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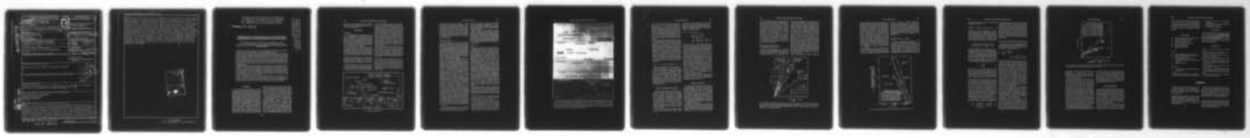

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Effects of non-equilibrium reaction on sound propagation are identified and studied by comparing the observed amplification rates with theoretical predictions. Experiments were conducted in a Pyrex tube filled with a homogeneous mixture of hydrogen, chlorine and argon of different initial compositions and pressures. During the photochemical reaction following ultraviolet irradiation, the amplitude of a two-cycle burst of variable frequency (generated at one end of the reaction tube) is monitored simultaneously with mixture temperature and chlorine concentration, as the sound burst propagates in the reaction tube and reflects back

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EXPERIMENTAL INVESTIGATION OF ACOUSTIC-KINETIC INTERACTIONS IN NON-EQUILIBRIUM H_2-Cl_2 REACTIONS

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Effects of non-equilibrium reaction on sound propagation are identified and studied by comparing the observed amplification rates with theoretical predictions.

Experiments were conducted in a Pyrex tube, filled with a homogeneous mixture of hydrogen, chlorine and argon of different initial compositions and pressures. During the photochemical reaction following ultraviolet irradiation, the amplitude of a two-cycle burst of variable frequency (generated at one end of the reaction tube) is monitored simultaneously with mixture temperature and chlorine concentration, as the sound burst propagates in the reaction tube and reflects back and forth at its two ends. After correcting for dissipation losses, one obtains the net amplification rate which would conceivably be observed in a non-dissipative reacting medium.

Significant amplification of the sound pressure fluctuations due to acoustic-kinetic interaction has been consistently observed at different acoustic frequencies and for different mixture compositions and pressures. The amplification rate is typically three times larger than what would be expected from simple consideration of conservation of the acoustic energy, thus demonstrating the significance of the additional contribution due to acoustic-kinetic coupling. (Total amplification of up to 80% of the initial sound amplitude was commonly observed over the sound residence time of 0.1 to 0.3 sec).

Within experimental accuracy, the measured amplification rates are found to agree with predictions, derived on the basis of Arrhenius kinetics, for all mixture compositions and pressures and acoustic frequencies tested. The observed effects can be interpreted by a quasi-steady theory, which is also shown to be valid for the tests reported in this paper.

Introduction

It has long been recognized that the coupling between chemical kinetics and acoustic wave propagation may be instrumental in the growth of small pressure disturbances, leading eventually to the nonlinear, large-amplitude instabilities often observed in practice. Considerable insight into this phenomenon has already been obtained in several theoretical studies.[1-6] In particular, sound propagation in an infinite, irreversibly reacting medium was examined for the case of a simple one-step reaction with Arrhenius kinetics.[5-6] Substantial amplification of the pressure fluctuations (as high as 300 to 400% under certain conditions) was predicted for exothermic reactions. Extensive theoretical results in regard to sound scattering, structure of acoustic and chemical instability, and energy transport processes involved in the acoustic-kinetic interactions have also been presented. Yet, to the knowledge of the authors, no systematic experimental investigation of this phenomenon has been reported so far; hence, the motivation for this work.

This paper presents the experimental results on sound propagation in a non-equilibrium hydrogen-chlorine reacting mixture. The sound amplitude, mixture temperature and chlorine concentration were simultaneously measured to determine quantitatively the effects of chemical reaction on sound amplification during the H_2-Cl_2 photochemical reaction. These results were then compared with the corresponding predictions based on the previous theoretical study.[5] The agreement observed in this comparison has contributed toward a better understanding of the acoustic-kinetic coupling involved.

Experimental

Apparatus

Sound propagation in a homogeneous mixture of hydrogen and chlorine (diluted with argon) undergoing non-equilibrium photochemical reaction was experimentally studied. This reaction was selected due to its relatively high degree of controllability and the possibility of initiating the reaction in a homogeneous manner by ultraviolet irradiation.

The experiments were conducted in a horizontal 5.5-m long, 8-cm diameter Pyrex tube, surrounded by three sets of dc fluorescent black-light lamps (General Electric F40 BL) and placed in a light-proof wooden enclosure. A schematic of the apparatus is shown in Fig. 1.

The overall reaction rate is measured by monitoring the uv light (from one of the fluorescent lamps) absorbed by molecular chlorine with a photomultiplier.[*] The temperature of the gaseous mixture is obtained by means of four 1-mil chromel-alumel thermocouples (T1, T2, T3, T4) placed at the center of the tube and at various axial positions. The longitudinal homogeneity of the reaction can then be checked by simultaneous monitoring of these thermocouples. Average temperature across one diameter of the reaction tube is also measured by means of a 0.2-mil tungsten resistance thermometer, denoted by W in Fig. 1. Note that W is placed very close to the photomultiplier tube. The average chlorine consumption rate and the corresponding mean temperature history are thus available for each experimental run.

Plane sound waves are generated at one end of the tube by means of a piston, activated by a mechanical shaker. The pulse generator-function generator-power amplifier combination is used to generate a 2-cycle burst of variable frequency which propagates down the reaction tube.[*] Sound pressure is monitored

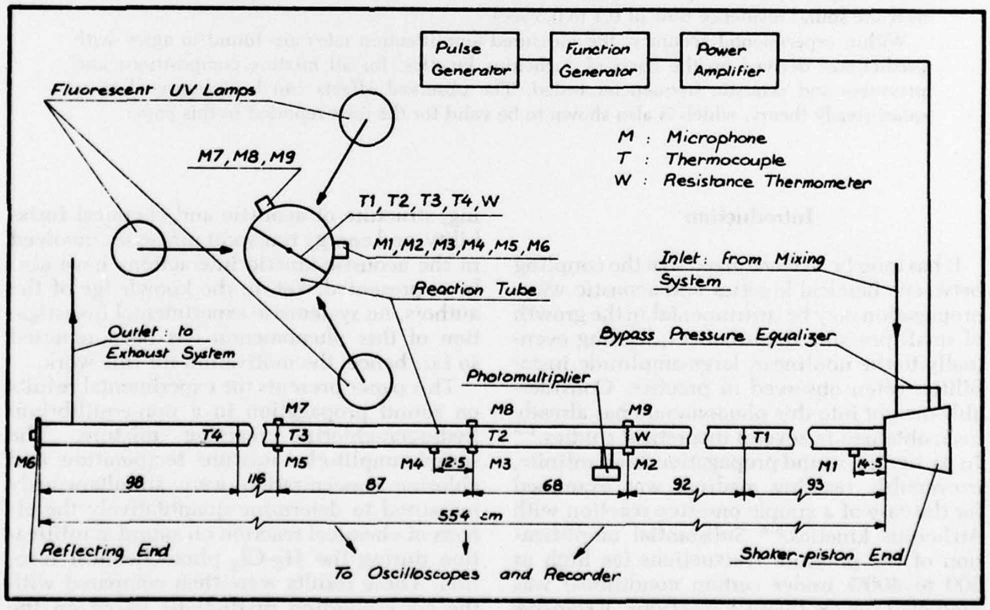

FIG. 1. Schematic of apparatus

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[*] The photomultiplier (RCA 931A) is equipped with a filter, centered at a wavelength (3340 Å) which corresponds approximately to the peak absorption of chlorine (with a width of 120Å at half-amplitude).

[*] Examination of the energy spectrum of such a 2-cycle burst at 300 Hz (which is the frequency employed in most of our experiments) shows that 93% of the energy is carried at that frequency, thus justifying the assumption that the acoustic signal is essentially one at a specific frequency (with negligible effect due to other Fourier components in such a pulse).

at various stations along the tube by means of miniature condenser microphones (M1 through M9), mounted flush with the inside surface of the tube. The incident sound burst subsequently reflects back and forth at both ends of the tube and as a result, one is able to examine a specific acoustic wave during a time-interval as long as 0.2 to 0.3 sec, before its amplitude reaches the noise level due to sound absorption.

Experimental Data

The data obtained from a typical experimental run are shown in Fig. 2. The sound signals monitored at two stations M4 and M5, the resistance thermometer signal indicating the average gas temperature and the uv light intensity indicating chlorine concentration are shown (as recorded by a recording oscillograph Visicorder) in (A) before reaction, (B) during reaction and (C) after reaction. Part (D) represents an analysis of the sound pressure amplitude and will be discussed later.

The incident 2-cycle 300-Hz sound burst followed by successive reflected bursts is shown on the microphone signal traces. Before reaction, the resistance thermometer signal[**] indicates that the temperature remains at its ambient value. In part (B) of Fig. 2, the H_2-Cl_2 reaction is initiated at time $t = 0$ by turning on the uv lamps. The photomultiplier signal indicates a 0.2 to 0.3 sec induction time in the photochemical reaction. (Note that the duration of the induction time is very much dependent on the impurity content of the mixture, such as O_2, H_2O and NCl_3). The reaction then enters its non-equilibrium phase during which the quantity of uv light absorbed decreases until the reaction is completed. Knowing the initial concentration and the absorption coefficient of chlorine, one can deduce its consumption rate from the uv intensity curve by means of the Beer-Lambert law. During reaction, the resistance thermometer indicates a temperature increase, peaking at 600°K, which is lower than the computed adiabatic temperature. This is due to inevitable heat losses to the surroundings. The sound-burst generation is delayed so that its residence time approximately coincides with the non-equilibrium part of the reaction. This is shown in part (B) of Fig. 2, where the incident and successive reflected bursts can be identified. Towards the end of the reaction, large-amplitude, low-frequency pressure oscillations sometimes develop. Although these oscillations complicate the analysis of the acoustic signal, they generally occur outside the region of current interest.

After completion of the reaction—approximately 2 seconds after initiation—another sound-burst is sent through the reacted mixture as shown in part (C) of Fig. 2. Note that, due to heat losses to the environment, the average temperature has returned to its ambient level. Note also that the photomultiplier signal indicates no further change in the average chlorine concentration.

Results

The approach taken in this investigation is to identify and study the effects of non-equilibrium reaction on sound propagation by comparing the acoustic amplitudes before, during and after the chemical reaction for given initial mixture composition and pressure and sound frequency. This comparison is illustrated in part (D) of Fig. 2 where the peak-to-peak amplitude of the second cycle of the 2-cycle burst in each successive reflection, normalized by the corresponding amplitude in the incident burst, is shown versus time in a semi-logarithmic plot. The amplitude change before and after reaction can be represented by one single straight line,[*] indicating that the sound absorption coefficient is the same[**] before and after reaction. During reaction, the sound attenuation is significantly reduced, indicating a net relative amplification of approximately 80% during the 0.08 sec residence time as shown in Fig. 2. Such reduced attenuation was consistently obtained in the course of these experiments and, in certain cases, amplification of the reflected bursts was even observed in the microphone signals.

Consideration of the various sound absorption mechanisms in the reaction tube indicates that the major cause of energy losses is due to the presence of boundaries.[7] Theory[8] shows that the attenuation coefficient (per unit time)

[**] The 60-cycle ripple (caused by the ambient 60-cycle electric field) on the resistance thermometer and photomultiplier signals should be ignored.

[*] In fact the data present a slight "saw-tooth" variation, possibly due to the different reflecting characteristics at the two ends of the tube.

[**] Note that the composition of the mixture does not differ significantly before and after reaction, as argon and hydrogen are usually predominant (typical composition: $1Cl_2 + 3H_2 + 17\,Ar$). Furthermore, the observed attenuation rates in a non-reacting mixture are found to agree well with values computed on the basis of classical acoustics theory.[7,8]

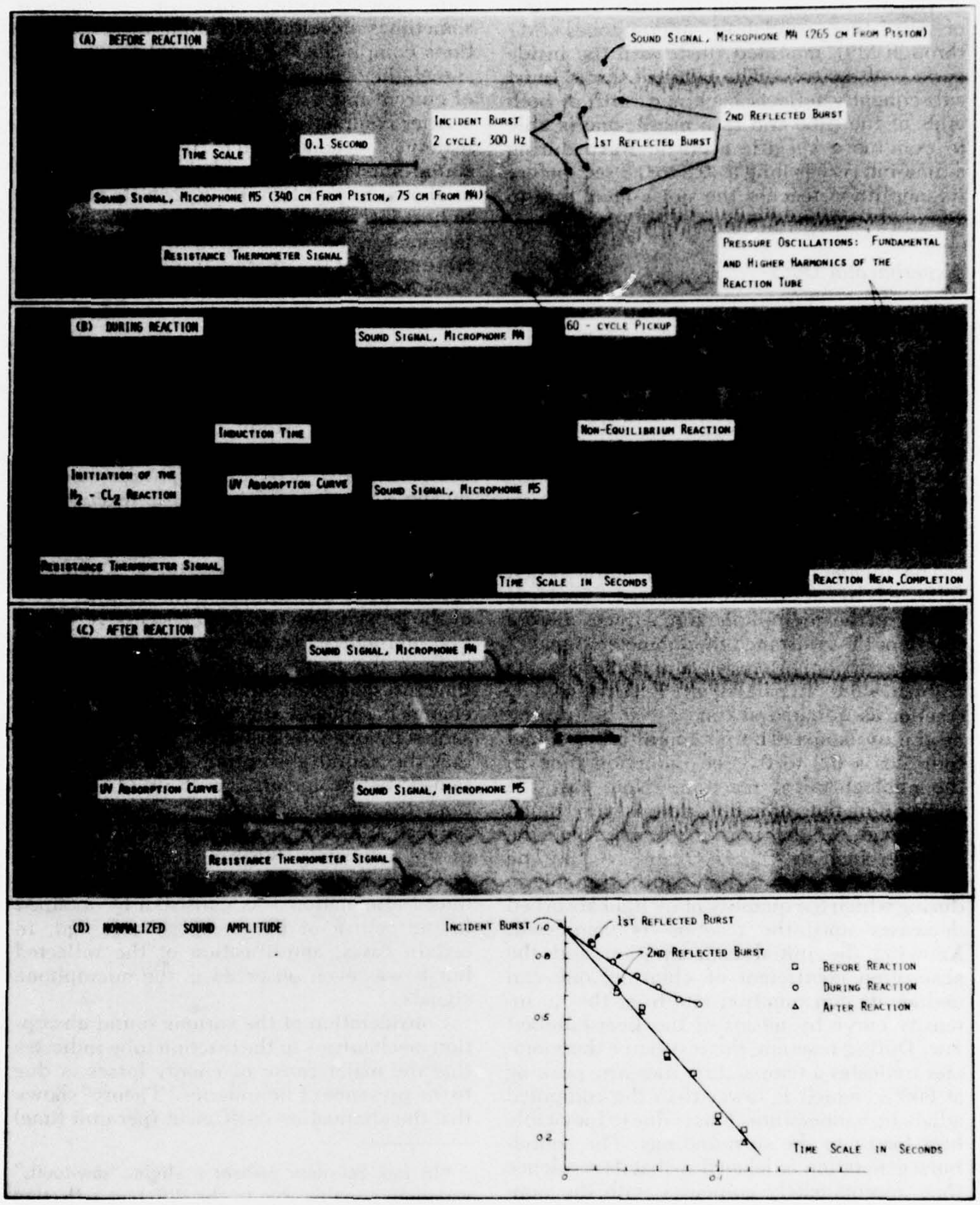


FIG. 2. Experimental data from a typical test (identified by ⬡ in Figs. 4 and 5). Mixture molal composition: 1 Cl_2: 2 H_2: 15 Ar. Initial pressure: 280 Torrs. Initial Temperature: 295°K. Acoustic frequency: 300 Hz. (A) Before reaction, showing sound signals at two microphones and temperature by resistance thermometer. (B) During reaction, showing sound signals, temperature rise and chlorine concentration decrease. (C) After reaction, showing sound signals, temperature and uv intensity. (D) Normalized sound amplitudes versus time, before, during and after reaction.

due to such losses decreases as the gas temperature outside of the boundary layer rises. Experiments[7] in a non-reacting medium at different temperatures further show that the attenuation coefficient varies inversely as $T_w^{1/4}$, where T_w is the average temperature measured by the tungsten resistance thermometer. The attenuation coefficient obtained before reaction is thus corrected for temperature effect to give the actual dissipation during chemical reaction.

At any time during chemical reaction, the observed attenuation coefficient (per unit time) is measured as the slope of the normalized amplitude curve (cf. part (D) of Fig. 2). The difference $\Delta\alpha(t)$ between this measured value and the dissipation coefficient, corrected for temperature effect as described above, is then regarded as the *net effect* on sound amplification due to acoustic-kinetic coupling that would conceivably be observed in a corresponding *non-dissipative* reacting medium. Thus, the instantaneous pressure amplitudes of an acoustic wave at a small time interval τ apart during chemical reaction can be represented by

$$|p_1(t_{ref} + \tau)| = |p_1(t_{ref})| \exp\{\Delta\alpha(t_{ref})\tau\} \qquad (1)$$

Significant amplification of the sound pressure fluctuations due to acoustic-kinetic interaction was consistently observed throughout this investigation at different acoustic frequencies and for different H_2-Cl_2-Ar mixture compositions and pressures (total amplifications of up to 80% of the initial sound amplitude were commonly obtained over the sound residence time interval). Analysis of the experimental results in terms of a previously published theory[5] will be presented in the following sections.

Review of Theoretical Predictions

A physical model for acoustic-kinetic interactions and the predictions derived therefrom have been reported in our earlier work.[1,4,5,6] Briefly, one considers a travelling plane acoustic wave of specified wave length in a homogeneous, stagnant, ideal gaseous medium of infinite extent, which is also inviscid, non-conducting, non-diffusive, and nonreacting. At time $t = 0$, a simple one-step reaction, obeying Arrhenius law, is initiated and the subsequent acoustic-kinetic interactions are studied.

For the quasi-steady limit (high acoustic frequency or slow reaction), which will be shown later to be the regime where the current experiments are, the following expression relating the amplitudes of the pressure fluctuations at two instants separated by a small time interval τ can be derived[5,7]:

$$|p_1(t_{ref} + \tau)| = |p_1(t_{ref})| \times \exp\left\{\frac{1}{2\gamma T_o(t_{ref})} \frac{dT_o}{dt} \times \left[m + \frac{\beta(\gamma - 1)}{(T_o/T_{o,i})} + \gamma\right]\tau\right\} \qquad (2)$$

where m and β are the reaction order and reduced activation energy, respectively, in the Arrhenius rate expression [cf. Eq. (3)]. (Other symbols are defined in the Nomenclature). The various terms in Eq. (2) represent the different possible effects on acoustic waves due to chemical reaction. First, these effects depend on the mean temperature as well as its rate of change, indicating amplification for exothermic reactions and attenuation for endothermic reactions. Furthermore, these effects depend on the kinetic parameters m and β, which represent the dependencies of the reaction rate on the concentration and the temperature, respectively. For constant reaction rate ($m = \beta = 0$), Patureau[7] has shown that the effect due to the third term inside the bracket in Eq. (2) results in the conservation of the acoustic energy in a non-dissipative but temperature-varying medium.

In the following section, the measured amplification rates of pressure amplitude according to Eq. (1) will be compared with the predictions based on Eq. (2).

Discussion of Results

As noted earlier, consideration of the various sound absorption mechanisms in the reaction tube and their behavior under changing temperature conditions enables one to separate the dissipative effects from the amplitude measurements during non-equilibrium reaction. More specifically, the effects due to tube boundaries can be subtracted. As a result, one obtains the net amplification rates of acoustic waves that would conceivably be observed in a corresponding non-dissipative, irreversibly reacting H_2-Cl_2 medium.

Attempts have been made to interpret the observed acoustic-kinetic interactions in terms of the elementary reactions.[7] Several difficulties present themselves. First, the reaction rate is known to be very sensitive to the presence of trace impurities, such as O_2, NCl_3 and H_2O. However, the kinetics involving the latter two impurities are not well known. Secondly, the concentrations of these impurities in various tests cannot be determined precisely. On the other hand, the measured temporal change in the chlorine concentration can be adequately modeled by Arrhenius kinetics (as is to be described later). Furthermore, for a direct comparison with the experimental observations, theoretical analysis of the acoustic-kinetic interactions is available in the literature for a simple one-step reaction, obeying Arrhenius law.[5,6] Such a comparison is presented in the following sections.

Demonstration of the Existence of Acoustic-Kinetic Interactions

In Fig. 3, the instantaneous rate of amplification $\Delta\alpha$ is plotted against the average rate of mean temperature increase dT_w/dt, at two constant temperatures, as measured by the resistance thermometer. Each point refers to a different experimental test of different mixture composition and pressure but at the same acoustic frequency of 300 Hz and initial temperature of 295°K. Typical confidence limits resulting from a 5 to 15% experimental error are shown for low and high amplification rates. The dashed lines represent the predictions derived on the basis of conservation of the acoustic energy only. These lines are easily obtained from Eq. (2) where m and β are set equal to zero. It is found that all data points lie above these lines by a significant margin. This is a clear indication that, in non-equilibrium H_2-Cl_2 reactions, conservation of the acoustic energy cannot, by itself, account for the observed sound amplification. The effects of the acoustic-kinetic coupling (through the parameters m and β in Eq. (2)) must, therefore, be considered, thus demonstrating on an experimental basis the existence of acoustic-kinetic interactions.

The experimental data show reasonable

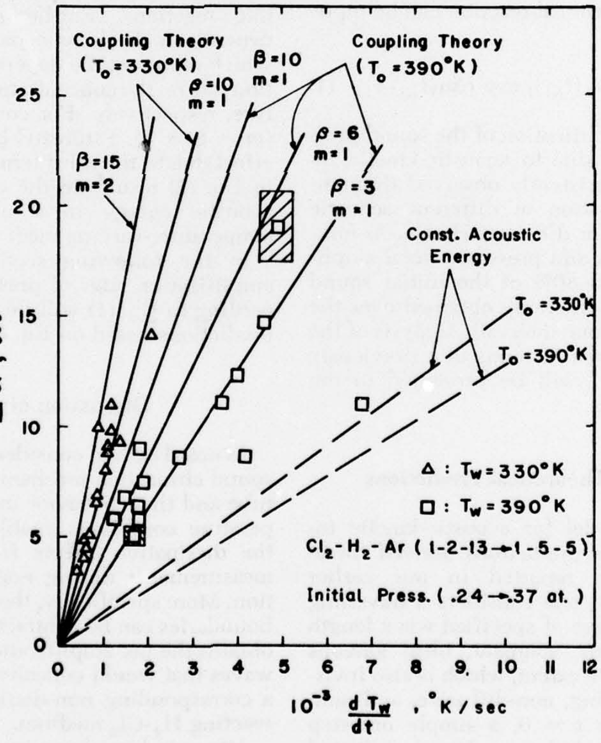


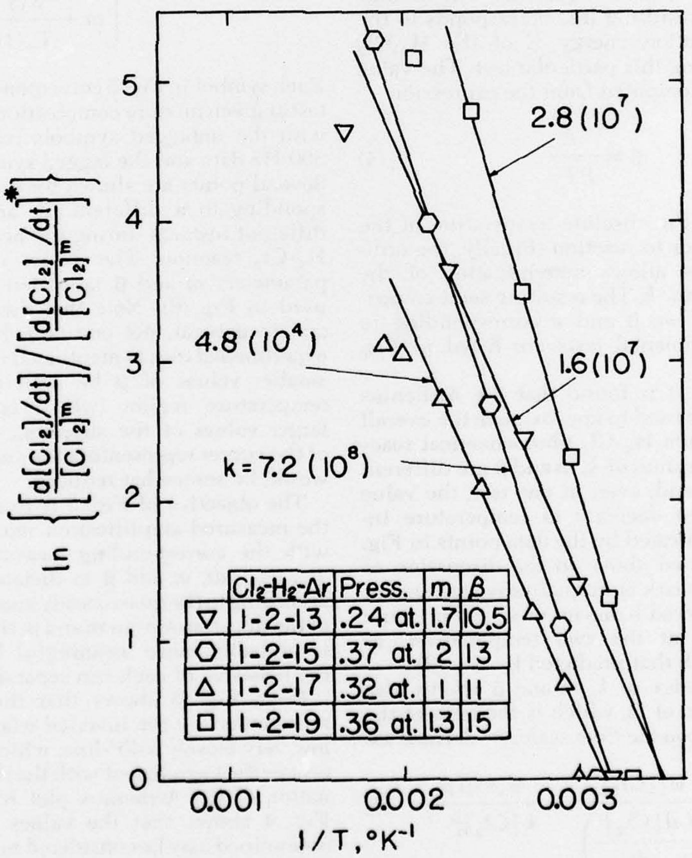
FIG. 3. Observed sound amplification rate versus rate of temperature rise at two mean temperatures, 330 and 390°K. Dashed lines show theoretical predictions according to Eq. (2) for constant acoustic energy ($m = \beta = 0$). Solid lines show predictions from Eq. (2) for different values of m and β, as indicated. Acoustic frequency: 300 Hz.

qualitative agreement with the predictions of the quasi-steady interaction model represented by Eq. (2) in the sense that, if one ignores the scatter for a moment, a fairly linear relationship is obtained between $\Delta\alpha$ and dT_w/dt at constant T_w. At constant T_o (which is equivalent to the measured T_w), Eq. (2) predicts a linear relationship as well, provided m, β and γ are the same for all tests. Also, when T_o is lowered, the theory predicts an increased slope of the linear relationship, all other conditions being the same. Except for possible effects due to varying m and β (to be discussed below), this is somewhat verified in the experimental data as the points corresponding to T_w = 330°K lie on a curve steeper than the one for 390°K.

For comparison with the experimental results, other theoretical curves are included in Fig. 3 for the same two temperatures. These curves are obtained from Eq. (2) for different values of m and β, as indicated. Note that the low-temperature points (T_w = 330°K) are bounded by theoretical curves at larger values of β than those for 390°K, thus suggesting that the reaction rate may not be adequately represented by an Arrhenius expression of constant β. Indeed, as shown in Fig. 4 below, one would expect that the value of β to be larger at lower temperatures.

Empirical Values of m and β

In order to compare the predictions of Eq. (2) with the experimental observations on a quantitative basis, one must determine the Arrhenius kinetic parameters m and β for the H_2-Cl_2 reaction. As mentioned earlier, the average chlorine consumption rate and the corresponding mean temperature history are available for each experimental test. These data



	Cl_2-H_2-Ar	Press.	m	β
▽	1-2-13	.24 at.	1.7	10.5
⬡	1-2-15	.37 at.	2	13
△	1-2-17	.32 at.	1	11
□	1-2-19	.36 at.	1.3	15

FIG. 4. Arrhenius plots of four tests, all at 300 Hz. (k in (liter/mole)$^{m-1}$/sec)

are arbitrarily represented by the following Arrhenius expression:

$$\frac{d[Cl_2]}{dt} = -k[Cl_2]^m \exp(-\beta\, T_{o,i}/T_w) \qquad (3)$$

where $[Cl_2]$ is the instantaneous chlorine molal concentration at temperature T_w (see also the Nomenclature for the definition of the other symbols). This operation yields optimum values of the parameters k, m and β, which would best fit the data for one specific test. Such procedure is illustrated in Fig. 4 where

$$ln\left\{\frac{d[Cl_2]/dt}{[Cl_2]^m} \bigg/ \left(\frac{d[Cl_2]/dt}{[Cl_2]^m}\right)^{*}\right\}$$

is plotted against the measured value of $1/T_w$ at the same instant of time (with the asterisk indicating a reference value). The parameter m is adjusted for each test until the data points fall on a reasonably straight line. The average slope of the resulting line corresponds to the overall activation energy E of the H_2-Cl_2 reaction during this particular test. The value of β is then computed from the expression

$$\beta \equiv \frac{E}{RT_{o,i}} \qquad (4)$$

where $T_{o,i}$ is the absolute temperature of the gas phase prior to reaction. Finally, the ordinate intercept allows determination of the frequency factor k. The resulting semi-empirical values of m, β and k corresponding to several experimental tests are listed in Fig. 4.

In general, it is found that the Arrhenius model may be used to approximate the overall non-equilibrium H_2-Cl_2 photochemical reaction. Yet, the values of k, m and β are different for each test and, even in one test, the value of β seems to decrease as temperature increases, as indicated by the data points in Fig. 4. As mentioned above in the discussion of Fig. 3, this remark is in qualitative agreement with the observed behavior of sound pressure amplification at the two temperatures, as compared with that predicted by Eq. (2).

The knowledge of k, m and β allows also the calculation of Ω, which is the ratio of the chemical to acoustic time scales,[5,6] defined as:

$$\Omega \equiv -\frac{\omega_i [Cl_2]_i}{\left(\dfrac{d[Cl_2]}{dt}\right)_i} = \frac{\omega_i \exp\beta}{k\,[Cl_2]_i^{m-1}} \qquad (5)$$

The computed values of Ω for the four experimental tests listed in Fig. 4 are between 100 and 300 at an acoustic frequency of 300 Hz. At these values of Ω, it is expected from the theoretical studies[5,6] that the acoustic-kinetic interactions would be in the quasi-steady regime. Therefore, Eq. (2) should be valid to predict the chemical effects on sound amplification. In the following section, the experimental results will be compared with such predictions.

Comparison Between Theory and Experiment

In Fig. 5, the observed amplification rate $\Delta\alpha$ is plotted versus the predicted rate A, which is deduced from Eq. (2) in terms of the corresponding measured quantities as:

$$A \equiv \frac{1}{2\gamma T_w(t)} \frac{dT_w(t)}{dt} \times \left[m + \frac{\beta(\gamma-1)}{T_w(t)/T_i} + \gamma \right] \qquad (6)$$

Each symbol in Fig. 5 corresponds to a specific test at given mixture composition and pressure, with the untagged symbols referring to the 300 Hz data and the tagged symbols, 900 Hz. Several points are shown for each test, corresponding to a different T_w and dT_w/dt at different instants during the non-equilibrium H_2-Cl_2 reaction. The values of the kinetic parameters m and β tabulated in Fig. 4 are used in Eq. (6). Note that these parameters are, in general, not constant during a given experimental test, as mentioned earlier. Should smaller values of β be used in the higher temperature region (which corresponds to larger values of the abscissa), the curvature of the curves representing the various test runs would be somewhat reduced.

The objective of Fig. 5 is to show whether the measured amplification rate is consistent with the corresponding measured values of T_w, dT_w/dt, m and β as dictated by Eq. (6) according to the quasi-steady analysis. Because of the uncertainties in m and β, the comparison is probably more meaningful by examining the behavior of each run separately.

First, Fig. 5 shows that the test results represented by the inverted triangles (▽) follow very closely a 45°-line, which would indicate perfect agreement with the theory. Examination of the Arrhenius plot for this test in Fig. 4 shows that the values of m and β determined may be considered to be quite good throughout the major part of the temperature

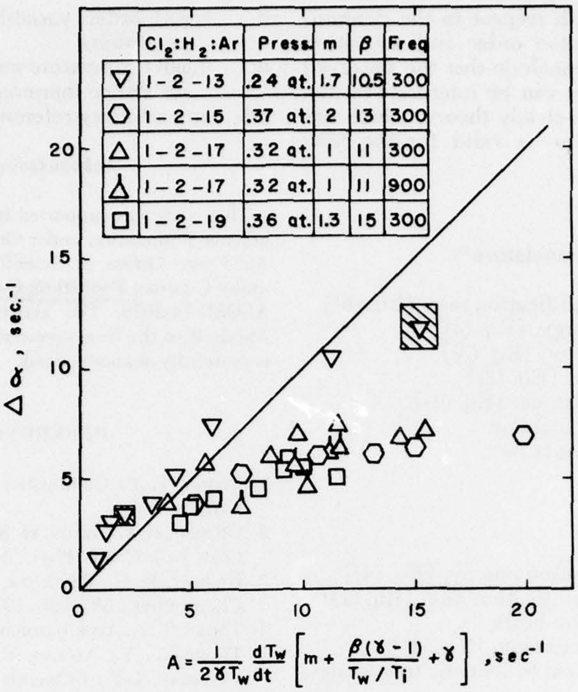


FIG. 5. Observed sound amplification rate versus predicted rate according to Eq. (6). Untagged symbols are identified in Fig. 4 for 300 Hz. Tagged symbols are for 900 Hz.

range (300 to 370°K) in which the pressure amplitudes were measured. The observed agreement thus indicates that the acoustic-kinetic interactions can indeed be interpreted by the quasi-steady theory.

The results of the other tests, however, do not follow the 45°-line as well. Since they include data at high temperatures at the large values of the abscissa shown, one expects that the values of β to be used in the computation of A in Eq. (6) should be less than those tabulated in Fig. 4, which were determined by fitting the low-temperature data. This remark is also supported by Fig. 3, which shows that the data at the higher temperature (390°K) are bounded by theoretical curves at smaller values of β. It is possible that, if m and β could be determined to fit the reaction rate exactly at any instant of time, the relationship between $\Delta\alpha$ and A might become more linear and closer to the 45°-line. However, the uncertainties in the concentration and the temperature measurements preclude such elaborate determination of the kinetic parameters.

According to Eq. (2), the quasi-steady theory further predicts that the amplification rate does not depend on the acoustic frequency, as long as the value of Ω is large enough. (This prediction means that the amplification per acoustic cycle is less at higher frequencies). Within experimental error, this is supported in Fig. 5 by the data represented by the tagged and the untagged triangles (△), which correspond to 900 and 300 Hz, respectively.

Concluding Remarks

The results of this investigation have identified the coupling between chemical kinetics and sound propagation during H_2-Cl_2 photochemical reaction. The observed effects on sound amplification cannot be fully accounted for by conservation of the acoustic energy alone. In addition, acoustic-kinetic coupling has to be considered, thus demonstrating experimentally its importance as predicted by previous theoretical studies.

The experimental results have been compared with the theoretical predictions which are derived on the basis of a simple Arrhenius kinetics. Within experimental accuracy (especially with respect to the determination of the reaction order and activation energy), one may conclude that the observed sound amplification can be interpreted satisfactorily by a quasi-steady theory, which has also been shown to be valid for the tests reported.

Nomenclature*

A	predicted amplification rate, [Eq. (6)]
E	activation energy, [Eq. (4)]
k	frequency factor, [Eq. (3)]
m	reaction order, [Eq. (3)]
$\|p_1\|$	pressure amplitude, [Eq. (1)]
R	universal gas constant
T	absolute temperature
t	time

Greek

β	reduced activation energy, [Eq. (4)]
$\Delta\alpha$	measured amplification rate, [Eq. (1)]
γ	ratio of specific heats
τ	small time increment, [Eq. (1)]
Ω	ratio of chemical to acoustic time scales, [Eq. (5)]
ω	acoustic frequency

Subscripts

i	initial conditions prior to start of chemical reaction
o	zeroth-order variable for undisturbed conditions
w	mean temperature measured by tungsten resistance thermometer
ref	any arbitrary reference time

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*Number of defining equation or equation of first appearance is shown in brackets where appropriate.

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REFERENCES

1. Toong, T. Y.: Combustion and Flame, *18*, 207, 1972.
2. Gilbert, R. G., Hahn, H. S., Ortoleva, P. J., and Ross, J.: J. Chem. Phys., *57*, 2672, 1972.
3. Gilbert, R. G., Ortoleva, P. J., and Ross. J.: J. Chem. Phys., *58*, 3625, 1973.
4. Toong, T. Y.: Acta Astronaut., *1*, (3/4), 317, 1974.
5. Toong, T. Y., Arbeau, P., Garris, C. A., and Patureau, J.-P.: Fifteenth Symposium (International) on Combustion, The Combustion Institute, 87, 1975.
6. Garris, C. A., Toong, T. Y., and Patureau, J.-P.: Acta Astronaut., *2*, 981, 1975.
7. Patureau, J.-P.: Acoustic-Kinetic Interactions in Non-Equilibrium H_2-Cl_2 Reactions. Sc.D. Thesis, Massachusetts Institute of Technology, 1976.
8. Morse, P. M., and Ingard, K. U.: Theoretical Acoustics, McGraw-Hill, 1968.

COMMENTS

Toshi Fujiwara, Nagoya University, Japan. Isn't it possible that there was some inhomogeneity of reaction in the axial direction of such a long tube? If so, there would be a reaction wave in addition to the acoustic wave.

Authors' Reply. As pointed out in the paper, the longitudinal homogeneity of the reaction has been checked by simultaneous monitoring of four thermocouples placed at the center of the reaction tube and at various axial positions. No inhomogeneity has been detected.

James A. Miller, Sandia Laboratories, USA. Do you expect any frequency dependence for amplification under "non-quasi-steady" conditions? Specifically, under conditions where τ_{acoustic} and τ_{chem} are of the same order (or where $\tau_{\text{acoustic}} \gg \tau_{\text{chem}}$), will certain frequencies be selectively amplified? Do you plan any experiments under these conditions?

Authors' Reply. Our theoretical studies indicate that there would be frequency dependence of chemical effects on acoustic waves under non-quasi-steady conditions. Experiments are now being conducted to study this dependence.