nase was purified as cellulase III by Okada.[3] Nevertheless, its extinction coefficient at 280 nm is much less than the value of endoglucanase II isolated by Schoemaker *et al.*[7] This coefficient for cellulase component was rarely to be reported. Moreover, the molecular weight of this enzyme is larger than the molecular weight corresponding to this enzyme.

Beldman *et al.*[8] purified three exoglucanases, and two of them as Exo I and II were isolated by the affinity chromatography using crystalline cellulose with pH gradient, which resulted in a high affinity to Avicel. Gum *et al.*[5] purified three exoglucanases from Meicelase P from *Trichoderma* species and suggested that their carbohydrate content is the principal factor which differentiates the cellobiohydrolase enzymes. However, it was reported that no distinct differences in the elution process were found. Exoglucanase II isolated in this study as a major *exo*-type enzyme gives a low activity toward CM-cellulose and Avicel as like as Exo III isolated by Beldman *et al.*[8] and CBH III by Gum *et al.*[5] These enzymes have produced only cellobiose from cellulose. Similar exoglucanase was isolated by Shikata *et al.*[4] from *T. viride.* All exoglucanase III-type enzymes reported showed a high affinity to crystalline cellulose with a very low activity to crystalline cellulose.

From the results presented here, these similarities between the enzyme components classified by several investigators indicate partially that the multiplicity of endoglucanases are determined genetically. Nevertheless, endoglucanases I and II showed a less similarity in hydrolytic and spectroscopic properties. Further work considering these differences is required to understand the hydrolytic characteristics of these component enzymes on insoluble cellulose.

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Theoretical Investigation on the Effects of Additive Oxygen in HF Chemical Laser Performance

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The effect of oxygen for the HF chemical laser performance has been theoretically investigated. Due to the inhibition mechanism of O_2 in H_2/F_2 chain reaction, the rate for the formation of HF is reduced by the addition of O_2. As the concentration of O_2 in the reaction mixture increases, the pulse power and temperature of the system becomes lower, while total output energy does not change significantly. But addition of O_2 makes the system easy to be controlled and the composition of H_2+F_2 can be high at constant total pressure. With this system, it is possible to obtain higher output energy than oxygen free environment.

Introduction

During last two dacades a great interest has been made for the utilization of hydrogen-fluorine reaction in HF chemical laser system.[1,2] The reaction of hydrogen with fluorine releases large exothermic energy and makes it possible to achieve highly efficient emission of intensely stimulated rediation from HF molecules.[3]

Although H_2/F_2 reaction has a merit described above, some drawbacks, which diminish the performance of the laser, still exist. H_2 reacts with F_2 spontaneously, and often explodes without ignition under some conditions.[4,5] The explosion produces less vibrationally excited HF than that from chain reactions. The population inversion is rapidly destroyed by a collisional deactivation process, which results in poor efficiencies of HF chemical laser.[2] Since the enhancement of specific output energy and lasing has been a major subject in the field of HF laser, there have been a lot of efforts to suppress the explosive properities of the chain reaction.

In 1968, Levy and Copland[6] reported that the chain reaction of H_2 and F_2, could be stabilized by O_2 gas in their experiment. Kerber and Ching[7] applied this effect for the improvement of the characteristics of HF laser. Upon these bases[6,7], Taylor *et al.*[8] performed detailed modeling and more systematic study on the reaction mechanism and kinetics of $H_2/F_2/O_2$ laser system. And it was continued by Dreiling[9] and many other researchers including us[10,11]. In their works, they showed the role of O_2 additive as a radical scavenger of F or H, which makes the chain reaction moderate. Therefore it made the system easily controlled than O_2 free system for the selection of initial lasing conditions such as mixing ratio of $H_2/F_2/O_2$ and total pressure of the system. The moderating effect of O_2 on the chain reaction, however, reduces the power of laser. The increment of O_2 contents in the initial mixture usually causes power decrement. Hence, to obtain a sufficient laser output in a given condition, the least amount of O_2 is required.

On the other hand, Chen *et al.*[12], Sullivan *et al.*[13] and Turby[14] had performed numerous experiments to explain the explosion phenomena by controlling the mixing ratio of initial reactants and gas additives. Through their gas kinetic studies they had demonstrated that explosion boundary exists. The chain reaction is limited at that mixing ratio without explosion. However, the relationship between explosion limit and laser performance has not yet been investigated intensively and it seems to be insufficient to explain the effects of O_2 on laser performance. In the present work, using the reported experimental explosion boundary as the initial condition of $H_2/F_2/O_2$ chemical laser system, the influence of O_2 on this laser performance will be analyzed theoretically by numerical model simulation. The variations of major chemicals, temperature, and lasing power in the system will be investigated as a function of time and be compared to that of O_2 free system.

Kinetic Model

The major reactions for the HF laser system with oxygen as an inhibitor, can be represented as follows;

a) Initiation

$$F_2 \longrightarrow 2F \tag{R-1}$$

b) H_2+F_2 chain reaction (pumping reaction)

$$F+H_2 \rightarrow HF(v)+H+31.6\ \text{kcal/mole} \tag{R-2}$$

$$H+F_2 \rightarrow HF(v)+F+98.0\ \text{kcal/mole} \tag{R-3}$$

c) Vibrational-Translational (V-T) deactivation

$$HF(v)+M \rightarrow HF(v-1)+M \tag{R-4}$$

d) Vibrational-Vibrational (V-V) exchange

$$HF(v)+HF(v') \rightarrow HF(v+1)+HF(v'-1) \tag{R-5}$$

$$HF(v)+H_2(v') \rightarrow HF(v+1)+H_2(v'-1) \tag{R-6}$$

e) Stimulated emission

$$HF(v+1) \rightarrow HF(v)+h\nu \tag{R-7}$$

f) Inhibition of O_2

$$H+O_2+M \rightarrow HO_2+M \tag{R-8}$$

$$F+O_2+M \rightarrow FO_2+M \tag{R-9}$$

where M is any molecules or atoms. The reactions from (R-1) to (R-7) represent the general mechanism of HF laser system without oxygen. The rate constants of these reactions are listed in Table 1. In the presence of oxygen the primary mechanism with the added O_2 is the chain termination. The oxygen reacts with F and H atoms, the chain carrier from the reaction of (R-1) through (R-3), to form HO_2 and FO_2. The HO_2 radicals react with H and O-atoms eventually to form H_2O through a set of reactions in the H_2/F_2 combustion sequence. The FO_2 which reacts with H, F and F_2 produces HF and F-atom. Namely, the oxygen terminates and/or inhibites the chain reactions by removing the number of chain

Table 1. Kinetic model for H_2/F_2 system

Reaction	Rate coefficient	Distribution constants			
		$v=0$	$v=1$	$v=2$	$v=3$
$F+H_2 \rightarrow HF(v)+H$	$k_1=1.62\times10^{14}$ exp $(-1600/RT)$	0.056	0.111	0.555	0.278
$H+F_2 \rightarrow HF(v)+F$	$k_2=1.2\times10^{14}$ exp $(-2400/RT)$	0.050	0.050	0.075	0.133
$HF(v)+HF \rightarrow HF(v-1)+HF$	$k_{HF}=6\times10^{16}T^{1.43}$	0	0.167	0.333	0.500
$HF(v)+H_2 \rightarrow HF(v-1)+F$	$k_{H2}=8.3\times10^{5}T^{2.2}$ exp $(-562/RT)$	0	0.965	0.035	0
$HF(v)+F \rightarrow HF(v-1)+F$	$k_F=5.4\times10^{9}T^{1.3}$	0	0.167	0.333	0.500
$2HF \rightarrow HF(v-1)+HF(v+1)$	$k_{2HF}=4.0\times10^{5}T^{22}$	0	0.333	0.333	0.333
$F+H_2 \rightarrow HF(v)+H$	$k_1(v)=10^{12}T^{0.67}$	$v=4\text{-}6$			
$H+F_2 \rightarrow HF(v)+F$	$k_2(v)=a_v k_2$	$a_4=0.167$; $a_5=0.257$; $a_6=0.250$			

$R=1.987$ cal/mole·K. All rate coefficients are in $(cm^3/mole)^{N-1}/sec$ where N is the reaction order.

Table 2. Kinetic model for $H_2/F_2/O_2$ system

Reaction	Rate Coefficient
$H+O_2+H_2 \rightarrow HO_2+H_2$	$k=5.07\times10^{15}$ exp (994/RT)
$H+O_2+H_2O \rightarrow HO_2+H_2O$	$k=3.153\times10^{16}$ exp (994/RT)
$H+O_2+M \rightarrow HO_2+M$	$k=1.489\times10^{15}$ exp (994/RT)
$H+HO_2 \rightarrow OH+OH$	$k=2.528\times10^{14}$ exp (−1888/RT)
$H_2+OH \rightarrow H_2O+H$	$k=2.167\times10^{13}$ exp (−5416/RT)
$H+OH+H_2O \rightarrow H_2O+H_2O$	$k=1.413\times10^{23}T^2$
$H+HO_2 \rightarrow H_2+O_2$	$k=2.528\times10^{13}$ exp (−695/RT)
$H+OH+M \rightarrow H_2O+M$	$k=2.174\times10^{22}T^2$
$H+O_2 \rightarrow OH+O$	$k=2.227\times10^{14}$ exp (−16790/RT)
$O+HO_2 \rightarrow OH+O_2$	$k=4.82\times10^{13}$ exp (−994/RT)
$H+H+H_2O \rightarrow H_2+H_2O$	$k=7.25\times10^{18}T^1$
$H+H+M \rightarrow H_2+M$	$k=6.52\times10^{16}T^1$
$H+O+M \rightarrow OH+M$	$k=6.616\times10^{16}T^2$
$O_2+O+O \rightarrow O_2+O_2$	$k=7.937\times10^{27}T^{1.5}$
$F+O+M \rightarrow FO_2+M$	$k=1.810\times10^{15}$
$F+F+M \rightarrow F_2+M$	$k=1.087\times10^{16}T^1$
$O+O+O \rightarrow O_2+O$	$k=2.247\times10^{20}T^{1.5}$
$O+H_2 \rightarrow OH+H$	$k=1.81\times10^{11}$ exp (−8902/RT)
$H+H+H_2 \rightarrow H_2+H_2$	$k=1.957\times10^{18}T^1$
$H+H+H \rightarrow H_2+H$	$k=1.087\times10^{19}T^1$
$OH+O+M \rightarrow HO_2+M$	$k=3.62\times10^{14}$
$H_2O+O \rightarrow OH+OH$	$k=6.62\times10^{13}$ exp (−18360/RT)
$H+F+M \rightarrow HF+M$	$k=2.61\times10^{18}T^1$
$O+O+M \rightarrow O_2+M$	$k=6.6161\times10^{15}T^{0.5}$

carrier. These are represented in the typical reaction (R-8) and (R-9). And the full list of reactions and reaction rate constants are given in Table 2.

Generally, the computer model simulations for the $H_2/F_2/O_2$ system are carried out by the addition of these 24 reactions in Table 2 to the multi-coupled differential equations of the HF system. The computer code of $H_2/F_2/O_2$ laser system in this study[15] has been developed and updated our previous model[10,11], by adding the differential equations for the species of $[HO_2]$, $[FO_2]$, $[O_2]$ etc.

Calculation and Initial Condition

To describe the infulence of added O_2 on the HF chemical laser performance in more detail, initial conditions are classified into two types. First, without considering the explosion limit like the previously reported results[8], the percent ratio of O_2 increased monotonically at fixed total pressure and composition of reactants. With constant H_2 and F_2 pressure, O_2 is varied from 0.0 to 0.4 percent for the 4 cases, *i.e.* $H_2 : F_2 : O_2 : He = 41.04 : 20.52 : x : 698.44\text{-}x$, $x=0.0$, 0.76, 1.52, 3.04 torr. In order to keep the pressure constant at 760 torr, inactive helium gas pressure is reduced as much as the percent of O_2 is increased. This condition is listed in Table 3.

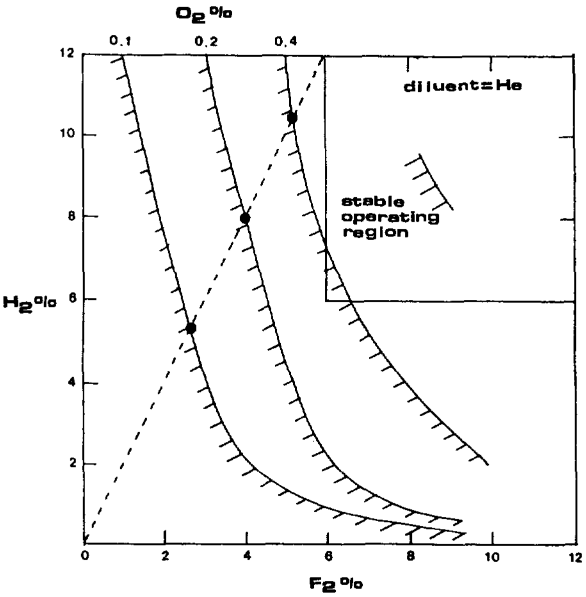

Figure 1. Position of boundary between the two regions in an $H_2/F_2/O_2/He$ mixture as a function of the reaction mixture composition.

Second, in order to consider the explosion limit, the calculation conditions are chosen from the data of H. C. Chen *et al.*[12] They reported that the distinct boundary condition between explosion and stable region can be altered by varying oxygen concentration. If the initial condition is selected close to the explosion boundary, its numerical solution becomes very unstable. The calculation becomes more difficult due to the abrupt concentration change of reactants such as H, and F, etc. Therefore, the initial H_2/F_2 ratio is fixed at 2, in which the numerical solution becomes stable. Because Chen's experiment was performed on 0.1, 0.2 and 0.4% O_2 as shown in Figure 1, only 3 calculation points was selected on the explosion boundary, keeping the H_2/F_2 ratio at 2. The initial partial pressure used in this calculation is represented as follows ; $H_2 : F_2 : O_2 : He = 41.04 : 20.52 : 0.76 :$

Table 3. Initial condition for $H_2/F_2/O_2$ system with addition of O_2

Condition	Pressure of Reactants (torr)				Ratio of O_2	Initial Temp.	Total Press.	Cavity Condition		
System	H_2	F_2	O_2	He	(%)	K	torr	r_0	r_1	L
Case 1	41.04	20.52	0	698.44	0.0	300	760	0.8	1.0	100
Case 2	41.04	20.52	0.76	697.68	0.1	300	760	0.8	1.0	100
Case 3	41.04	20.52	1.52	696.92	0.2	300	760	0.8	1.0	100
Case 4	41.04	20.52	3.04	695.40	0.4	300	760	0.8	1.0	100

Table 4. Initial condition for $H_2/F_2/O_2$ system with considering the explosion limit

Condition	Pressure of Reactants (torr)				Ratio of O_2	Initial Temp.	Total Press.	Cavity Condition		
System	H_2	F_2	O_2	He	(%)	K	torr	r_0	r_1	L
Case 5	41.04	20.52	0.76	697.68	0.1	300	760	0.8	1.0	100
Case 6	60.80	30.40	1.52	667.28	0.2	300	760	0.8	1.0	100
Case 7	77.52	38.76	3.04	640.68	0.4	300	760	0.8	1.0	100

697.68, 60.80 : 30.40 : 1.52 : 667.28 and 77.52 : 38.76 : 3.04 : 640.68 in torr. Table 4 summarizes these conditions.

Results and Discussion

The concentration of Chemical Species. Figure 2 shows the calculated temporal changes of [H], [F], [HO_2], [O_2] and [HF] for the conditions without considering explosion limit (Table 3). In this figure, [H_2] and [F_2] are not plotted but can be obtained from the initial concentrations minus twice that of [HF]. The concentration of F atom decreases in the earlier stage ($<10^{-7}$ sec). After passing minimum point, it increased very slowly, while the concentration of H atom increases maximum point, then decreases gradually. As the O_2 added more, the concentration of both species, [H] and [F] decreases due to termination reaction of (R-8) and (R-9). In this figure, these are marked as a, b and c for 0.1, 0.2 and 0.4 percent ratio of O_2 respectively. In order to proceed chain reaction contineously, a steady state condition can be assumed;

$$k_2[H_2][F] \approx k_3[F_2][H]$$

And the relative removal rates of the chain terminating reactions are given as

$$\frac{\mathrm{Rate}_{(H+O_2)}}{\mathrm{Rate}_{(F+O_2)}} = \frac{k_8 k_2 [H_2]}{k_9 k_3 [F_2]}$$

where, the rate constants for $k_{2,3}$-$k_{8,9}$ can be evaluated at room temperature with 20x [H_2]/[F_2]. At our calculation condition the value of [H_2]/[F_2] is 2, so the formation rate of HO_2 is faster than that of FO_2 by an order of magnitude. Thus the F + O_2 can not be a major species, so the concentration of FO_2 is omitted in Figure 2. The concentration of HO_2 is over 10^{-10} M after 10^{-7} sec and reaches maximum after 1 μsec. (near the end point of lasing) And this increases higher as the amount of added O_2 increases. The concentration of O_2, however, is nearly unchanged during lasing. Only small portion of added O_2 is reacted.

Since the output power of the laser depends dominantly on the [HF] generated from the H_2/F_2 chain reaction, the temporal change of [HF] and the effect of O_2 pressure on [HF] is of interest. In Figure 2, the concentration of HF increases continuously. And the production rate of HF is reduced according to the increments of O_2 mole percent. This effect can be explained by inhibition of O_2.

On the other hand, the results obtained from the calculation with considering the explosion limit data in Table 4 are shown in Figure 3. To compare the results with Figure 2, [H], [F], [HO_2], [O_2], and [HF] are plotted in the same

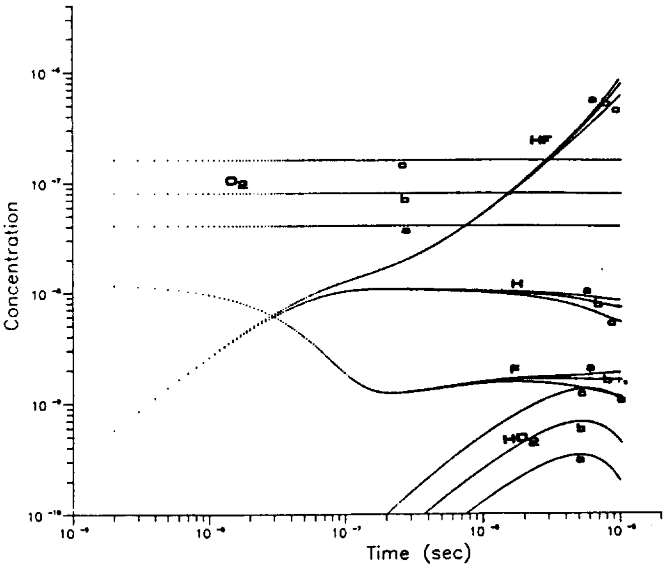

Figure 2. Temporal profile of the concentrations of main species, H, F, HF, HO_2, and O_2, for the lasing conditions. $H_2 : F_2 : O_2 : He = 41.04 : 20.52 : x : 698.44\text{-}x$, $x =$ a) 0.76. b) 1.52. c) 3.04 torr. $P = 760$ torr.

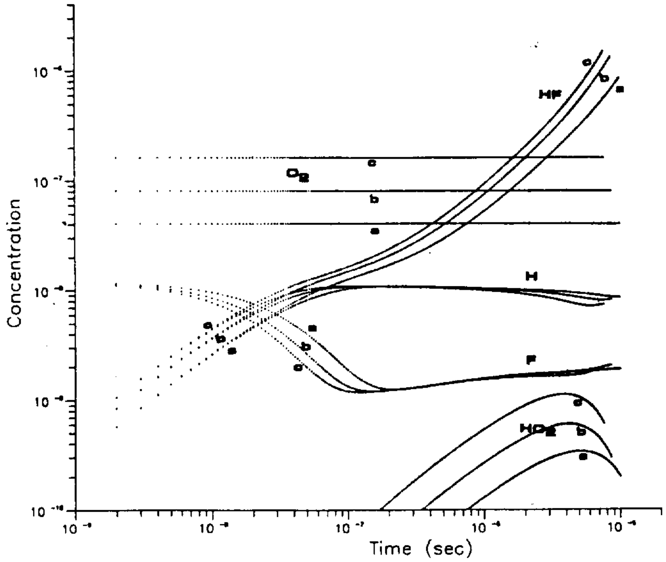

Figure 3. Temporal profile of the concentrations of main species, H, F, HF, HO_2, and O_2, for the lasing conditions. $H_2 : F_2 : O_2 : He =$ a) 41.04 : 20.52 : 0.76 : 697.68, b) 60.80 : 30.40 : 1.52 : 667.28 and c) 77.52 : 38.76 : 3.04 : 640.68 torr. $P = 760.$ torr.

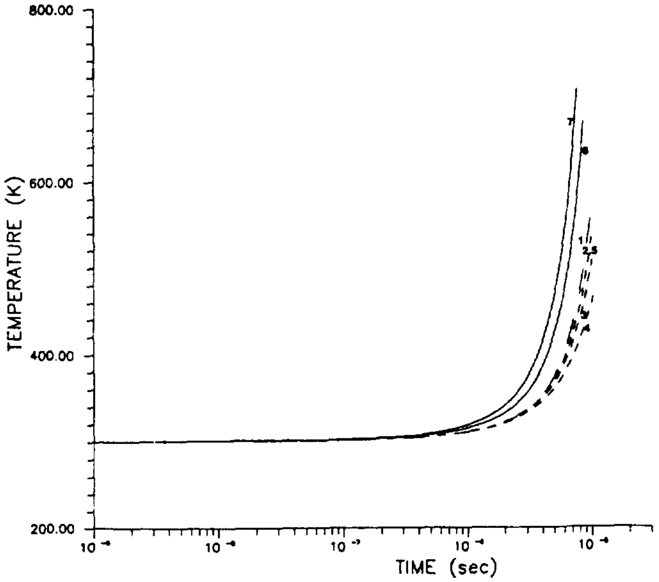

Figure 4. Effects of O_2 on temperature change in $H_2/F_2/O_2$ system. (Number 1-7 are the same as case 1-4 in Table 3 and case 5-7 in Table 4).

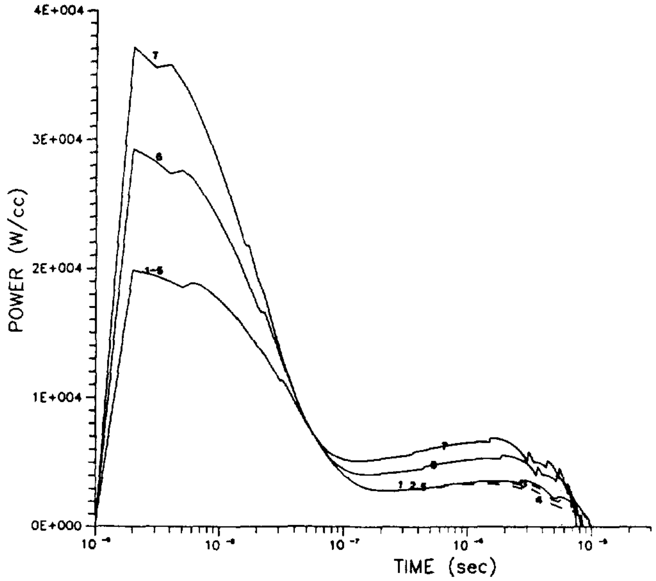

Figure 5. Effects of O_2 on power characteristics and duration time in $H_2/F_2/O_2$ system. (Number 1-7 are the same as case 1-4 in Table 3 and case 5-7 in Table 4).

scale as Figure 2. The time dependence of these species is similar to the results calculated without considering the expolsion limits. The effect of O_2 pressure on HF laser system, however, is quite different from the results in Figure 2. In Figure 3, as the amount of O_2 increases, the concentration of HF rises. Due to the moderating effect of O_2, the system can be controlled easily and the concentration of $H_2 + F_2$ could be high with constant total pressure. Since the reaction (R-9) can be negligible and $k_2[F][H_2] \approx k_3[H][F_2]$ in steady state condition, the temporal change of F is approximately expressed as

$$\frac{d[F]}{dt} = 2k_1[F_2] - k_2[F][H_2] + k_3[F][H_2] - k_9[F][O_2][M]$$
$$\approx 2k_1[F_2]$$

and

$$[F] = \int^t 2k_1[F_2]\ dt$$

where *t* is time. The formation rate of HF is expressed as

$$\frac{d[HF]}{dt} = k_2[F][H_2] + k_3[H][F_2]$$
$$\approx 2k_2[F][H_2]$$
$$\approx 4k_1k_2[H_2] \int^t [F_2]\ dt$$

Therefore the generation rate of HF mainly depends on the concentration of H_2 and/or F_2. From the condition of Table 4, the product HF can be generated more as the sum of reactants $[F_2]+[H_2]$ increases. In this result, the role of added O_2 is not only to stabilize the H_2/F_2 chain reaction but also to increase the extent of this reaction.

Reaction temperature. Since the H_2/F_2 chain reaction provides large exothermic energy, the temperature of the system increases contineously. The temperature rise in the cavity is depicted in Figure 3. For the condition of O_2 free system (case 1 in Table 3), it rises about 200 K (from 300 to 580 K) within 10 μsec. As the O_2 mole percent varies to 0.1, 0.2 and 0.4% (case 2, 3 and 4 in Table 3 respectively), the maximum temperature of the system gradually decreases to 540, 480 and 450 K respectively. The addition of O_2, therefore, makes the increasing rate of temperature lower. This effect can also be explained by the chain temination reaction of O_2. But, as mentioned above, the stabilizing effect of O_2 increases the extent of this reaction. This is observed in the condition of case 6 and 7. Here, the increment of O_2 from 0.2 to 0.4%, makes the temperature of the system rise up to 670 and 710 K respectively. Ultimately, the addition of O_2 makes exothermicity, or the extent of reaction, higher.

The output power of chemical laser. For all calculated conditions in Table 3 and 4, the time dependence of output power in HF chemical laser is shown in Figure 4. The output of HF laser increases rapidlly with time, gives maximum peak within 10 nsec, then decreases fast near to lowest level, and disappears.

For O_2 free system (case 1 in Table 3), the maximum output is about 2×10^4 W/cc and the duration time is about 10 μsec. In Figure 4, the effect of O_2 on lasing power is shown clearly. The dotted lines (case 2, 3 and 4 in Table 3) represent the dependence of O_2 on the output without considering the explosion limit. The increment of O_2 reduces the output power and elongates the duration time, but this influence is insignificant. However, considering the expolsion limit, this situation is changed. Only 0.2% addition of O_2 (case 6 in Table 4) makes the maximum output rise up to 2.9×10^4 W/cc. And 0.4% addition of O_2 (case 7 in Table 4) makes the maximum ouput power up to 3.8×10^4 W/cc. Namely, by the addition O_2, the maximum output power can be increased approximately twice. The duration time is slightly shortened, but negligible. From these results, we could point out the important fact that the role of O_2 is not the degradation but the improvement of the HF laser performance.

Conclusion

Many experiments reported that the addition of O_2 for H_2/F_2 chemical laser system makes the performance of chemical laser improved. In this paper, we calculated theoretically the illustration of this phenomena. The effects of the concentration of HF and other products and the output power were demonstrated. The added O_2 reacts with H and F, which makes the reaction explosive, and reduces the formation rate of HF. The dominating chain inhibition step is the production of HO_2, whereas the production of FO_2 is unimportant. As the concentration of O_2 in the reaction mixture increases, the pulse power and temperature of the system becomes low, while the total energy does not change significantly. But the addition of O_2 makes the system easily controlled and the concentration of H_2+F_2 could be high without changing total pressure. In the case of our calculation condition, as the addition of O_2 increases to 0.1, 0.2 and 0.4%, the sum of H_2+F_2 can be as high as 41.04+20.52 torr, 60.80+30.40 torr and 77.52+38.76 torr respectively without explosion at total pressure ($H_2+F_2+O_2+He$) of 760 torr. Since the increment of reactant, H_2+F_2, means the increment of product, HF, the output power of laser would be high. By the addition of 0.4% O_2, the maximum output power increases about twice (1.8). This ratio varies depending upon the condition of initial mixture. Unfortunately the choice of initial calculation condition is not diverse enough due to the limited number of experimental data and due to the barriers in numerical analysis at abrupt change of concentration. However, we have shown a possible way to achieve higher output energy than that from oxygen free system.

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15. This computer code is programmed by FORTRAN using Runge-Kutta and/or GEAR Method, and excuted in IBM PC 386 series.
16. This figure is adapted from ref. 12 and modified.

Acid-Promoted Ring Cleavage Reactions of Silacyclohex-3-ene Derivatives

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The acid-promoted cleavage of the *E*- and *Z*-isomers of 1-phenyl-6-neopentyl-1,3,4-trimethyl-1-silacyclohex-3-ene(II) under various conditions gave clean and nearly quantitative formation of the ring-opened 2,3,7,7-tetramethyl-5-(X)silyl-1-octene products (X=OMe, Cl, OH). The possible mechanism for the formation of the ring-opened products was suggested that the initial protonation of II at C-4 would give a carbocation oriented so that they are β to the silicon atom, and the subsequent nucleophilic attack at silicon would give rise to the observed products (VI, VII, VIII).

Introduction

Unsaturated organosilanes often exhibit unusual reactivity towards electrophiles in comparison to their carbon analogues. One important characteristic of their unusual reactivity is that a silicon-carbon σ bond exerts a greater stabilizing effect on a carbocation ion β to the silicon than does a carbon-carbon or carbon-hydrogen bond.[1] In all of the above