



PHOTOLYSIS OF AN ARYLALKYL-TRIAZENIDO-PLATINUM-IV COMPLEX

T. LIPPERT,¹ J. DAUTH,² B. DEUBZER,² J. WEIS² and A. WOKAUN^{1†}

¹Physical Chemistry II, University of Bayreuth, D-95440 Bayreuth, Germany and ²Wacker-Chemie GmbH, D-84489 Burghausen, Germany

(Received 1 September 1994; accepted 29 May 1995)

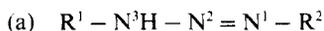
Abstract—The photolytic decomposition of tetrakis(1-phenyl-3-hexyl-triazenido)-platinum(IV) is studied in a variety of media, and found to proceed according to simple first order kinetics. Two excimer laser wavelengths, an excimer-laser pumped dye laser, and a broadband mercury lamp are used for excitation. As referred to the incident power, selective irradiation near the complex-specific absorption maximum is found to be most efficient for inducing the photolytic decomposition. A different influence of degassing and oxygen saturation is observed for tetrahydrofuran and for technical siloxane solvents. To elucidate the origins of the observed behaviour, decomposition products of the complex, and products of hydrosilylation reactions catalyzed by this compound, are identified by GC/MS analysis. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

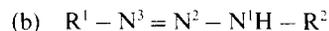
The properties of metal complexes containing triazenido ligands have met intense research interest during the past few years (Moore and Robinson, 1986). Studies on the coordination chemistry of triazenes were initiated around the turn of the century (Meldola and Streatfield, 1887, 1888; Cuisa and Pestalozza, 1911, Meunier, 1900, 1903; Niementowski and Roszkowski, 1897). A second period of high activity in the field of triazenido complexes was started in the 1940's (Dwyer, 1939, 1941).

In this study we are focussing on the class of 1-aryl-3-alkyl-triazene ligands. In view of the multitude of available triazene ligands, and of possible variations in their coordination geometries, the number of characterized arylalkyl-triazenido transition metal complexes is still comparatively small (Julliard *et al.*, 1982; Dauth *et al.*, 1993). Recently we have succeeded in synthesizing several homoleptic arylalkyltriazenido-platinum(IV) complexes.

The discovery of disubstituted aryl-triazene compounds can be traced back to the work of Griess (1861). Alkyl-aryl-triazenes have been first synthesized by Dimroth (1905); in solution, the substituents at the N=N bond are found in the *trans* configuration, in either of the following tautomeric forms,



or



The equilibrium between the two tautomers is strongly dependent on the substituents, R¹ and R² (Ahern and Vaughan, 1973; Kelly *et al.*, 1982).

Triazenes are the most simple representatives of a class of compounds containing chains of nitrogen atoms (Benson, 1984). Depending on substitution, these molecules are remarkably stable in the ground state, but subject to decay under elimination of nitrogen at higher temperatures (Albert *et al.*, 1976; Lippert *et al.*, 1992). Acidolysis (Jones *et al.*, 1982) induces an ionic decay into the corresponding diazonium ion and a primary amine, which in formal notation corresponds to the reverse of the coupling reaction used for synthesis.

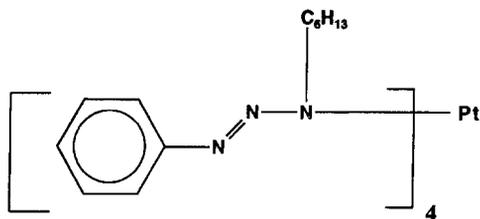
Furthermore, alkyl-aryltriazenes may be decomposed photochemically; the decomposition reaction again involves the elimination of nitrogen, in this case however on a radical pathway.

The photolytic decomposition of 1-aryl-3,3-dialkyltriazenes due to continuous irradiation or pulsed laser excitation has recently been studied (Lippert *et al.*, 1994; Stasko *et al.*, 1993), quantum yields of photolysis have been determined (Lippert *et al.*, 1994), and the radicals created in the course of reaction were identified by ESR spectroscopy (Stasko *et al.*, 1993).

This photolability of the ligands is the basis for the present study in which the photolysis reaction of platinum complexes with triazene ligands is investigated. The photodecomposition is of interest because reactive and coordinatively unsaturated platinum species may be generated in solution by a controlled light-induced reaction. Here we are focussing on the influence of various reaction parameters on the

†Author to whom all correspondence should be addressed.

Present address: ETH Zürich and Paul Scherrer Institute, General Energy Technology Department, CH-5232 Villigen, Switzerland, Fax +41 56 310 44 16.



Scheme 1. Structure of the Pt-triazenido complex.

photolysis of a typical representative, i.e. tetrakis(1-phenyl-3-hexyl-triazenido)-platinum(IV). The reactivity of a series of related compounds containing various, differently substituted triazenido ligands will be the subject of a forthcoming communication.

EXPERIMENTAL

Materials

The structure of the investigated tetrakis(1-phenyl-3-hexyl-triazenido)-platinum(IV) complex is shown in Scheme 1. The synthesis procedure has been described in detail (Dauth *et al.*, 1993). The molar extinction coefficient at the XeCl excimer laser wavelength of 308 nm amounts $\epsilon = 39,100$.

The solvent THF was supplied from Merck; various siloxane-based solvents, as specified below, were obtained from Wacker Chemie GmbH, and were used without degassing. Solutions of the triazenido complex were prepared in a concentration range of $1-8 \times 10^{-5}$ M (unless otherwise stated), such that UV/visible spectra could be recorded without any further dilution.

Photolysis, spectroscopy, and analysis

Photolysis experiments were carried out in quartz cuvettes, containing 3 ml of the platinum complex

solution. Concentrations were varied in the range $1-8 \times 10^{-5}$ M. A high pressure Hg lamp (Oriel, 500 W), a KrF* excimer laser (248 nm, Lambda Physik, model LPX 105e), a XeCl* excimer laser (308 nm, Lambda Physik, model 120i), and an excimer pumped dye-laser (345 nm, Lambda Physik, model FL 3002) have been used alternatively as irradiation sources. The lasers were operated at pulse energies of 1.3 mJ (dye-laser), 70 mJ (KrF) and 88 mJ (XeCl), respectively, with a repetition rate of 2 Hz.

UV/visible spectra were recorded on a conventional double-beam spectrometer (Perkin-Elmer, model Lambda 17). Gas chromatograms (GC) of product mixtures were recorded on an HP instrument (model 5890A) equipped with a $25 \text{ m} \times 0.32 \text{ mm} \times 0.52 \mu\text{m}$ column (type HP-1). Gas chromatography/mass spectrometry (GC/MS) analyses were carried out on a Finnegan mass spectrometer (model MAT 312).

RESULTS

Kinetic measurements

From ESR spectroscopy, a radical pathway of the photochemical decomposition of triazenido-platinum complexes has been derived (Rapta *et al.*, 1995). In an earlier communication (Dauth *et al.*, 1993) we have stated that the photolysis of our Pt complex followed a simple one-step decomposition. This behaviour is illustrated in Fig. 1. The linearity of the absorption-difference diagram (Mauser, 1968), as shown in Fig. 2, confirms that the photochemical reaction is of type $A \Rightarrow B$. A first order analysis according to the Swinbourne approximation (Swinbourne, 1960) was used to calculate the rate constant. Absorbance values were recorded after delivery of equal incremental

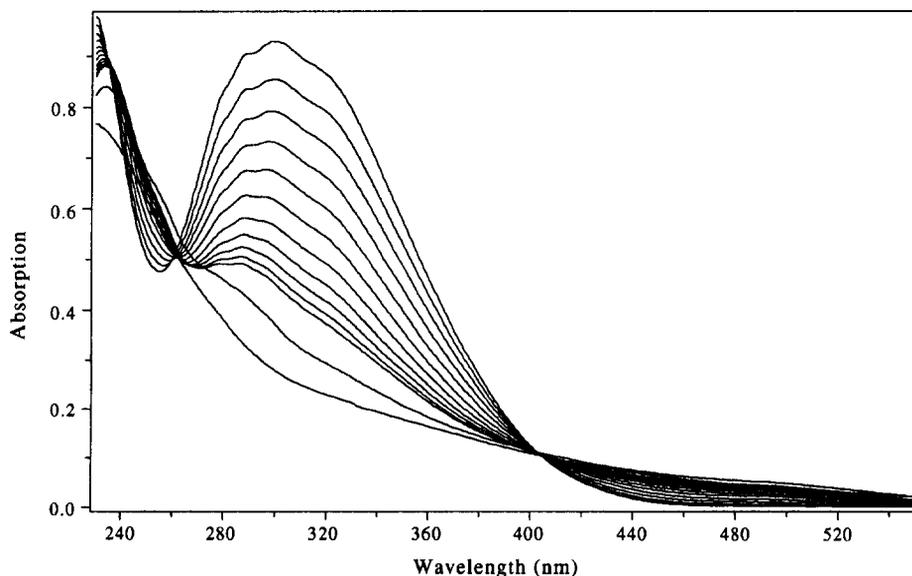


Fig. 1. Irradiation of the Pt complex (conc. 3.8×10^{-5} M in PS III) with 0, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 400 and 2000 XeCl* excimer laser pulses (308 nm, 88 mJ, 2 Hz).

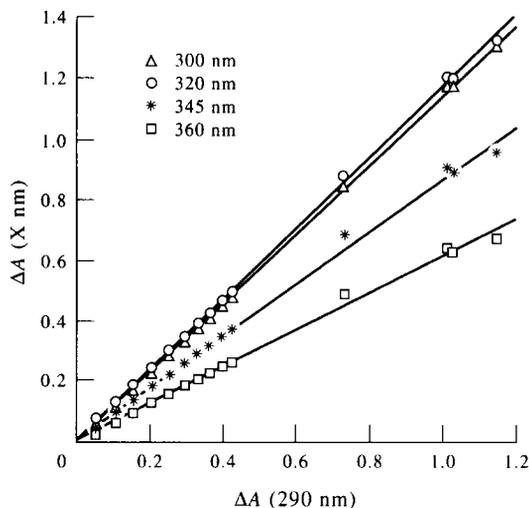


Fig. 2. Absorption difference diagrams for the photolysis of the complex in PS III, as shown in Fig. 1.

numbers of excimer laser pulses to the sample. These increments correspond to the constant time interval Δt of the standard data analysis (Swinbourne, 1960),

$$A_{\lambda,t+\Delta t} = A_{\lambda,t}(1 - e^{-k_1\Delta t}) + A_{\lambda,t}e^{-k_1\Delta t}$$

A plot of $A_{t+\Delta t}$ vs A_t yields a straight line of slope $e^{-k_1\Delta t}$. Such a linear Swinbourne plot is illustrated in Fig. 3. From the slope of the Swinbourne plots, apparent first order rate constants k_1 have been determined.

Of course, the absolute values of k_1 do depend on the experimental conditions. Except for Table 3 where the influence of the excitation wavelength is explicitly investigated, all the results presented (Tables 1, 2, and 4) refer to XeCl excimer laser irradiation at 308 nm. In these experiments, pulses of 88 mJ energy were incident onto an area $10 \times 22 \text{ mm}^2$ in size; the irradiated volume in the quartz cuvette

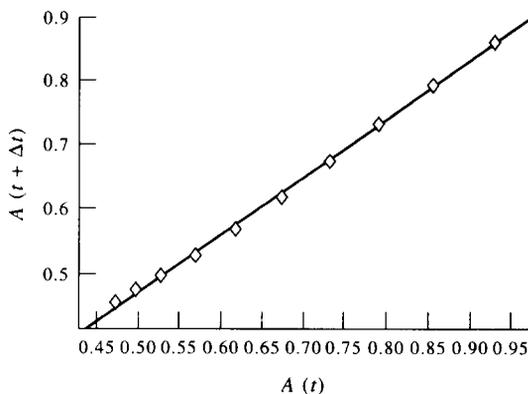


Fig. 3. Swinbourne-plot for the photolysis of the complex in PS III.

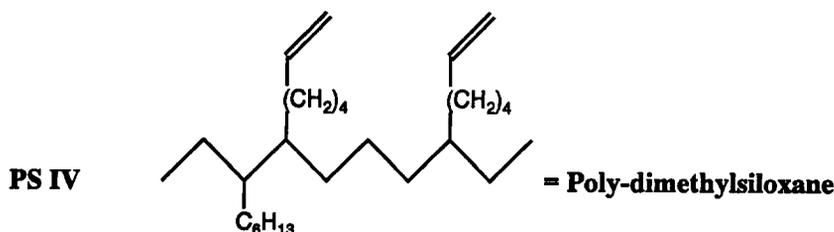
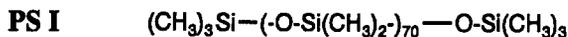
corresponded to 3.5 cm^3 . *Relative* values of the first order rate constants k_1 represent a measure of photochemical reactivity under various experimental conditions, with the irradiation parameters being held constant.

In addition, quantum yields (QY) of photolysis were calculated from the decrease in absorption in response to a given number of laser pulses. As a consequence of the low values (*ca* 0.2%) of the quantum yields, the associated error bars are quite large.

The above mentioned effective rate constants are obtained with higher precision, as they are determined from the Swinbourne fit of an entire photolysis data set. Therefore, these rate constants will be referred to when comparing the various photolysis conditions.

Variation of solvent

In view of an envisaged use of the complex as a hydrosilylation catalyst (Boardman, 1992; Hux and Puddephatt, 1992; Brune *et al.*, 1992; Hennig *et al.*, 1989), various polysiloxanes (PS I-IV) and THF were



Scheme 2. Solvents used for the photolysis. The 'zig-zag' line drawn for the backbone of PSIV represents a poly-dimethylsiloxane chain.

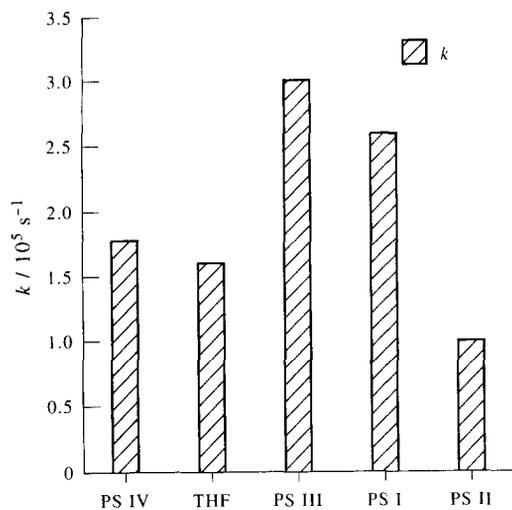


Fig. 4. Photolysis rate constant in different solvents.

used as solvents; structural formulas are displayed in Scheme 2. These solvents may be ranked according to polarity and viscosity as follows

Viscosity: THF < PS II < PS I < PS III = PS IV

Polarity: PS I < PS III < PS IV < PS II < THF

THF was also used as a "co-solvent" in order to overcome the poor solubility of the crystalline complex in the polysiloxanes. To this aim, the compound was dissolved in a small quantity (<1 ml) of THF. After addition of the silicon oil, the THF component was removed by vacuum evaporation. The rate constants of the photolysis were determined using the XeCl* excimer laser (308 nm) as the irradiation source.

The results obtained in the various solvents are compared in Table 1 and in Fig. 4. The lowest rate constant is observed for PS II, the solvent with the highest polarity and lowest viscosity among the investigated series of PS. The polar solvent PS IV should be regarded as an exceptional case as it is not completely transparent at 308 nm (absorbance = 0.3 for 1 cm path length).

The value recorded in THF lies between the rate constants found in PS II and PS I. In order to check whether the use of THF as a co-solvent was producing additional effects, the rate constant of photolysis

Table 1. Rate constants for photolysis of the Pt-complex in various solvents

	$k_1 \dagger / 10^5 \text{ s}^{-1}$	QY/%
PS II	1.002	0.159
PS I	2.595	0.163
PS III		
(THF evaporated)	3.011	0.28
(THF not evaporated)	2.396	0.233
PS IV	1.770	0.164
THF	1.605	0.126

†This photolytic first order "rate" constant refers to the effective illumination time, as given by 20 ns pulse length of the XeCl* excimer laser ($\lambda_{irr} = 308 \text{ nm}$). Pulses of 88 mJ energy were incident onto an area $10 \times 22 \text{ mm}^2$ in size on the front face of a quartz cuvette, containing 3.5 cm^3 of solution.

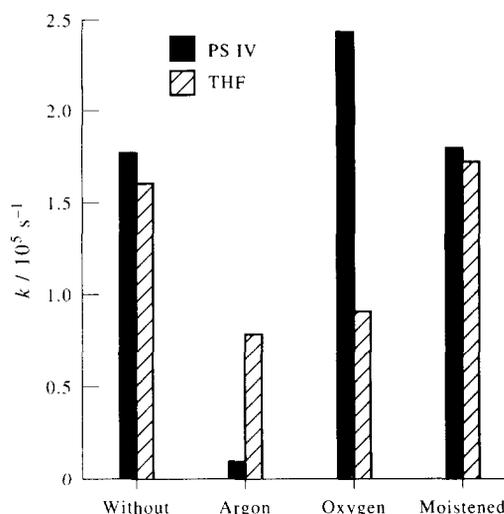


Fig. 5. Photolysis rate constants for different types of solvent preconditioning.

was determined with and without evaporation of the added THF. For the case of PS III, the solvent with the highest rate constant, the removal of the THF resulted in an increase of k , in agreement with the result (Table 1) that the value for PS III is higher as compared to the one determined in neat THF.

Conditioning of the photolysis medium

In view of technical applications in hydrosilylation, it was deemed important to clarify the influence of oxygen and water content of the solvent. The solvent PS IV was chosen as it represents a possible candidate for the hydrosilylation reaction; THF was tested for use as a co-solvent, which would not be removed by evaporation in a technical process.

Rate constants are compared in Table 2 and Fig. 5 for the solutions used without any pretreatment, saturated with argon, with moistured argon, and with oxygen.

In PS IV, the highest rate constants were obtained for the oxygen saturated solution. The moistured and unpretreated solutions gave rise to similar values, whereas the sample saturated with Ar showed a very low k value.

For the pure THF solution, the oxygen and argon saturated solutions exhibited the lowest rate constants, whereas for the untreated and moistured solutions, similar rate constants as in PS IV solution were obtained.

Table 2. Rate constants[†] determined for various preconditionings of the solvent

Solvent	PS IV	THF
No pretreatment	1.770	1.605
Saturated with argon	0.100	0.779
Saturated with moistured argon	1.790	1.715
Oxygen saturated	2.430	0.904

† k_1 in units of 10^{-5} s^{-1} , irradiation wavelength 308 nm, irradiation geometry as in Table 1.

Table 3. Dependence of the rate constant in THF on irradiation wavelength

	k_1/s^{-1}	$k_1 P^{-1}/s^{-1} W^{-1}$
Hg lamp	2.52×10^{-2}	0.003×10^{-2}
KrF excimer laser (248 nm, 70 mJ)	4.404×10^4	0.1573×10^{-2}
XeCl excimer laser (308 nm, 88 mJ)	7.794×10^4	1.772×10^{-2}
Dye laser (345 nm, 1.3 mJ)	1.01×10^4	7.770×10^{-2}

Wavelength dependence of the photolysis

Rate constants for different irradiation wavelengths are listed in Table 3. For a rough direct comparison, the rate constants obtained with different irradiation sources were normalized with respect to the average power P (last column of Table 3). The differences between the values thus obtained, as shown in Fig. 6, may be due to both wavelength and peak power dependent effects.

Not unexpectedly, the normalized photolysis rate constant for irradiation with a mercury lamp is lowest, as a large fraction of the power is emitted at wavelengths where the complex does not exhibit absorption. For the three laser wavelengths employed, the relative values of the normalized rate constants are increasing with the laser wavelength.

Temperature dependence

In order to test whether thermolytic decomposition was running in parallel with the photolysis reaction at the temperatures used, rate constants have been determined at different temperatures, and are summarized in Table 4. For a photochemical elementary step, no influence of the temperature on the rate constant is expected. With radical decompositions, a modest increase of the rate at higher temperatures is often observed, and is ascribed to a higher escape rate of the radicals from the primary solvent cage as the viscosity of the latter is decreased. This effect typically amounts to a factor of 2–3 for a temperature change from -20 to 20°C .

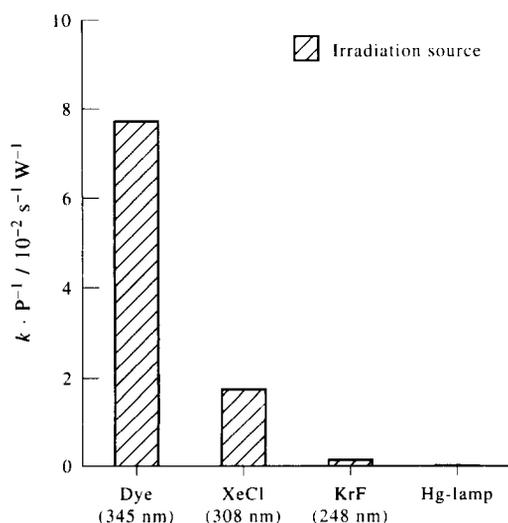


Fig. 6. Normalized values of the rate constant for different irradiation wavelength.

Below 0°C , the expected increase with temperature is detected (Table 4). However, for solvent temperatures of 20 and 40°C the rate constant is found to decrease again.

Product analysis

Hydrosilylation activity. To test the ability of the Pt complex to act as a catalyst for the hydrosilylation, the test reaction shown in Scheme 3 has been used. Compounds A and B were mixed in a volume ratio of 3:1, and the Pt complex was added at a concentration of 100 ppm (calculated as pure platinum). The solution was irradiated with 5000 pulses at 308 nm (88 mJ, 2 Hz). The resulting products, as identified from GC/MS analysis, are shown in Scheme 3.

After activation with the XeCl* excimer laser the Pt-triazenido complex acts as a catalyst for the hydrosilylation reaction. Besides the main products of the hydrosilylation reaction $(AB)_x$, further components resulting from side reactions are detected. The cyclization yielding the cyclic AB-dimer, and the generation of hydrogenated products have been previously described (Speier, 1979). Possible side reactions are isomerizations of the olefin and the "dehydrogenating silylation" (cf. Scheme 5). In addition, isomers of the main products are detected, which may be due to the possibility of either α or β addition during hydrosilylation.

Products of the catalyst. The fate of the ligands of the Pt complex after photolysis has also been investigated by GC/MS analysis. For this purpose, saturated solutions of the complex in either of the two components of the hydrosilylation reaction were again irradiated with 5000 excimer laser pulses (308 nm, 88 mJ, 2 Hz), and the product solution was analyzed.

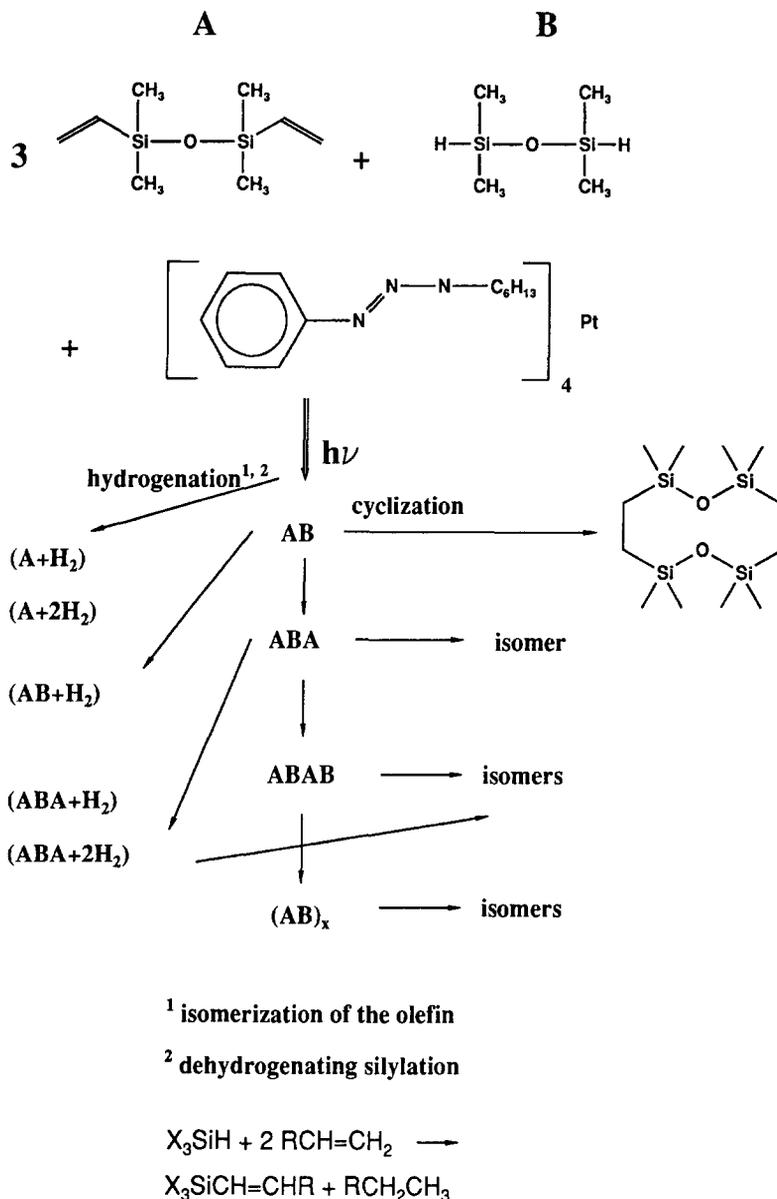
If the divinyl-disiloxane was used as the solvent, aniline and various tertiary amines were detected (cf. Scheme 4). In the hydrogen-carrying siloxane, a tertiary amine is again detected; in addition, higher homologues (n -mers) of the siloxane reactant are found.

Reaction rate. To determine relative values of the hydrosilylation reaction rate, a model reaction has

Table 4. Temperature dependence of the rate constant† in PS III

	$k_1/10^{-5} s^{-1}$
40°C	2.899
20°C	3.062
0°C	4.210
-20°C	3.657
-35°C	2.487

† k_1 in units of $10^{+5} s^{-1}$, irradiation wavelength 308 nm, irradiation geometry as in Table 1.



Scheme 3. Products of the hydrosilylation reaction.

been used. The time dependence of this reaction, which is shown in Scheme 5, can be followed on line by monitoring the decreasing integral intensities of the reactant in the gas chromatograph.

As shown in Fig. 7, the Pt complex itself is very stable in the mixture of the reactants. Also for solutions irradiated with 20 or 200 pulses, the reaction did not take place. After 1000 pulses, the reaction was already complete after 5 min.

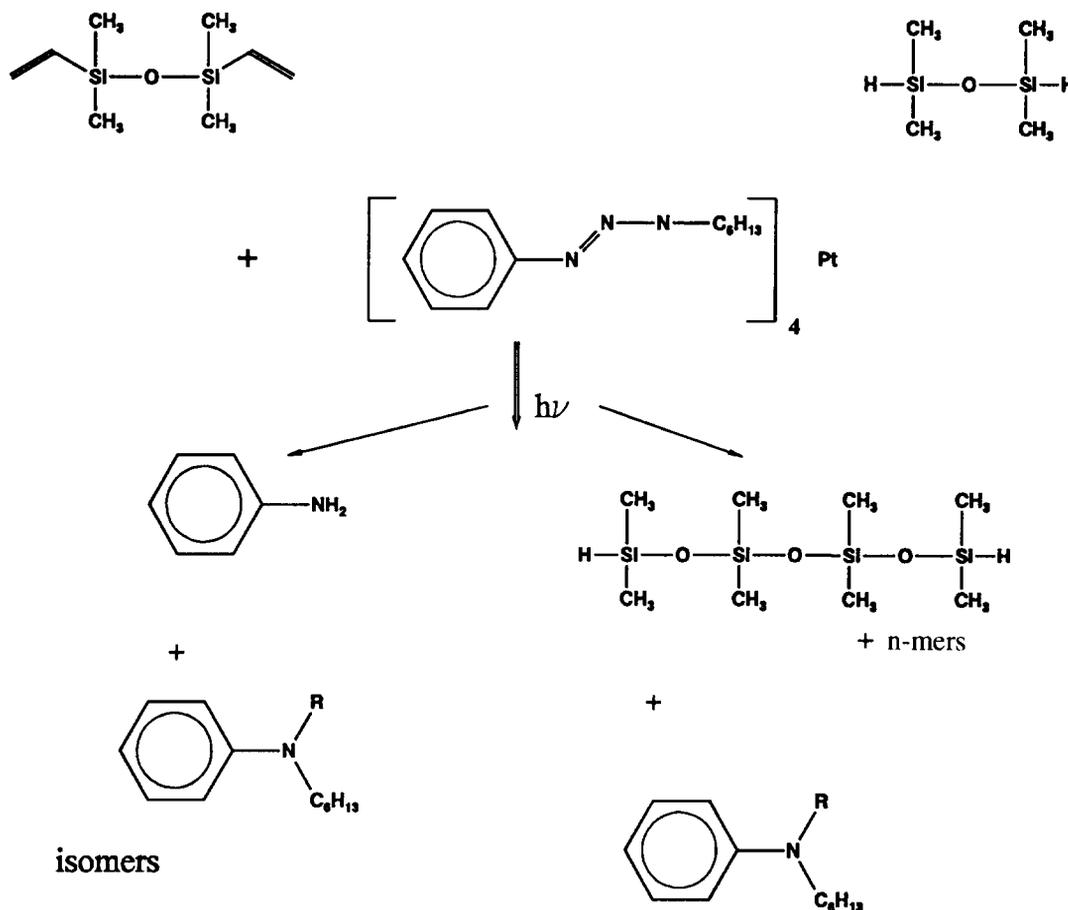
DISCUSSION AND CONCLUSIONS

Influence of the solvent

A wide variety of polysiloxanes may, in principle, be used as solvents for the hydrosilylation reaction.

In an effort to provide guidelines for solvent selection, the influence of physico-chemical properties, such as polarity and viscosity, have been probed. For the tested solvents, no direct correlation of these parameters with the photolytic activity of tetrakis (1-phenyl-3-hexyl-triazenido)-platinum(IV) has been found. As both the polarity (formation of hydrogen bonds) and the viscosity (which influences the radical recombination rates) are expected to influence the effective photolysis rate constant, an *a priori* prediction of the latter appears to be difficult, and any further solvents of interest will have to be tested by experiment.

However, it is worthwhile to point out that the reaction medium has a pronounced influence on the



Scheme 4. Reaction products of the Pt complex.

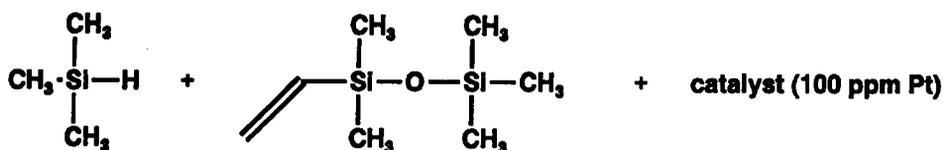
photolysis rate of tetrakis (1-phenyl-3-hexyl-triazenido)-platinum(IV). High polarity solvents are generally found to increase the photolysis rate, whereas high viscosity tends to lower the rate due to geminate recombination of the primary radicals produced.

Reaction conditions

Whereas photochemical studies are normally performed under well-defined laboratory conditions, i.e. in UV-grade, degassed and water free solvents, technical hydrosilylation reactions are typically carried out in the presence of water, oxygen, and solvents such as THF. Therefore, it was deemed important to assess the influence of these parameters. First, the role of oxygen is addressed. Formation of charge transfer complexes is a well-known feature for oxygen satu-

rated solutions of organic solvents (Tsubomura and Mulliken, 1960; Stenbeg *et al.*, 1970; Kulevsky *et al.*, 1969). These CT complexes, which result from radical chain mechanisms in the case of THF (Tsubomura and Mulliken, 1960), have higher absorbance values and are hence competing with the photolysis of the Pt-complex. A further aspect should be borne in mind: oxygen is thought to act as a “co-catalyst” (Lewis, 1990; Marciniak and Gulinski, 1993) during the hydrosilylation reaction. This effect is either due to the development of Pt–oxygen intermediates during the activation of the Pt catalyst, or by stabilization of Pt colloids, which are discussed as possible reaction products of the photolysis.

In argon-saturated PS IV no stabilization of intermediates or products can take place, leading to the lowest rate constant of photolysis, or reversely to the



Scheme 5. Model reaction for direct monitoring of the extent of reaction by GC analysis.

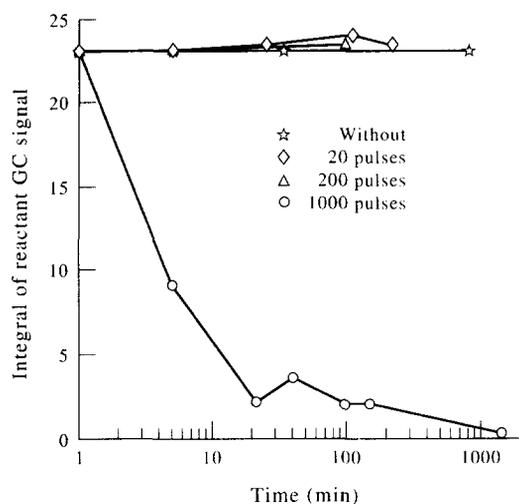


Fig. 7. Time dependent decrease of the vinyl reactant concentration, as monitored by GC in the model reaction of Scheme 5. An unirradiated solution, as well as solutions irradiated by 20, 200 and 1000 excimer laser pulses, have been studied.

highest half life of the Pt complex in light-exposed solution. In the degassed THF solution, oxygen containing photolysis products of the solvent (such as water, butyrolactone and α -hydroxy-THF) (Tsubomura and Mulliken, 1960; Steberg *et al.*, 1970; Kulevsky *et al.*, 1969) can act as stabilizers. An additional effect of the radicals from the photolysis of THF can not be excluded. These factors may account for the higher k value in argon-saturated THF, as compared to PS IV. Water in moisture-containing samples appears to act in a similar way as the THF photolysis products.

In order to assert the above-mentioned role of oxygen in connection with the radical chain decomposition of THF, the stability of a solution of the complex in THF and in benzene was compared. After 30 days of storage, the benzene solution still contained 95% of the starting material, whereas in THF only 65% of the complex remained. This observation confirms the role of oxygen, and of the photolysis products of the CT complex.

In the solvent PS IV which is relevant for technical applications, preconditioning of the medium by degassing is not required. Addition of oxygen is even found to enhance the photolysis rate, as oxygen is acting as a co-catalyst in the decomposition. For the same reason, saturation with argon causes a drastic lowering of the photodecomposition rate as the co-catalyst is lacking.

The behaviour in the spectroscopic solvent THF is different. Here an addition of oxygen lowers the photolysis rate, due to the formation of absorbing charge transfer complexes between THF and O_2 . In argon, the photolysis rate remains high as the decomposition products of THF may act as secondary stabilizers for the photolyzed platinum complex.

Wavelength and temperature dependence

In order to discuss the different efficiencies of the three laser wavelengths employed, it is necessary to analyze the UV-spectrum of the complex in more detail (cf. Fig. 1). The UV band around 240 nm is assigned to the $\pi \Rightarrow \pi^*$ transition of the aromatic ring system. Close inspection of the broad band between 280–360 nm, belonging to the triazenido system, shows that more than one electronic transition is involved.

The excitation of the more stable aromatic system with the 248 nm emission of the KrF* laser results in the lowest normalized k value. From semiempirical calculations of structurally similar 1-aryl-3,3-dialkyl-triazenes (Panitz *et al.*, 1993), it emerges that irradiation at 308 nm (XeCl* laser) leads to an excitation of the N=N—N system. Finally, with an excitation wavelength of 345 nm the N—N—Pt system can be excited. If the bond breakage between platinum and the coordinated nitrogen atom is the rate determining step in the photolysis of the complex, an irradiation with the dye laser is expected to lead to the highest normalized rate constant.

A similar mechanism has been suggested for the thermolysis of the Pt complex. From an analysis of DSC-measurements, a reaction sequence of type $A \Rightarrow B \Rightarrow C$ has been derived (Dauth *et al.*, 1993). The first step is thought to be the breaking of the Pt—N bond leading to an unstable triazenido intermediate, which has not been isolated. It appears possible that the photolysis follows the same sequence. However, on the timescale of our measurements the intermediate is not detected, such that a simple one-step mechanism is observed.

In conclusion, the study of the wavelength dependence reveals that selective irradiation near the long-wavelength absorption maximum of the complex is more effective as compared to either short wavelength (308, 248 nm) or broadband excitation.

The temperature-dependent studies revealed a non-monotonic behaviour. Below 0°C the photolysis rate constant was found to decrease with temperature as expected, due to the higher viscosity of the solvent resulting in higher recombination rates. However, the decrease of the rate constant at temperatures higher than 0°C is an unusual result. This observation is attributed to a thermal transformation of the complex into a photochemically more stable conformer.

In summary, the presented results show that a thermolytic component of the decomposition is not significant in the temperature range used for the photolysis experiments. However, there is a definite and unusual effect of temperature on the course of photochemistry above 0°C.

Product analysis

Analysis of irradiated solutions of the Pt complex provided information on the mechanism of the photochemical decomposition, as well as on the fate of

the triazenido ligands. Products such as the tertiary amine shown in Scheme 4, which were identified by GC/MS analysis, are compatible with a radical decomposition mechanism of the triazenido ligands.

The reaction between divinyl-disiloxane (A) and a dihydro-disiloxane (B) (3:1 by volume) was used to test the ability of the platinum complex (100 ppm of Pt) to act as a catalyst for hydrosilylation reactions (Speier, 1979; Marciniak and Gulinski, 1993). Besides the expected (AB)_n chains, the products from all well-known side reactions of the Pt catalyzed hydrosilylation reaction (e.g. isomerization, cyclization, hydrogenation of the terminal vinyl groups, and dehydrogenating silylation) were detected (Scheme 3). This result shows that the novel, photochemically activated Pt triazenido complex catalyzes hydrosilylation in the same way as conventional, thermally activated systems.

A minimum number of laser pulses, which is equivalent to an incubation period, is required to start the catalytic hydrosilylation reaction. From these observations we conclude that a minimum concentration of reduced Pt appears to be necessary to start the reaction. An alternative explanation is based on the exothermicity of the hydrosilylation reaction. Once a minimum turnover has been achieved in the laser-assisted reaction, the associated temperature rise will provide the required energy of activation for the catalytic dark reaction.

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