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Chloranil-Sensitized Photolysis of Benzyltrimethylsilanes. Solvent Effect on the Competition between Carbon−Hydrogen and Carbon−Silicon Bond Cleavage

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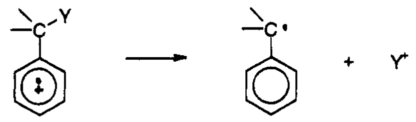
A steady state and laser flash photolysis study of the chloranil (CA)-sensitized oxidation of benzyltrimethylsilane (BTS) and (4-methoxybenzyl)trimethylsilane (MBTS) in different solvents (benzene, CH_2Cl_2, and MeCN) has been carried out. In benzene, BTS reacts with $^3\mathrm{CA}^*$ to give exclusively α-substituted benzyltrimethylsilane, whereas with MBTS the α-substituted silane is formed together with benzylic desilylation products. The latter situation also holds in CH_2Cl_2 for BTS. Only desilylation products are obtained from MBTS in CH_2Cl_2 and from both BTS and MBTS in MeCN. Higher quantum yields in the reactions with BTS than in those with MBTS have been observed in benzene and CH_2Cl_2. In MeCN, no significant change in quantum yield has been observed on going from BTS to MBTS. In MeCN with both BTS and MBTS and in CH_2Cl_2 with MBTS, the laser photolysis experiments have shown evidence for the formation of transients which can be attributed to $\mathrm{MBTS}^{\bullet+}$ and $\mathrm{CA}^{\bullet-}$ (MBTS in MeCN and CH_2Cl_2) and to $\mathrm{CA}^{\bullet-}$ (BTS in MeCN). This indicates that quenching of $^3\mathrm{CA}^*$ has taken place *via* an electron transfer process. Once formed, both $\mathrm{BTS}^{\bullet+}$ and $\mathrm{MBTS}^{\bullet+}$ undergo exclusive C−Si bond cleavage. In CH_2Cl_2, this reaction is promoted by $\mathrm{CA}^{\bullet-}$, and accordingly, $\mathrm{MBTS}^{\bullet+}$ decays by a second-order kinetics. In MeCN, $\mathrm{MBTS}^{\bullet+}$ decays by a first-order kinetics and desilylation is promoted by the solvent itself. The same holds for $\mathrm{BTS}^{\bullet+}$ as the decay reaction of this cation radical in MeCN appears much faster than that of $\mathrm{CA}^{\bullet-}$. In fact, only the transient assigned to the latter species has been observed in the laser photolysis experiments. A different situation has been found for both MBTS and BTS in benzene and BTS in CH_2Cl_2, where quenching of $^3\mathrm{CA}^*$ occurs *via* a partial charge transfer (CT) triplet complex. The reversible formation of this complex with MBTS in benzene is clearly indicated by the dependence of the observed rate constant for $^3\mathrm{CA}^*$ quenching on the substrate concentration, which has allowed the association constant for the complex (*ca.* 400 M^{-1}) to be determined. With BTS in benzene and CH_2Cl_2, the formation of the CT triplet complex is irreversible and rate determining, and the main evidence in this respect comes from the absence of a sizable deuterium kinetic isotope effect for the $^3\mathrm{CA}^*$ quenching rate. With BTS in benzene, the CT complex undergoes C−H bond cleavage as the exclusive chemical reaction. With MBTS in benzene and BTS in CH_2Cl_2, both C−H and C−Si bond cleavages take place, and it is suggested that the cleavage of the latter bond requires more transfer of charge in the complex than the cleavage of the C−H bond. Alternatively, in CH_2Cl_2, the CT complex might evolve in part to a solvent-separated radical ion pair, exclusively leading to the C−Si bond cleavage products. The above results have also allowed an assessment of the scope of the benzyltrimethylsilane probe to detect electron transfer mechanisms.

There is a continuous and increasing interest in the study of photoinduced electron transfer (PET) reactions for the very relevant theoretical and practical aspects associated with these processes.[1] These include the direct study of ion pair dynamics,[2] solar energy storage,[3] and the possibility of accomplishing synthetically useful transformations.[4,5] In addition, PET reactions have been shown to be a very useful tool for the generation and the study of radical ions, a class of reaction intermediates that in the last decade has acquired an importance comparable to that of the longer known carbocations, carbanions, and carbon radicals.

Scheme 1



One of the major problems in PET processes is the energy-wasting back-electron transfer reaction, where the radical ions return to ground state starting materials. However, this problem can, at least partially, be overcome if the radical ions undergo fast chemical reactions which can compete with back-electron transfer. For the case of aromatic radical cations side-chain fragmentation reactions, involving the cleavage of a β bond (Scheme 1), often fulfill this purpose. Y is hydrogen in most cases, but other groups (i.e., SiR_3, SnR_3, CR_3) can be involved.

In order to increase the chance of observing a chemical reaction in PET processes, the use of aromatic carbonyl compounds, as photosensitizers, has also received considerable attention.[6] When excited, aromatic carbonyl

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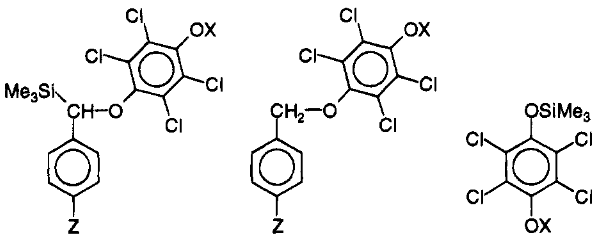
compounds undergo a very fast intersystem crossing to the triplet state, which is the species involved in the electron transfer step. This results in a slowing of the spin-forbidden back-electron transfer reaction.

Alkylaromatic compounds as the substrates and aromatic carbonyl compounds as the photosensitizers have therefore represented a very convenient system for the study of PET processes and of the properties of alkylaromatic radical cations. However, most reported studies have so far examined reactions of alkylaromatics involving the cleavage of the benzylic C−H bond,[6] whereas much less is known about the corresponding processes where the electrofugal group is different from the proton. This issue, however, is beginning to attract attention, especially with reference to the nucleofugal trialkylsilyl group. Thus, a very extensive mechanistic study has been carried out by Mariano and his group on the enone-sensitized photochemical reactions of tertiary α-silylamines.[7] In this study, an important effect of solvent polarity upon the competition between the deprotonation and desilylation in the α-trimethylsilyl amine cation radical $Et_2NCH_2SiMe_3{}^{\bullet+}$ has been observed. The role of the solvent has also been studied by Kochi and coworkers[8] in the photochemical reactions induced by chloranil of trimethylsilyl enol ethers, where there is competition between C−H and O−Si bond cleavage.

In this context, our attention has been directed at the study of solvent effects on the PET reactions of benzyltrimethylsilanes induced by chloranil (CA). It is well known that benzyltrimethylsilane cation radicals undergo fast C−Si bond cleavage, when generated in solvents (i.e., MeCN, AcOH, ROH), which can provide nucleophilic assistance to this cleavage.[9,10] Much less is known about the properties of these cation radicals in non-nucleophilic solvents, where the only nucleophile they can react with is the reduced form of the oxidant. Actually, the problem of medium effects on the reactivity of benzyltrimethylsilane cation radicals has been addressed in some studies where these species have been generated in photoinduced electron transfer processes. However, when different solvents have been used either all were sufficiently nucleophilic as to always promote C−Si bond cleavage in the cation radical[11] or the actual fate of the cation radical could not be established with certainty.[10,12]

Chart 1



1: Z = H, X = H
2: Z = H, X = SiMe$_3$
7: Z = OMe, X = H
8: Z = OMe, X = SiMe$_3$

3: Z = H, X = H
4: Z = H, X = SiMe$_3$
9: Z = OMe, X = H
10: Z = OMe, X = SiMe$_3$

5: X = H
6: X = SiMe$_3$

In this paper, we report on a study of the photolysis of benzyltrimethylsilane (BTS) and (4-methoxybenzyl)trimethylsilane (MBTS) sensitized by CA, in three solvents, benzene, CH_2Cl_2, and MeCN, which significantly differ in polarity as well as in nucleophilic character. Quenching of the CA triplet excited state with a variety of aromatic hydrocarbons is well known, occurring either by electron transfer or by formation of charge transfer complexes,[13−16] and similar behavior is expected to be displayed by benzyltrimethylsilanes. By a combination of steady state and laser photolysis experiments, it was hoped to obtain significant information on the role of the solvent in the formation and on the fate of benzyltrimethylsilane cation radicals.

It is important to note that this information also has a bearing with respect to the scope of the recent proposal that benzyltrimethylsilanes can be exploited as a mechanistic probe to differentiate ET from hydrogen atom transfer (HAT) mechanisms in chemical and enzymatic oxidations of alkylaromatic compounds[17−19] since different products are expected for the two mechanisms. Accordingly, when an ET step occurs, benzyltrimethylsilane cation radicals form and then undergo carbon−silicon bond cleavage to produce benzylic derivatives as reaction products. In contrast, a HAT mechanism is revealed from the formation of silicon retaining α-substituted products or benzaldehydes, if further oxidation is possible. Whereas this probe appears to work quite well in nucleophilic solvents, there is less certainty about the validity of the probe in solvents where, as mentioned before, no nucleophilic assistance to C−Si bond cleavage in the cation radical is possible.

Results

Steady State Experiments. Photolysis experiments were performed at 40 °C, by external irradiation (Pyrex filter) of an equimolar solution (0.08 M) of CA and benzyltrialkylsilane, in a Rayonet photoreactor, with a bank of 16 × 24 W black light phosphor lamps (λ_{max} = 360 nm, range of emission 340−380 nm). The reaction mixtures, after being deoxygenated, were irradiated for 3 h under magnetic stirring. After workup (see Experimental Section) products were identified by ^{1}H NMR and GC−MS comparison with authentic samples. Product yields were determined by ^{1}H NMR in the presence of an internal standard; in all cases the material balance was excellent (>95%).

Product quantum yields were determined by irradiating the reactants (0.01 M) at 366 nm, until the CA

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Table 1. Products Formed in the CA-Sensitized Photolysis of BTS and MBTS in Benzene, CH_2Cl_2, and MeCN together with Chemical (%) and Quantum (Φ)Yields

substrate	solvent	products[a] (%)	Φ_{C-H}[b]	Φ_{C-Si}[c]
BTS	benzene	**1** (76)	0.17	
	CH_2Cl_2	**1** (16), **2** (4), **3** (35), **4** (5), **5** (10), **6** (10)	0.13	0.22
	MeCN	**3** (84)		0.43
MBTS	benzene	**7** (5), **8** (3), **9** (6), **10** (3), **5** + **6**[d] (4)	0.04	0.03
	CH_2Cl_2	**9** (25), **10** (5), **5** + **6**[d] (25)		0.07
	MeCN	**9** (85)		0.42

[a] Yields (±5%) determined with respect to the initial moles of substrate; [substrate] = [CA] = 0.08 M, irradiation time 3 h. [b] Quantum yields (±10%) of the products arising from the cleavage of the C−H bond. [c] Quantum yields (±10%) of the products arising from the cleavage of the C−Si bond. [d] Yield determined by PMR as the sum of the two ethers.

absorbance had decreased by 10−20%. In these experiments, as well as in the preparative photolyses, light was almost completely absorbed by "free CA" and not by the benzyltrialkylsilane/CA CT complex. The products obtained in the photolyses of BTS and MBTS are summarized in Chart 1. Chemical and quantum yields are collected in Table 1.

The photolysis of BTS and CA in benzene leads exclusively to the (α-phenoxybenzyl)trimethylsilane **1**. A single product, the tetrachlorohydroquinone monobenzyl ether **3**, is also formed in the photolysis of BTS in MeCN, whereas a more complex mixture of products is obtained when the solvent is CH_2Cl_2. In this case, together with **1** and **3**, their trimethylsilyl ethers **2** and **4** are also formed. Other products are the mono- and bis(trimethylsilyl) ethers of tetrachlorohydroquinone, **5** and **6**, respectively.

The outcome of the photolysis of MBTS in benzene was a complex mixture of products including α-(phenoxy-*p*-methoxybenzyl)trimethylsilanes **7** and **8** and the *p*-methoxybenzyl ether of tetrachlorohydroquinone **9** and its trimethylsilyl ether **10**, together with **5** and **6**. In the photolysis of MBTS in CH_2Cl_2, the products observed are **5**, **6**, **9**, and **10**. In acetonitrile, **9** was the exclusive product of the photochemical process.

Control experiments showed, however, that under the photolysis conditions, partial conversion of the trimethylsilyl ethers **2**, **4**, **8**, and **10** into **1**, **3**, **7**, and **9**, respectively, takes place. For this reason, it was considered appropriate not to give the quantum yields for each compound, but rather for the pairs of compounds **1** + **2** and **7** + **8** (products of C−H bond cleavage from BTS and MBTS, respectively) and the pairs of compounds **3** + **4** and **9** + **10** (products of C−Si bond cleavage from BTS and MBTS, respectively).

Finally, it is worth noting that in benzene and in CH_2Cl_2 both chemical and quantum yields for the photolysis of MBTS are significantly lower than those obtained for the corresponding reactions of BTS. No difference in yields is, however, observed in MeCN.

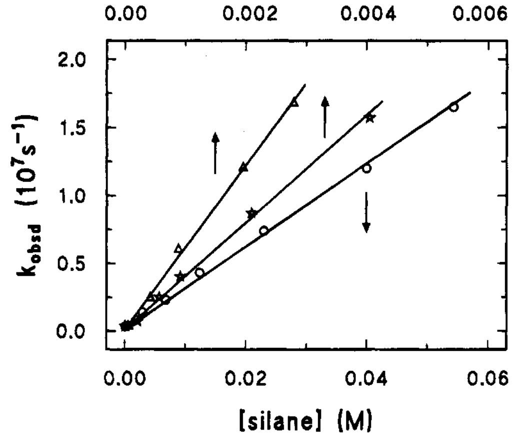


Figure 1. Dependence of the decay rate constant (k_{obsd}) of $^3CA^*$ on the concentration of BTS in benzene (○) and CH_2Cl_2 (☆) and of MBTS in CH_2Cl_2 (△) (λ_{exc} = 347 nm).

Table 2. Spectral and Kinetic Properties of the BTS and MBTS Transients Sensitized by Triplet CA[a]

compd	solvent	λ_{max} (nm)	τ[b] (μs)	$t_{1/2}$[c] (μs)	k_q[d] (10^9 M^{-1} s^{-1})
BTS[e]	benzene	320		5	
		365, 440	0.07[f]	10	
		490, 520	0.09		0.29
	CH_2Cl_2	320, 425 (sh), 440		20	
		360, 425 (sh), 435		8	
		520	0.05		4.0
	MeCN	320, 420 (sh), 435		20	4.3
		450		3.5	
		510	0.02		4.3
MBTS[g]	benzene	370, 440		45	
		450, 520	0.15		
	CH_2Cl_2	320, 425 (sh), 440		17	
		330, 450		~2[h]	
		330, 510		1.5	
		520	<0.05		6.1
	MeCN	320, 440		20	
		330, 450		2.0	
		500	0.48		
HMDS	CH_2Cl_2	325, 425 (sh), 435		18	

[a] [CA] = 4.0 × 10^{-4}, 4.0 × 10^{-3} and 3.6 × 10^{-3} M in benzene, CH_2Cl_2, and MeCN, respectively. [b] τ (= k_{obsd}^{-1}) is the time at which the initial signal was reduced to 1/*e*. [c] $t_{1/2}$ is the time at which the initial signal was halved. [d] Quenching rate constant of $^3CA^*$, measured at λ_{max}. [e] [BTS] = 3 × 10^{-2}, 5 × 10^{-3}, and 0.10 M in benzene, CH_2Cl_2, and MeCN, respectively. [f] Rise-time value. [g] [MBTS] = 1.5 × 10^{-3}, 10^{-2}, and 6.4 × 10^{-3} M in benzene, CH_2Cl_2, and MeCN, respectively. [h] With a large error, owing to overlap between the absorptions of different transients (see text).

Laser Photolysis Experiments. Quenching of Triplet CA by BTS and MBTS. The quenching rate constants (k_q) for the reaction of $^3CA^*$ with BTS and MBTS were determined by measuring the rate of decay at 510 nm, where the triplet absorbs, as a function of the concentration of silane. This was, however, not possible for MBTS in MeCN, due to the overlap between the absorption spectrum of $^3CA^*$ and $MBTS^{•+}$ and the similar lifetimes of the two transients (see below). In all cases, except for MBTS in benzene, the decay rate constant of triplet CA (k_{obsd}) increased linearly with silane concentration (Figure 1). The k_q values (reported in Table 2) were obtained from the slopes of the linear plots. With the exception of that for BTS in benzene, these constants are not far from the diffusion-controlled limits (k_{diff} = 1.0 × 10^{10} M^{-1} s^{-1} in benzene, 1.5 × 10^{10} M^{-1} s^{-1} in CH_2Cl_2, and 1.9 × 10^{10} M^{-1} s^{-1} in MeCN).[20] For benzyltrimethylsilane, deuterated in the ring and in the methylene group (BTS-d_7), the quenching rate constants of $^3CA^*$ in benzene and in CH_2Cl_2 were the same, within

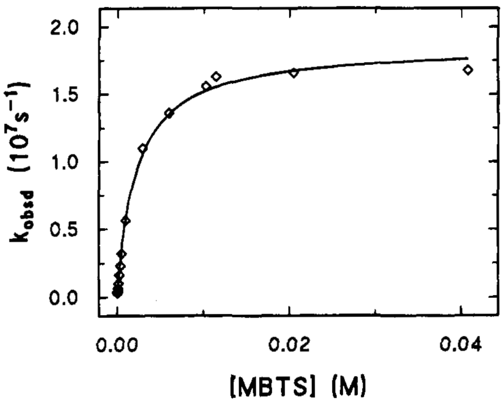
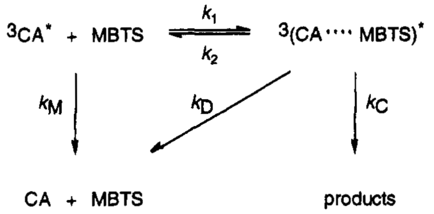


Figure 2. Dependence of the decay rate constant (k_{obsd}) of $^3CA^*$ on the concentration of MBTS in benzene (λ_{exc} = 347 nm).

Scheme 2



experimental error, as that with BTS, indicating a negligible kinetic deuterium isotope effect.

In the case of MBTS in benzene, however, the plot of k_{obsd} *vs* [MBTS] does not increase linearly with the concentration of the substrate but reaches a plateau (Figure 2), which suggests the existence of an intermediate in equilibrium with the reactants. The process can be written as follows (Scheme 2).

By assuming that the intermediate is formed in a fast equilibrium, one obtains eq 1

$$k_{obsd} = \frac{k_M}{1 + K[MBTS]} + \frac{(k_C + k_D)K[MBTS]}{1 + K[MBTS]} \quad (1)$$

where [MBTS] is the initial substrate concentration (with [MBTS] $\gg$ [$^3CA^*$] at any time), K is defined as the k_1/k_2 ratio, k_M is the rate constant for the decay of the unquenched $^3CA^*$, and k_C and k_D are the decay rate constants of the exciplex to the products and to the ground state reactants, respectively. The best fit of the experimental data to eq 1 was obtained with $K = (400 \pm 70)\ M^{-1}$, $k_M = (3 \pm 0.5) \times 10^5\ s^{-1}$, and $k_C + k_D = (2 \pm 0.4) \times 10^7\ s^{-1}$.

Transient Absorption Spectra. (a) Photolysis in Benzene. Photolysis, by laser excitation, of an Ar-saturated benzene solution of CA (4×10^{-4} M) in the presence of BTS (3×10^{-2} M) produced three transient species. Triplet CA was detected at the end of the laser pulse (λ_{max} = 490 and 520 nm and lifetime τ_T = 90 ns, see Table 2 and Figure 3a),[13,14] while at a longer delay time, three other absorption bands replaced that of the triplet (λ_{max} = 320, 365, and 440 nm).

The decay of $^3CA^*$ at 520 nm was synchronous with the buildup of the transient at 440 nm ($\tau_{rise} \approx$ 70 ns, Table 2 and Figure 4a). The rise times of the longer-lived transients at 320 and 365 nm were not determined, owing to the overlap, in this region, between the absorption of the triplet CA and those of the other transients. Anyway, since the decay kinetics recorded at 365 and 440 nm were similar (second order with $t_{1/2} \approx 10\ \mu s$, see Figure 4b) the absorptions were assigned to the same transient, which should be CAH$^•$ on the basis of literature data.[13,14] The absorption band centered at 320 nm (complex decay kinetics with $t_{1/2} \approx 5\ \mu s$) was difficult to assign because three transients, certainly $^3CA^*$ and probably CAH$^•$ and BTS(−H)$^•$, could contribute to the absorption in this region.

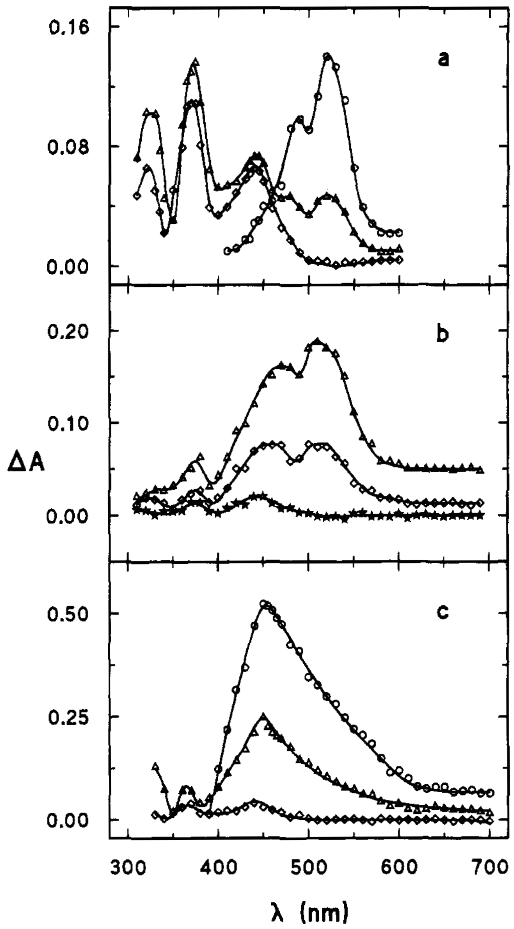


Figure 3. Time-resolved absorption spectra in benzene obtained by laser photolysis of 4.0×10^{-4} M CA in the presence of (a) 3×10^{-2} M BTS, recorded at the end of the pulse (○) and 0.12 (△) and 1.5 (◇) μs after the laser pulse, (b) 1.5×10^{-3} M MBTS, recorded 0.07 (△), 0.22 (◇), and 1.6 (☆) μs after the laser pulse, and (c) 0.02 M MBTS, recorded at the end of the pulse (○) and 0.10 (△) and 1.6 (◇) μs after the laser pulse (λ_{exc} = 347 nm).

For the CA/MBTS system, laser flash photolysis measurements in benzene were carried out at different MBTS concentrations, since the formation of a triplet excited complex was suggested by the substrate concentration dependence of the observed $^3CA^*$ decay rates (see above). Figure 3b shows the time-resolved absorption spectra recorded upon irradiation of 1.5×10^{-3} M MBTS in this solvent. Two absorption bands (λ_{max} = 450 and 510 nm, respectively) were formed within the laser pulse, as shown by the absorption spectrum recorded 70 ns after the laser pulse. However, these bands are no longer detected in the absorption spectrum recorded 1.6 μs after the laser pulse, where two new absorption bands (λ_{max} = 370 and 440 nm) appear.

The short-lived transient(s) showed the same first-order decay in the whole 400-600 nm range with lifetime

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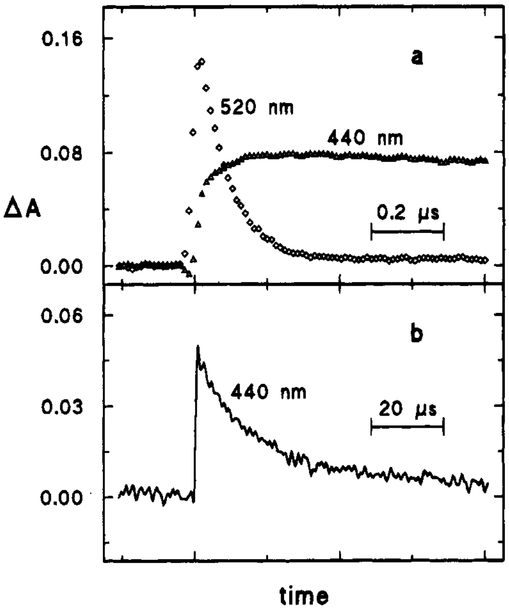

Figure 4. Changes in optical density with time following photolysis of 4.0 × 10^{-4} M CA and 0.03 M BTS in benzene solution recorded over (a) 1 μs and (b) 100 μs.

of *ca* 0.15 μs, whereas the longer-lived transient showed a second-order decay with half-life of 45 μs measured at λ = 370 and 440 nm. The latter transient is attributed to CAH$^\bullet$, and the former is assigned to the excited triplet complex. The efficiency of radical formation (shown by the small ΔA values at larger delay time) with CA/MBTS is much lower than that with CA/BTS, and this can explain the longer half-life of CAH$^\bullet$ in the former system.

The transition absorption spectra recorded upon irradiation of 2 × 10^{-2} M MBTS are shown in Figure 3c. Under these conditions the plateau shown in Figure 2 has been reached and therefore the equilibrium in Scheme 2 has been completely shifted toward the complex. Thus, the absorption spectra recorded at the end of the laser pulse and after 0.1 μs (shown in Figure 3c) correspond to the absorption of the triplet complex (a strong absorption at 450 nm, with a shoulder at 510 nm).

In this spectrum, there is no signal which can be attributed to MBTS$^{\bullet+}$, and therefore, also considering the reversibility of the process, we suggest that the triplet complex is a charge transfer complex, rather than a contact ion pair. The formation of a CT complex has also been suggested in the photooxidation of mesitylene, induced by CA.[14] In that case an equilibrium constant of 28 M^{-1} for the formation of the complex has been calculated, a value much lower than that measured by us for the ^{3}CA*/MBTS complex. Clearly, the interaction between ^{3}CA* and MBTS appears to be much stronger than that between ^{3}CA* and mesitylene, which is in line with the lower oxidation potential (1.35 V *vs* SCE[21] or even lower[22]) of MBTS with respect to that of mesitylene (2.11 V).[23] On the other hand, a significant interaction between ^{3}CA* and MBTS is also suggested by the fact that the exciplex presents an absorption spectrum strongly different from that of triplet chloranil.

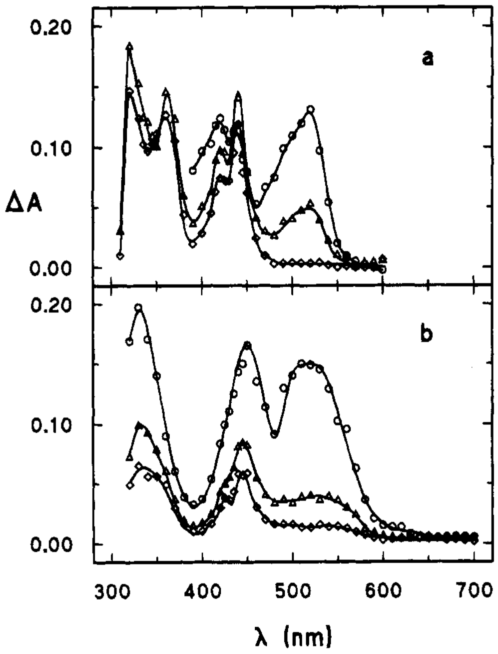

Figure 5. Time-resolved absorption spectra in CH_2Cl_2 obtained by laser photolysis of 4.0 × 10^{-3} M CA in the presence of (a) 5.0 × 10^{-3} M BTS, recorded at the end of the pulse (○) and 0.08 (△) and 1.5 (◇) μs after the laser pulse, and (b) 0.01 M MBTS, recorded at the end of the pulse (○) and 0.26 (△) and 4.0 (◇) μs after the laser pulse (λ_{exc} = 347 nm).

The small absorption with λ_{max} = 370 and 440 nm was assigned, as above, to the CAH$^\bullet$ radical, on the basis of its spectral and kinetic properties.[13,14] It is very likely that CAH$^\bullet$ derives from the CT complex, but, owing to the overlap between the absorption spectra of the detected transient species, a direct measure of the formation rate constant of CAH$^\bullet$ could not be performed. The presence of **9** and **10** among the products suggests that CASiMe$_3^\bullet$ should also be formed. However, as already mentioned, the efficiency of radical production of the CA/MBTS system (see quantum yields, Table 1) is significantly smaller than that of the CA/BTS system and the detection of the low intensity absorptions due to CASiMe$_3^\bullet$ (see below) may become impossible, especially in a quite complex spectrum.

(b) Photolysis in CH_2Cl_2. Upon irradiation of a 4 × 10^{-3} M CA solution containing 5 × 10^{-3} M BTS, the time-resolved absorption spectra reported in Figure 5a were obtained. As in benzene, the decay of triplet CA was very short (≤50 ns). At a delay time of 80 ns its absorption band was replaced by a structured spectrum (λ_{max} = 320, 360, and 440 nm). In the 350–460 nm range, the change of absorbance (ΔA) built up with a rise time corresponding to the lifetime of the triplet CA. The absorption bands showed two decay components; both of them followed a second-order kinetics with half-lives of 8 and 20 μs (Table 2). The transient with $t_{1/2}$ = 8 μs and λ_{max} = 360, 420(sh), and 440 nm was assigned to CAH$^\bullet$ on the basis of its absorption spectrum and also taking into account the photoproduct analysis.

Again, on the basis of photoproduct analysis, the transient with $t_{1/2}$ = 20 μs was thought to be CASiMe$_3^\bullet$. To test this hypothesis, laser photolysis experiments with the CA/hexamethyldisilane (HMDS) system in CH_2Cl_2 were carried out, which are expected to lead to the formation of CASiMe$_3^\bullet$ according to the reactions described in eqs 2–4.

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[21] Baciocchi, E.; Crescenzi, M.; Fasella, E.; Mattioli, M. *J. Org. Chem.* **1992**, *57*. 4684.

[22] A value of 1.38 V (vs SCE) for PhCH$_2$SiMe$_3$ has also been reported. On this basis, the $E°$ value for MBTS should be much lower than 1.35 V. Fukuzumi, S.; Fujita, M.; Otera, J.; Fujita, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10271.

[23] Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.* **1986**, *90*, 3747.

$$^{3}CA^{*} + Me_3SiSiMe_3 \rightarrow CA^{\bullet -} + Me_3SiSiMe_3^{\bullet +} \quad (2)$$

$$Me_3SiSiMe_3^{\bullet +} + CA^{\bullet -} \rightarrow SiMe_3^{\bullet} + CASiMe_3^{\bullet} \quad (3)$$

$$CASiMe_3^{\bullet} + SiMe_3^{\bullet} \rightarrow CA(SiMe_3)_2 \quad (4)$$

The absorption spectrum recorded 1.5 μs after the laser pulse (Figure 6) showed strong absorption bands at 440 and 325 nm with shoulders at 420 and 360 nm, respectively. The absorptions at 325 and 440 nm decayed by second-order kinetics with similar half-lives ($t_{1/2}$ = 18 μs) and were assigned to the same transient, $CASiMe_3^{\bullet}$,[24] which is therefore also the longer-lived transient observed in the CA/BTS system.

Upon irradiation of CA in the presence of 10^{-2} M MBTS, an absorption spectrum with maxima at 450 and 520 nm was recorded at the end of the laser pulse (Figure 5b). The decay of $^{3}CA^{*}$ followed at 520 nm was very fast (τ < 50 ns), and a strong signal, assigned to $CA^{\bullet -}$ (ΔA at λ_{max} 450 nm), was detected just after the laser pulse. Another transient, which absorbs in the 450–600 nm range and decays by a second-order kinetics ($t_{1/2}$ = 1.5 μs), is assigned to the cation radical $MBTS^{\bullet +}$.[10] The transient absorption spectrum recorded 4 μs after the laser pulse (Figure 5b) is reminiscent of that reported in Figure 6; the decay kinetics was also similar (second-order with $t_{1/2}$ = 17 μs). Therefore, the longer-lived transient obtained upon irradiation of the CA/MBTS system was assigned to the radical $CASiMe_3^{\bullet}$.

The decay kinetics at 450 nm were rather complex because, in addition to $CA^{\bullet -}$ and $^{3}CA^{*}$, two other transients ($MBTS^{\bullet +}$ and $CASiMe_3^{\bullet}$) absorb significantly at this wavelength. Likewise, at 320 nm, the decay was too complex to obtain unequivocal kinetic information for the short-lived transients.

(c) Photolysis in MeCN. Photolysis of 3.6 × 10^{-3} M CA in Ar-saturated MeCN in the presence of 0.1 M BTS produced the time-resolved absorption spectra reported in Figure 7a. Under these experimental conditions the $^{3}CA^{*}$ was too short-lived to be detected ($\tau \leq$ 20 ns). In fact, 0.1 μs after the laser pulse a broad band between 400 and 500 nm appeared together with an absorption with λ_{max} = 320 nm. The system produced two transients which decayed by second-order kinetics with $t_{1/2}$ = 3.5 and 20 μs, respectively. The short-lived transient, with $\lambda_{max} \approx$ 450 nm (not well resolved owing to the overlap between the absorptions of the two transients) was attributed to the anion radical $CA^{\bullet -}$. Probably, the cation radical $BTS^{\bullet +}$ is too short-lived to be observed because it decays by the efficient interaction with the solvent to give the desilylation products $MeCNSiMe_3^{+}$ and $PhCH_2^{\bullet}$[10] (see below). The longer-lived transient (λ_{max} = 325 and 440 nm) was assigned to the radical $CASiMe_3^{\bullet}$.

In the case of MBTS (6.4 × 10^{-3} M), a transient with λ_{max} = 500 nm and τ = 0.48 μs, recorded just after the laser pulse (Figure 7b), has been assigned to the cation radical $MBTS^{\bullet +}$. The absorption of the anion radical $CA^{\bullet -}$ has been detected at the same delay time. The decay of $MBTS^{\bullet +}$ takes place by a first-order process, with a rate constant of 2.1 × 10^{6} s^{-1}. The kinetic analysis of the decay of $CA^{\bullet -}$ was not possible, due to the overlap between the absorption of $CA^{\bullet -}$, $MBTS^{\bullet +}$, and a longer-lived transient. The latter turned out to be identical to that observed in the CA/BTS system (Figures 5a and 7a) and was therefore assigned to $CASiMe_3^{\bullet}$.

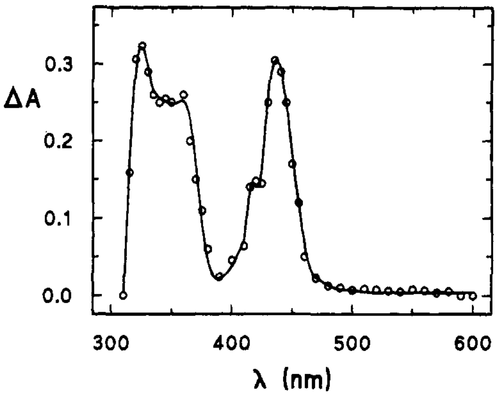

Figure 6. Transient absorption spectrum of the CA/HMDS system in CH_2Cl_2 (4.0 × 10^{-3} M CA and 4.0 × 10^{-2} M HMDS) recorded 1.5 μs after the laser pulse (λ_{exc} = 347 nm).

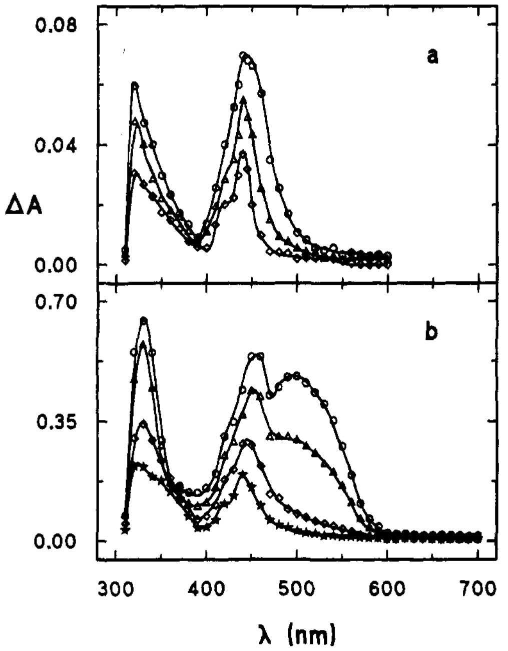

Figure 7. Time-resolved absorption spectra in MeCN obtained by laser photolysis of 3.6 × 10^{-3} M CA in the presence of (a) 0.10 M BTS, recorded at the end of the pulse (○) and 1.8 (△) and 8.0 (◇) μs after the laser pulse, and (b) 6.4 × 10^{-3} M MBTS, recorded at the end of the pulse (○) and 0.30 (△), 1.2 (◇), and 4.0 (☆) μs after the laser pulse (λ_{exc} = 347 nm).

Discussion

Photolysis in Benzene. There are a number of reports suggesting that electron transfer quenching of triplet CA by methylbenzenes and methylnaphthalenes ($ArCH_3$) in benzene leads to a polar exciplex, which has been assigned the character of a tight radical ion pair ($CA^{\bullet -}$, $ArCH_3^{\bullet +}$) retaining the triplet multiplicity (triplet excited CT complex).[13,15] In this complex, proton transfer between the two species is competitive with intersystem crossing to regenerate the reactants.

Indeed, with MBTS as the substrate, laser photolysis experiments (ns time scale) have provided clear evidence for the reversible formation of a transient intermediate which, however, as previously discussed, appears to have more the character of a partial charge transfer (CT)

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[24] Craw, M. T.; Albert, A.; Depew, M. C.; Wan, J. K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3675.

triplet complex than that of a contact radical ion pair. A CT complex is most probably formed also in the reaction with BTS since it has been found that the ^{3}CA* quenching rates of BTS and BTS-d_7 are the same, within the experimental error. However, in this case the complex is formed irreversibly since, as seen before, the quenching rate exhibits a linear dependence on BTS concentration. Probably, since BTS is a weaker donor than MBTS, a shorter-lived complex is formed, which undergoes chemical reactions and/or regenerates ground state reactants at a faster rate than it reverts back to ^{3}CA* and BTS.

The formation of charge transfer complexes as key intermediates in the photolysis of alkylaromatics sensitized by aromatic ketones has clearly been shown by Wagner and his associates,[25] and the same mechanism might also hold in the reactions under study. Even though with CA and silanes the energetics are strongly in favor of a complete electron transfer with the formation of ion pairs (with BTS and MBTS substantially negative $\Delta G°$ values < -8 kcal mol^{-1} for the electron transfer step can be calculated, taking 2.38 V *vs* NHE as the reduction potential of triplet chloranil),[13] this process could be highly unfavored in benzene which is a solvent of very low polarity.

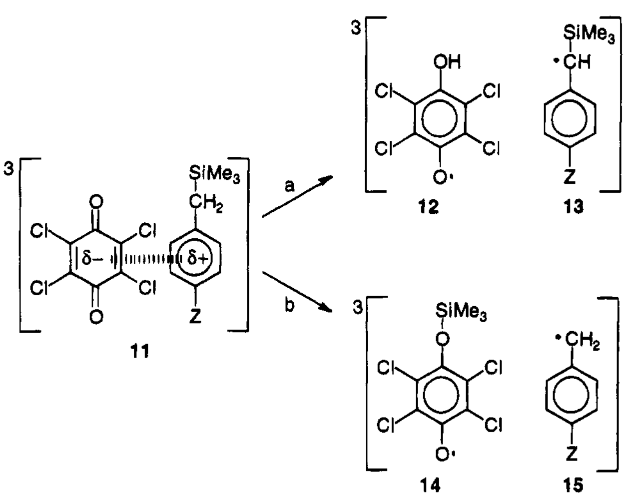
Wagner and his associates have also suggested that the partial transfer of charge in the CT complex is expected to weaken the C−H bond, so inducing its cleavage which then assumes the partial character of proton transfer. The same might also be envisaged for the C−Si bond even though there is no precedent, the transfer of the trimethylsilyl group assuming the partial character of silicenium cation transfer.

Exclusive formation of **1** in the photolysis of BTS indicates that in the CT complex only the cleavage of the C−H bond occurs, whereas with MBTS the products study indicates that both the C−H and C−Si bonds are cleaved. An interesting conclusion is that the relative rate of C−H and C−Si bond breaking appears to depend on the degree of charge transfer in the complex; more precisely, the importance of the C−Si bond cleavage increases with increased charge transfer character of the complex.

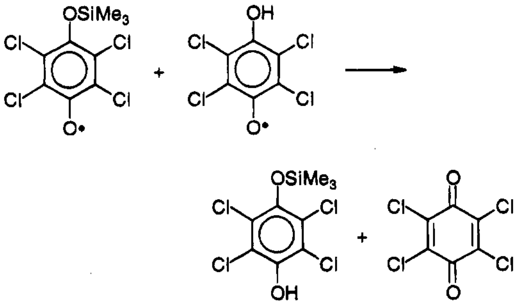
A possible explanation is that the C−Si bond appears to be much less liable than the C−H bond to be cleaved in homolytic reactions, as also shown by the observation that in the reaction of BTS with *t*-BuO$^\bullet$ radicals only products of hydrogen atom transfer are observed.[26] Thus, it is plausible that more charge has to be transferred in the exciplex to induce C−Si bond cleavage than to induce C−H bond cleavage.

As shown in Scheme 3 (path a) C−H bond cleavage in the ^{3}CA*/BTS CT complex (**11**) leads to the radical pair **12** and **13** (Z = H) in the triplet state, which, after spin inversion or, more probably (see below), diffusive separation, can recombine to give **1**, the observed reaction product. With the ^{3}CA*/MBTS complex, in addition to path a, C−Si bond cleavage is also possible (path b in Scheme 3), and two radical pairs in the triplet state, **12** and **13** (Z = OMe) and **14** and **15** (Z = OMe) are formed. The observation of **7**−**10** among the reaction products clearly indicates that the radicals have diffused from the cage. Accordingly, in addition to the reaction between **12** and **13** (Z = OMe) and **14** with **15** (Z = OMe) to form **7** and **10**, respectively, we also observe that **13** reacts with **14** to give **8** and **12** reacts with **15** to form **9**. It can be noted that no product deriving from combination reactions involving C−C bond formation (i.e., reaction of **13** with **15**) is observed.

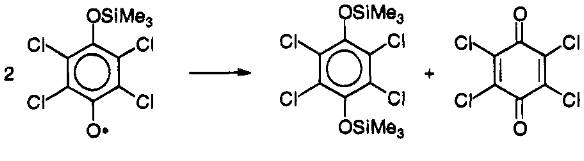
Scheme 3



It has also been found that the amounts of **7** and **9** in the final reaction mixture after 3 h irradiation are always significantly larger than those of the silylated **8** and **10**. Control experiments (see Experimental Section) have shown that this is due to partial photooxidation of **8** and **10** into **7** and **9**, respectively, under the reaction conditions. In these desilylation reactions, induced by ^{3}CA*, CASiMe$_3^\bullet$ (**14**) is formed, from which the other two reaction product **5** and **6** can be obtained as described in eqs 5 and 6.



(5)



(6)

As already noted, the quantum yields, as well as the extent of radical production in the laser experiments, is significantly lower in the photolysis of MBTS than with BTS. A possible explanation is that, with MBTS, the reactions forming products inside the charge transfer complex are slower than with BTS, since, as mentioned above, MBTS forms a more stable complex. Thus, the ground state regenerating path (k_D in Scheme 2) may become more competitive with the route leading to products in the photolysis of MBTS than in that of BTS.

Photolysis in CH$_2$Cl$_2$. The rate of quenching of ^{3}CA* by BTS in CH$_2$Cl$_2$ does not exhibit any significant deuterium isotope effect, and this indicates that, as for

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[25] Wagner, P.; Park, B. S. *Organic. Photochem.* **1991**, *11*, 227−366.

[26] Swenton, J. S.; Platz, M.; Venham, L. D. *J. Org. Chem.* **1988**, *53*, 2764.

the reaction in benzene, a CT complex is most probably formed as intermediate.

Since, differently than in benzene, products of both C−H and C−Si bond cleavage are observed, it can be suggested, on the basis of the above reasonings, that the degree of charge transfer in the ^{3}CA*/BTS complex is higher in CH_2Cl_2 than in benzene. This is plausible in view of the fact that CH_2Cl_2 ($\epsilon = 9.08$) is more polar than benzene ($\epsilon = 2.3$), and therefore, in the former solvent a more polar complex can be formed. Nevertheless, the rate of decay of the complex has to be very high, since no evidence for its formation has been obtained in the laser photolysis experiments.

Alternatively, it is also possible that, in CH_2Cl_2, the ^{3}CA*/BTS CT complex partially evolves to a solvent-separated radical ion pair (SSRIP). Thus, it might be that, whereas the CT complex undergoes exclusive C−H bond cleavage (as observed in benzene), only C−Si bond cleavage takes place in the SSRIP.

Whatever the detailed mechanism, two radical pairs **12** and **13** (Z = H) and **14** and **15** (Z = H) are formed. **12** and **14** have also been observed in the laser photolysis experiments. After diffusional separation, the same kind of radical combination reactions, discussed for the case of MBTS in benzene, occur with formation of **1-4**. The major reaction products are **1** and **3** (Table 1), which indicates that, also in this case, **2** and **4** undergo a desilylation reaction by triplet chloranil under the reaction conditions, being converted into **1** and **3**, respectively. In this process, **5** and **6** are also formed as already discussed.

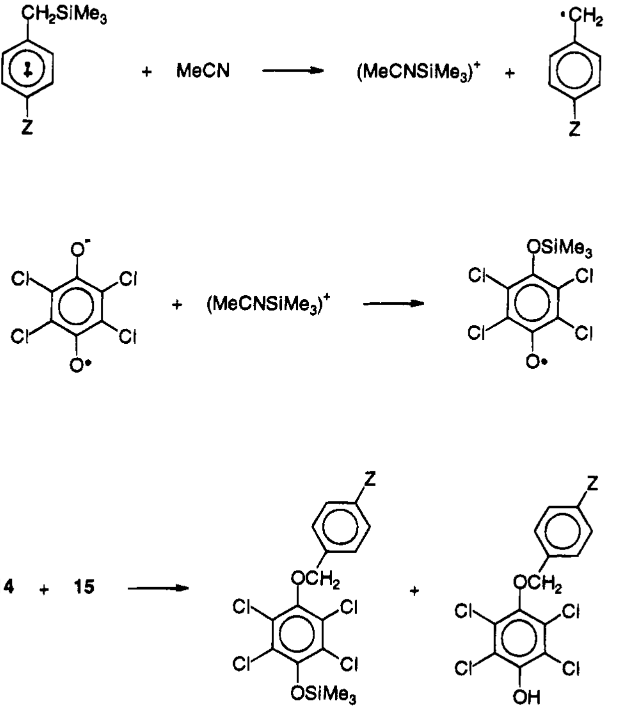
With MBTS, full electron transfer between ^{3}CA* and the substrate is possible. The formation of $\mathrm{MBTS}^{\bullet+}$ and $\mathrm{CA}^{\bullet-}$ is clearly shown by the laser experiments. $\mathrm{MBTS}^{\bullet+}$ decays by second-order kinetics, and most likely it reacts with $\mathrm{CA}^{\bullet-}$ in a desilylation process with formation of the transient $\mathrm{CASiMe_3}^{\bullet}$, which, accordingly, has also been observed. The second-order kinetics suggest that separated radical ions are probably formed.

The formation of the benzylic derivatives **9** and **10** in the steady state experiments and the lack of any evidence for products arising from C−H bond cleavage clearly indicates that the nucleophilic attack on silicon by $\mathrm{CA}^{\bullet-}$ is the exclusive reaction path of the cation radical, leading to **14** and **15** (Z = OMe). After cage escape and recombination, **10** is obtained, which is then partially converted into **9** under the reaction conditions. Concerning the other reaction products **5** and **6**, these can be formed from **14**, which is also an intermediate in the conversion of **10** into **9**, as described in eqs 5 and 6.

The lower quantum yield found in the photolysis of MBTS than in that of BTS probably has the same explanation suggested above for the corresponding phenomenon observed in benzene.

Photolysis in MeCN. With both BTS and MBTS, the chemistry observed in MeCN is in line with a dominant role played by solvated ions, and accordingly, exclusive carbon−silicon bond cleavage products are observed. With MBTS, both $\mathrm{MBTS}^{\bullet+}$ and $\mathrm{CA}^{\bullet-}$ have been detected in the laser experiments. With BTS, $\mathrm{BTS}^{\bullet+}$ has not been detected, but evidence for the formation of $\mathrm{CA}^{\bullet-}$ has been obtained. Interestingly, $\mathrm{MBTS}^{\bullet+}$ decays by a first-order process, with a rate constant of 2.1×10^6 s^{-1}, which is almost the same as that measured when this cation radical has been generated in MeCN by either excited DCA[10] or nitrate radical.[27] This clearly indicates that $\mathrm{MBTS}^{\bullet+}$ is desilylated in a reaction with the solvent and not with the counterion, as already suggested by Dinnocenzo *et al.*[10] This should also be the case with $\mathrm{BTS}^{\bullet+}$, since its lifetime appears much shorter than that of $\mathrm{CA}^{\bullet-}$. Accordingly, as already mentioned, the latter transient is observable in the laser photolysis experiments, whereas the former is not.

Scheme 4



Interestingly, the laser photolysis experiments have shown that $\mathrm{CASiMe_3}^{\bullet}$ (**15**) is, nevertheless, a reaction intermediate in the photolysis of both BTS and MBTS. Since **3** from BTS and **7** from MBTS are the only products observed in the two reactions, we suggest the reaction sequence shown in Scheme 4.

The solvent-induced desilylation leads to the benzyl radicals **15** (Z = H and Z = OMe) from $\mathrm{BTS}^{\bullet+}$ and $\mathrm{MBTS}^{\bullet+}$, respectively, and to the cation $\mathrm{MeCNSiMe_3}^{+}$, which then might react with $\mathrm{CA}^{\bullet-}$ to form **14**. Reaction of **14** with **15** (Z = H) and **15** (Z = OMe) produces **4** and **10**, respectively. Control experiments have accordingly shown that the latter are rapidly desylilated in the solvent itself (presumably by traces of water) giving **3** (from **4**) and **9** (from **10**) as the final reaction products.

It is interesting to note that, at variance with what observed with BTS, in the photolysis of $\mathrm{Et_2NCH_2SiMe_3}$ in MeCN, sensitized by cyclohexenone, desilylation was only a minor pathway, deprotonation accounting for more than 80% of the fate of the radical cation. Certainly, the basicity of the enone-derived anion radical (pK_a *ca.* 10 in H_2O)[28] is much higher than that of $\mathrm{CA}^{\bullet-}$ (pK_a *ca.* −1.9 in H_2O).[29] However, this factor should largely be overcome by the much greater acidity of benzyltrimethylsilane

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[27] Baciocchi, E.; Del Giacco, T. Unpublished results.

[28] Hasegawa, E.; Xu, W.; Mariano, S. P.; Yeon, U. C.; Kim, U. H. *J. Am. Chem. Soc.* **1988**, *110*, 8099.

[29] Calculated in H_2O by a thermochemical cycle, using the following values: BDE(OH) in $\mathrm{CAH}^{\bullet}$ = 64 kcal mol^{-1},[30] $E°$ ($\mathrm{H^+/H^{\bullet}}$) in H_2O = −2.29 V (vs NHE),[31] $E°$ ($\mathrm{CA/CA^{\bullet-}}$) = 0.25 V (*vs* NHE).[13]

[30] Friedrich, L. E. *J. Org. Chem.* **1983**, *48*, 3851.

[31] Wayner, D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287.

cation radical (pK_a *ca.* −16)[32] than that of $Et_2NCH_2SiMe_3^{\bullet+}$ (pK_a *ca.* 8).[28] Moreover, it is likely that proton basicity parallels silicon nucleophilicity (in fact, the Si−O bond is stronger than the O−H bond), so that the competition between desilylation and deprotonation may not be very sensitive to the base strength of the nucleophile. In this respect, it should also be considered that the deprotonation of alkylaromatic cation radicals exhibits a low sensitivity to the basicity of the proton-abstracting species.[33]

A more plausible explanation is that in benzyltrimethylsilane cation radical deprotonation is intrinsically disfavored with respect to desilylation by stereoelectronic effects.[34] Accordingly, in the preferred conformations of these species, it is the carbon−silicon bond, not the carbon−hydrogen bond, which assumes the geometric arrangement most suitable for cleavage (bond collinear with the π-system). An additional possibility is that the formation of contact ion pairs or excited CT complexes is much more important in the reaction of triplet cyclohexenone with $Et_2NCH_2SiMe_3$ than in the reaction of $^3CA^*$ with BTS or MBTS, due to the higher basicity of the cyclohexenone anion radical. Thus, in the reaction of $Et_2NCH_2SiMe_3$, the formation of these species, which lead to C−H bond cleavage products for steric reasons, is dominating also in MeCN,[7,28] whereas in the CA/BTS system solvated radical ions are formed.

Summary and Conclusions

The present results clearly indicate a very important role of the solvent and the substrate structure in the CA-induced photolysis of benzyltrimethylsilanes, particularly with respect to the mechanism of quenching of triplet chloranil as well as to the reaction regiochemistry (competition between the cleavage of the benzylic C−H bond and the C−Si bond). In benzene, the quenching of $^3CA^*$ by both BTS and MBTS occurs *via* the formation of a charge transfer complex, which is formed irreversibly with BTS and reversibly with MBTS. In the reaction with MBTS, direct evidence for the formation of the exciplex has been obtained and an association constant of 400 M^{-1} has been measured. In the reaction with BTS (a worse donor than MBTS), the exciplex is much less stable and its formation is suggested by the fact that BTS and BTS-d_7 quench $^3CA^*$ at a very similar rate (no kinetic deuterium isotope effect). In the $^3CA^*$/BTS complex hydrogen transfer to $^3CA^*$ occurs as the exclusive chemical reaction. Both C−H and C−Si bond cleavage are observed with MBTS, and it is suggested that the different behavior is due to the fact that the $^3CA^*$/MBTS complex has a higher CT character than the $^3CA^*$/BTS complex.

A complex with relatively high CT character is probably the reaction intermediate in the photolysis of BTS in CH_2Cl_2 (a solvent more polar than benzene), which, accordingly, leads to products of C−H and C−Si bond cleavage. Alternatively, in this solvent it is also possible that the $^3CA^*$/BTS CT complex partially evolves to a solvent separated radical ion pair (SSRIP). From the CT complex only products of C−H bond cleavage are formed, as observed in benzene, whereas the C−Si bond cleavage products derive from the SSRIP.

With MBTS in CH_2Cl_2 and with both BTS and MBTS in MeCN a different quenching mechanism has been observed, as a full electron transfer between $^3CA^*$ and the substrate takes place leading to separate ions. Under these conditions, only C−Si bond cleavage is observed with the formation of benzylic products. In CH_2Cl_2, the cleavage is assisted by $CA^{\bullet-}$, in MeCN by the solvent itself.[35]

With respect to the use of benzyltrimethylsilanes as a mechanistic probe to detect ET processes, the results in the present work suggest that some caution has to be used in applying the probe to reactions occurring in nonpolar solvents. Under these conditions, the observation of a product resulting from C−Si bond cleavage is not a clean-cut probe that a cation radical is formed, since such a cleavage can also be associated with the formation of a CT complex. Certainly, however, a purely homolytic mechanism of cleavage can be excluded. On the other hand, the exclusive formation of products resulting from C−H bond cleavage appears to be a strong indication that an ET mechanism is not operating.

Finally, MBTS is a better mechanistic probe than BTS. Accordingly, with the former substrate, formation of the corresponding cation radical and exclusive C−Si bond cleavage are observed even in a solvent of polarity as low as CH_2Cl_2.

Experimental Section

General Aspects. ^1H NMR spectra were generally recorded on a 80 MHz spectrometer in $CDCl_3$. In some cases (especially, for products analysis), a 300 MHz spectrometer was also used. GC−MS analyses were performed on an instrument equipped with a 12 m × 0.2 mm silica capillary column coated with methylsilicone gum. GLC analyses were performed using a 25 m × 0.2 mm silica capillary column coated with methylsilicone gum.

Materials. High purity commercial solvents (Carlo Erba) were used as obtained or dried with the following procedures: MeCN by refluxing over CaH_2, CH_2Cl_2 by refluxing over P_2O_5, and benzene was distilled and then placed over sodium wires. Deuterated solvents were purchased from Janssen and kept over anhydrous sodium sulfate.

Chloranil was a commercial (Aldrich) product and was purified by sublimation under reduced pressure before use. Benzyltrimethylsilane (Aldrich) was distilled under reduced pressure before use. (4-Methoxybenzyl)trimethylsilane was prepared by reaction of (4-methoxybenzyl)magnesium chloride with trimethylsilyl chloride in anhydrous tetrahydrofuran (THF) and was purified by chromatography on a silica gel column (eluent petroleum ether 40−70 °C).[36] For the preparation of (heptadeuteriobenzyl)trimethylsilane-*2,3,4,5,6,α,α′-d₇* (BTS-d_7), benzyl chloride-d_7 (Janssen) was used to prepare the Grignard reagent.

The reaction products were obtained as described in the following.

Tetrachlorohydroquinone monobenzyl ether (3) and **tetrachlorohydroquinone *p*-methoxybenzyl ether (9)** were prepared by reaction of tetrachlorohydroquinone (Sigma) with the corresponding benzylic halide in THF and potassium carbonate. Purification was carried out by chromatography on silica gel (hexane−diethyl ether). **5**: mp 136−137 °C; ^1H

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[32] Calculated by a thermochemical cycle, using the following values: BDE (CH) in BTS = 75 kcal mol^{-1},[10] $E°$ ($BTS^{\bullet+}$/BTS) = 2.06 V *vs* NHE,[21] $E°$ ($H^+/H^\bullet$) in MeCN = −1.77 V (*vs* NHE).[31]

[33] Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290 and references therein.

[34] Baciocchi, E.; Mattioli, M.; Romano, R.; Ruzziconi, R. *J. Org. Chem.* **1991**, *56*, 7154 and references therein.

[35] After this work was under way, we learned that Albini and his associates were studying the photolysis of BTS and MBTS induced by aromatic ketones in MeCN and in MeCN/MeOH mixtures. Their excited acceptors have a lower reduction potential than $^3CA^*$, and in most cases, they observe exciplex formation, followed by deprotonation. Desilylation predominates when solvent-separated radical ion pairs are formed (trifluoroacetophenone/MBTS).

[36] Coughlin, D. J. ; Salomon, R. G. *J. Org. Chem.* **1979**, *44*, 3784.

NMR δ 4.98 (s, 2H), 5.9 (bs, 1H, OH), 7.5–6.8 (m, 5H, arom); MS *m/z* 338 (M$^+$, 0.9), 247 (1), 92 (8), 91 (100), 65 (13). Anal. Calcd for $C_{13}H_8Cl_4$: C, 46.16; H 2.38. Found: C, 45.95; H 2.45. **9**: mp 138–139 °C; ^{1}H NMR δ 3.81 (s, 3H, OCH_3), 4.92 (s, 2H), 5.82 (bs, 1H, OH), 7.6–6.8 (5H, arom). Anal. Calcd for $C_{14}H_{10}O_3Cl_4$: C, 45.69; H, 2.64. Found: C, 45.39; H, 2.55. **Tetrachlorohydroquinone benzyl trimethylsilyl ethers** (**4**) and (**10**) were prepared by reaction of **3** and **9** with the silylating agent *N,O*-bis(trimethylsilyl)trifluoroacetamide (Carlo Erba) in THF.[37] **4**: ^{1}H NMR δ 0.34 (s, 9H), 4.99 (s, 2H), 7.5–6.8 (m, 5H, arom); MS *m/z* 410 (M$^+$, 0.4), 395 (0.5), 267 (0.4), 113 (1.4), 92 (8), 91 (100), 73 (17), 65 (9). **10**: ^{1}H NMR δ 0.34 (s, 9H), 3.81 (s, 3H, OCH_3), 4.94 (s, 2H), 7.3–6.5 (bm, 4H, arom); MS *m/z* 425 (M$^+$ − 15, 0.2), 305 (0.2), 267 (0.4), 121 (100), 73 (11). **[α-(2,3,5,6,-Tetrachlorophenoxy)benzyl]trimethylsilane** (**1**) and **(4-methoxybenzyl)trimethylsilane** (**7**) were prepared by reaction of the corresponding (α-bromobenzyl)trimethylsilane[26] with tetrachlorohydroquinone in THF and potassium carbonate and were purified by TLC chromatography (silica gel, eluent hexane–diethyl ether) and crystallization. **1**: mp 96–97 °C; ^{1}H NMR δ 0.13 (s, 9H), 5.54 (s, 1 H), 5.7 (sb, 1H, OH), 7.2 (s, 5 H, arom). Anal. Calcd for $C_{16}H_{16}O_2SiCl_4$: C, 46.85; H, 3.93. Found: C, 46.60; H, 3.85. Compound **7** undergoes partial decomposition in the chromatographic column; thus, further purification from the reaction mixture was not possible and only an NMR analysis is available. ^{1}H NMR δ 0.138 (s, 9H), 3.73 (s, 3H, OCH_3), 5.45 (s, 1H), 5.92 (bs, 1H, OH), 7.2–6.5 (mb, 4H, arom). The trimethylsilyl ethers of **1** and **7** (**2** and **8**, respectively) were prepared by reaction of **1** and **7** with the silylating agent *N,O*-bis(trimethylsilyl)trifluoroacetamide in THF. **2**: ^{1}H NMR δ 0.13 (s, 9H), 0.25 (s, 9H), 5.55 (s, 1H), 7.2 (sb, 5H, arom). **8**: ^{1}H NMR δ 0.134 (s, 9H), 0.26 (s, 9H), 3.81 (s, 3H, OCH_3), 5.45 (s, 1H), 7.3–6.5 (bm, 4H, arom). **Tetrachlorohydroquinone bis(trimethylsilyl) ether** (**6**) was prepared by reaction of tetrachlorohydroquinone with a molar excess of *N,O*-bis(trimethylsilyl)trifluoroacetamide in THF and was purified by two crystallizations: mp 66–67 °C; MS *m/z* 392 (M$^+$, 26.6), 377 (28.6), 269 (22.8), 267 (22.0), 93 (36.8), 73 (100.0); ^{1}H NMR δ 0.31 s. Anal. Calcd for $C_{12}H_{18}Si_2O_2Cl_4$: C, 36.74; H 4.62. Found: C, 36.50; H, 4.55. **Tetrachlorohydroquinone mono(trimethylsilyl) ether** (**5**) was prepared by reaction of tetrachlorohydroquinone with the same molar amount of *N,O*-bis(trimethylsilyl)trifluoroacetamide in THF. Unfortunately, this compound was always contaminated by traces of tetrachlorohydroquinone and **6**, and attempts to purify it by crystallization or by chromatography were unsuccessful; thus, for **5** only the mass spectral and PMR analysis are available: ^{1}H NMR δ 0.31 s; MS *m/z* 320 (M$^+$, 27.2), 307 (37.4), 305 (72.6), 303 (54.9), 270 (40.6), 268 (43.2), 93 (59.7), 73 (100.0).

Products Analysis. Product yields were determined by PMR in the presence of diphenylmethane as the internal standard. When the δ values of the reaction products were very similar, PMR spectra were recorded at 300 MHz. In the case of the quantitative determination of the tetrachlorohydroquinone mono- and bis(trimethylsilyl) ethers **5** and **6**, since we could not obtain a good separation of the PMR signals of the two compounds, the analysis was carried out by GLC chromatography in the presence of an internal standard.

Stability of the Reaction Products. A suspension of BTS and CA in CH_2Cl_2 was irradiated in the Rayonet photoreactor and analyzed by GC at intervals of time. The **3**/**4** molar ratio was determined after 5, 30, 70, 130, and 180 min of irradiation and turned out to be 0.8, 2.2, 3.2, 3.6, and 5, respectively. This clearly indicates that **4** is converted into **3**. During that process **5** and **6** are also formed. The same result was obtained in the photolysis of **4** in the presence of CA. Thus, when an equimolar mixture of **4** and CA (0.05 M) in CH_2Cl_2 was irradiated in the Rayonet photoreactor for 3 h and then analyzed by GC at intervals of 15 min, the almost complete conversion of **4** into **3**, **5**, and **6** was observed. Similar control experiments showed that **2**, **8**, and **10** are converted into **1**, **7**, and **9**, respectively.

It was also found that, when **4** was kept in CD_3CN for 1 h at 25 °C in the dark, it was completely transformed into **3**. Under the same conditions, **10** was converted into **9**.

Laser Flash Photolysis. Excitation wavelength of 347 nm from a ruby laser (J. K., second harmonic) was used in ns flash photolysis experiments (pulse width *ca.* 20 ns and energy < 10 mJ per pulse).[38] The transient spectra were obtained by a point-to-point technique, monitoring the absorbance change (ΔA) values after the flash at intervals of 5–10 nm over the spectral range 300–700 nm and obtained by averaging at least 4 decays at each wavelength. $\tau = 1/k_{obsd}$ (the time at which the initial signal is reduced to $1/e$) and $t_{1/2}$ (the time at which the initial signal is halved) are reported for the transients showing first-order and second-order kinetics, respectively. The experimental errors were estimated to be (i) ±10% for τ and $t_{1/2}$ and (ii) ± 15% for k_q. The solutions containing silane and CA, after saturation by bubbling with argon, were flowed through a quartz photolysis cell. All measurements were carried out at 22 ± 2 °C.

Photochemical Experiments. Photolyses were performed at 40 °C, by external irradiation in a Rayonet photoreactor, with a bank of 16 × 24 W black light phosphor lamps (center of emission 360 nm, range of emission 340–380 nm), of a mixture of chloranil (0.08 M) and the benzyltrialkylsilane (0.08 M) in the reaction solvent (1–3 mL) contained in a Pyrex vessel. Reaction mixtures were capped with a rubber septum and deoxygenated by bubbling with argon before the irradiation. After irradiation for 3 h, under magnetic stirring, the solvent was evaporated and the raw photolysate was analyzed by GC–MS and PMR. When photolyses were carried out on a larger scale (50 mL), isolation of the reaction products from the raw photolysate was carried out by preparative TLC (silica gel, eluent hexane–diethyl ether). UV spectra of the isolated products showed that there is no product absorption at wavelengths higher than 330 nm. Product identification was carried out by comparison of the spectral properties (UV, NMR, GC–MS, GLC) with authentic samples prepared as described below.

Quantum Yields. Typically a 1 mL solution of the reactants (0.01 M each) was placed in a quartz cuvette with a magnetic stir bar, capped with a rubber septum, and purged with argon before irradiation with a high-pressure Hg lamp (366 nm filter), while being magnetically stirred. Chemical reaction was evaluated by following the decrease of the chloranil absorbance at 366 nm until it was decreased by 10–20%. Then the internal standard was added and products yields were determined by PMR. Light intensity was evaluated by ferrioxalate actinometry. The reported quantum yields are an average of duplicate independent measurements and were reproducible within 10%.

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