

Thermal and Photochemical Reactions of Aromatic Compounds in Trifluoroacetic Acid, Involving Carbocations and Radical Cations

Lennart Ebersson*[‡] and Finn Radner

MAX Chemistry, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

Ebersson, L. and Radner, F., 1992. Thermal and Photochemical Reactions of Aromatic Compounds in Trifluoroacetic Acid, Involving Carbocations and Radical Cations. – Acta Chem. Scand. 46: 630–643.

Upon dissolution of 2,2',3,3',4,4',5,5',6,6'-decamethyldiphenylmethane (**1**) in trifluoroacetic acid (TFA), a deep-seated transformation takes place with eventual formation of 1,2,3,4,5,6,7,8-octamethylanthracene (OMA) and its radical cation. The formation of OMA is initiated by the establishment of an equilibrium involving proton-induced cleavage of **1** to give pentamethylbenzyl cation and pentamethylbenzene. Species **1-H**⁺ undergoes intramolecular methyl transfer to pentamethylbenzene, to give a nonamethyldiphenylmethane with one free *ortho* position (NMDM) and hexamethylbenzene. Pentamethylbenzyl cation then acts as a hydride-transfer oxidant toward NMDM (at the 2-methyl position), yielding 9,10-dihydro-OMA, from which OMA is obtained by a second hydride-transfer step and proton loss.

The oxidation of OMA to OMA^{•+} in TFA is light-dependent, most likely by excitation of OMA to ¹OMA* followed by electron transfer to the TFA dimer. If electron transfer is synchronous with or very rapidly followed by proton transfer within the dimer, the back electron transfer step is blocked. As an experimentally convenient model, the electron transfer reaction between 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene and TFA was studied in detail, showing that this process is strongly dependent on light. Under dark conditions, one can also detect a thermal component of the electron transfer reaction, but it is very slow ($k = 10^{-6}$ – $10^{-7} \text{ M}^{-1} \text{ s}^{-1}$) and not definitively established.

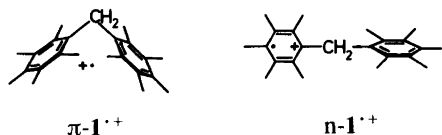
Dedicated to Professor Lars Skattebøl on the occasion of his 65th birthday.

It has recently been proposed¹ that 2,2',3,3',4,4',5,5',6,6'-decamethyldiphenylmethane (**1**) would be converted into a π -stabilized radical cation (π -**1**^{•+}) upon dissolution in trifluoroacetic acid (TFA) or oxidation by nitrosonium ion in dichloromethane. Evidence for the structure of π -**1**^{•+} was based on EPR and time-resolved UV–VIS spectroscopy and an estimate of the stabilization energy of π -**1**^{•+} with respect to the 'normal' radical cation of **1** (*n*-**1**^{•+}) was made from cyclic voltammetric data. From the fact that **1** had an E_{pa} of 1.55 V and the reverse reduction of π -**1**^{•+} seemed to take place at $E_{\text{pc}} = 0.95 \text{ V}$, this stabilization energy was estimated to be $\approx 10 \text{ kcal mol}^{-1}$.

However, previous experience from anodic and metal ion oxidation of polymethylaromatic compounds in our

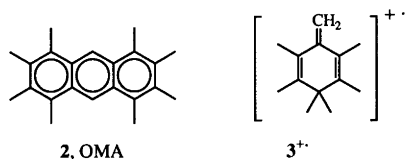
laboratory² indicated that such compounds easily undergo intermolecular alkyl transfers and/or cyclizations to anthracene derivatives under oxidative/acidic conditions. Thus oxidation of durene by Co(III) or Mn(III) in TFA afforded significant amounts of 2,2',4,4',5,5'-hexamethyldiphenylmethane and 1,2,4,5,6,8-hexamethylanthracene in addition to the expected product from an ECE-type mechanism, 2,2',3,4',5,5',6-heptamethyldiphenylmethane.^{2b} It was thus reasonable to assume that the radical cation observed in the **1**/TFA system might have been formed via a more deep-seated transformation, leading to a particularly stable radical cation.

In a preliminary communication³ we showed that the radical cation observable by EPR spectroscopy in the **1**/TFA system is derived from 1,2,3,4,5,6,7,8-octamethylanthracene (**2**, OMA), which also was identified as a product formed in 3% yield. The origin of the EPR spectrum was independently verified by isolation and X-ray crystallographic analysis of the hexachloroantimonate of OMA^{•+}, synthesized by SbCl₅ oxidation of **1** in dichloromethane.⁴ Perusal of the 'golden age' EPR literature revealed that the same characteristic EPR spectrum had been obtained^{5,6} from treatment of hexa- or penta-methylbenzene with sulfuric acid and at that time assigned to the radical cation of 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene (**3**^{•+}).

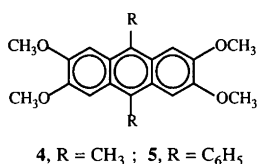


* To whom correspondence should be addressed.

‡ In part presented at the National Meeting of Organic Chemistry, June 10–12, 1991 in Ystad, Sweden and the 16th Organic Electrochemistry Meeting, June 14–17, 1991 at Sandbjerg Castle, Denmark.



While the skeletal transformation of **1** → **2** is of some interest, we show below that well-known carbocation chemistry⁷ is probably responsible for it. Of considerable current interest is the fact that OMA, with an $E^\circ(\text{OMA}^{\cdot+}/\text{OMA}) = 1.04$ vs. NHE (normal hydrogen electrode) in dichloromethane, is oxidized to its radical cation by dissolution and standing for a few hours in neat TFA. The oxidizing properties of TFA are well documented⁸ but less well understood, having been explained either as an inherent electron transfer (ET) reactivity of TFA or by TFA catalysis of dioxygen ET reactivity. Since the reactivity and UV-VIS spectral properties of OMA and OMA^{·+} are not well suited to convenient studies of the formation of OMA^{·+}, our attention was directed to the easily oxidizable anthracene derivatives **4** and **5**.⁹ With **4** [$E^\circ(\text{ArH}^{\cdot+}/\text{ArH}) = 0.99$ V vs. NHE in acetonitrile⁹] as the substrate, we have reported¹⁰ that the formation of **4**^{·+} is light-dependent. This fact has already been utilized for



some time by the EPR research community¹¹ for obtaining radical cation solutions in TFA and other acids, although the connection between the forcing conditions of high-effect UV lamps inflicted upon small EPR samples and the effect of diffuse daylight on similar solutions on a larger scale was not made.

This paper is a detailed account of these and other observations on the thermal and photochemical reactions of aromatic compounds in TFA. We believe that the long-standing enigma of the redox reactivity of TFA has now been solved.

Results

Nature of the problem. Before reporting our results, we emphasize that the transformation of **1** into OMA^{·+} has two facets which are largely independent of each other. The first is the conversion of **1** into OMA which, although seemingly drastic, can be easily explained in terms of conventional carbonium ion chemistry. The second is the one-electron oxidation of OMA to OMA^{·+} which seems to take place with great ease and produces the characteristic EPR spectrum of OMA^{·+}. Because of the high sensitivity of the EPR method, this species is easily detected and monitored in low concentrations (down to ≈ 0.01 mM), giving the

impression that OMA^{·+} is a major product from **1**. We stress that this is not so: even if OMA can be formed in yields of 10–20%, its (light-dependent) conversion into the radical cation is normally only of the order of 1–10%.

Formation of OMA^{·+} from 1. When **1** was dissolved in TFA (≈ 2 mM) a strong EPR signal was detectable after 4 h [Fig. 1(a)]. This spectrum has a 1:2:1 splitting with coupling constant 0.545 mT, assigned to the 9,10 hydrogens of OMA. The second largest splitting, 0.334 mT, is ascribed to coupling with the 12 hydrogens of the 1,4,5,8-methyl groups and the third one, 0.167 mT, to the hydrogens of the remaining four methyl groups. This assignment is based on the known coupling constants of the ring hydrogens of several anthracene radical cations,¹² where $a^{\text{H}1,4,5,8} > a^{\text{H}2,3,6,7}$. The peak-to-peak line-width was, on average, 0.012 mT and the g value 2.00278 (in dichloromethane; in TFA $g = 2.0023$). The spectrum was, in all respects, identical with that of a solution of authentic OMA, synthesized¹³ from 1,2,3,4-tetramethylbenzene and formaldehyde, followed by chloranil dehydrogenation of 9,10-dihydro-OMA.

The spectrum of Fig. 1 could be adequately simulated by the number of hydrogen atoms and parameters given above, provided the line-width was taken to be ≤ 0.02 mT. It must however be noted that the number of hydrogens connected with the 0.167 mT coupling cannot easily be ascertained from the spectrum. As mentioned above, the EPR spectrum of OMA^{·+} has been reported earlier^{5,6} from the reaction between hexamethylbenzene and sulfuric acid but then ascribed to structure **3**^{·+}, with six hydrogens in the group of $a^{\text{H}} = 0.167$ mT. Since the ratio of the intensity of the center peak to that of the outermost signal would be 1.3×10^6 for a 2:12:12 hydrogen atom pattern, this problem is not easily settled from EPR spectral data. However, by accumulating ca. 300 000 spectra [from the sample of Fig. 1(a); see the left part of spectrum (a)] it was at least possible to show that the 0.167 mT group has more than six hydrogens. The final assignment of the spectrum to OMA^{·+} must rest on the fact that OMA could be detected or isolated in significant yields from mixtures where the EPR spectrum of OMA^{·+} could be obtained (see below).

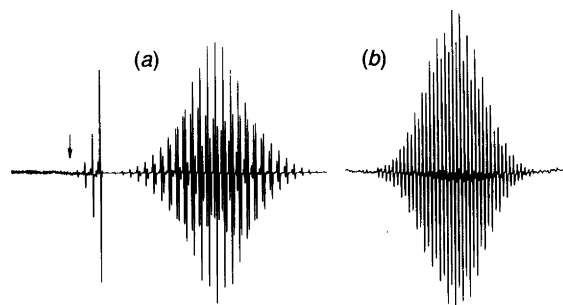


Fig. 1. EPR spectrum of (a) **1** in TFA after 20 h and (b) in TFA-d after 20 h. The left part of (a) is a superposition of ca. 300 000 spectra, showing at least four lines outside the outermost line of the left 13-line group with $a = 0.334$ mT. The arrow marks the position of the outermost line visible.

As also observed in the sulfuric acid studies,^{5,6} the use of deuteriated acid leads to the exchange of two hydrogens for deuteriums with a concomitant change in the spectrum. The 1:2:1 pattern with $a^{2H} = 0.545$ mT was replaced by a 1:2:3:2:1 group with $a^{2D} = 0.545/6.5 = 0.083$ mT [Fig. 1(b)], and again exactly the same EPR spectrum was obtained from OMA in TFA-*d*.

Table 1 shows that the OMA^{•+} EPR spectrum indeed appeared in a number of systems comprising TFA and (a) polymethylbenzenes alone (entries 3, 4), (b) a source of pentamethylbenzyl cation plus a polymethylbenzene (entries 7–10), or (c) any of the two possible nonamethylphenyldiphenylmethanes (methyls in the rings; entries 12, 13). However, mesitylene and hexamethylbenzene alone (entries 2, 5) did not produce any spectrum, and the spectrum from the latter in combination with pentamethylbenzyl acetate was very weak (entry 11). Thus it seems as if a recipe for the successful production of OMA^{•+} in TFA must contain (1) a source of pentamethylbenzyl cation and (2) a polymethylbenzene capable (if necessary) of accepting one further methyl group. In a strongly oxidizing acid, such as sulfuric acid,^{5,6} these restrictions need not apply; here, for example, hexamethylbenzene can form pentamethylbenzyl cation after initial ET oxidation to the hexamethylbenzene radical cation, proton loss from the latter and ET oxidation of the pentamethylbenzyl radical.

Table 1 also shows more obvious ways to produce OMA^{•+} modelled after the reported synthesis,¹³ namely dissolution of 1,2,3,4-tetramethylbenzene + paraformaldehyde in TFA (entries 14, 15), or dissolution of 9,10-

dihydro-OMA in itself in TFA in the absence or presence of DDQ (entries 16–19).

Formation and synthesis of OMA from various systems. While monitoring of OMA^{•+}-containing solutions by EPR spectroscopy is a simple, and sometimes a deceptively simple, method, it really does not say much about the actual yield of OMA. We therefore determined the yields of OMA in various systems (Table 2) and consistently found 3–30% yields of OMA. In line with the qualitative results of Table 1, a combination of 1,2,3,4-tetramethylbenzene and pentamethylbenzyl acetate was a good source of OMA (entries 6,7). In sulfuric acid, both penta- or hexa-methylbenzene in themselves gave OMA (entries 1, 2), lending support to the above assignment of the observed EPR spectra. These spectra were reproduced by us, including very minor changes of coupling constants on going from TFA to sulfuric acid or sulfuric acid-*d*₂. The system 1,2,3,4-tetramethylbenzene/pentamethylbenzyl acetate in TFA/sulfuric acid (entry 10) actually turned out to provide an exceptionally simple and fast (≈ 1 h) synthesis of OMA (24% yield of >99% quality; see the Experimental).

Entry 4 of Table 2 indicated that it might be possible to lower the reactivity of TFA by dilution with an inert solvent to the point that only proton-induced cleavage of **1** to give pentamethylbenzene and pentamethylbenzyl trifluoroacetate [eqn. (1)] would be observed. Table 3 shows that this was possible. In neat TFA with sodium trifluoroacetate present, the acidity was still high enough to drive the reac-

Table 1. Systems leading to the formation of 1,2,3,4,5,6,7,8-octamethylanthracene radical cation, as shown by EPR spectroscopy. Solvent = TFA, unless otherwise stated.

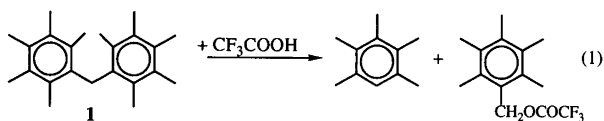
Entry No.	System	Time elapsed before recording the EPR spectrum/h	Nature of EPR signal
1	2,2',3,3',4,4',5,5',6,6'-Decamethyldiphenylmethane	4 3 × 10 ³	Strong Very strong
2	Mesitylene	72	None
3	1,2,3,4-Tetramethylbenzene	48	Weak
4	Pentamethylbenzene	72	Weak
5	Hexamethylbenzene	120	None
6	Pentamethylbenzyl acetate	120	Very weak ^a
7	Pentamethylbenzyl acetate + mesitylene	21	Medium
8	Pentamethylbenzyl acetate + 1,2,3,4-tetramethylbenzene	48	Very strong ^a
9	Pentamethylbenzyl acetate + durene	40	Strong
10	Pentamethylbenzyl acetate + pentamethylbenzene	20	Strong
11	Pentamethylbenzyl acetate + hexamethylbenzene	21	Very weak
12	2,2', 3,3',4,4',5,5',6-Nonamethyldiphenylmethane (6)	20	Strong
13	2,2',3,3',4,4',5,6,6'-Nonamethyldiphenylmethane	2	Medium
14	1,2,3,4-Tetramethylbenzene + formaldehyde	0.1	Strong
15	2,2',3,3',4,4',5,5'-Octamethyldiphenylmethane + formaldehyde	0.2	Strong
16	2,2',3,3',4,4',5,5'-Octamethyldiphenylmethane	2	Medium
17	1,2,3,4,5,6,7,8-Octamethyl-9,10-dihydroanthracene	1	Weak
18	1,2,3,4,5,6,7,8-Octamethyl-9,10-dihydroanthracene/DDQ	<0.1	Very strong
19	1,2,3,4,5,6,7,8-Octamethyl-9,10-dihydroanthracene/DDQ	<0.1 ^b	Very strong

^aRatio between signal intensities of entries 8 and 6 $\approx 10^2$. See the text. ^bIn dichloromethane/TFA (2:1).

Table 2. Product yields from the reaction of methylaromatics in acidic systems. TMB = 1,2,3,4-tetramethylbenzene; PMB = pentamethylbenzene; HMB = hexamethylbenzene; NMDM = 2,2',3,3',4,4',5,5',6-nonamethyldiphenylmethane; PMBzOAc = pentamethylbenzyl acetate; TFAAn = trifluoroacetic anhydride; RY = relative yield; AY = absolute yield.

Entry No.	Substrate (conc./mM)	Reaction conditions	Time/h	Products (%)					RY
				PMB	HMB	NMDM	1	OMA	
1	PMB (14)	H ₂ SO ₄ ^a	20	26	34		18	6 ^b	RY
2	HMB (14)	H ₂ SO ₄ ^a	20	1	72			14 ^{b,c}	RY
3	1 (15)	TFA	40	17	62		4	17	RY
4	1 (32)	CH ₂ Cl ₂ , [TFA] = 80 mM; [TFAAn] = 3 mM	170	46	29		21	0 ^d	RY
5	PMB (34) + PMBzOAc (23)	CH ₂ Cl ₂ [CF ₃ SO ₃ H] = 34 mM	170	32	4		2	3 ^e	RY
6	TMB (350) + PMBzOAc (70)	CH ₂ Cl ₂ /TFA ^f	1	–	31	69		0	AY
7	TMB (250) + PMBzOAc (75)	CH ₂ Cl ₂ /TFA ^f [CF ₃ SO ₃ H] ^g = 50 mM	48	62		1		23	AY
8	Same as #7	CH ₂ Cl ₂ /TFA ^f [CF ₃ SO ₃ H] = 60 mM	1	–	49	49		1	RY
9	TMB (300) + PMBzOAc (90)	CH ₂ Cl ₂ /TFA/H ₂ SO ₄ (2/2/1 v/v)	100					18	AY
			0.02	–	51	34		12	RY
			0.08	–	82	0		18	RY
			0.5	–	69	0		31	RY
			1	–	76	0		24	RY
1.5	–	73	0		27 ^h	RY			

^a100%. ^bIn addition, a compound (12%) with M^+ = 164 was formed. ^cIn addition, two compounds (4 and 2%) with M^+ = 164 and 178, respectively, were formed. ^dIn addition, pentamethylbenzyl trifluoroacetate (33%) was formed. ^eIn addition, 1,2,3,4-tetramethylbenzene (52%) was formed. ^f1/1 (v/v). ^gWithout CF₃SO₃H, no OMA was formed under these conditions. ^hCorresponded to an absolute (isolated) yield of 29%.



tion past the pentamethylbenzyl trifluoroacetate stage (entries 2, 3) and the same was true for dichloromethane/TFA (1/1 v/v) (entry 4). Further dilution with dichloromethane eventually gave an almost perfect cleavage according to eqn. (1) (entry 7) with no further reactions occurring. At twice the [TFA] (entry 9), these manifested themselves in

the transfer of a methyl group from 1-H⁺ to pentamethylbenzene, to give hexamethylbenzene and 2,2',3,3',4,4',5,5',6-nonamethyldiphenylmethane (NMDM, 6). At still higher [TFA] and/or longer reaction times, OMA formation became noticeable.

Formation of OMA⁺⁺ from OMA and its EPR and UV-VIS spectral properties. The UV-VIS spectrum of OMA in (a) dichloromethane (these solutions had to be freshly prepared since OMA was consumed over days in what, presumably, were light-induced processes) and (b) TFA (see

Table 3. Product yields from the reaction of 1 (30 mM) in TFA-containing systems. TMB = 1,2,3,4-tetramethylbenzene; PMB = pentamethylbenzene; HMB = hexamethylbenzene; NMDM = 2,2',3,3',4,4',5,5',6-nonamethyldiphenylmethane; PMBzOCOCF₃ = pentamethylbenzyl trifluoroacetate. Yields are relative.

Entry No.	Reaction conditions	Time/h	Products (%)						
			PMB	HMB	PMBzOCOCF ₃	NMDM	1	OMA	
1	CH ₂ Cl ₂ /TFA (20/1 v/v) [TFAAn] = 110 mM	24	44	1	32		1	11	
2	TFA; [CF ₃ COONa] = 250 mM	4	5	21	0		5	65	0.5
		80	19	68	0		1	0	12
3	TFA; [CF ₃ COONa] = 1250 mM	80	15	61	0		3	16	4
4	CH ₂ Cl ₂ /TFA (1/1 v/v) [TFAAn] = 100 mM	80	13	66	0		18	2	0.5
5	CH ₂ Cl ₂ /TFA (20/1.5 v/v) [TFAAn] = 220 mM	20	59	1	30		1	10	
6	CH ₂ Cl ₂ ; [TFA] = 220 mM	20	23	0	17		0	59	
7	CH ₂ Cl ₂ ; [TFA] = 420 mM	20	43	<0.2	35		0	22 ^a	
8	CH ₂ Cl ₂ ; [TFA] = 800 mM	20	48	0.5	37		0.5	14	
9	CH ₂ Cl ₂ ; [TFA] = 1500 mM	20	31	11	22		6	6 ^b	

^aAbsolute yields of PMB and PMBzOCOCF₃, respectively, after 44 h were > 95%, based on unrecovered 1. ^bAbsolute yields of PMB, HMB and PMBzOCOCF₃ were 62, 38 and 55% after 44 h, based on unrecovered 1.

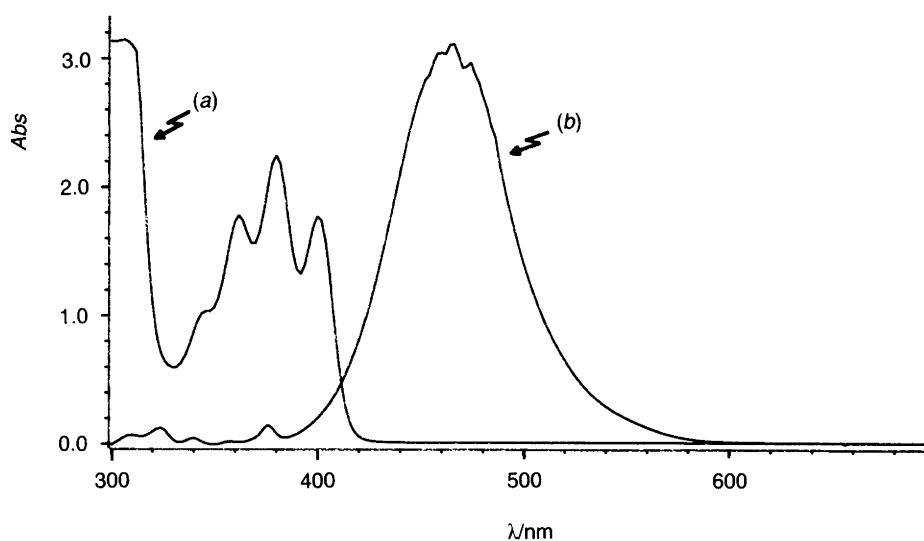


Fig. 2. UV-VIS spectrum of 1,2,3,4,5,6,7,8-octamethylanthracene in (a) dichloromethane (0.93 mM) and (b) TFA (1.28 mM).

Fig. 2) showed a large difference in appearance owing to almost complete protonation of OMA in TFA. This change is analogous to that experienced by anthracene itself upon protonation, except that the corresponding species have their UV spectral maxima at shorter wavelengths.¹⁴ In dichloromethane/TFA mixtures both species were clearly seen at low [TFA], as shown in Fig. 3, where the effect of incremental additions of TFA to a 0.35 mM solution of OMA in dichloromethane is shown. The EPR spectrum of the orange-red solution obtained immediately after dissolution of OMA in TFA was low in intensity, but this was strongly and instantly increased by addition of an oxidant such as DDQ, Pd(II)(CH₃CN)₄BF₄, tris(4-bromophenyl)aminium hexachloroantimonate or NO⁺ (see further below). The EPR signal was also increased strongly merely by leaving the sample in the dark overnight.

However, irradiation of the TFA solution even by diffuse daylight increased the rate of formation of OMA^{•+} significantly. In order to accelerate this effect, a flash-lamp set-up capable of delivering a focussed light pulse of 5–10 J over 1/200 s into the cuvette was used for irradiation of an OMA solution (0.35 mM) in dichloromethane/TFA (75/25 v/v). UV spectra were taken for solutions obtained from irradiation by a series of consecutive flashes. As seen from Fig. 4 the 474 nm band of OMAH⁺ decreased in intensity whereas peaks originating from OMA^{•+} appeared in the range of 340–380 nm and above 820 nm (λ_{\max} separately determined to be 907 nm). There was also a shoulder at \approx 450 nm on the 474 nm band that could be better visualized by tris(4-bromophenyl)aminium oxidation of an OMA/dichloromethane solution (see the insert, showing the two bands at 448 and 476 nm belonging to OMA^{•+}).

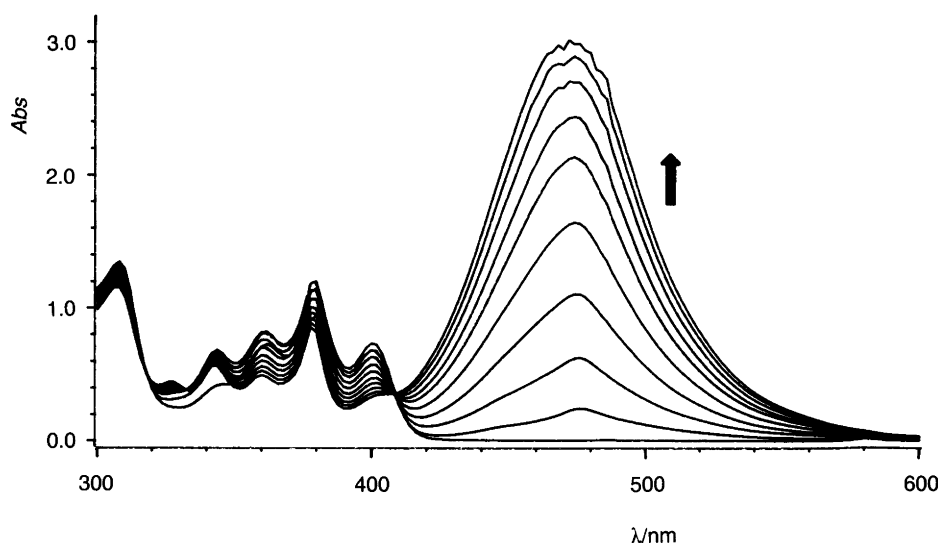


Fig. 3. Effect of adding TFA in 50 μ l increments to a solution of 1,2,3,4,5,6,7,8-octamethylanthracene (0.35 mM) in dichloromethane.

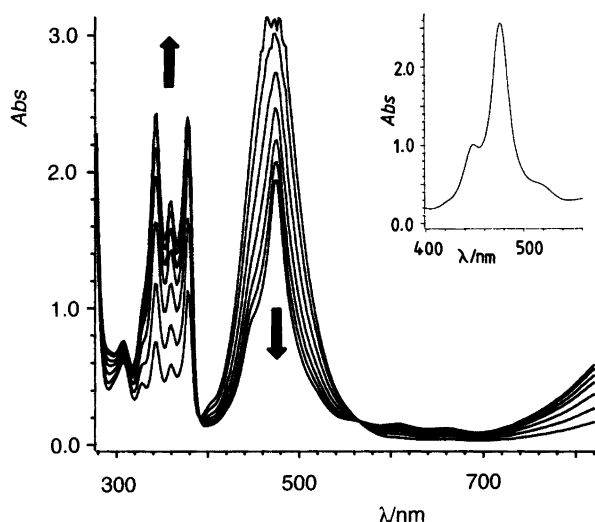


Fig. 4. Effect of light flashes on a solution of 1,2,3,4,5,6,7,8-octamethylanthracene (0.35 mM) in dichloromethane/TFA (75/25 v/v). The insert shows separately the two bands at 448 and 478 nm obtained by oxidation of an OMA solution in dichloromethane by tris(4-bromophenyl)aminium hexachloroantimonate.

Each flash caused an average change in absorbance (*Abs*) of -0.131 at 474 nm (decrease of OMAH^+) and $+0.235$ of the 376 nm band (increase of $\text{OMA}^{\cdot+}$). For comparison, the corresponding absorbance changes in the same solution after 20 h in the dark were -0.42 and $+1.1$, respectively, which means that 3–4 light flashes are equivalent to 20 h of what presumably must be the purely thermal oxidation of OMA by TFA. A more detailed study of the light-induced one-electron oxidation of 2,3,6,7-tetramethoxy-9,10-dimethylanthracene (**4**) is described below. This substrate has a similar redox reactivity to OMA [$E^\circ(4^{\cdot+}/4) = 0.99$

(NHE) V compared with 1.04 V (NHE) for OMA] but its UV-VIS spectral properties are experimentally more convenient.

The solution of $\text{OMA}^{\cdot+}$ in neat TFA eventually attained a brown-yellowish color and the UV spectrum, taken after the solution had been exposed to the light of the laboratory for three months, was in agreement with that expected from the two components of Fig. 4, all OMAH^+ having disappeared (see Fig. 5). The EPR signal of the solution was very strong.

Having identified the main features of the UV-VIS spectrum of $\text{OMA}^{\cdot+}$ it was possible to trace the colour development of a solution of **1** in TFA in more detail. Fig. 6 shows repetitive UV-VIS spectral scans (16×20 min) of a 1.2 mM solution of **1** in TFA, showing the growth of the $\text{OMA}^{\cdot+}$ peaks in the 340 – 380 nm region, the shoulder around 470 nm and the rising part of the peak at $\lambda_{\text{max}} = 907$ nm. Also the growing peak (rate constant ca. $6 \times 10^{-3} \text{ min}^{-1}$) around 470 nm due to OMAH^+ is clearly identifiable. There is also a strong absorption centred around 510 nm which must be responsible for the red-purple colour of the solution at this stage of the experiment and which was originally¹ assigned to $\pi\text{-1}^{\cdot+}$. Continuation of the experiment for another 20×90 min produced no additional features of interest (see the insert of Fig. 6) except for a colour change in the direction of that of an $\text{OMA}^{\cdot+}$ solution (brown-yellowish).

In TFA, the spontaneous oxidation of OMA gives rise to an EPR spectrum, in all respects identical with that shown in Fig. 1 (see the inserts in Fig. 5 and compare with Fig. 1). The same change as that between Fig. 1(a) and 1(b) was also obtained when TFA was replaced by TFA-*d*. The same spectrum was obtained when various oxidants were employed in TFA, e.g., tris(4-bromophenyl)aminium ion or DDQ. However, attempts to oxidize OMA in dichloro-

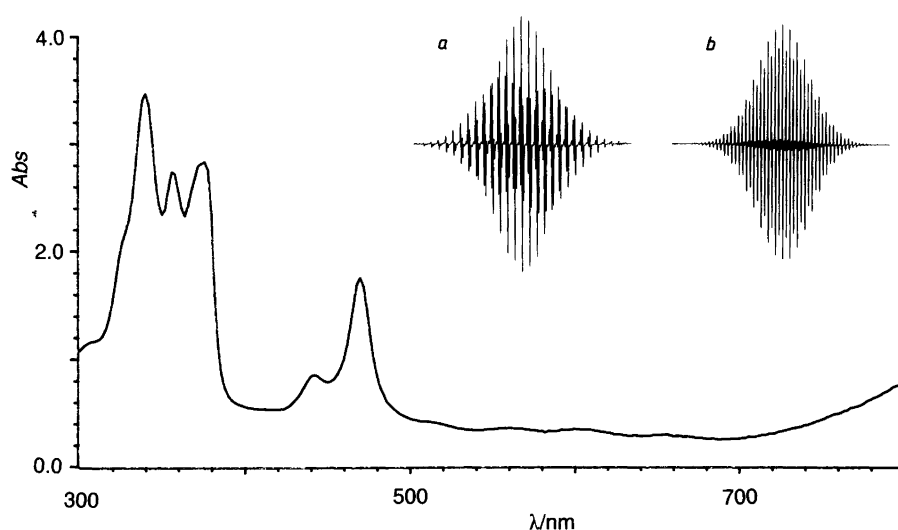


Fig. 5. UV-VIS spectrum of a solution of 1,2,3,4,5,6,7,8-octamethylanthracene (1.2 mM, 2 mm cell path) in neat TFA after 30 days. the insert shows the EPR spectrum of $\text{OMA}^{\cdot+}$ in (a) TFA (same solution as UV spectrum) and (b) in TFA-*d*. The sweep width was 5.0 mT in both cases.

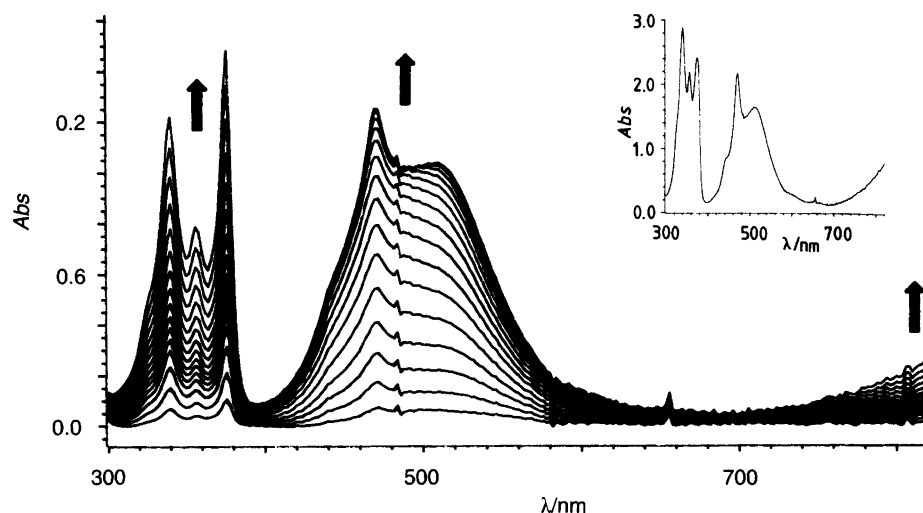


Fig. 6. Repetitive UV-VIS spectral scan of an initially 1.2 mM solution of 2,2',3,3',4,4',5,5',6,6'-decamethyldiphenylmethane in neat TFA at 20 min intervals. The insert shows the spectrum after 20 h from the start of the reaction.

methane with NO^+ , $\text{Pd(II)(CH}_3\text{CN)}_4^{2+}$ and tris(4-bromophenyl)aminium ion gave EPR spectra of $\text{OMA}^{\cdot+}$ which could be simulated by the same parameters and number of hydrogens as in Fig. 1 only if a larger line-width was employed (see Fig. 7). Presumably this is due to the fact that electron exchange occurs between $\text{OMA}^{\cdot+}$ and OMA (prevented by protonation of OMA in TFA) or the components of the redox system employed for oxidation. Also trichloroacetic acid/nitromethane could be used for the production of $\text{OMA}^{\cdot+}$.

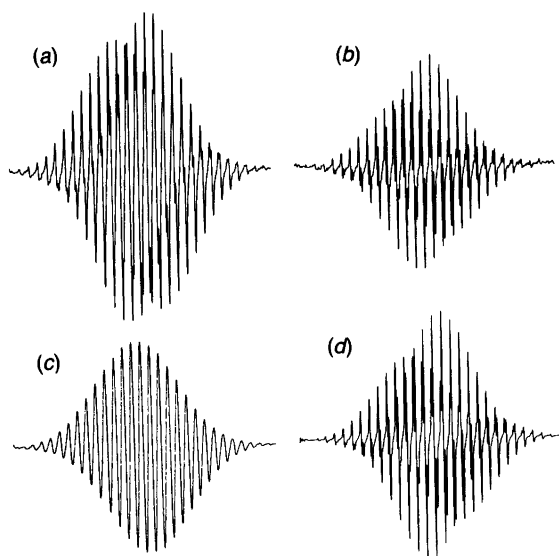


Fig. 7. EPR spectra of $\text{OMA}^{\cdot+}$ in dichloromethane, obtained by oxidation of OMA by (a) nitrosonium hexafluorophosphate, (b) $\text{Pd(II)(CH}_3\text{CN)}_4(\text{BF}_4)_2$ and (c) tris(4-bromophenyl)aminium hexafluorophosphate. Spectrum (d) developed spontaneously by dissolution of OMA in trichloroacetic acid/nitromethane (2/1). Satisfactory simulations of these spectra were obtained with the same parameters as those used for $\text{OMA}^{\cdot+}$ in neat TFA, except that the linewidths were taken to be (a) 0.040, (b) 0.030, (c) 0.10 and (d) 0.035 mT.

The spontaneous oxidation of OMA to $\text{OMA}^{\cdot+}$ in TFA under dark conditions prompted us to search for other substrates with similar redox properties, i.e., with E° ($\text{ArH}^{\cdot+}/\text{ArH}$) values in a range around or preferably somewhat lower than 1 V vs. NHE. Tris(4-methoxyphenyl)amine, *N*-methylphenothiazine and the anthracene derivatives studied by Parker *et al.*,⁹ 9,10-dimethyl- (**4**) and 9,10-diphenyl-2,3,6,7-tetramethoxyanthracene (**5**), turned out to have the desired properties, in particular **4** with its characteristically coloured protonated form (purple) and radical cation (blue). It was the distinct colour difference between the upper (exposed to daylight for ca. 1 h) and lower (located in the cavity) part of the EPR sample tubes containing solutions of **4** in TFA that eventually focussed our attention on the all-important photochemical aspects of TFA chemistry.

Photochemical oxidation of 4 to 4^{·+} in TFA-containing media. A repetitive (120 min between spectra) scanning UV-VIS spectroscopic experiment with ca. 0.4 mM **4** in dichloromethane/TFA (3/2, v/v), thoroughly degassed with argon and kept in the semidarkness of the spectrophotometer cuvette housing during the run (shutter closed between spectral recordings), is shown in Fig. 8. The radical cation absorption maxima above 400 nm were located at 462, 492 and 698 nm, the last maximum providing an excellent way of monitoring the progress of the reaction. The maximum at 540 nm originates from the protonated form, 4-H^+ (see below). The inserts show the EPR spectrum of $4^{\cdot+}$ in (a) TFA and (b) TFA-*d*, corresponding to the following parameters: $a^{6\text{H}(9,10\text{-CH}_3)} = 0.724$ mT, $a^{4\text{H}(1,4,5,8)} = 0.289$ mT, $a^{12\text{H}(2,3,6,7\text{-MeO})} = 0.0077$ mT and $a^{\text{AD}(1,4,5,8)} = 0.289/6.51 = 0.044$ mT. The *g* value was 2.00280. The change in replacing TFA with TFA-*d* corresponds to a reduction of the 4 H coupling constant by the expected factor of 6.5 (to 0.044 mT).

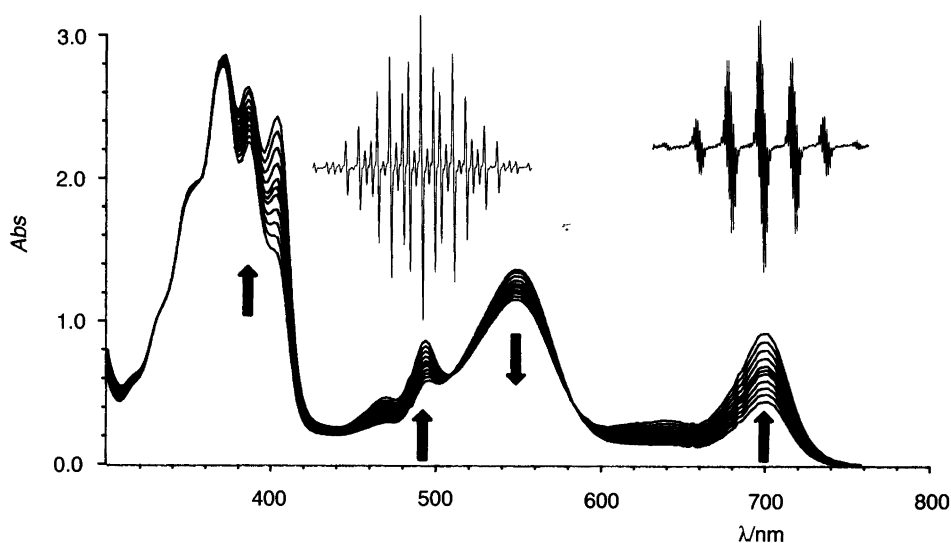


Fig. 8. Spectra of a 0.36 mM solution of 4 in dichloromethane/TFA (3/2, v/v), recorded at 120 min intervals under conditions of 'semidarkness' (Table 1). The EPR spectrum of $4^{\bullet+}$ (sweep width = 5.0 mT), recorded on the final solution, is shown in the left insert; the right insert shows the EPR spectrum of $4^{\bullet+}$ in TFA-*d*.

Fig. 9 shows an absorbance/time plot (curve 1) of the radical cation maximum at 698 nm, the straight line representing the regression line. Curve 2 shows the effect of bubbling oxygen through the initial solution before the commencement of repetitive scanning; there is a significant but not drastic rate increase. To establish a zero level, an Ar-degassed solution kept in complete darkness between spectral measurements showed an even lower rate of production of $4^{\bullet+}$ (curve 0, drawn as a straight line by back extrapolation of *Abs*/time data taken over 240 h). The rate constant was $\approx 2 \times 10^{-4} \text{ min}^{-1}$, corresponding to a second-order rate constant for the reaction between 4 and TFA of $\approx 1 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$.

Irradiation of the quartz cuvette by diffuse daylight near a north-facing window strongly increased the rate of production of $4^{\bullet+}$ (curve 3). Even higher rates were obtained

by irradiation by a 300 W 'sun lamp' (unfocussed light) at a fixed distance (curves 4 and 5, see also the insert of Fig. 9 for more detail). Change of co-solvent to carbon tetrachloride increased the rate even further (Fig. 10, circles; the regression line was drawn for the rising part only). In this medium $4^{\bullet+}$ was unstable (see Fig. 10), whereas it was relatively stable in dichloromethane/TFA. Any error in the measured rates in carbon tetrachloride/TFA must thus be on the lower side, since some $4^{\bullet+}$ must decay during the rising part of the curve. With acetonitrile as a co-solvent, practically no net production of $OMA^{\bullet+}$ was noticeable, again possibly explicable by the instability of the radical cation in acetonitrile (rate constant for its disappearance under the conditions employed $\approx 0.1 \text{ min}^{-1}$). The slopes of the regression lines in Figs. 9 and 10 were converted into $d[Abs]/dt$ values, where *t* was chosen to be 200 s in order to

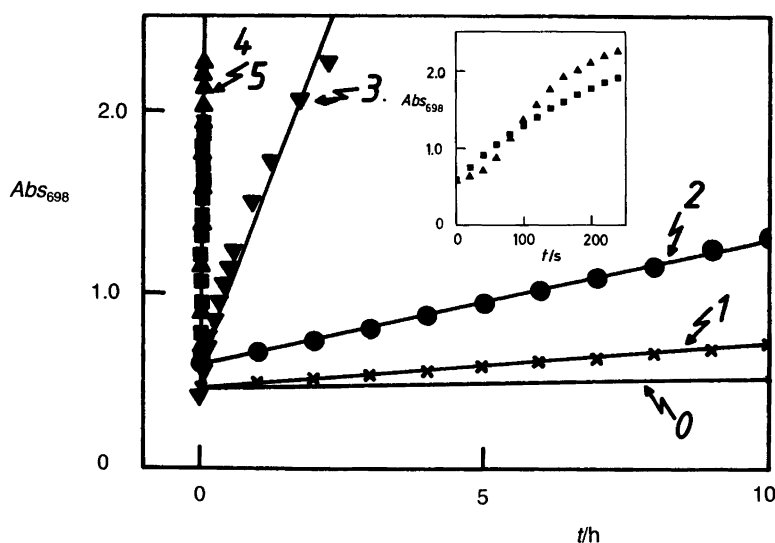


Fig. 9. Time development of Abs_{698} (representing $[4^{\bullet+}]$) under different light conditions in a solution of 0.36 mM 4 in dichloromethane/TFA (3/2, v/v) at $25 \pm 1^\circ \text{C}$, degassed with Ar if not otherwise stated. 0, darkness; 1, semidarkness; 2, semidarkness, bubbled with O_2 ; 3, diffuse daylight; 4 (■), 'sun lamp'; 5 (▲), 'sun lamp', bubbled with O_2 . Lines represent least-squares computed $d[Abs]/dt$ (see Table 1). Insert: Curves 4 (■) and 5 (▲) on a shorter timescale.

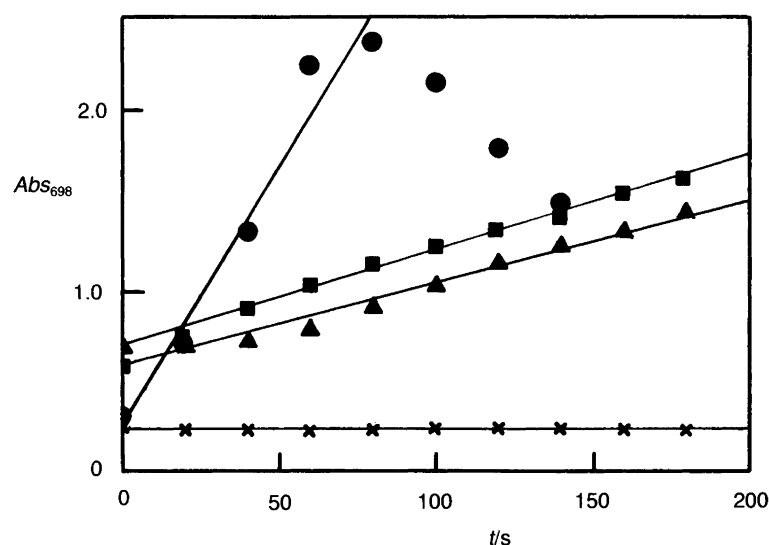


Fig. 10. Time development of Abs_{698} (representing $[4^+]$) of a solution of 0.36 mM **4** in neat TFA or mixtures of TFA with a co-solvent (ratio co-solvent/TFA was 3/2, v/v) irradiated with a 300 W sun lamp. ●, CCl_4 (average of two runs); ×, acetonitrile; ■, dichloromethane; ▲, neat TFA. Lines represent least-squares computed $d[Abs]/dt$ (see Table 1).

give a value around unity for the 'sun lamp' runs. These values are shown in Table 4.

The protonation of **4** in carbon tetrachloride/TFA (3/2, v/v) proved to be a slow process. Immediately after dissolution of **4** in this medium, the solution took on a faint blue colour owing to a low concentration of the radical cation. Repetitive scanning (21×2 min, see Fig. 11) showed that the 548 nm maximum of 4-H^+ increased with a rate constant of $0.021(1) \text{ min}^{-1}$ at 20.0°C and only after a few hours was the red-purple colour of 4-H^+ fully developed. The photochemical experiments with $4/CCl_4/TFA$ solutions were performed with solutions where the protonation equilibrium concentrations had been attained. In dichloromethane/TFA (3/2, v/v) protonation of **4** occurred on a much faster timescale, k for protonation being $\gg 10 \text{ s}^{-1}$.

Table 4. Values of $d[Abs]/dt$ (t taken to be 200 s) for the reactions of Figs. 9–10. $[4]_0 = 0.36 \text{ mM}$, solvent = TFA in admixture with a co-solvent (co-solvent/TFA = 3/2, v/v), temperature 20.0°C .

Light source	Co-solvent	Cell bubbled before run with	$d[Abs]/dt$
Sun lamp ^a	None	Ar	0.9
Sun lamp ^a	CH_2Cl_2	Ar	1.1
Sun lamp ^a	CCl_4	Ar	6
Sun lamp ^a	CH_3CN	Ar	<0.01
Sun lamp ^a	CH_2Cl_2	O_2	1.6
Diffuse daylight ^b	CH_2Cl_2	Ar	0.05
Laboratory light ^c	CH_2Cl_2	Ar	0.007
Semidarkness ^d	CH_2Cl_2	Ar	0.0015
Semidarkness ^d	CH_2Cl_2	O_2	0.004
Semidarkness ^d	CCl_4	Ar	<0.001
Darkness	CH_2Cl_2	Ar	0.0003

^a300 W 'sun lamp' (Osram ULTRAVITALUX) at a distance of 15 cm. ^bNear north-facing window (June–August). ^cConventional ceiling neon light. ^dIn spectrophotometer (HP-8452A) cell housing, shutter closed between measurements, semidark room.

While the experiments described in Table 4 were reproducible within a range of $\pm 20\%$, they should be considered as semiquantitative because of the relative lack of control over the light conditions. These results merely show how light in the laboratory environment affects solutions of **4** in TFA and, by inference, of other organic compounds in TFA. Experiments under well-reproducible conditions of light intensity were performed with the spectrophotometer light source at open shutter (Table 5). This light source (covering the whole spectral range of 190–820 nm with a total light effect of the order of 1 W) gave $d[Abs]/dt$ in dichloromethane/TFA of 0.099(5). Insertion of a filter of cut-off 435 or 545 nm after a certain reaction period with unfiltered light decreased this variable to 0.013, showing that UV light is mainly responsible for the photochemical effect. The same was true in carbon tetrachloride/TFA, where $d[Abs]/dt$ was actually lower than in dichloromethane/TFA (see also Table 4) with unfiltered light owing to the instability of 4^+ ; this is also seen in the form of negative $d[Abs]/dt$ when filters were inserted after a reaction period with unfiltered light. The radical cation formed then slowly decayed while the production almost completely ceased. Light from the flash-lamp set-up gave very high $d[Abs]/dt$, the ratio between reactions with carbon tetrachloride and dichloromethane being within the same the error limits as with the sun lamp (Table 4).

These results bring us to the problem of a possible promoting effect of light. From Table 4 we see that a solution of **4** in dichloromethane/TFA, mixed in the dark under argon, under 'semidarkness' conditions has $d[Abs]/dt = 0.0015$, while it is 0.013 when a reaction under 'open shutter' conditions (Table 5) is interrupted by insertion of a filter. This is a significant increase. Likewise, the negative $d[Abs]/dt$ observed in similar experiments in carbon tetrachloride/TFA were numerically too low to be compatible with the rate of disappearance of 4^+ . Also, irradiation of a carbon tetrachloride/TFA solution of **4** by the 'sun lamp' for 150 s gave rise to a reaction period with $d[Abs]/dt$ of

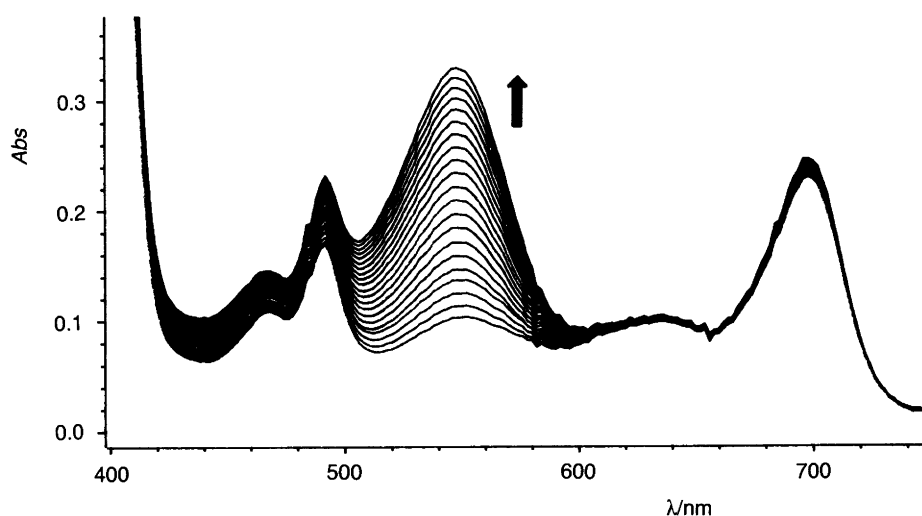


Fig. 11. Time development of Abs_{548} (representing $[4-H^+]$) in an initially 0.42 mM solution of **4** in carbon tetrachloride/TFA (3/2, v/v) at 20.0 °C. The interval between the scans was 2 min.

0.020, significantly larger than that obtained under 'semi-darkness' conditions, < 0.001 . Thus we can detect a weak promoting effect of light which is, however, completely overshadowed by the effect of ongoing irradiation.

Reaction between 2,2',3,4',5,5',6-heptamethyldiphenylmethane (7) and TFA. The oxidative self-coupling of durene by Co(III) or Mn(III) in TFA gave the expected **7** as the main product, but a hexamethylantracene derivative

was formed as a side-product, most likely 1,2,4,5,6,8-hexamethylantracene (**8**).^{2b} To determine whether **7** undergoes the same type of chemistry in TFA as **1**, solutions of **7** in TFA were monitored by EPR spectroscopy. After enough time had elapsed, a weak EPR spectrum of a persistent radical was detectable (Fig. 12). Presumably this is due to the presence of $8^{\cdot+}$. The same spectrum* has been recorded from the solution resulting from the oxidation of **7** by Pd(II) trifluoroacetate in TFA.¹⁵ We will address this problem in more detail in a future publication.

Table 5. Values of $d[Abs]/dt$ (t taken to be 200 s) for the formation of $4^{\cdot+}$ under well-reproducible conditions of light control. $[4]_0 = 0.36$ mM, solvent = TFA in admixture with a co-solvent (co-solvent/TFA = 3/2, v/v), temperature 20.0 °C.

Light source	Co-solvent (3/2 v/v)	$d[Abs]/dt$
Spectrophotometer light ^b	CH ₂ Cl ₂	0.099 ^a
		0.013 ^c
Spectrophotometer light ^b	CCl ₄	0.052 ^d
		0.007 ^e
		-0.0053 ^f
		-0.008 ^g
		-0.0037 ^h
Flash lamp ⁱ	CCl ₄	6.3×10^3
Flash lamp ⁱ	CH ₂ Cl ₂	1.2×10^3

^aAverage of three runs. ^bIn spectrophotometer cell housing, shutter open, semidark room. ^cWith cut-off filter at 435 or 545 nm inserted after a 1000 s reaction period with open shutter. ^dAverage of five runs. ^eWith cut-off filter at 290 nm inserted after a 1000 s reaction period with open shutter. ^fWith cut-off filter at 400 nm inserted after a 1000 s reaction period with open shutter. ^gWith cut-off filter at 435 nm inserted after a 1000 s reaction period with open shutter. ^hWith cut-off filter at 545 nm inserted after a 1000 s reaction period with open shutter. ⁱLight temperature 5600 K, corresponding to daylight conditions.

Discussion

As pointed out above, the formation of OMA $^{\cdot+}$ from **1** by TFA treatment, involves two problems, namely the skeletal transformation of **1** into OMA and the further one-electron oxidation of OMA to OMA $^{\cdot+}$. The finding (Table 3) that TFA, at a sufficiently low level of reactivity, can cleanly cleave **1** to give pentamethylbenzene and pentamethylbenzyl trifluoroacetate and, at the next higher level of reactivity, can induce formation of NMDM and hexamethylbenzene, suggests that the equilibria of eqns. (2) and (3) are set up first. This gives pentamethylbenzene, capable of acting as an acceptor of a methyl cation, and pentamethylbenzyl cation, a good acceptor of hydride ion. The need for these intermediates is also clearly indicated by the results in Tables 1 and 2; pentamethylbenzyl acetate in combination with a polymethylbenzene with at least one free nuclear position gave significant yields of OMA/OMA $^{\cdot+}$ in TFA.

The next step is transfer of a methyl cation from **1-H**⁺ (protonated in any *ortho* position) to pentamethylben-

* We thank Prof. I. Kozhevnikov for providing a copy of the complete spectrum of this sample.

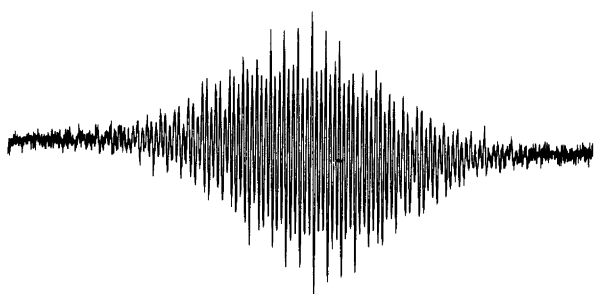
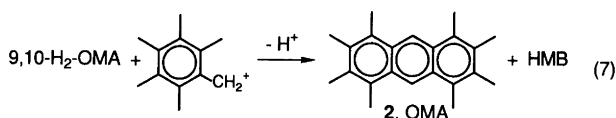
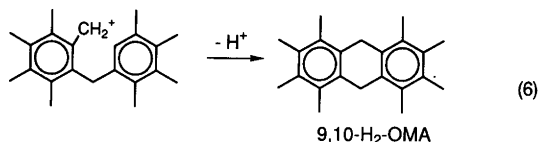
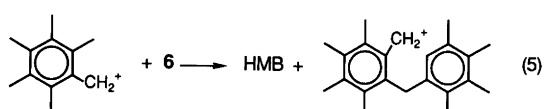
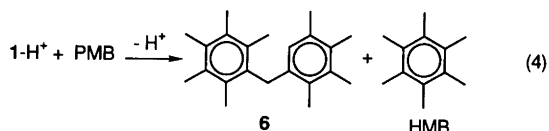
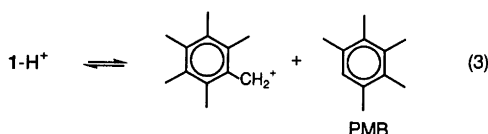
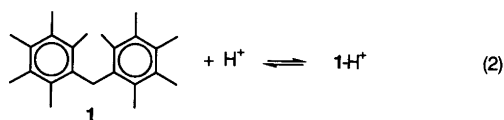


Fig. 12. EPR spectrum of a solution of 2,2',3,4,4',5,5'-heptamethyldiphenylmethane (7) in neat TFA, kept for ca. 400 h in laboratory light.

zene,¹⁶ presumably favoured by relief of strain in 1-H^+ [eqn. (4)]. This gives NMDM (6), from which productive chemistry can be induced by hydride transfer from one of the *ortho* methyls in the fully methylated ring to pentamethylbenzyl cation [eqn. (5)]. Ring closure of the new benzyl cation formed gives 9,10-dihydro-OMA [eqn. (6)], from which a second hydride transfer, followed by loss of a



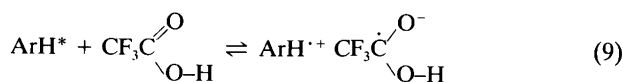
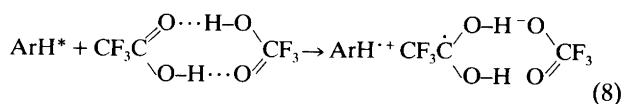
proton, completes the formation of OMA [eqn. (7)]. This is all carbonium ion chemistry for which ample precedence can be found in the literature.⁷ It is also easily understood why nitrosonium ion, with its blend of one-electron, electrophilic and hydride acceptor reactivity,¹⁷ can effect¹ the transformation $1 \rightarrow \text{OMA} \rightarrow \text{OMA}^{\cdot+}$.

The final electron transfer (ET) step converting OMA into $\text{OMA}^{\cdot+}$ was shown to be light induced (Fig. 4), even though there seemed to be a slow component of thermal ET. Samples kept under argon in complete darkness still experienced a slow but consistent increase in $[\text{OMA}^{\cdot+}]$, and so did similarly treated samples of tris(4-methoxyphenyl)amine and *N*-methylphenothiazine.³ The rate constants for formation of the corresponding radical cations under these conditions were $\approx 4 \times 10^{-7}$ and $2 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$, respectively. Also for 4/TFA solutions, a slow, seemingly spontaneous build-up of radical cation was noticeable (rate constant $\approx 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$).

If the recorded rate constants for these three systems really correspond to thermal ET steps of outer-sphere type, TFA would possess an $E^\circ(\text{TFA}/\text{TFA}^{\cdot-})$ of $\approx 0 \text{ V}$ vs. NHE, as can be calculated on the basis of the Marcus theory with reasonable estimates of the self-exchange reorganization energies involved.⁸ However, as demonstrated for 4, radical cation production seems to be promoted by light, which indicates that even the limited light exposures necessitated by intermittent measurements might induce an ET reaction which continues under dark conditions.

However, the thermal ET reaction, if it exists, is an insignificant cause of radical cation production compared with the effect of light. We stress that the facile photochemical production of radical cations from aromatic and heteroaromatic compounds in sulfuric acid, TFA or TFA/Hg(II) trifluoroacetate (Kochi's reagent)¹⁹ has been an established method in the EPR research community for some time,¹¹ although the implications have not been carried over to other uses of TFA. Generally, strong UV sources have been employed in this context and the connection with the everyday use of TFA solutions in diffuse day- or laboratory-light was not obvious.

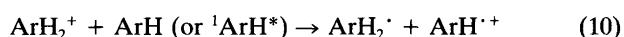
TFA has been shown to be an efficient quencher of naphthalene fluorescence, especially in less polar or non-polar solvents.²⁰ The rate constant for quenching [eqn. (8)] of naphthalene singlet by the dimer of TFA in isooctane, benzene and 1,2-dichloroethane was $\approx 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The finding that the dimer is the active quencher is probably highly significant. As written in eqn. (8) the ET step between ArH^* and $(\text{TFA})_2$ avoids the potentially unproductive back ET step from the $\text{ArH}^*/\text{monomer}$ reaction [eqn. (9)]; by synchronous electron/proton transfer the



radical cation is formed together with a less strongly reducing species than $\text{TFA}^{\cdot-}$ and thus has a chance to survive. The radical $\text{CF}_3\dot{\text{C}}(\text{OH})_2$ in eqn. (8) has been detected in the photoreduction of TFA in methanol at -60°C .²¹

The ET reducing properties of $^1(\text{naphthalene})^*$ are such that the ET step should be facile. $E^\circ[(\text{naphthalene})^{\cdot+}/^1(\text{naphthalene})^*]$ has been estimated to be -2.2 V vs. NHE,²² certainly a value that would provide a strong driving force in eqn. (8). The substrates under investigation here should have similarly low, or even lower $E^\circ(\text{ArH}^{\cdot+}/^1\text{ArH}^*)$ and thus undergo reaction (8) with great efficiency. The need for light of wavelengths < 400 nm indicates that it is the singlet state that is the active ET reagent.

A previously described mechanism for the production of radical cations in acidic media assumed ArH_2^+ to be the oxidizing species, as shown in eqn. (10).^{8a,b} The ArH_2^+



radical formed would then be oxidized further by the acid. The same mechanism is possible in TFA, but then requires $\text{ArH}_2^{\cdot+}$ to be oxidized to ArH_2^+ in a thermal ET process. We will address the mechanistic problem in more detail in forthcoming publications.

Conclusions

From the results reported here and by others the following picture emerges of radical cation production from organic compounds (denoted RH) in TFA. The substrate undergoes more or less extensive protonation by TFA, RH being the photochemically active species. Photochemical excitation of RH to $^1\text{RH}^*$ occurs, followed by ET to the TFA dimer [as in eqn. (8)]. This step derives its efficiency from the fact that synchronous proton transfer can take place within the dimer. Higher efficiencies can be observed in the presence of a better electron acceptor, such as mercury(II) trifluoroacetate,¹⁹ where charge-transfer complex formation also enhances the range of wavelengths accessible for excitation. However, the presence of an additional electron acceptor in TFA is probably not mandatory. The stability of $\text{RH}^{\cdot+}$ in TFA is dependent on several factors,²³ of which the basicity of RH may be the most important. If RH is extensively protonated, bimolecular reactions between $\text{RH}^{\cdot+}$ and RH will be retarded and thus oxidative coupling reactions are prevented. For EPR studies this is presumably important for deciding which radical cation species is formed, $\text{RH}^{\cdot+}$ or $(\text{RH})_2^{\cdot+}$ in relatively stable systems. Again, extensive protonation of ArH should prevent formation of the dimeric species. Addition of a second, stronger acid (such as sulfuric acid) to the TFA solution should help to prevent dimer formation. However, at extremely high degrees of protonation one may run into the problem that [RH] becomes so low that the photooxidation process becomes too slow for any radical cation production occur. We think this is the case for *N,N,N',N'*-tetramethyl-1,4-phenylenediamine [$E^\circ(\text{ArH}^{\cdot+}/\text{ArH}) = 0.25$ V vs. NHE] which cannot be photochemically oxidized in TFA.^{11j} We can confirm this observation but have found that facile photooxidation of *N,N,N',N'*-tetramethyl-1,4-phenylenediamine takes place in dichloromethane, 20 mM in TFA,

and even in acetic acid. Thus in neat TFA this very easily oxidizable compound is protected from ET oxidation by protonation; upon extensive dilution of the acid, enough neutral compound will be present for photooxidation to take place.

The most important conclusion is that TFA is not such an innocent Brønsted acid as usually believed. It is acidic enough to induce deep-seated transformations of alkylaromatic compounds, and its light dependent ET oxidizing capability is high enough to make possible photooxidation of compounds as difficult to oxidize as pyrene and thianthrene with $E^\circ(\text{ArH}^{\cdot+}/\text{ArH})$ around 1.6 V vs. NHE. This combination of reactivities might well be detrimental to investigations where TFA is used as the solvent.

Experimental

Materials. Mesitylene, 1,2,3,4-tetramethylbenzene, penta- and hexa-methylbenzene, 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ), tetrachlorobenzoquinone (chloranil), tris(4-bromophenyl)aminium hexachloroantimonate, nitrosonium hexafluorophosphate, Pd(II)(CH₃CN)₄(BF₄)₂ and paraformaldehyde were obtained in the highest possible commercial quality. 2,2',3,3',4,4',5,5'-Octamethyldiphenylmethane and 1,2,3,4,5,6,7,8-octamethyl-9,10-dihydroanthracene were synthesized according to known procedures,¹³ as was 2,3,6,7-tetramethoxy-9,10-dimethylanthracene (**4**).²⁴ 2,2',3,3',4,4',5,5',6,6'-Decamethyldiphenylmethane (**1**), 2,2',3,3',4,4',5,5',6- and 2,2',3,3',4,4',5,6,6'-nonamethyldiphenylmethane, 2,2',3,4',5,5',6-heptamethyldiphenylmethane (**7**), pentamethylbenzyl acetate and tris(4-methoxyphenyl)amine were available from earlier work.²⁵ Sulfuric acid (100%) was prepared by mixing 96% sulfuric acid (Merck, SUPRAPUR) and 20% fuming sulfuric acid (Merck, analytical grade). Sulfuric acid-*d*₂ (98%) was purchased from Dr. Glaser AG, Basel. Dichloromethane (*zur Rückstandsanalyse*), TFA and acetonitrile (both of UVASOL quality), carbon tetrachloride (analytical grade), trichloroacetic acid (analytical grade) and nitromethane (*zur Synthese*) were from Merck AG.

Instrumentation. The UV-VIS spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer, equipped with an HP 89500 UV-VIS ChemStation. The temperature of the cells was kept at 20.0°C and the cell path of the quartz cuvettes used was 10 mm, unless otherwise stated. The VIS spectrum of OMA^{·+} above 820 nm was recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Filters were from Hewlett-Packard (290 nm), Schott (GG 400 and 435) and Corning (3/69; 545 nm). Kinetic runs and data analysis were performed by means of HP 89512 UV/VIS Kinetics Software. NMR spectra were recorded on a Varian 300 MHz instrument, chemical shifts being given with respect to tetramethylsilane. GLC analyses were performed on an HP 5830A gas chromatograph, equipped with an HP 15580A integrator and using a short column (50 cm 10% UCW-982 on 80-100 mesh WAW-DMCS B343)

with pentamethylbenzyl acetate as an internal standard. GLC/MS analyses were performed on a Finnegan 4021 mass spectrometer. Cyclic voltammetry was performed on a BAS-100 Electrochemical Analyzer with a platinum button working electrode, an Ag/AgCl reference electrode and a Pt wire counter-electrode. The EPR spectra were recorded on a Bruker ER-200D SRC instrument, using solid diphenylpicrylhydrazyl (DPPH, $g = 2.00354$)²⁶ as a reference for determinations of g .

The flash set-up consisted of a large commercial (MECABLITZ 60 CT-4 from Metz-Werke, Germany) photo flashgun with an approximate light effect of 5–10 kW, equipped with a tele-attachment 60–42. The light was focussed onto an area of ca. 2×6 cm by means of a condenser lens (11 cm diameter, focal distance ca. 10 cm) where the cell was placed with a reflecting parabolic surface behind.

1,2,3,4,5,6,7,8-Octamethylanthracene (2, OMA). 9,10-Dihydro-OMA¹³ (0.46 g, 1.64 mmol) and chloranil (0.49 g, 2.0 mmol) were heated to 90 °C for 120 min in *p*-xylene. At this stage all of the starting material had been consumed (GLC). The mixture was left overnight, and solid **2** was collected by filtration. The yield of **2** after one recrystallization from benzene was 81 % (0.38 g, 1.34 mmol), m.p. 230–235 °C (by melting point microscope; the sample resolidified partially upon further heating and became dark brown with signs of extensive decomposition; lit.¹³ m.p. 298–299 °C). ¹H NMR (CDCl₃): 2.48 (s, 12 H), 2.79 (s, 12 H), 8.68 (s, 2 H), matching the reported²⁷ spectrum exactly, except for a constant difference of 0.15 ppm. MS [m/z (rel. int/%)]: 291 (22), 290 (100), 275 (18), 145 (38).

A very simple synthesis of OMA was performed in the following way. Pentamethylbenzyl acetate (10.0 g, 0.045 mol) and 1,2,3,4-tetramethylbenzene (20.0 g) were dissolved in 150 ml of dichloromethane. A mixture of 75 ml of concentrated sulfuric acid (98 %) and 150 ml of TFA was added in one portion, the flask was stoppered and the dark red–brown solution stirred for 15 min. After addition of 750 ml of dichloromethane, 1 l of ice–water was added with stirring. The organic layer was separated, washed twice with water and dried (MgSO₄). After evaporation of the volatile components, the yellow–brown residue was suspended in 25 ml of pentane. The solid was filtered off and washed with 25 ml of pentane. After drying, 3.3 g (0.011 mol, 24 % yield) of pure (>99 %, GLC), yellow OMA, were obtained, its spectral properties being identical with those of authentic OMA (see above).

The small-scale reactions in Table 1 were performed on 0.5–2 mM solutions of the substrate in TFA (volume 10–20 ml). After the appropriate time, small samples were withdrawn and transferred to EPR tubes, degassed thoroughly with argon and sealed. The reactions of Tables 2 and 3 were performed by weighing the substrate (plus additives, if any) into a 25 ml Erlenmeyer flask, followed by addition of the solvent. The mixtures were stirred and protected from ex-

posure to daylight during the reaction period, and then poured into water, extracted with dichloromethane and the organic layer dried (MgSO₄). The reported yields were determined by GLC either without (relative) or with (absolute) addition of an internal standard.

Acknowledgements. Financial support from the Swedish Natural Science Research Council, the Knut and Alice Wallenberg Foundation and the Crafoord Foundation is gratefully acknowledged. We thank Dr. Börje Folkesson, Inorganic Chemistry for recording a spectrum, Professors Ulf Litzén and Indrek Martinsson, Department of Physics for the loan of lenses and Professor Michael Hartshorn for valuable comments.

References

- Sankararaman, S., Lau, W. and Kochi, J. K. *J. Chem. Soc., Chem. Commun.* (1991) 396. For a case of a doubly π -stabilized radical cation, see: Grimme, W., Kämmerling, H. T., Lex, J., Gleiter, R., Heinze, J. and Dietrich, M. *Angew. Chem., Int. Ed. Engl.* 30 (1991) 205.
- (a) Nyberg, K. *Chem. Scr.* 5 (1974) 115 and references quoted therein; (b) Nyberg, K. and Wistrand, L.-G. *Chem. Scr.* 5 (1974) 234.
- Eberson, L. and Radner, F. *J. Chem. Soc., Chem. Commun.* (1991) 1233.
- Sebastiano, R., Korp, J. D. and Kochi, J. K. *J. Chem. Soc., Chem. Commun.* (1991) 1481. We thank Prof. Kochi for sending us a preprint.
- Singer, L. S. and Lewis, I. C. *J. Am. Chem. Soc.* 87 (1965) 4695.
- Hulme, R. and Symons, M. C. R. *J. Chem. Soc. A* (1966) 446.
- Olah, G. A. and Schleyer, P. von R. (Eds.) *Carbonium Ions*, Vols. I–IV, Wiley, New York, 1968, 1970, 1972 and 1973.
- (a) Bard, A. J., Ledwith, A. and Shine, H. J. *Adv. Phys. Org. Chem.* 13 (1976) 155; (b) Fava, A., Sogo, P. B. and Calvin, M. *J. Am. Chem. Soc.* 79 (1957) 1078; (c) Aalbersberg, W. I., Hoijtink, G. J., Mackor, E. L. and Weijland, W. P. *J. Chem. Soc.* (1959) 3049; (d) Shine, H. J. and Piette, L. *J. Am. Chem. Soc.* 84 (1962) 4798; (e) Castagnola, M., Floris, B., Illuminati, G. and Ortaggi, G. *J. Organomet. Chem.* 60 (1973) C17; cf. however Bitterwolf, T. E. and Ling, A. C. *J. Organomet. Chem.* 40 (1972) C29; (f) Ronlán, A. and Parker, V. D. *J. Chem. Soc., Chem. Commun.* (1974) 33; (g) Eloranta, J. and Kolehmainen, S. *Finn. Chem. Lett.* (1977) 10; (h) Gerson, F., Kaupp, G. and Ohya-Nishiguchi, H. *Angew. Chem.* 89 (1977) 666; (i) Hart, H., Teuerstein, A. and Babin, M. A. *J. Am. Chem. Soc.* 103 (1981) 903; (j) Mäkelä, R., Oksanen, M. and Vuolle, M. *Acta Chem. Scand., Ser. A* 38 (1984) 73; (k) Dinno-cenzo, J. P. and Schmittel, M. *J. Org. Chem.* 53 (1988) 4147; (l) Kozhevnikov, I. V. and Eberson, L. *New J. Chem.* 16 (1991) 351.
- Andersen, M. L., Handoo, K. L. and Parker, V. D. *Acta Chem. Scand.* 45 (1991) 983.
- Eberson, L. and Radner, F. *Acta Chem. Scand.* 45 (1991) 1093.
- (a) Hulme, R. and Symons, M. C. R. *J. Chem. Soc.* (1965) 1120; (b) Courtneidge, J. L., Davies, A. G. and Yazdi, S. N. *J. Chem. Soc., Chem. Commun.* (1984) 570; (c) Chan, W., Courtneidge, J. L., Davies, A. G., Djap, W. H., Gregory, P. S. and Yazdi, S. N. *J. Chem. Soc., Chem. Commun.* (1984) 1541; (d) Courtneidge, J. L. and Davies, A. G. *Acc. Chem. Res.* 20 (1987) 90; (e) Courtneidge, J. L., Davies, A. G., McGuchan, D. C. and Yazdi, S. N. *J. Organomet. Chem.* 341

- (1988) 63; (f) Davies, A. G., Julia, L. and Yazdi, S. N. *J. Chem. Soc., Perkin Trans. 2* (1989) 239; (g) Davies, A. G. and Schiesser, C. H. *J. Organomet. Chem.* 389 (1990) 301; (h) Avila, D. V. and Davies, A. G. *J. Chem. Soc., Faraday Trans. 86* (1990) 3243; (i) Depew, M. C., Zhongli, L. and Wan, J. K. S. *J. Am. Chem. Soc.* 105 (1983) 2480; (j) Craw, M. T., Depew, M. C. and Wan, J. K. S. *Can. J. Chem.* 64 (1986) 1414.
12. Börnstein, L. *Numerical Data and Fundamental Relationships in Science and Technology*, Vol. 9d2, Springer-Verlag, Berlin 1980, pp. 6–20.
13. Welch, C. M. and Smith, H. A. *J. Am. Chem. Soc.* 73 (1951) 4391.
14. Olah, G. A., Pittman, C. U., Jr. and Symons, M. C. R. In: Ref. 7, Vol. 1, Chap. 5.
15. Kozhevnikov, I. V., Kim, V. I., Talzi, E. P. and Sidelnikov, V. N. *J. Chem. Soc., Chem. Commun.* (1985) 1392.
16. For a review, see McCaulay, D. A. In: Olah, G. A., Ed., *Friedel-Crafts and Related Reactions*, Vol. II, Part 2, Interscience, New York 1964, Chap. XXIV.
17. Williams, D. L. H. *Nitrosation*, Cambridge University Press, Cambridge, UK 1988; Olah, G. A., Salem, G., Staral, J. S. and Ho, T.-L., *J. Org. Chem.* 43 (1978) 173; Olah, G. A. *J. Org. Chem.* 45 (1980) 3532; Ebersson, L. and Radner, F. *Acc. Chem. Res.* 20 (1987) 53.
18. Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, Heidelberg 1987.
19. Lau, W. and Kochi, J. K. *J. Org. Chem.* 51 (1986) 1801.
20. Bunce, N. and Bergsma, M. D. *J. Org. Chem.* 45 (1980) 2083; Bunce, N. J., Kumar, Y. and Ravanal, L. *J. Org. Chem.* 44 (1979) 2612.
21. Kaiser, T., Grossi, L. and Fischer, H. *Helv. Chim. Acta* 61 (1978) 223.
22. Juillard, M. and Chanon, M. *Chem. Rev.* 83 (1983) 425; Chanon, M. and Ebersson, L. In: Fox, M. A. and Chanon, M., Eds., *Photoinduced Electron Transfer*, Part A, Elsevier, Amsterdam 1988.
23. Dannenberg, J. J. *Angew. Chem.* 87 (1973) 7114.
24. Chung, Y., Duerr, B. F., McKelvey, T. A., Nanjappan, P. and Czarnik, A. W. *J. Org. Chem.* 54 (1989) 1018.
25. Nyberg, K. *Chem. Scr.* 4 (1973) 143; Ebersson, L., Barry, J. E., Finkelstein, M., Moore, W. M. and Ross, S. D. *Acta Chem. Scand., Ser. B* 40 (1986) 283.
26. Forrester, A. R., Hay, J. M. and Thomson, R. H. *Organic Chemistry of Free Radicals*, Academic Press, London 1968.
27. Krysin, A. P., Bodoev, N. V. and Koptuyug, V. A. *Zh. Org. Khim. (Engl. Transl.)* 13 (1977) 1183.

Received October 11, 1991.