Spectrochimica Acta, Vol. 43A, No. 2, pp. 257–264, 1987.
Printed in Great Britain.

0584–8539/87 $3.00+0.00
Pergamon Journals Ltd.

THE INFRARED LASER PHOTOCHEMISTRY OF SILANE[1]

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1. INTRODUCTION

In view of the close match of an R branch transition in the ν_4 vibrational mode of SiH_4 at 944.21 cm^{-1} with the P(20) line of the 10.6 µm band of a CO_2 laser at 944.19 cm^{-1}, it is not surprising that monosilane decomposition by infrared laser irradiation has been known since the early days of the field.[2-6] Monosilane does not, however, decompose in the collision-free region. For the decomposition to occur, collisional assistance is required. That this is a photodecomposition and not a thermal decomposition is a result of V-V collisional transfer being significantly faster than V-T relaxation, permitting SiH_4 molecules to be pumped (with collisional assistance) into the quasicontinuum and then by multiple photon absorption to the dissociation limit before relaxation to translational modes occurs.[7] Such a collisionally assisted multiple photon decomposition can not be carried out in PH_3 with a pulsed laser, even though absorption was complete; presumably this was because the lower density of states in PH_3 rendered the quasicontinuum inaccessible at 1 J/cm^2 fluence.[8]

The primary dissociation in the collisionally assisted multiple photon decomposition of SiH_4 is that of lowest energy, namely

$$SiH_4 + nh\nu \xrightarrow{n \geq 21} SiH_2 + H_2 \qquad (1)$$

The dissociation path, (2) which is the next higher energy process,

$$SiH_4 + nh\nu \xrightarrow{n \geq 33} SiH_3 + H \qquad (2)$$

does not appear to occur to any significant extent.[7] Among the various methods of decomposition of SiH_4 that have been employed, this essentially exclusive formation of SiH_2 by (1) is unique to infrared laser decomposition and provides, therefore, a useful means to produce SiH_2 and study its reactions with other molecules.

In all of the systems studied a solid powder and/or poorly adhering film is observed as a product of the photodecomposition. Material balances and infrared examination demonstrate this solid to contain silicon, hydrogen and the other heavy element of the substance added to silane, i.e. P, Ge, Cl, etc. The reaction mechanisms discussed in this paper do not address the formation of solid products but rather deal exclusively with the gaseous products that have been unambiguously identified.

2. Pure SiH_4

The fractional yields per pulse, $\Delta N(i)/N^o(SiH_4)$ for a fluence of 1.0 J/cm^2 are shown in Figures 1 and 2,[7] with the pressure threshold at this fluence being about 8 torr. The strong dependence of the decomposition rate of SiH_4 on the pressure, i.e. Rate α $P^{5.5}(SiH_4)$ demonstrates the collisional assistance required in the process. The increase in the rates of formation of Si_2H_6 and Si_3H_8 with increasing total pressure and/or partial pressure of He indicate that the decomposition is a photodecomposition and not a thermal process. If it were a thermal decomposition induced by laser-energy absorption followed by V-T relaxation, one would expect a decrease in these formation rates due to the higher heat capacity at the higher pressures.

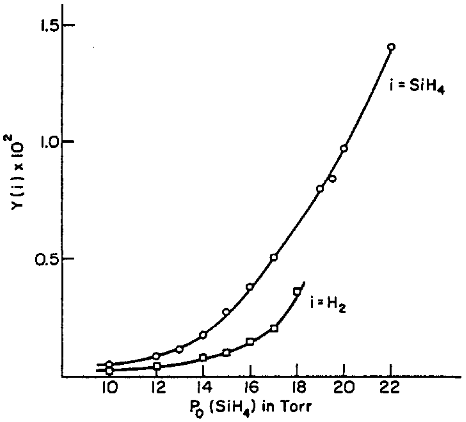

Figure 1. Dependence of the rates of decomposition of SiH_4 and formation of H_2 on SiH_4 pressure. ○, SiH_4 decomposition; □, H_2 formation. Fluence = 1.0 J/cm^2.

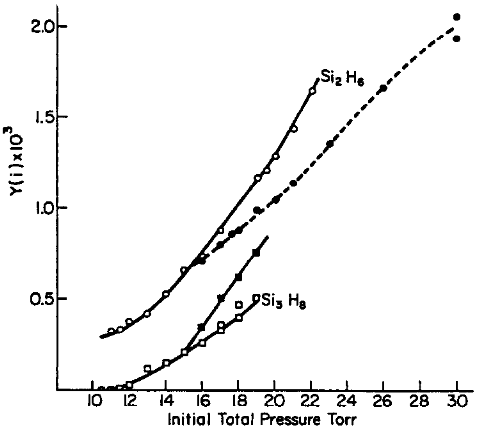

Figure 2. Dependence of the rates of formation of Si_2H_6 and Si_3H_8 on total pressure. ○, Si_2H_6 formation from pure SiH_4; □, Si_3H_8 formation from pure SiH_4; ●, Si_2H_6 formation from SiH_4 (15 torr) + He mixtures; ■, Si_3H_8 formation from SiH_4 (15 torr) + He mixtures. Fluence = 1.0 J/cm^2.

The chemistry of the infrared laser photodecomposition of SiH_4 is to be understood in terms of the occurrence of the following reactions subsequent to (1).[7,9]

$$\begin{array}{llll}
SiH_2 + SiH_4 \rightleftharpoons & Si_2H_6^* & & (3,-3) \\
Si_2H_6^* \longrightarrow & SiH_3SiH + H_2 & & (4) \\
Si_2H_6^* + M \longrightarrow & Si_2H_6 + M & & (5) \\
SiH_3SiH + SiH_4 \rightleftharpoons & Si_3H_8^* & & (6,-6) \\
SiH_3SiH \longrightarrow & SiH_2SiH_2 & \text{wall} & (7) \\
Si_3H_8^* + M \longrightarrow & Si_3H_8 + M & & (8)
\end{array}$$

The collisional assistance required in the infrared laser photodecomposition of SiH_4 suggests that a Boltzmann distribution might be a useful approximation to the actual distribution of vibrational energy carried by the energy absorption and collisional V-V transfer. Indeed, the fractional yields per pulse can be accounted for quantitatively[7] using the following assumptions:

(a) A Boltzmann distribution of vibrational quanta in SiH_4 exists.
(b) SiH_2 and SiH_3SiH are taken to be at the same vibrational temperature as SiH_4.
(c) RRKM calculations of the unimolecular decompositions can be based on the vibrational frequencies of Si_2H_6 and Si_3H_8 with simple removal of the reaction coordinate in the transition states of $Si_2H_6^*$ and $Si_3H_8^*$.
(d) Collisional stabilization rate constants can be taken to be 1.7×10^{-11} cm^3/s.
(e) All molecules of SiH_4 with $n \geq 21$ can be assumed to decompose.

3. SiH_4-PH_3 Mixtures

Phosphine does not absorb the P(20) line of the 10.6 μm band of the CO_2 laser so that when SiH_4-PH_3 mixtures are irradiated only SiH_4 absorbs energy from the laser. The products observed are H_2, Si_2H_6, Si_3H_8 and SiH_3PH_2, with the reaction rates or yields of the pulsed irradiations being shown in Figure 3.[10] We attribute the formation of Si_2H_6 and SiH_3PH_2 to a competition between SiH_4 and PH_3 for the SiH_2 that is formed as a result of absorption of laser energy, i.e. in addition to the reactions that occur in pure SiH_4, i.e. (3,-3)-(8), we have in the mixture

$$\begin{array}{lll}
SiH_2 + PH_3 \rightleftharpoons & SiH_3PH_2^* & (9) \\
SiH_3PH_2^* + M \longrightarrow & SiH_3PH_2 + M & (10)
\end{array}$$

Making the reasonable assumption that the fractions of $Si_2H_6^*$ and $SiH_3PH_2^*$ that are stabilized by (5) and (10) are the same, we may use the initial formation rates of SiH_3PH_2 and Si_2H_6 to estimate the following rate constant ratio

$$\frac{k_9}{k_3} = 0.92 \text{ at } 300 \text{ K.} \qquad (11)$$

SiH_3PH_2 is not stable in the presence of the reaction products even when the irradiation is stopped. It appears to decompose thermally at 300 K by a first-order process having a half-life of about 14 minutes.[10]

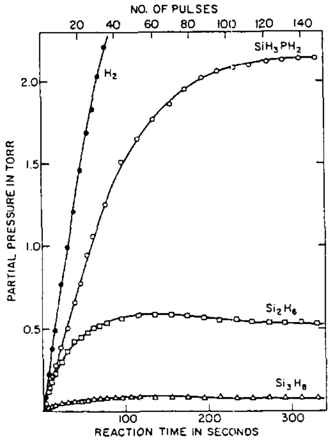

Figure 3. Time dependence of product formation in the IR laser irradiation of SiH_4-PH_3 mixtures at 944.19 cm^{-1} and a fluence of 1.0 J cm^{-2}: ●, H_2; ○, SiH_3PH_2; □, Si_2H_6; △, Si_3H_8.

4. SiH_4-GeH_4 Mixtures

The infrared spectrum of GeH_4[11-14] indicates that this molecule should be essentially transparent to the emission from the CO_2 laser and, consistent with this indication, we could detect no absorption of laser energy or decomposition when pure GeH_4 was irradiated. While GeH_4 does not absorb the P(20) line, the addition of GeH_4 to a cell containing SiH_4 enhances the fraction of the laser energy absorbed. Such enhancement has been reported previously[6,7,10] and is attributed to the collisional redistribution of vibrational energy that repopulates the low-lying ν_4 states of SiH_4; GeH_4 also participates in this collisional redistribution, although not as effectively as SiH_4 itself.

Irradiation of SiH_4-GeH_4 mixtures with 1-20 pulses of 944 cm^{-1} radiation at a fluence of 0.53 J/cm^2 results in the formation of SiH_3GeH_3 in addition to the expected products of the pure SiH_4 photodecomposition, namely H_2, Si_2H_6 and Si_3H_8. Although we searched for Ge_2H_6 the concentration of this expected product was below our detection sensitivity (i.e. 10% of the SiH_3GeH_3 concentration) in all experiments.

Since GeH_4 does not absorb energy from the laser beam, it is very probable that the sole primary photodissociation process is SiH_2 formation via (1). This is followed by the reactions

$$\begin{aligned}
&SiH_2 + GeH_4 \rightleftharpoons SiH_3GeH_3^* && (12,-12)\\
&SiH_2 + SiH_4 \rightleftharpoons Si_2H_6^* && (3,-3)\\
&SiH_3GeH_3^* + M \longrightarrow SiH_3GeH_3 + M && (13)\\
&Si_2H_6^* + M \longrightarrow Si_2H_6 + M && (5)
\end{aligned}$$

The very small amounts of Si_3H_8 indicate that (5) is the predominant fate of $Si_2H_6^*$ and the absence of Ge_2H_6 suggests that $SiH_3GeH_3^*$ does not decompose to any signficant extent to SiH_4 and GeH_2.[15,16] Since dissociation to GeH_2 and SiH_4 is expected to be the lowest energy decomposition path of SiH_3GeH_3, (13) is very probably the dominant fate of $SiH_3GeH_3^*$.

A standard kinetic treatment of this reaction scheme, assuming (5) and (13) dominate the reactions of $Si_2H_6^*$ and $SiH_3GeH_3^*$, respectively, leads to the expression in (14) for the rate ratio (or yield per pulse ratio)

$$\frac{R(SiH_3GeH_3)}{R(Si_2H_6)} = \frac{k_{12}[GeH_4]}{k_3[SiH_4]} \qquad (14)$$

and the linearity of the plots in Figure 4 attest to the basic correctness of this expression.

An Arrhenius plot of the slopes of the lines in Figure 4 (i.e. k_{12}/k_3) is shown in Figure 5, from which we may derive the relative Arrhenius parameters:

$$\begin{aligned}
A_{12}/A_3 &= 5.2 \pm 1.4\\
E_{12}-E_3 &= 5330 \pm 670 \text{ J/mole}
\end{aligned}$$

Recent mesurements[17] of the absolute value of k_3 at 300 K report a value of k_3 = 1.1 x 10^{-10} cm^3/s. This value is so near the collision limit, that it may be concluded that

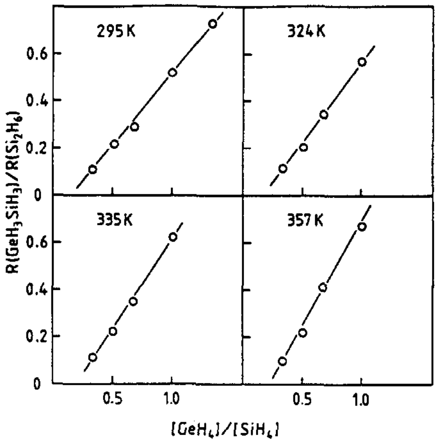

Figure 4. Dependence of the initial-rate ratio, $R(SiH_3GeH_3)/R(Si_2H_6)$, on the initial concentration ratio, $[GeH_4]/[SiH_4]$, at various temperatures.

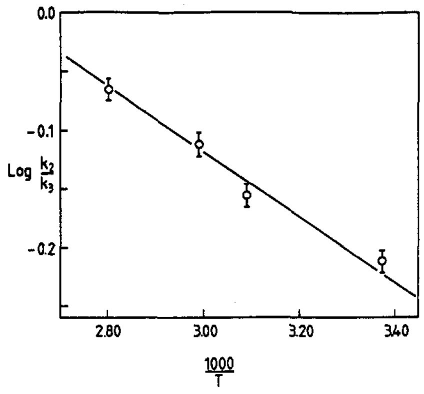

Figure 5. Arrhenius plots of slopes of lines in Figure 3, i.e. log (k_2/k_3) vs. 1/T.

$E_3 \approx 0$ and $E_{12} = 5330$ J/mole. Since the average SiH_4 molecule in the system contains 4-5 kcal/mole of vibrational energy from the laser, it is even more likely in this system that (3) proceeds with zero energy of activation.

5. SiH_4-HCl Mixtures

The insertion reactions of SiH_2 into Si-H, P-H and Ge-H bonds, as described above, appear to proceed with very little activation energy, i.e. are very fast reactions near the bimolecular collision limit. It is of interest to ask if rapid insertion of SiH_2 into relatively strong bonds will occur also. To examine this question we have studied the infrared laser multiphoton decomposition of SiH_4-HCl mixtures,[18] HCl neither absorbing laser energy nor showing any decomposition when irradiated in the pure state.

The gaseous products of the irradiation are H_2, Si_2H_6, Si_3H_8, SiH_3Cl, SiH_2Cl_2 and $SiHCl_3$. Continuous mass spectrometric monitoring of pertinent masses, as shown in Figure 6, demonstrates that all products are formed simultaneously, i.e. all are primary products of the reaction.

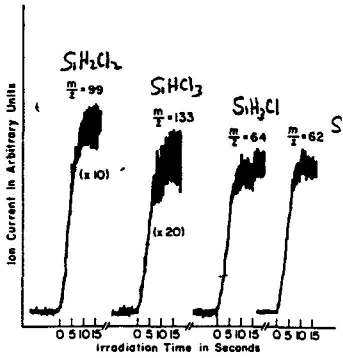

Figure 6. Dependence of ion currents of reaction products on irradiation time.

The reaction products and the dependence of the rates of formation of these products on reactant partial pressures, pressure of inert gas and temperature are described satisfactorily by (1), (3)-(8), i.e. the reactions in pure SiH_4, and the additional processes shown by (15)-(22).

$SiH_2 + HCl \rightleftarrows SiH_3Cl^*$ (15,-15)
$SiH_3Cl^* \longrightarrow SiHCl + H_2$ (16)
$SiH_3Cl^* + M \longrightarrow SiH_3Cl + M$ (17)
$SiHCl + HCl \rightleftarrows SiH_2Cl_2^*$ (18,-18)
$SiH_2Cl_2^* \longrightarrow SiCl_2 + H_2$ (19)
$SiH_2Cl_2^* + M \longrightarrow SiH_2Cl_2 + M$ (20)
$SiCl_2 + HCl \rightleftarrows SiHCl_3^*$ (21)
$SiHCl_3^* + M \longrightarrow SiHCl_3 + M$ (22)

This reaction scheme is more complicated kinetically than those of the previous systems discussed because of the propensity of SiH_3Cl^* and $SiH_2Cl_2^*$ to decompose to H_2 and retain the newly found Si-Cl bond. Nevertheless, it can be shown by kinetic analysis[18] that the rate ratio $R(SiH_3Cl)/R(Si_2H_6)$ should be a linear function of the concentration ratio $[HCl]/[SiH_4]$ and that a plot of the logarithm of the slopes of the linear plots versus 1/T represents the activation energy difference $E_{15}-E_3$. Such plots are shown in Figures 7 and 8, respectively.

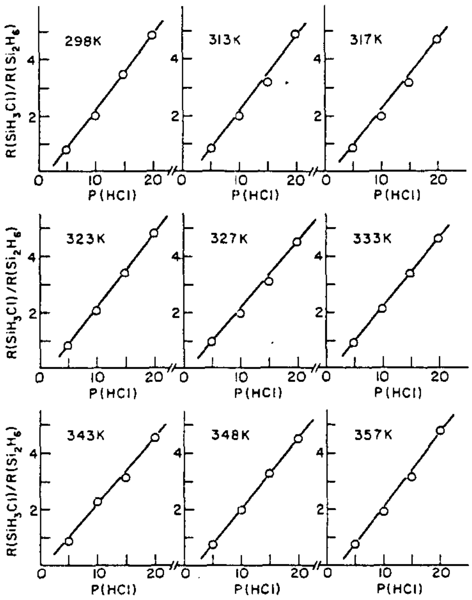

Figure 7. Dependence of the initial rate ratio $R(SiH_3Cl)/R(Si_2H_6)$ on partial pressure of HCl at various temperatures ($P(SiH_4)$ = 30 torr).

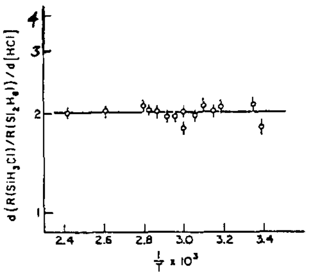

Figure 8. Arrhenius plots of data in Figure 3: i.e., $dR[(SiH_3Cl)/R(Si_2H_6)/d[HCl]$ vs. 1/T.

Clearly from Figure 8, $E_{15}-E_3 \approx 0$ and since, as already discussed, $E_3 \approx 0$, E_{15} is also near zero and (15) must also be very near its bimolecular collision limit at all temperatures studied.

6. SiH_4-CH_3Cl Mixtures

Our experience with the SiH_4-HCl system[18] led us to expect that SiH_2 would insert readily into the C-Cl bond of CH_3Cl with formation of CH_3SiH_2Cl. Accordingly we carried out CO_2-laser irradiation of SiH_4-CH_3Cl using the P(20) line at 944 cm^{-1} and a fluence of 0.70 J/cm^2. Contrary to our expectation, CH_3SiH_2Cl was not a major product, being observed only in tace amounts. The major products were H_2, CH_4, Si_2H_6 and SiH_3Cl. Addition of small amounts of NO to the system were made to test for the presence of CH_3 radicals through the formation of CH_3NO and $(CH_3)_2NOCH_3$.[19] No evidence of the presence of CH_3 could be found.

Since CH_3Cl does not absorb radiation at the frequency used, the reaction is considered to be initiated by SiH_2 produced in (1). Then, in addition to (3)-(8), the reactions best describing our studies of the effects of $[CH_3Cl]/[SiH_4]$ ratio, pressure of inert gas, and total pressure on the rates (or yields per pulse) are as follows:

$$SiH_2 + CH_3Cl \rightleftarrows CH_3SiH_2Cl^* \qquad (23,-23)$$
$$CH_3SiH_2Cl^* \longrightarrow SiHCl + CH_4 \qquad (24)$$
$$SiHCl + SiH_4 \longrightarrow SiH_3Cl + SiH_2 \qquad (25)$$
$$SiHCl \longrightarrow \text{wall} \qquad (26)$$

The data require that in this reaction scheme $k_{24} \gg k_{-23}$, a not too surprising requirement when the much greater exothermicity of (24) as compared to (-23) is taken into account. RRKM calculations of the respective unimolecular decomposition rates bear out this conclusion. Further evidence of the correctness of this conclusion lies in the fact that in the irradiation of CH_3SiH_3-HCl mixtures, in which CH_3SiH molecules are produced in the favored primary dissociation act, i.e. (27), CH_3SiH_2Cl is observed as

$$CH_3SiH_3 + nh\nu \longrightarrow CH_3SiH + H_2 \qquad (27)$$

a major product. The formation of this product most probably occurs via (28), since

$$CH_3SiH + HCl \rightleftarrows CH_3SiH_2Cl^* \qquad (28)$$

$$CH_3SiH_2Cl^* + M \longleftarrow CH_3SiH_2Cl + M \qquad (29)$$

thermochemical data[20,21] indicate that $CH_3SiH_2Cl^*$ energized by (28) contains 290 kJ/mole of excess energy, while $CH_3SiH_2Cl^*$ energized by (23) contains 424 kJ/mole of excess energy. RRKM calculations of the lifetimes indicate that in the former case the lifetime is long enough for collisional stabilization to occur, while in the latter case it is not. Therefore CH_3SiH_2Cl will be a major product of the CH_3SiH_3-HCl reaction but not of the SiH_4-CH_3Cl system.

7. SiH_4-NO Mixtures

For many years the addition of NO to reacting silane systems has been used as an indicator to differentiate between reactions involving SiH_2 and SiH_3, it being thought[22] that SiH_3 will react with NO and the Si_2H_6 formation rate retarded, while SiH_2 will not react with NO and the reaction rate will be unaffected. The infrared laser multiphoton decomposition of SiH_4 produces only SiH_2 and therefore provides a convenient method of testing this long held view of NO scavenging in reacting silane.

When SiH_4-NO mixtures containing less than 12% of NO are irradiated with the P(20) line at a fluence of 0.7 J/cm^2, the gaseous reaction products are: H_2, Si_2H_6, Si_3H_8, Si_4H_{10} and very small amounts of N_2O. In this region of composition the rate or yield per pulse of Si_2H_6 formation decreases with increasing value of the ratio $[NO]/[SiH_4]$, as shown in Figure 9. The rates of formation of all other products increase with increasing concentration ratio. The conversion in this composition range is, therefore, best described by (1) followed by (3)-(8) and competition of SiH_4 and NO for SiH_2. Thus in addition to (1), (3)-(8) we have (30). We have not been able to identify the products other than to note they comprise N_2O, solid siloxy-compounds and perhaps N_2.

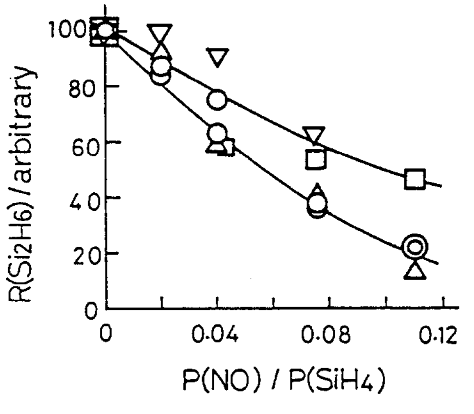

Figure 9. Rate of Si_2H_6 Formation in Arbitrary Units as a Function of $P(NO)/P(SiH_4)$.

$$SiH_2 + NO \longrightarrow Products \qquad (30)$$

A kinetic analysis of the retardation of Si_2H_6 formation by NO indicates

$$\frac{k_{30}}{k_3} = 2.3$$

This finding does not negate the conclusions of many studies using NO to differentiate between SiH_3 and SiH_2 because at the concentration ranges of NO usually used (~1-2%), the fast reaction of SiH_2 with SiH_4 still is the predominant fate of SiH_2. On the other hand,

SiH_3 undergoes no reaction that can compete with its rapid reaction with NO and SiH_4 to form N_2O and siloxanes.[24]

When $[NO]/[SiH_4] > 0.15$ the laser initiated reaction under the same conditions becomes explosively rapid, with 75% of SiH_4 decomposed by a single pulse and with the products of this explosive reaction being only H_2 and brown powder. The explosive nature of the reaction is shown in Figure 10. Material balance considerations indicate that all the H-atoms of the SiH_4 that is consumed during the explosive reaction are liberated as H_2. Thus the powder formed does not contain hydrogen and H_2 must arise mostly via processes other than the initial dissociation of SiH_4.

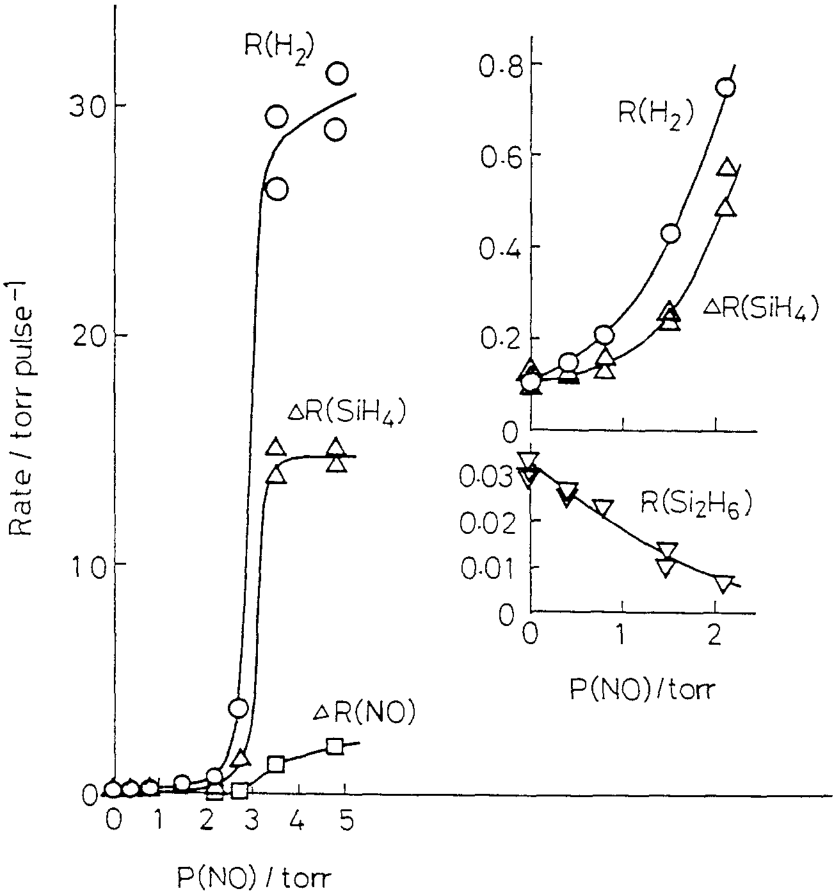

Figure 10. Rates of depletion (ΔR) of the reactants and of formation (R) of H_2 and Si_2H_6 as a function of pressures of NO added: initial pressure of SiH_4, 20 torr.

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