant difference in detonation velocities. The gases were forced into the evacuated pipe by lubricating oil flowing into the flasks. In order to avoid the rupture of cellophane diaphragms both sections of the pipe were filled simultaneously. According to all previous work neither small changes of initial temperature nor those of initial pressure cause significant variations in detonation velocities. The pressures in the experimental section were kept near 760 mm., the temperature was that of the room, averaging about 24°.

The Results and Interpretation

A correlation of experimental detonation rates with the theory is possible only when the observed velocities are those of stationary waves. The only criterion of stationarity in this, as well as previous, work is the constancy of detonation rates. A gradual development of detonations, sometimes over distances measured in many meters, is characteristic of the less readily detonable mixtures when initiation is by a flame. Some doubt should be felt regarding the significance of earlier data with such mixtures unless the velocity was observed, and shown to be constant, over long distances. With the presently used technique this critique does not apply because the detonation waves in experimental mixtures were started by still stronger waves. Therefore the initial velocities in weaker mixtures were measurably greater than the steady values. This excess velocity is imparted to the experimental mixtures by the momentum of the initiating wave. A rough estimate allowing for the rate of energy dissipation in the wave and the relative lengths of the initiating and the experimental compartments makes it improbable that the "overdrive" could persist over the major portion of the experimental section. After extensive preliminary experimentation with numerous gages along the experimental section, the measurements of velocities near the cellophane diaphragm were discontinued as beclouding the clarity of the records by the hash from the first gages. Instead the velocities were measured only over the last sixty cm. of the pipe, divided by three gages into two equal intervals. We believe that a steady velocity over these two intervals is positive proof that a stationary detonation wave is propagating through the pipe.

The accuracy of the present measurements is best tested by the data of Table I. It shows the time intervals between the pips of adjacent gages, placed at 5- and 10-cm. intervals along the pipe and also time intervals for the same distances calculated from the average values of the velocities of the two runs over the entire length of the pipe. An acetylene–oxygen mixture filled the entire pipe in these experiments to ensure good steadiness of detonation velocities. Table I shows that measured time intervals are reliable to 0.3 microsecond, the average deviation being less than 0.2 microsecond. Allowing for other sources of error, such as uncertainties of absolute time scale, of gas composition, etc., we believe that velocities measured over 30 cm. intervals are accurate to 0.5% or better, depending on velocity.

TABLE I

REPRODUCIBILITY OF TIME MEASUREMENTS

Gage distance	Run 643		Run 647	
	Actual time	Calcd. time	Actual time	Calcd. time
10.82	45.0	44.6	45.1	44.8
4.91	19.9	20.2	20.0	20.3
5.00	20.7	20.6	20.6	20.7
5.00	20.5	20.6	21.0	20.7
4.99	20.7	20.6	20.4	20.7
4.97	20.2	20.5	20.6	20.6
5.00	21.0	20.6	20.7	20.7
4.97	20.4	20.5	20.3	20.6
4.97	20.3	20.5	20.6	20.6
5.00	20.7	20.6	20.8	20.7
4.96	20.3	20.4	20.5	20.5
4.96	20.4	20.4	20.7	20.5
10.01	41.0	41.2	41.3	41.4
9.97	41.1	41.1	41.3	41.3
9.98	41.1	41.1	41.4	41.3
Tot. 95.51 cm.	393.3	microseconds	395.3	microseconds
	Av. vel. 2428 m./sec.		Av. vel. 2416 m./sec.	

Table II presents the results of measurements on hydrogen–oxygen mixtures. The two values for each mixture in a pipe are the velocities over the two adjacent intervals, starting, respectively, 60 and 90 cm. from the cellophane diaphragm. More extreme compositions could not be detonated with stationary detonation velocities.

Significant changes of velocity from the first to the second interval were observed only at the extremes of the investigated composition range. In a few experiments the changes are so large that even the velocity in the last interval may be suspected as being higher than the steady value. The error thus committed is not likely to be greater than 1%, however. It should be noted that the data of Tables II and III were obtained with the weakest compositions of the acetylene–oxygen initiator mixtures still producing detonation in the experimental gases. Other runs, not shown here, made with stronger initiating mixtures gave results for the last interval which did not differ significantly from the data here shown, although the decrease from the first to the second interval was larger. Table III presents the velocities measured by the same procedure in three-component mixtures. In order to facilitate comparison with the data of Table II, the velocities have been interpolated to an exactly stoichiometric ratio of hydrogen to oxygen and are shown on the last lines of Table III. The agreement between these values and the measurements of Dixon, Lewis, etc., is on the whole very good, although our velocities in the 10-cm. pipe are consistently higher than those given in earlier publications. This is not surprising because then pipes of small diameter were used. The com-

TABLE II

EXPERIMENTAL DETONATION VELOCITIES IN HYDROGEN–OXYGEN MIXTURES, M./SEC.

% H_2 in O_2	10-cm. pipe First 30 cm.	10-cm. pipe Last 30 cm.	1.2-cm. pipe First 30 cm.	1.2-cm. pipe Last 30 cm.
87.8			3606	3609
87.3			3637	3568
86.9	3990	3867		
86.1			3600	3575
85.2	3825	3695		
82.9			3492	3475
82.6	3562	3555		
81.4			3452	3408
80.1	3387	3390		
78.8			3288	3267
75.9			3197	3170
71.6			3033	3032
71.0			3038	3031
67.8			2872	2863
67.5			2872	2850
66.9				2823
66.7	2833	2825		
66.4	2839	2836		
63.8			2742	2735
62.8	2703	2728		
58.9			2579	2578
58.8			2572	2579
51.5	2360	2365		
50.0	2332	2323	2315	2325
43.5			2160	2151
33.6				1937
33.5	1954	1969		
31.0			1891	1866
25.3			1764	1735
25.2	1768	1763		
20.8			1636	1605
20.5	1644	1635		
18.9			1553	1508
17.6			1497	1417
16.6			1340	1347

TABLE III

EXPERIMENTAL DETONATION VELOCITIES IN HYDROGEN–OXYGEN–RARE GAS MIXTURES

H_2, %	He, %	10-cm. pipe First 30 cm.	10-cm. pipe Last 30 cm.	1.2-cm. pipe First 30 cm.	1.2-cm. pipe Last 30 cm.	Chosen values	
44.4	32.8	3097	3098			3097	
44.4	33.7			3089	3110		3110
24.3	63.2	3388	3407			3395	
24.8	62.7			3339	3307		3307
	A, %						
44.5	33.2	2145	2153			2149	
44.6	33.4			2132	2125		2125
24.7	62.9	1773	1781			1778	
24.9	62.3				1757		1757
Interpolated to Stoichiometric Mixtures							
44.4	33.3		3121		3098		
25.0	62.5		3385		3307		
	A %						
44.4	33.3		2151		2125		
25.0	62.5		1782		1757		

parison of these velocities with our 1.2-cm. pipe data shows indeed as good a degree of agreement as can be expected after allowance for combined experimental errors.

The calculation of detonation velocities by the Chapman–Jouguet theory is quite straightforward but laborious. A method of successive approximations[8] was used in which first a trial value of the temperature in the wave was chosen. From it and the thermodynamic data was calculated a value of the gas density in the wave. Substitution of this into the Chapman–Jouguet equations led to a new value of the final temperature and so forth. With some practice in the choice of the starting values the calculation converged rapidly, to give the desired degree of accuracy, 0.1%, in the velocity. For these calculations thermodynamic data as given recently by the Bureau of Standards[9] were used throughout, chemical equilibria allowed for being

$$2H_2 + O_2 \rightleftarrows 2H_2O$$
$$H_2 \rightleftarrows 2H$$
$$O_2 \rightleftarrows 2O$$
$$H_2 + O_2 \rightleftarrows 2OH$$

Formation of HO_2 was disregarded because of uncertainty over its thermodynamic potential. Formation of hydrogen peroxide and ozone is insignificant at the temperatures and densities of detonation waves. Table IV gives the results of these calculations. Largely because of the use of different values for heat capacities, the calculated velocities are somewhat higher than those given by Lewis and Friauf. In Fig. 2 we have plotted the differences between experimental values of Tables II and III and the theoretical ones, deduced from a smooth curve drawn

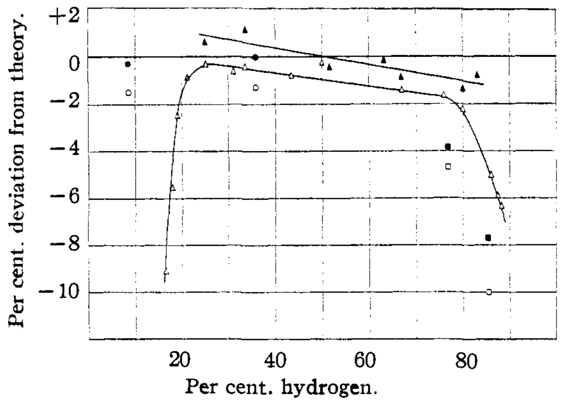

Fig. 2.—Deviations of experimental velocities from theory: triangles = $H_2 + O_2$; squares = $H_2 + O_2 + He$; circles = $H_2 + O_2 + A$; solid = 10-cm. pipe; open = 1.2-cm. pipe.

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[8] *Cf.* Lewis and Friauf, ref. 4; also Kistiakowsky and Wilson, O. S. R. D. Report No. 69 (1941). Their procedure was largely followed here.

[9] "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Standards, 1947, 1948.

TABLE IV

CALCULATIONS FROM HYDRODYNAMIC THEORY

	Initial		Final								
H_2, %	O_2, %		Vol., m./sec.	Temp., °K.	Press., atm.	H_2O %	H_2 %	O_2 %	OH %	H %	O %
89.9	11.1		3943	2440	12.78	20.0	79.7	0.0	0.0	0.3	0.0
80.0	20.0		3427	3439	17.31	42.8	45.2	0.1	3.6	8.2	0.4
66.7	33.3		2852	3678	18.06	54.3	16.5	5.1	12.5	7.8	3.8
50.0	50.0		2332	3467	17.09	48.0	4.0	26.5	13.2	2.5	5.6
33.3	66.7		1940	3031	15.32	34.8	0.6	55.7	6.2	0.3	2.5
25.0	75.0		1747	2675	13.80	26.7	0.1	69.6	2.6	0.0	0.9
		He, %									
44.4	22.2	33.3	3249	3515	17.67	35.2	9.8	3.1	7.2	4.4	2.2
25.0	12.5	62.5	3672	3198	16.25	21.7	3.9	1.3	2.6	1.3	0.6
		A, %									
44.4	22.2	33.3	2153	3515	17.67	35.2	9.8	3.1	7.2	4.4	2.2
25.0	12.5	62.5	1788	3198	16.25	21.7	3.9	1.3	2.6	1.3	0.6

through the points given in Table IV. The experimental points for three-component mixtures were so placed on the abscissas that the mean molecular weights of these mixtures are identical with those of hydrogen–oxygen mixtures indicated in the figure. In the middle composition range the agreement between calculations and experimental data in the 10-cm. pipe is exceedingly good, well within the estimated maximum error of our measurements. The uncertainty in the calculated values is even smaller and therefore it may be concluded that the Chapman–Jouguet theory applies rigorously to these mixtures. This is meant in the sense that detonation velocity may be set equal to the sum of acoustic and mass velocities of the equilibrium mixture, making it the lowest velocity consistent with the Rankine–Hugoniot conditions for this mixture. The converse conclusion, that the experimental mixtures truly reach the state of thermodynamic equilibrium in the Chapman–Jouguet plane of a detonation wave, is proven less rigorously by these measurements. This is so because in mixtures not far from stoichiometric composition formation of water is very far from complete due to high temperatures. The large concentrations of reactant molecules, radicals and atoms have a stabilizing or buffering effect on detonation velocities because of a particular relation between density and temperature in these mixtures. For instance, a calculation for the stoichiometric mixture in which the degree of reaction (into water) was in error by several per cent. gave a detonation velocity agreeing with that of Table IV to better than 0.1%. Calculations of Lewis and Friauf and of Scorah[10] neglect some of the dissociation processes here included and employ different data for heat capacities, yet their results for the stoichiometric mixtures differ from ours by only 1.6 and 1.1%, respectively. The agreement of calculated and experimental velocities is therefore no proof that thermodynamic equilibrium is accurately established in the detonation wave.

Significant differences between calculated and observed velocities exist at the extremes of the composition range. Here also the difference of velocities measured in wide and narrow pipes is larger. This immediately suggests that energy losses to the walls of the pipe are the cause. Such losses may be produced by two mechanisms,[11] that of heat conduction and that of friction. Although ordinary heat conductance is not fast enough to reduce the temperature of the detonation gases appreciably in the few microseconds that count, it may do so through formation of a rarefaction wave. This happens because the gases in contact with the walls are instantly cooled with a corresponding reduction of volume. This starts a gas flow toward the walls; in other words, a rarefaction wave moves into the interior of the pipe with the acoustic velocity of the hot gases. If the rarefaction waves coming from the opposite walls of the pipe meet each other still within the stationary region of the detonation wave, reduction of detonation velocity should result. This reasoning is completely analogous to the theory of the reduction of detonation velocities in cylindrical explosive charges of finite diameter by radial expansion of product gases.[12] Also algebraically the relation between the tube diameter and the decrease of detonation velocity should be similar to that in charges of condensed explosives. Therefore the small difference of velocities observed in the 1.2- and the 10-cm. tubes is evidence that in the latter the effect of tube diameter is negligible.

The effect of friction at the walls might appear as turbulence on a macroscopic scale. However, the walls, joints and gages presented a smooth surface and special experiments[13] showed that the front of the detonation waves was plane to within 2 mm. or better. Turbulence on a gross scale was therefore not involved. Friction would also

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[10] Scorah, *J. Chem. Phys.*, **3**, 424 (1935).

[11] A third, radiation losses, is readily shown to be insignificant.

[12] Jones, *Proc. Roy. Soc.* (*London*), **189A**, 415 (1947); Eyring, *et al.*, *Chem. Rev.*, **45**, 69 (1949).

[13] See Paper II of this series.

cause a non-turbulent reduction of mass velocity of the material in the wave, which should propagate into the interior of the pipe with acoustic velocity. Its effect should therefore be indistinguishable experimentally from that of heat conduction. It may be thus reliably concluded that limiting velocities have been observed in the 10-cm. pipe.

A comparison in Fig. 2 of 10-cm. pipe velocities with the theoretical values brings out the following features: (1) in the compositions having the highest detonation velocities (excess hydrogen or helium) the experimental velocities are lower than calculated, (2) in the compositions having the lowest detonation velocities (excess oxygen or argon) the experimental values are slightly higher than theoretical when oxygen is in excess, but are equal to them in presence of argon. The excess of experimental over theoretical velocity in the case of oxygen-rich mixtures appears to us as the clue for the interpretation of these phenomena. It should be noted that once the correct heat capacities and heats of reaction have been used in the calculation of detonation velocities, the inclusion of additional side reactions normally leads to a reduction of calculated detonation rates because of attendant lowering of temperature. This would be the case if HO_2, H_2O_2, O_3, etc., were included in the present calculations. Since the thermodynamic data here used are adequately accurate, we believe that the present theoretical detonation velocities should be looked upon as the upper limits to the true values. Therefore the mentioned excess of experimental velocities, although small, appears to be a real one. Its most plausible explanation is that the heat capacities of the components due to internal degrees of freedom of the molecules do not reach complete statistical equilibrium[14] within the reaction zone of the detonation waves. In mixtures rich in argon, which has virtually no internal heat capacity, this effect should be minimized and so the observed and theoretical detonation velocities agree perfectly. The same reasoning applies to the differences observed between hydrogen-rich and helium-rich mixtures. Superimposed on this effect, however, is a lowering of all experimental velocities in these fast detonating mixtures. One might suggest that it is caused by excessively rapid heat losses to the walls of the tube owing to the very high acoustic velocities in these mixtures. However, the relatively small differences in velocities between the 1.2- and the 10-cm. pipe make this a rather dubious explanation. As a hypothesis which we hope to test later, the following may be suggested. The v. Neumann treatment of the structure of detonation waves was deduced for what amounts to a zero-order chemical reaction, *i. e.*, one which proceeds with constant speed to completion. The reactions involved in experimentally observed detonations undoubtedly reach equilibrium asymptotically. Consequently the rate of production of useful energy may drop below the rate of consumption, due to the rarefaction wave, even before the equilibrium is attained. In that case v. Neumann's identification of the Chapman–Jouguet plane as the state of "complete reaction" (*i. e.*, chemical equilibrium) must be modified. The Chapman–Jouguet condition, *i. e.*, the equality of detonation with the sum of acoustic and material velocities, should then hold for the plane in which the evolution of useful energy is just balanced by its losses. The rest of the spontaneous reaction occurs in the rarefaction wave and has no effect on the propagation of the detonation wave.[15] If this is the case, one must expect detonation velocities lower than those calculated on the assumption of complete equilibrium because some of the energy is not utilized. With the progress of the wave through the medium and the accompanying reduction of the pressure gradient in the rarefaction wave one might expect in these cases a slow rise in detonation velocity as the Chapman–Jouguet plane gradually shifts to the state of more nearly complete equilibrium. Two factors should cause this phenomenon to be especially pronounced in hydrogen- or helium-rich mixtures: (1) the temperatures of the wave are relatively low, making chemical reactions slower; (2) the acoustic velocities in these mixtures are very high, effectively contracting the time scale of hydrodynamic processes in the wave.

If both the incomplete equilibration of internal heat capacities and the incomplete attainment of chemical equilibria are present, it may seem strange indeed that experimental and Chapman–Jouguet detonation velocities agree so well in other mixtures. There is indeed no cause to believe that in such mixtures the equilibria, both thermal and chemical, are exactly attained. They may be approached more closely because of high temperatures producing more frequent elementary chemical reactions. The main reason, however, is the buffering action of the largely dissociated reaction systems on the detonation velocities. They can produce seemingly perfect agreement of experiment and theory without the theory being accurate in detail. To test this it would be necessary to measure not only the velocities but also temperatures and densities in the Chapman–Jouguet plane.

Summary

Detonation velocities in hydrogen–oxygen mixtures with and without addition of argon and helium have been determined in tubes of two diameters over a wide range of concentrations.

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[14] Kantrowitz, *J. Chem. Phys.*, **14**, 150 (1946); there earlier literature.

[15] In detonations of acetylene–oxygen mixtures the oxidation of carbon monoxide to dioxide appears not to contribute to the propagation of the wave, presumably because it is much slower than the primary oxidation of acetylene, *cf.* Bone and Townend, "Flame and Combustion in Gases," Longmans Green, London, 1927.

Comparison with velocities calculated by the Chapman–Jouguet theory shows agreement only for mixtures with a ratio of hydrogen to oxygen not far from stoichiometric. The deviations from the theory are only partially explainable by losses of energy to the walls of the tube. Evidence is presented to show that the internal heat capacity of polyatomic gases may not be fully excited and also that the chemical reactions may not reach the state of thermodynamic equilibrium in the Chapman–Jouguet plane of some detonation waves.

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Gaseous Detonations. II. Initiation by Shock Waves[1]

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Extensive studies of the initiation of gaseous detonation have shown no single sequence of events.[1a] The primary result of a thermal initiation appears always to be a flame, which propagates with subsonic speed. Where conditions are such that the flame causes adiabatic compression of the still unreacted material ahead of it, its velocity speeds up. In some of the observations the speed of the flame seems gradually to rise until it equals that of the detonation wave. Normally a discontinuous change of velocity is observed from the low flame velocity to the high speed of detonation. In still other observations the detonation wave has been observed to originate apparently spontaneously some distance ahead of the flame front. The place of origin has been shown to coincide with the location of a shock wave sent out by the expanding gases of the flame. The observed phenomena are quite complex and exceptions may easily be taken to this synopsis, but we believe that it is as accurate as a brief summary can be.

The theoretical problem of transitions from flames to detonations has not been extensively treated, except by Zeldovich[2] and by Shchelkin[3] who attribute it to turbulence near the front of the flame. Other less quantitative ideas attribute the initiation of detonations to chain carriers,[4] etc. Le Chatelier proposed that adiabatic compression by a shock is the cause of detonations and initiation by shock waves has been a subject of extensive experimental work, Laffitte,[5] Wendlandt,[6] Payman,[7] Dixon,[8] Bone[9] and others having participated in it. The gist of their findings is that detonation waves may be started by shock waves, even when these arrive from chemically inert media. Very intense shocks appear to start the detonation instantly and even to overdrive it initially to an excess velocity. Weaker shocks appear to cause ignitions, which eventually change into detonations. Still weaker shocks produce no chemical effects. In view of the usually discontinuous character of detonation initiation by flames and other evidence[10] it may be surmised that shocks are the normal if not the exclusive cause of detonation waves. This mode of initiation has therefore particular interest and yet previous experimental work has been far from exhaustive or even quantitative. The initiation by shocks arriving from inert media should possess, relatively speaking, maximum simplicity because the transfer of the reaction by chain carriers is excluded and the theory of shocks is sufficiently well developed so that initial conditions in the explosive gas mixture may be deduced, except for the uncertainty of incomplete equilibration of the internal degrees of freedom in the molecules.

The present paper describes experiments on the initiation of gaseous detonations by plane shock waves transmitted by inert gases.

Experimental Details

The same equipment as described in the preceding paper, but with suitable additions, was used. The experiments were carried out in the 10-cm. pipe, which was assembled by bolting together flanged sections 50, 20, 10 and 100 cm. long. The first two sections contained the initiating mixture. Separated from it by a cellophane diaphragm 0.001″ thick was a 10-cm. buffer layer of air and beyond the next cellophane diaphragm was the experimental gas mixture. Gases were taken from commercial high-pressure cylinders without further purification. The first piezoelectric gage was located about 5 cm. ahead of the first cellophane diaphragm and was used to trigger the oscilloscope sweep. The next gage was located midway in the buffer section. The experimental section had twelve gages spaced 5 cm. apart, followed by three more at 10-cm. intervals. The same piezoelectric gages and amplifiers were used as described in the first paper, except that the resistances on the diode filters were altered when weaker waves were expected, or the diodes were even omitted altogether to permit the amplification of still weaker signals.

Some of the phenomena observed suggested the possibility that the waves transmitted through the cellophane

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(1a) For a review see Lewis and v. Elbe, "Combustion, Flames and Explosions of Gases," Cambridge University Press, Cambridge, England, 1938.

(2) Zeldovich, *J. Exp. Theor. Phys. U. S. S. R.*, **10**, 542 (1940); *J. Tech. Phys., U. S. S. R.*, **17**, 3 (1947).

(3) Shchelkin, *Comp. rend. acad. sci. U. R. S. S.*, **23**, 636 (1939); **47**, 482 (1945).

(4) Lewis, THIS JOURNAL, **52**, 3120 (1930).

(5) P. Laffitte, *Compt. rend.*, **177**, 178 (1923).

(6) W. Wendlandt, *Z. physik. Chem.*, **116**, 227 (1925).

(7) Payman, *Proc. Roy. Soc. (London)*, **A120**, 90 (1928).

(8) Lean and Dixon, *Manch. Lit. Phil. Soc.*, **5**, 16 (1891).

(9) Bone, *et al.*, *Phil. Trans. Roy. Soc. London*, **A235**, 29 (1936).

(10) Kistiakowsky, Third Symposium on Combustion, Flame and Explosion Phenomena, Madison, Wisconsin, 1948.