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Gaseous Detonations. X. Study of Reaction Zones

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The resolution time of the apparatus for rapid measurements of gas densities in shock and detonation waves by the absorption of x-rays was evaluated by studies of shock waves and found to be largely determined by the slit width. The rotational relaxation of N_2 , O_2 , H_2 , and CH_4 in mixtures with xenon and the vibrational relaxation of O_2 , H_2 , and CH_4 were too fast for observation. The dissociation rate constants were determined for hydrogen: $k_D = 2.5$ and 4.2×10^{-16} cc/sec at 2850 (?) and 3250°K and for oxygen: $k_D = 2.3$ and 6.8×10^{-16} cc/sec at 3100 and 3500°K. The initial (shock front) densities in $2H_2 + O_2 + \frac{1}{2}Xe$ detonating mixtures were found to be consistent with calculations based on full rotational but no vibrational relaxation, when it was assumed that the rates of exothermic reactions rise to a maximum within less than one μ sec and then decrease somewhat faster than in a second order reaction. The pre-exposure of the cold gases to x-rays for a few seconds results in faster initial reaction rates, while a pre-exposure of only a few milliseconds has no measurable effect. No effect of pre-exposure on the rates after about 50% completion of the reaction is evident. These findings indicate a highly branched mechanism of chain carrier generation. The effects of total pressure and gas composition on the duration of the reaction zone were investigated with several mixtures. Substitution of deuterium for hydrogen reduces the rate by about 30%. The retarding effect of water vapor on the rate of the hydrogen-oxygen reaction is not pronounced.

A RECENT paper described rapid measurements of gas density changes in detonation waves by the method of x-ray absorption.¹ The Zeldowitch-Doering-v. Neumann representation¹ of the wave as a shock in unreacted gases, followed by a steady-state zone of spontaneous chemical reactions was in general confirmed. The reactions (in $H_2 + O_2$, $CO + H_2 + O_2$ and $CH_4 + O_2$ mixtures, with small additions of xenon) were found to occur so fast, even at the low pressures employed, that the conversions were of the order of 50% within the estimated resolution time of the apparatus. Taking this time as compounded only of the transit time of the waves by the x-ray slit and of the usual slight tilts and distortions of the wave front, the extrapolations of the observed gas density ratios to the shock front suggested considerably lower ratios than expected from the shock waves theory. The present investigation was largely concerned with the causes of this apparent anomaly but included also some new studies of the reaction kinetics in detonation waves.

EXPERIMENTAL DETAILS

Except as noted below and for some refinements of electronic circuits the apparatus employed was the same as previously described.¹ The beryllium covered slits of the original design formed narrow recesses on the inside of the detonation tube which could disturb the density measurements. The slits were rebuilt so as to place the curved beryllium sheets flush with the inner walls of the tube. The new slits were only 1 mm wide. In the previous measurements the full x-ray beam was turned on for several seconds before the passage of the detonation wave by the slits and therefore, cold gases were exposed

to intense x-ray radiation. There was the possibility that this pre-exposure produces considerable numbers of free atoms and radicals. These then might initiate branching chain reactions when the gases are heated by the shock wave. A shutter was interposed, therefore, between the x-ray tube and the entrance slit to the detonation tube. The motion of the shutter triggered the spark igniting the acetylene-oxygen mixture in the driver section of the detonation tube. By trial-and-error it was possible to stagger the spark and the opening of the slit so that the gases were exposed to x-rays for as little as 1 millisecond before the passage of the wave. This change in operation made it necessary to use dc amplification in the Tektronix scope displaying gas density changes. By adjusting the vertical centering controls the trace was kept off the face of the tube until the output of the photomultiplier, generated by the x-rays, brought it into the middle of the tube face. The increase in the gas density caused by the detonation wave, which reduces the transmitted x-ray intensity, gave then entirely adequate deflections of the trace. This modified procedure made necessary some changes in the method of the calibration of the vertical position of the trace *versus* gas density¹ but they resulted in an over-all improvement of the accuracy. The gas density ratios reported here are accurate to better than 10%, insofar as the calibration errors are involved.

For the experiments with pure shock waves a fine Nichrome wire was strung axially the full length of the driver section of the detonation tube. This section was filled with rich hydrogen-oxygen mixtures to about atmospheric pressure and the wire was exploded by discharging through it a large high-voltage condenser. The radially expanding flame provided the necessary uniform high pressure to rupture the Mylar diaphragm and produce shocks with negligible attenuation.

* Present address: Department of Chemistry, Yale University.
¹ G. B. Kistiakowsky and P. H. Kydd, *J. Chem. Phys.* **25**, 824 (1956).

RESULTS

Extensive experiments were made with shock waves, both to determine the time resolution of the apparatus and to gain information on the relaxation times of the internal degrees of freedom of the gases used subsequently in detonating mixtures. The initial plan was to study shocks of Mach numbers approximating those characteristic of gases in the shock fronts of detonation waves. It was found, however, that the ionization gauges used to determine wave velocities and to trigger the scopes did not operate satisfactorily when the shock temperatures were of the order of 2000°K, although they responded well to detonation waves. Since these gauges depend for their proper functioning largely on the spontaneous ionization of the gases in the wave front, the degree of ionization, at the same temperature, is apparently higher in detonation waves than in shocks. This must be the result of exothermic reactions characteristic of the former. The shock wave experiments were made, therefore, at somewhat higher shock temperatures. In all these experiments the observed density rise-times exceeded those calculated from the transit times of the wave front through the x-ray beam (0.5 to 0.8 μ sec) by not more than 0.5 μ sec. The shock fronts, therefore, had almost negligible distortions, as compared with detonation waves.

In experiments with xenon alone, at 10 mm initial pressure, the density ratios immediately after the passage of the wave agreed well with calculations,² but were followed by further gradual density increases. The final values of $\sigma = \rho_s/\rho_i$ were about 0.5 unit higher than calculated at 4000–6000°K. The pumping system in all experiments consisted of only a good mechanical oil pump and, therefore, the dissociation of residual oil vapors could be responsible for the observations. Indeed, on increasing the initial pressure and so reducing the contribution from the residual oil vapors, good agreement with calculations and nearly complete absence of gradual density changes was obtained. Thus,

starting with 19.6 mm xenon, at a wave velocity of 1470 m/sec, the observed density ratio was 3.90 against 3.95 calculated. Starting with 4.75-mm xenon and 15.2 mm helium, the observed ratio was 3.67 against 3.68 calculated, at a wave velocity of 2035 m/sec.

Table I shows the results of experiments with mixtures of xenon and nonmonatomic gases. In all cases the initial rapid rise of the density ratio was followed by a slower change. Since the temperatures in these shocks are too low to be concerned about the dissociation of traces of large organic molecules present, the gradual rises must be due either to internal relaxation or the dissociation of the major constituents of the mixtures. The vibrational relaxation times, τ , were calculated by the method of Blackman,³ only a rough fit of the equation to the experimental curves being possible because the observed changes in σ were rather small, substantially less than one unit in σ . Blackman finds, in the temperature range of the present measurements, that the vibrational relaxation time of oxygen is less than one μ sec and, therefore, the much longer lasting observed rise in the density ratio must be due to oxygen dissociation. The initial rate of dissociation was calculated by the equation:

$$k_D = \frac{C_p T_s}{\sigma^2 c \Delta H} \frac{d\sigma}{dt} \quad (1)$$

in which T_s is the shock temperature calculated without allowing for dissociation, c is the concentration of the dissociating gas, and t is the observer's time counted from the instant of the passage of the shock front by the slits and related to the true time spent in the shock by the dissociating gas by the relation:

$$\tau = \int_0^t \sigma dt = \sigma_{Nt}. \quad (2)$$

From the observed dissociation rate constants shown

TABLE I. Shock waves in mixtures of xenon and nonmonatomic.

Gas	P ₁₀ mm	Xenon %	D m/sec	σ_{\max} obs.	σ_s calc. ^a		T_s °K ^a with C _{vibr}	τ μ sec	P ₁₀	k _D × 10 ¹⁶ cc/molecule sec
					No C _{vibr}	With C _{vibr}				
N ₂	18.64	25.0	1870	6.0	5.07	6.08	3160	22	4.7 × 10 ⁻⁵	
H ₂	20.25	25.1	2150 ^b	5.3	4.99	5.45	2850 ^b	53	5.4 × 10 ⁻⁴	2.5
	23.57	25.1	2310	5.6	5.06	5.65	3250	32	8.2 × 10 ⁻⁴	4.2
O ₂	20.72	25.1	1940	7.7	5.11	6.31	3500			6.8
	20.61	25.1	1815	6.4	5.07	6.15	3110			2.3
CH ₄	15.07	33.3	2440 ^b	11.0	5.59	11.9	2500 ^b			
	5.42	77.7	1400	7.5	4.37	6.75	3150			
C ₂ H ₄	5.71	77.7	1597	7.8	4.41	7.91	3650			
C ₂ H ₆	5.84	76.6	1580 ^b	9.9	4.45	9.52	3060			
	5.25	76.6	1580	9.1	4.45	9.52	3060			

^a Without dissociation.

^b Uncertain because of the malfunctioning of the gages.

² W. Doering and G. Burkhardt, Theory of Detonations, Tech. Report F-TS-1227 1A, GDAM A9T46, Air Materiel Command.

³ V. Blackman, J. Fluid Mech. 1, 61 (1956).

in Table I and thermodynamic equilibrium constants,⁴ the association rate constants for oxygen are calculated to be 1.3 and 3.3×10^{-33} cc² sec⁻¹ at 3500 and 3100°K, respectively. The errors of measurements are such that only the average of these values is significant. Since the vibrational relaxation times of hydrogen have not been previously determined, both these and the dissociation rate constants were calculated and are shown in Table I. In calculating τ it was assumed that k_D is zero, in calculating k_D that τ is immeasurably short. From the dissociation rate constants shown, the recombination rate constants are obtained as 9.7 and 1.9×10^{-33} cc² sec⁻¹, only the average value being significant. In experiments with CH₄, C₂H₄, and C₂H₆ the density ratios attained nearly 90% of their final values after times equal to the transit times of the waves by the slit. The rest of the density changes occurred in about 5 μ sec of observer's time, the ratios remaining then constant for as long as 20 to 30 μ sec.

Experiments with detonation waves were mainly concerned with hydrogen-oxygen-xenon mixtures. The improvements of the apparatus produced no drastic changes in the appearance of the density records when compared with earlier work.¹ The observed peak density ratios, however, increased from values in the range of 2.0–3.3 to 2.8–3.8 in the present experiments. This is readily accounted for by the reduction of slit width, more accurate calibration procedure and the selection of lower initial pressures, with attendant lengthening of reaction zones. It was noted that longer reaction zones were accompanied by higher peak density ratios. An extensive series of runs with the 2H₂+O₂+ $\frac{1}{2}$ Xe mixture at 35 mm initial pressure showed that seconds-long pre-exposure of the gases to x-rays reduced the peak density ratio from about 3.7 to 3.4. The effect of this pre-exposure on the later portions of the density profiles was statistically not significant. Experiments were then made with the mixture 2D₂+O₂+ $\frac{1}{2}$ Xe, also at 35 mm initial pressure. The scatter of the data was somewhat larger and the rise-time to peak density longer (2.5 rather than 2.0 μ sec). The duration of the reaction zone was increased by *ca* 30% and the effect of pre-exposure was barely significant statistically. In various experiments with the shutter the pre-exposure to x-rays varied between 1 and 5 milliseconds. This caused no significant change in the shape of the density profiles.

Systematic experiments were made to study the effects of gas composition and of initial pressure on the density profiles. These measurements were reproducible to better than 10% of the time to attain a given value of σ , except in the first two to three μ sec of observer's time. Occasionally, however, the rise-times were excessively long, indicating serious distortions of the wave fronts, which was confirmed by the signals of the

“planarity” gauges.¹ In these runs the remainder of the density profiles was also abnormal and it is suspected that spinning detonations were generated in the tube. The results of these infrequent runs are not considered in the following. In the previous publication¹ the density profiles were characterized by two parameters, t_{50} and t_{75} , defined as the (observer's) times for the density to decrease halfway and three-quarters of the way, respectively, from the initial empirically extrapolated values of σ to the density ratio of the Chapman-Jouguet state. Different parameters, τ_{50} and τ_{75} , are used in the following, which are closer to the true times to attain 50 and 75% completion of the reaction, as discussed later. The following regularities were established for these parameters: (1) τ_{75} is approximately twice as long as τ_{50} ; (2) τ_{50} and τ_{75} are inversely proportional to the initial pressure of a 2H₂+O₂+ $\frac{1}{2}$ Xe mixture, which was varied from 24 to 70 mm; (3) τ_{50} remains constant at 7 μ sec and τ_{75} decreases from 18 to 12 μ sec when the oxygen pressure is increased in several steps from 5 to 20 mm, while the hydrogen and xenon partial pressures remain at 20 and 5 mm, respectively; (4) τ_{50} decreases from 10 to 7 μ sec and τ_{75} decreases from 18 to 11 μ sec when the partial pressure of hydrogen is increased from 10 to 40 mm, while the partial pressures of oxygen and xenon remain at 10 and 5 mm, respectively; (5) τ_{50} and τ_{75} remain unchanged when the partial pressure of xenon is increased from 5 to 15 mm, while those of hydrogen and oxygen remain constant at 20 and 10 mm; and (6) τ_{50} and τ_{75} are approximately doubled and the peak density ratio is increased from 3.7 to 4.0 when 0.9 H₂O is added to 2H₂+O₂+ $\frac{1}{2}$ Xe.

Experiments were made with methane-oxygen-xenon mixtures to determine what effect oxygen has on the rate of this reaction. Holding methane pressure at 15 mm and that of xenon at 7 mm, the pressure of oxygen was increased from 23 to 200 mm in several steps. τ_{50} and τ_{75} increased by a factor of two starting at 2.7 and 4.5 μ sec.

The observed effect of long pre-exposure to x-rays upon the initial reaction rates in detonating mixtures suggested the formation of kinetically significant concentrations of free atoms and radicals. To gain an idea of the magnitudes involved, the ionization produced by the x-rays was measured in the mixtures used for the detonation wave experiments. After determining the geometry of the x-ray beam by exposing photographic film inside the detonation tube, parallel plates were placed into the tube, so as not to be struck by x-rays. The tube was then filled with a typical gas mixture, a variable potential was applied to one plate and the current from the other was determined with the aid of an electrometer tube amplifier. To obtain a reasonably flat ion current plateau it was necessary to reduce the x-ray tube emission current from the normally used 38 ma to 4 ma (while holding the voltage at the normal 28.5 kv) and to lower the gas pressure to 10 mm. A fairly flat plateau was obtained then between 50 and

⁴ Selected Values of Thermodynamic Properties (National Bureau of Standards, Washington, D. C.), Ser. III, Vol. 1.

250 v applied potential, the observed current corresponding to the generation of 5×10^9 ion pairs per cc sec of irradiated volume.

DISCUSSION

Shock Waves

The experiments with monatomic gases demonstrate that the static calibration technique relating the scope trace deflection to the density ratio does apply to dynamic measurements; also, that the time resolution of the apparatus is given by the transit time of the wave through the x-ray beam and the distortion of the wave front. The secondary comparatively slow density ratio increases observed with nonmonatomic gases can be, therefore, reliably attributed to either internal relaxation or dissociation or both. In all experiments with shock waves the density ratios attained values within the resolution time of the apparatus, which were as large or larger than those calculated for complete rotational relaxation. Therefore, the tentative suggestion¹ that rotational relaxation may be comparatively slow at high temperatures can be definitely discarded.

The gradual density rise observed in experiments with nitrogen is undoubtedly due to vibrational relaxation because the observed values of τ agree well with the interpolated data of Blackman.³ In hydrogen experiments it probably is not. Penny and Aroeste⁵ have calculated vibrational transition probabilities P_{10} for N_2 , O_2 , and H_2 . For the former two their calculations agree well with the measurements of Blackman.³ For hydrogen at 3000° their value is 2.1×10^{-2} , whereas the average of values in Table I is 6.8×10^{-4} . This suggests that the observed density rise is due to dissociation, the vibrational relaxation in hydrogen being too fast for observation. The recombination rate constants calculated from the data of Table I fall indeed in the range of theoretical estimates by Rice⁶ (0.9×10^{-33} cc²/sec) and by Careri⁷ (2.5×10^{-32} cc²/sec). The vibrational relaxation of oxygen is known³ to be too fast for observation by the present technique and, therefore, the dissociation rate constants are definitely established by the data of Table I.

Detonation Waves

The gauge groups used to determine the nonplanarity of the detonation wave front¹ indicated consistently larger tilts or curvatures than in experiments with pure shocks. The observed longer rise-times are completely explained by this finding, since the wave velocities were not markedly different. A general conclusion which can be drawn from various experiments with detonation waves is that the longer is the reaction zone, either because of a lowering of the pressure or a change in gas

composition, the more distorted is the wave front and hence the longer is the rise-time to peak density. The previously mentioned experiments with hydrogen and deuterium mixtures illustrate this point. A regrettable consequence is that an apparatus of the type used cannot be used to study in detail the initial portion of the reaction zone, no matter how narrow is the slit chosen. A limited information on this portion may be obtained, however, by fitting empirical density curves to experimental data. Trials were made with curves derived by double integration for slit transit time and wave distortion¹ from the equation:

$$\sigma_t = \frac{\sigma_s - \sigma_2}{t_2^n} (t_2 - t)^n + \sigma_2, \quad (3)$$

where σ_t is the desired density ratio at an (observer's) time t , counted from the midpoint on the initial rising part of the curve, σ_2 is the Chapman-Jouguet density ratio, usually 1.8 in the present experiments, t_2 is the somewhat arbitrarily chosen time when the observed density ratio becomes constant and equal to the Chapman-Jouguet ratio and σ_s is the density ratio in the shock front. Very good fits of the later portions of the observed reaction zone density profiles were obtained assuming for σ_s an immeasurably fast rotational relaxation in the shock front and values of 2 to 3 for the parameter n , but the calculated peak density ratios were consistently too high and sharp. Higher values of n reproduced the initial but not the later portions of the reaction zone. A satisfactory fit with the entire observed density profiles was obtained by using a steep linear density decrease from the calculated shock density to 4.0 for the first 0.5 μ sec (observer's time) and from then on using Eq. (3) with $\sigma_s = 4.0$. Typical of the results obtained are Figs. 1 and 2. In Fig. 1 the barred vertical lines show the total range of experimental points in five runs made under identical conditions. In Fig. 2 are shown individual measurements of two runs. In both figures no smoothing of the junction between the two segments of the assumed density profile is shown. Such smoothing is, of course, entirely possible without loss of agreement with the experi-

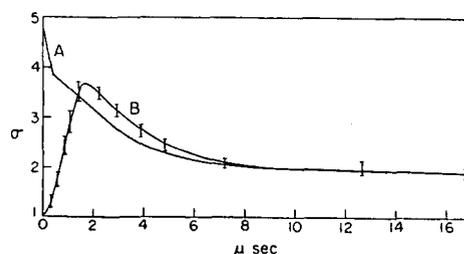


FIG. 1. The observed density ratios (barred vertical lines) in five experiments with a $2H_2 + O_2 + 0.5Xe$ mixture at 35 mm pressure. Line A is the assumed density profile; line B is the same after the correction for slit width and wave-front distortion. Abscissas are observer's time.

⁵ H. Penny and H. Aroeste, *J. Chem. Phys.* **23**, 1281 (1955).

⁶ O. K. Rice, *J. Chem. Phys.* **21**, 750 (1953).

⁷ G. Careri, *J. Chem. Phys.* **21**, 749 (1953).

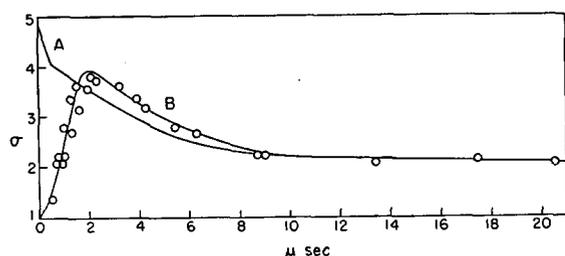


FIG. 2. The observed density ratios in two experiments with a $2\text{H}_2 + \text{O}_2 + 0.5\text{Xe} + 0.9\text{H}_2\text{O}$ mixture at 44 mm pressure. Line A is the assumed density profile; line B is the same after the correction for slit width and wave-front distortion.

mental measurements, provided the adjacent portions of the two segments of the assumed curve are suitably modified. From the plots like those shown in Figs. 1 and 2 the (observer's) times to reach $\sigma_{50} = (\sigma_1 + \sigma_2)/2$ and $\sigma_{75} = (\sigma_1 + 3\sigma_2)/4$ were read off and were converted to τ_{50} and τ_{75} by Eq. (2).

The σ_s used in Figs. 1 and 2 assumes rotational but no vibrational relaxation. The experimental data can be represented also by curves which start from σ_s corresponding to complete internal relaxation. However, the initial linear segment must be made much steeper than shown in Figs. 1 and 2. Not only is it started at a higher value of σ_s but either the junction with the segment represented by Eq. (3) must be made at a lower value of σ than 4 or the time of the junction chosen as less than $0.5 \mu\text{sec}$. Otherwise the calculated peak density ratios are consistently higher than observed. This modified representation would not be appropriate in the case of hydrogen-oxygen mixtures because the rate of vibrational relaxation under the conditions existing in the shock front of detonation waves is such^{3,6} that it is nearly complete only at the instant when the assumed linear segment is joined to the curve of Eq. (3). The density decrease during the first $0.5 \mu\text{sec}$ (of observer's time or *ca* $2.5 \mu\text{sec}$ of gas time) is the net result of a decrease due to exothermic chemical reactions and an increase due to vibrational relaxation. When converted from observer's time to gas time, the linear segments of Figs. 1 and 2 become slightly convex but definitely do not allow for significant (e.g., $1 \mu\text{sec}$ of gas time) induction periods in chemical reactions. If such are introduced into the assumed density profiles the agreement with experimental data is completely lost. It is therefore certain that rapid formation of water (and not only of intermediate free radicals) starts within less than $1 \mu\text{sec}$ after shock compression and before the vibrational relaxation is completed. In these early stages of the reaction the rate of formation of water molecules must be assumed to be 5 to 10 times faster than it is at the instant of 50% completion of the reaction. With these provisos, the present measurements of reaction zones in hydrogen-oxygen mixtures may be said to be consistent with the predictions of the Zeldowitch-v. Neumann theory and, therefore,

they largely resolve the difficulties discussed in the previous paper.¹

Drawn in observer's time the linear segments of the density profiles of methane-oxygen detonation waves are even steeper, relative to the segments represented by Eq. (3) because the calculated shock front densities are higher due to higher heat capacities but the observed peak density ratios were very nearly the same. After a correction for the difference in the gas and observer's time scales, however, the profiles of the reaction zones were quite similar to those observed in hydrogen-oxygen mixtures: the large initial density ratios are hidden from observation by the compression of the time scale due to these high density ratios, provided the relative rates of change are approximately the same.

Reaction Kinetics

The conversion of the measured rate of ion pair production to conditions existing in detonation wave experiments gives values in the range of 10^{11} ions per cc/sec. It is not known with certainty to how many atoms and free radicals this corresponds, but a one-to-one correspondence appears probable.^{8,9} At such rates of generation the atomic lifetime due to recombination is many seconds. The lifetime due to such reactions as: $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$; $\text{O} + \text{H}_2 = \text{OH} + \text{H}$; $\text{O} + \text{O}_2 + \text{M} = \text{O}_3 + \text{M}$ and attacks on organic impurities is very much shorter. However, the products of such reactions still must react with each other to form really stable end products and should be quite capable of rapidly starting reaction chains under the conditions of detonation shock fronts (2000°K). The effective lifetime at room temperature of chain initiators generated by the x-rays is, therefore, in the range of seconds and their concentration after a pre-exposure of milliseconds is several orders of magnitude lower. Furthermore, when the pre-exposure is in the millisecond range, this concentration must be proportional to the pre-exposure time and the initiators are present only in the volume traversed by the x-rays because the time is too short for diffusion. After a pre-exposure of seconds, the initiators spread, due to diffusion, through a gas layer several cm thick. These considerations lead to several conclusions: (1) since the changing of the pre-exposure from 1 to $5 \mu\text{sec}$ has no observable effect on the density profile, the seeding of the gas with chain initiators in numbers of the order of $10^8/\text{cc}$ is not important for the initiation of the thermal reaction in hydrogen-oxygen mixtures; (2) the seeding with numbers of the order of $10^{11}/\text{cc}$ does have a measurable but not a striking effect on the initial rate of reactions; (3) the seeding has no effect on the reaction rates after the first few microseconds. This follows because in experi-

⁸ G. Friedlander and J. Kennedy, *Nuclear Radiochemistry* (John Wiley and Sons, Inc., New York, 1955).

⁹ Zuller, Hamill, and Williams, *J. Chem. Phys.* **23**, 1263 (1953).

ments with the pre-exposure limited to milliseconds, the seeded gas is swept by the wave past the slits and the later portions of the reaction zone are observed in gases which were not seeded by the x-rays. The reverse is true of experiments with long pre-exposure and yet the later portions of the reaction zones are identical in the two types of experiments. In the first two microseconds of gas time something like 10^{18} molecules of water per cc are formed (Figs. 1 and 2), while an average molecule suffers about 10^4 collisions. Clearly, the 10^{11} of chain initiators per cc could not affect measurably this rate unless an extremely effective chain branching takes place. The lack of an observable effect of seeded chain initiators, when their concentration is in the range of 10^8 /cc, means that the thermal rate of generation of chain initiators is substantially in excess of 10^8 per μ sec. This is entirely in accord with the observed rates of dissociation of diatomic molecules,¹⁰ even not allowing for such reactions¹ as $\text{H}_2 + \text{O}_2 = 2\text{OH}$, but these reactions must attain a substantial fraction of their steady-state rates before the vibrational relaxation in the gases is well advanced.

The finding that τ_{75} is twice as long as τ_{50} and the good fit of Eq. (3) with $n=2$ to experimental density profiles mean that reaction is formally second order over most of its course. However, very soon after the beginning of the reactions, in the part represented by the linear segment (Figs. 1 and 2), the relative rates appear to be substantially higher than expected in a reaction of second order. This is quite puzzling, since the addition of water (Fig. 2) has an only minor effect on the density profile, so that it is not the accumulation of the final reaction product which makes the net branching factor less than unity. Unfortunately, the interpretation of experimental data in the early stages of the reactions is subject to such uncertainties that the speculation on this problem may be premature.

The experiments with deuterium-oxygen mixtures gave density profiles quite similar to those obtained with hydrogen, except for a lengthening of the time scale by about 30%. Hinshelwood *et al.*¹¹ have observed

¹⁰ See the foregoing, for instance.

¹¹ Hinshelwood, Williamson, and Wolfenden, Proc. Roy. Soc. (London) A147, 48 (1934).

a considerably greater retarding effect of deuterium on the rate of the slow thermal reaction with oxygen at lower temperatures. They were able to interpret this quantitatively as the effect of the isotopic zero point energy change on the rate of elementary reactions involved. Such effect, when extrapolated to the temperatures existing in the reaction zones of detonation waves agrees well with the observed 30% retardation. Moreover, the initial portions of the isotopic reaction zones are very much alike, insofar as it can be established by the methods outlined above. Thus, there is no evidence that the faster diffusion of hydrogen atoms from the main body of the reaction zone to the shock front has a significant effect on the start of the reaction.

The parameters τ_{50} and τ_{75} have a much closer relation to the times for 50 and 75% completion of the reaction than the parameters t_{50} and t_{75} previously used,¹ but they are not identical with such times, as should have become clear from the preceding discussion. As regards the formal kinetics, both the ratio τ_{75}/τ_{50} and the dependence of these parameters on total pressure indicate a second order reaction and their variation with composition indicates that hydrogen affects the rate more than oxygen. This difference, however, is not as pronounced as was suspected earlier.¹

Over the entire range of compositions studied, an increase in oxygen concentration was observed to retard the rate of reaction with methane. Some of this may be simply the cooling effect of excess oxygen, but a parallelism with the observations made on slow oxidations of hydrocarbons at lower temperatures¹² is unmistakable. It is unfortunate that the compression of time scale in the initial portions of such reactions by the high density ratios make kinetic studies by the present method quite unprofitable.

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¹² B. Lewis and G. v. Elbe, *Combustion, Flames and Explosions* (Academic Press, Inc., New York, 1951).