The Detection of O=$SiCl_2$ as an Intermediate During the Combustion Process of $SiCl_4$ with O_2

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Dedicated to Professor G. Fritz on the occasion of his 80th birthday

Keywords: $SiCl_4$ Combustion / $OSiCl_2$ / Matrix isolation / Thermodynamic data / DFT calculations

During the technical important combustion of $SiCl_4$ with oxygen [$SiCl_4(g) + O_2(g) = SiO_2(s) + 2\cdot Cl_2(g)$] many intermediates have been detected in the past. However, the presence of the primary species O=$SiCl_2$ has been discussed controversially until today. With the help of matrix isolation technique we have now been successful to monitor O=$SiCl_2$ via its IR spectrum. With the help of quantum chemical calculations the thermodynamic data have been calculated first. On this basis it was possible to find the optimal conditions to trap $OSiCl_2$ from the high-temperature equilibrium. Furthermore it could be shown via IR spectroscopy and quantum chemical calculations, that the radical OSiCl does not play a significant role within this combustion process.

Introduction

The reaction of silicontetrachloride with oxygen at temperatures far above 1000 °C ends up with solid SiO_2, which can be obtained as an industrial produced fine grained aerosil, if special reaction conditions are applied. At temperatures of about 1000 °C a great variety of chlorosiloxanes have been isolated, which can be regarded as metastable intermediates of this reaction.[1] The large number of products – the reaction yields hundreds of different molecules – allows the conclusion, that there must be an high reactive species involved in a primary step of the reaction.

Some time ago we did the presumption that this reactive intermediate is $OSiCl_2$.[2] Assuming its existence, most resultant products can easily be elucidated, for example Si_2OCl_6 can be regarded as a reaction product between $OSiCl_2$ and $SiCl_4$. A reaction of $OSiCl_2$ with a catenasiloxan $Si_nO_{n-1}Cl_{2n+2}$ yields chain prolongation, an oligomerisation leads to cyclosiloxanes $Si_nO_nCl_{2n}$. The formation of higher condensed siloxanes [$n(O) > n(Si)$] can be explained via elimination of $SiCl_4$ from siloxanes containing a smaller amount of oxygen.

In order to prevent consecutive reactions yielding higher condensed siloxanes and to detect $OSiCl_2$, the reaction of $SiCl_4$ and O_2 was performed at very low pressure. Performing the reaction first in the inlet system of a mass spectrometer, only a significant increase of the signal at m/z = 44 (SiO) and no signal, that could be assigned to $OSiCl_2$, was found. Therefore we tried to detect this molecule via matrix IR-spectroscopy. These investigations are mainly reported in the following paper.

However, first of all we want to discuss the results of DFT calculations on OSiCl and $OSiCl_2$ and their thermodynamic data, which are the basis for the high-temperature gas-phase equilibrium calculations, which will presented further on.

Results and Discussion

Quantum Chemical Calculations

Though we have described matrix isolated $OSiCl_2$, generated via a photoinduced reaction between Cl_2 and SiO in solid argon, some years ago,[3] literature provides no direct information about the thermodynamic stability of this species. Though we have published some quantum chemical SCF calculations on the structure and energetic relation of this molecule, the results have not been analysed with respect to a possible gas-phase stability.[4] In order to test the reliability of our DFT-calculations presented here,[5] we first applied the similar method to get the well-known values of $\Delta H_f^0(298)$ and $S^0(298)$ of Cl_2CO. Due to the excellent agreement between both couples of values [$\Delta H_f^0(298)$: (exp.) −220.078 kJ/mol[17]/(theor.) −227.2 kJ/mol and $S^0(298)$: (exp.) 283.852 J/(mol·K)[17]/(theor.) 283.84 J/(mol·K)], we assessed the calculated data for $OSiCl_2$ as reliable too. First we determined the enthalpy and entropy of the following reaction (1) to be $\Delta H_R^0(298) = -336$ kJ/mol and $\Delta S_R^0(298) = -137$ J/(mol·K).

$$Cl_2(g) + SiO(g) = OSiCl_2(g) \qquad (1)$$

On the basis of the experimental data of $Cl_2(g)$ and $SiO(g)$,[17] the $\Delta H_f^0(298)$ and $S^0(298)$ values for $OSiCl_2$ can be calculated to be:

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$$\Delta H_f^0(298) = -440.0 \text{ kJ·mol}^{-1}$$
$$S^0(298) = 302.4 \text{ J·(mol·K)}^{-1}$$

The geometry of $OSiCl_2$, which is a further result of these calculations, shows the expected differences to the former SCF calculation, e.g. the bond lengths are shortened [Si−O: 148.4 pm (SCF)/152.5 pm (DFT) and Si−Cl: 200.8 pm (SCF)/203.4 pm (DFT)], while the bond angles obtained by both methods are nearly identical: 109.1° (SCF)/ 108.9°(DFT). In order to calculate the thermodynamic data and to check the assignment of the matrix spectra, the following vibration frequencies (IR intensities [km/mol] in brackets) for $OSiCl_2$ have been determined.

Table 1. Calculated vibrational frequencies for $OSiCl_2$ (IR intensities [km/mol] in brackets)

Character	Frequencies in cm^{-1} (IR intensities in km/mol)		
A_1	1257.7 (99.4)	485.7 (24.1)	200.7 (2.8)
B_1	625.8 (249.2)	271.4 (25.3)	
B_2	274.7 (38.6)		

The excellent agreement between these calculated frequencies and the experimental values of the argon matrix isolated $OSiCl_2$ we published some years ago.[3]

[A_1: 1239.9/501.1 (200 estimated); B_1: 637.5/269.0; B_2: 279.9] confirms the reliability of the calculations about the high-temperature equilibrium presented further on.

During the combustion of $SiCl_4$ in principle one must also expect the radical species OSiCl, which recently has been characterised by our group.[6] The following thermodynamic values for OSiCl which are also the basis for the equilibrium calculations presented in the next chapter have been determined: $\Delta H_f^0(298) = -167.2$ kJ·mol^{-1}; $S^0(298) =$ 279.1 J·(mol·K)$^{-1}$[6]

Equilibrium State Considerations

To answer the question what should happen in the first steps of the considered reaction between $SiCl_4$ and O_2 we have carried out thermodynamic calculations of an equilibrium between the atoms and molecules given in Table 2. The computation was performed under the restriction, that no solid SiO_2 and higher molecular chlorosiloxanes are formed, that means only a homogeneous gas phase reaction is assumed.

The total pressure in the reaction tube cannot be measured exactly, therefore it is fixed to be 10^{-7} bar, which seems to be a realistic value, according to our experiments.

These data together with the presumed molar ratios 7:3, 5:5, and 3:7 of the species $SiCl_4$ and O_2 are the basis of our calculation. The results are shown in the diagrams Figure 1 to Figure 3, in which the partial pressures versus temperature are plotted.

Table 2. Thermodynamic data of those molecules which are involved in the equilibrium state calculations

Compound	$\Delta H°_{298}$/kJ/mol	$S°_{298}$/J/(K·mol)	Ref.
$SiCl_4$	−662.8	330.9	[17]
$SiCl_3$	−390.4	318.2	[17]
$SiCl_2$	−168.6	281.3	[17]
SiCl	198.3	237.8	[17]
Cl_2	0	223.1	[17]
Cl	121.3	165.2	[17]
O_2	0	205.1	[17]
O	249.2	161.1	[17]
SiO	−100.4	211.6	[17]
$OSiCl_2$	−440.0	302.4	cf. text
OSiCl	−167.2	279.1	cf. text

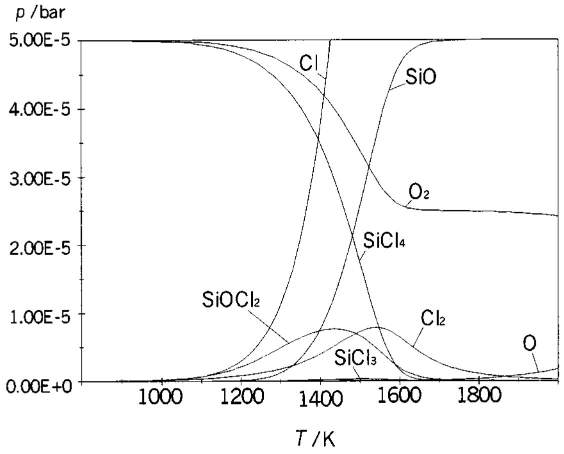

Figure 1. Equilibrium state partial pressures of the gaseous species in the system O/Si/Cl at a total pressure of 10^{-4} mbar; $SiCl_4$/ O_2 = 1:1

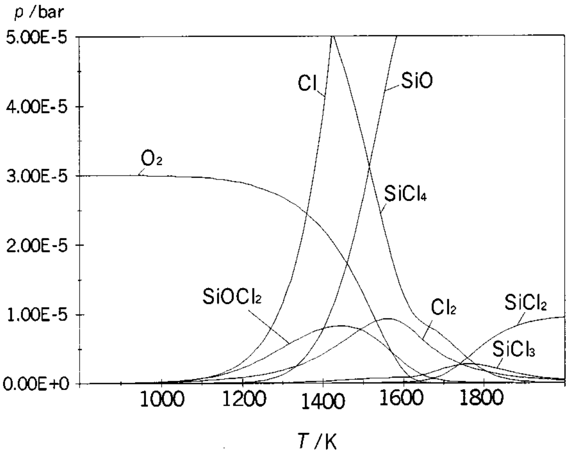

Figure 2. Equilibrium state partial pressures of the gaseous species in the system O/Si/Cl at a total pressure of 10^{-4} mbar; $SiCl_4$/ O_2 = 7:3

Although we cannot be sure that the system has been equilibrated all results of the computations are in good

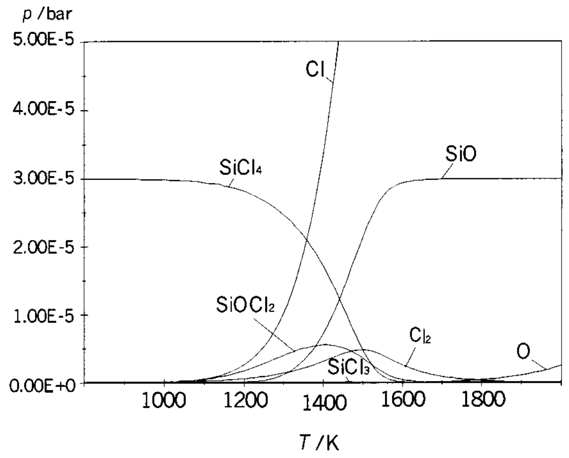

Figure 3. Equilibrium state partial pressures of the gaseous species in the system O/Si/Cl at a total pressure of 10^{-4} mbar; SiCl$_4$/O$_2$ = 3:7

agreement with experimental observations. It is evident that the reaction should start at a temperature of about 1000 K since the partial pressures of the starting materials SiCl$_4$ and O$_2$ begin to decrease there. Preparative and spectroscopic observations confirm this prediction. The formation of the oxygen containing species (e.g. OSiCl$_2$) is nearly completed at a temperature of 1400 K. Above this temperature mainly the dissociation of SiCl$_4$ and O$_2$ occurs. From all three diagrams it can be concluded that only two molecules containing Si and O appear at temperatures above 1000 K: SiO and OSiCl$_2$.[7]

The highest partial pressure of SiO is about one order of magnitude above that of OSiCl$_2$. The existence of the latter one is coupled to a rather narrow temperature range ΔT of about 300 to 400 K with a maximum of the partial pressure at about 1400 K. Based on these equilibrium state calculations the detection of OSiCl$_2$ via matrix IR spectroscopy should be possible without problems, because at a temperature of 1200 °C only SiO and SiCl$_4$ should be present in addition to OSiCl$_2$ and the IR-absorptions of the former ones are well-known and separated from those of OSiCl$_2$.

IR-Spectroscopic Investigations on Matrix-Isolated OSiCl$_2$

Matrix IR spectroscopy seemed to be the proper technique in order to investigate the combustion of SiCl$_4$ with O$_2$, since the starting materials as well as the products have already been studied by this method: SiCl$_4$,[8] SiO,[9] OSiCl,[6] and OSiCl$_2$.[3] Some time ago the OSiCl$_2$ molecule has been produced in the following way:[3] The high-temperature species SiO was cocondensed together with chlorine and a hundredfold excess of argon. The IR spectrum after cocondensation exhibited only the bands of SiO and its oligomers. Subsequently OSiCl$_2$ was generated from of SiO and Cl$_2$ in the matrix after irradiation with UV light of 254 nm. The IR spectrum of OSiCl$_2$ was analysed with the help of its isotopic shifts (^{16}O − ^{18}O/^{35}Cl − ^{37}Cl) and by means of a normal coordinate analysis.

In order to perform matrix investigations of the combustion process of SiCl$_4$ the gaseous components SiCl$_4$ and O$_2$ were first mixed in a ratio of 1:1. This gaseous mixture was passed under high-vacuum conditions through a high-temperature reactor at 1240 °C with a molar flow rate of 10^{-3} mmol/h. The mixture of gases leaving the high-temperature furnace was diluted with a hundredfold amount of gaseous argon and then was condensed onto a copper block of 15 K. The IR spectrum of a matrix after 30 minutes of condensation time of this gaseous mixture is shown in Figure 4.

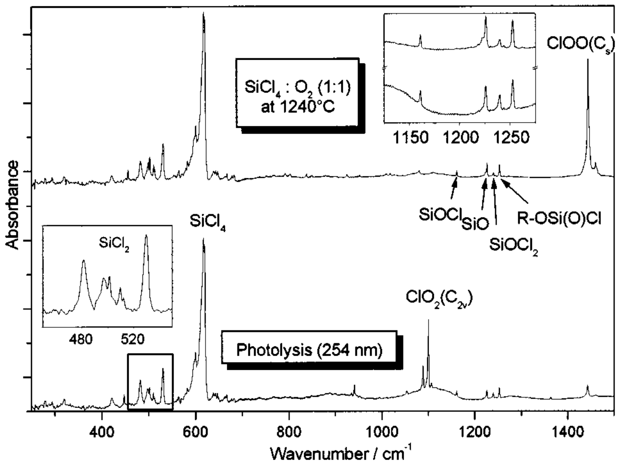

Figure 4. Top: argon matrix IR spectrum of the reaction products of the 1:1 SiCl$_4$/O$_2$-mixture at 1240 °C; below: following photolysis of the matrix with 254 nm for 10 min

The absorption bands of OSiCl$_2$ (1240 cm^{-1}, 637.5 cm^{-1}, 501.1 cm^{-1}), SiCl$_4$ (616.1 cm^{-1}), OSiCl (1161 cm^{-1}, 509.4 cm^{-1}), SiO (1226 cm^{-1}), SiCl$_2$ (512.0 cm^{-1}, 510.1 cm^{-1}, 501.4 cm^{-1}, 498.0 cm^{-1}), and ClO$_2$ (1100 cm^{-1}) can be observed. The molecule ClOO is formed spontaneously in the matrix by a reaction of chlorine atoms from the high-temperature equilibrium and O$_2$ molecules. The band at 1442 cm^{-1} can be assigned to the ClOO isomer (C_s symmetry).[10] After irradiation (254 nm) of the matrix the ClOO-molecule rearranges to the more stable C_{2v} isomer ClO$_2$ (1100 cm^{-1}). A spectrum over the whole range after photolysis is shown in Figure 4.

Starting with a molar ratio between SiCl$_4$ and O$_2$ of 5:1 a much smaller amount of ClO$_2$ is formed. This observation is plausible since no free O$_2$ molecules are present in the matrix due to the fact, that they have already reacted with the Si species which are present in large excess.

The most unexpected observation in Figure 4 is the larger intensity of the bands belonging to OSiCl, compared to those of OSiCl$_2$. Based on theoretical investigated integral extinction coefficients[14] of the "SiO absorption bands" (in [km/mol] SiO: 52.1; OSiCl: 56.8; OSiCl$_2$: 114) an OSiCl/OSiCl$_2$ ratio of about ten, averaged over eight experiments is observed, whereas SiO and $OSiCl_2$ are produced in nearly equimolar amounts (with an light weight excess of SiO). While the molar ratio of $SiO/OSiCl_2$ roughly corresponds to our expectations of a high-temperature equilibrium at 1500 K, there is by far too much OSiCl in the matrix compared to the amount of $OSiCl_2$. This discrepancy can only be understood if OSiCl is not formed in the gas phase but in the matrix from SiO molecules and Cl atoms. To confirm this hypothesis some experiments have been performed, in which exclusively SiO and Cl atoms from two separate high-temperature reactors were cocondensed with an excess of argon.[6] The resulting spectra exhibited unchanged SiO and only OSiCl as a Si-containing species. No $OSiCl_2$ was formed. Even after a subsequent photolysis (254 nm) no $OSiCl_2$ is observed, i.e. in the high-temperature equilibrium nearly no Cl_2 was present, because, if it would be present, $OSiCl_2$ should be obtained after irradiation.[3]

The conclusion of all these experiments is, that the observed $OSiCl_2$ species during the matrix experiments are unambiguously formed in the high-temperature equilibrium. The observation of the first matrix experiments showing an OSiCl amount to be one or two orders of magnitude too high do not correspond to the equilibrium conditions at 1240 °C, for OSiCl is nearly exclusively produced by the spontaneous reaction of chlorine atoms and SiO in the matrix. However the higher concentrations of $OSiCl_2$ and SiO, concluded from the analysis of these matrix spectra after correction for spontaneously formed OSiCl, are in good agreement with the presented equilibrium calculations.

In the spectrum presented in Figure 4 a SiO valence band appears at 1250 cm^{-1}. It is only observed in those experiments starting with a molar ratio of $SiCl_4$ and O_2 of 1:1. With respect to the intensity of this band in several experiments it must be assigned to a different species than these discussed so far. Due to the high frequency range a $-O(Cl)Si=O$ group can be expected, since ν(Si−O) in $OSiF_2$ is observed at 1309.4 cm^{-1}.[11] This estimation is confirmed by DFT calculations[12] from which the following SiO frequencies of the molecules under discussion result: SiO (1245 cm^{-1}), OSiCl (1149 cm^{-1}), $OSiCl_2$ (1258 cm^{-1}), and $Cl_3SiOSi(O)Cl$ (1299 cm^{-1},[13]). This variation in the frequency range reflects to a certain degree the variation in the SiO bond strength. However, for entropy reasons the species $Cl_3SiOSi(O)Cl$ should not exist in the high-temperature equilibrium, that means it should be formed in the matrix. However it is astonishing, that $Cl_3SiOSi(O)Cl$ and not the molecule $Cl_2SiO_2SiCl_2$ (with an central SiO_2Si four-membered ring) is formed, though according to analogous DFT calculations[12] the latter one is expected to be more stable by about 162 kJ/mol.

After the combustion of $SiCl_4$ we have also pyrolysed hexachlorodisiloxan (Figure 5) and octachlorotrisiloxan (Figure 6) at temperatures of 1240 °C.

These experiments clearly show the formation of the molecules SiO and $SiCl_4$. The species OSiCl and especially $OSiCl_2$ are only produced in small portions, that means the observed band intensities are below the limit of detection of this spectroscopic method.

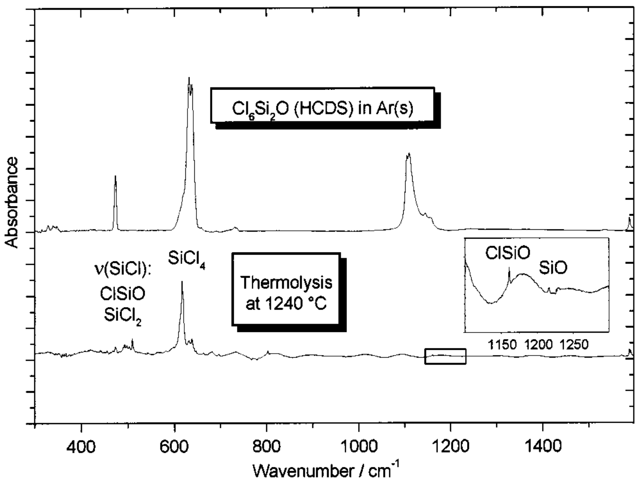

Figure 5. Top: argon matrix IR spectrum of hexachlordisiloxane, below: matrix IR spectrum of the thermolysis products (1240 °C)

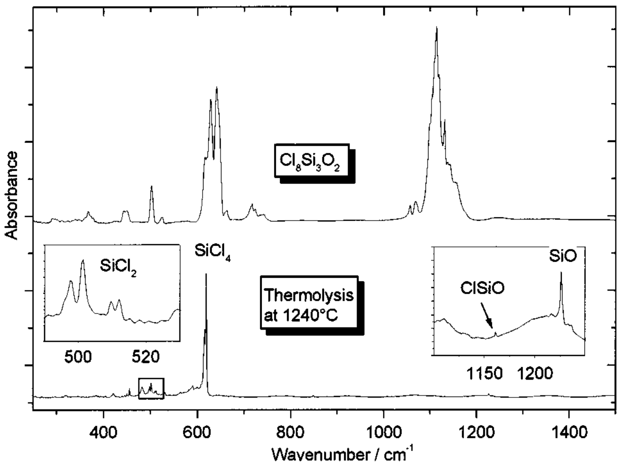

Figure 6. Top: matrix IR spectrum of octachlortrisiloxane in solid argon, below: matrix IR spectrum of the thermolysis products (1240 °C)

Conclusion

The quantumchemical calculations about the thermodynamic stability of OSiCl and $OSiCl_2$ and the equilibrium calculations based on these data are in good agreement with the experimental results of the matrix IR spectra. That means theory as well as experiments show that $OSiCl_2$ is an essential reactive intermediate in the combustion process of $SiCl_4$ with O_2. Therefore the presented results may be important as well for further synthetic investigations as for every kind of high-temperature processes, in which chlorine containing species are in a thermodynamic equilibrium with SiO containing species (e.g. chemical processes in quartz vessels). Since similar relations are expected for the reaction between $SiBr_4$/SiI_4 and O_2, the analogous species $OSiBr_2$/$OSiI_2$ may also be important for the understanding of the gas phase reactions in halogen lamps.

Experimental Section

$SiCl_4$ (> 99 %, Merck GaA, Darmstadt) and O_2 (4.8, Messer-Griesheim, Krefeld) were mixed in a glass vessel and the pressure was measured by means of a capacity instrument (Mks Instruments Deutschland GmbH). The same instrument was used in order to monitor the flow rate (10^{-5} mol/h) passing the reaction vessel (quartz) of the high-temperature furnace (alumina).

The relative amount of argon (4.8, Messer-Griesheim, Krefeld) mixed with the gaseous species after passing the high-temperature area to the Si/O/Cl species was estimated to be about 200:1. After a condensing period of 30 min, IR absorptions were recorded. The IR absorptions were recorded by means of a reflection unit, in which the copper plate for deposition of the matrix gases was cooled by a closed-cycle refrigerator (RGD 510, Leybold Köln).

All spectra were recorded with a Bruker IFS 113v FT-IR Spectrometer (Bruker GmbH, Karlsruhe). A MCT detector and a Ge/KBr beamsplitter have been applied in order to obtain the spectra presented.

The DFT calculations were carried out on IBM RS 6000/390 workstations using the B3-LYP functional and a TZVPP basis. The program packages Gaussian 94[14] and Turbomole[15] have been used. Contour line diagrams have been realised using the program Molden[16].

Photochemical activation has been performed with the help of a low-pressure Hg lamp (Gräntzel, Karlsruhe, Germany).

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Atom	Basis	Contraction pattern	Exponent of the polarisation function
H	TZVPP	(5s2p1d) / [3s2p1d] {311/11/1}	η_p = 1.407; 0.388 η_d = 1.057
C	TZVPP	(11s6p2d1f) / [5s3p2d1f] {62111/411/11/1}	η_d = 1.097; 0.318 η_f = 0.761
O	TZVPP	(11s6p2d1f) / [5s3p2d1f] {62111/411/11/1}	η_d = 2.314; 0.645 η_f = 1.428
Si	TZVPP	(14s9p2d1f) / [5s5p2d1f] {73211/51111/11/1}	η_d = 0.481; 0.159 η_f = 1.428
Cl	TZVPP	(14s9p2d1f) / [5s5p2d1f] {73211/51111/11/1}	η_d = 1.046; 0.344 η_f = 0.706

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[7] Furthermore the radical OSiCl has also been involved in the equilibrium state calculations[6] which are presented in the diagrams 1−3. However, the resulting partial pressure of OSiCl is too small to be seen in these figures, it vanishes in the base line.

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Received April 23, 1999
[99145]