Letter

Why is Trifluoroacetic Acid such an Effective One-Electron Oxidant?

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Trifluoroacetic acid (TFA) is an excellent solvent for the generation of radical cations from their parent compounds,[1] either anodically[2] or by various one-electron oxidants, for example thallium(III)[3] or cobalt(III)[4] trifluoroacetate, 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ),[5] aminoxyls,[6] palladium(II) acetate or trifluoroacetate[7,8] and 4-nitrobenzenediazonium ion.[9] However, there are numerous reports[1,8,10] that TFA *by itself* can oxidize easily oxidizable compounds, a process sometimes ascribed to the presence of dioxygen,[10e,j] but which sometimes occurs even in the absence of oxygen. Thus Illuminati *et al.*[10d] found that ferrocene is oxidized in neat TFA with a rate constant of 1.1×10^{-3} s^{-1} at 25 °C, whereas decamethylferrocene reacted 'in a few minutes'. Finally and importantly for the problem at hand, it should be noted that EPR spectroscopists have made extensive use of photolysis of hydrocarbons in TFA and other acids to generate radical cations.[11]

In view of our recent finding[12] that 2,2',3,3',4,4',5,5',6,6'-decamethyldiphenylmethane (E_{pa} = 1.55 V) is converted into 1,2,3,4,5,6,7,8-ocatamethylanthracene radical cation

(OMA$^{\cdot+}$) by dissolution in TFA, we were prompted to take a fresh look into the problem of the oxidizing properties of TFA. Even if most of the chemistry involved in that particular transformation must be of rather well-known carbonium-ion type, there must an oxidant present that is capable of oxidizing OMA to OMA$^{\cdot+}$ ($E°$ = 0.86 V vs. Ag/AgCl) in the absence of oxygen.

In searching for other, more convenient substrates (OMA reacts slowly in TFA and its radical cation has an absorption maximum at > 820 nm, inaccessible with our instrumentation) susceptible to oxidation by TFA, we noticed that 2,3,6,7-tetramethoxy-9,10-dimethylanthracene (DMTMA) has a suitable $E°$ (0.94 V vs. NHE)[9] for our purpose; upon closer inspection,[13] it turned out to have the desired UV–VIS spectral properties.

A repetitive scanning experiment with ca. 0.4 mM DMTMA in dichloromethane/TFA (3/2, v/v), thoroughly degassed with argon and kept in semi-darkness during the run, is shown in Fig. 1. The radical cation absorption maxima above 400 nm are located at 462, 492 and 698 nm, and we have used the band at 698 nm to monitor the progress of the reaction. Fig. 2, curve *1*, shows the change in absorbance with time of the radical cation, 698 nm

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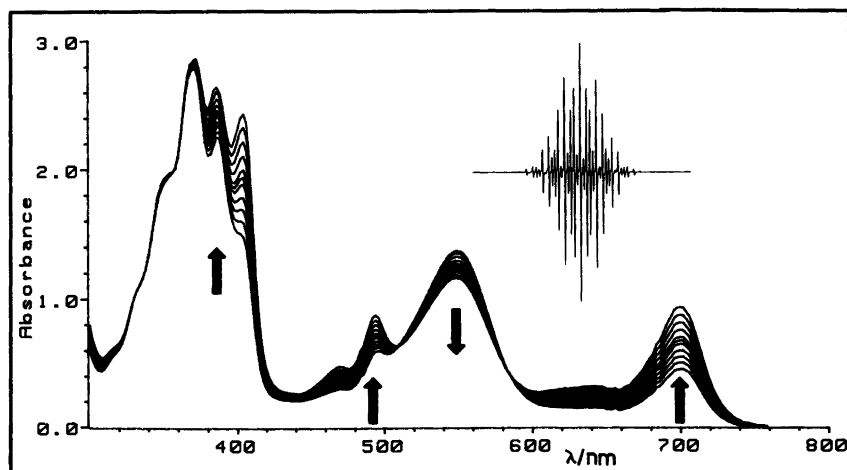* To whom correspondence should be addressed.

Fig. 1. Spectra of a 0.4 mM solution of DMTMA in dichloromethane/TFA (3/2, v/v), recorded at 120 min intervals under conditions of "semi-darkness" (Table 1). The ESR spectrum of DMTMA$^{\cdot+}$ (sweep width = 10.0 mT), recorded on the final solution, is shown in the insert; $a^{6H(9,10\text{-}CH_3)}$ = 0.724 mT, $a^{4H(1,4,5,8)}$ = 0.289 mT and $a^{12H(2,3,6,7\text{-}MeO)}$ = 0.0077 mT.
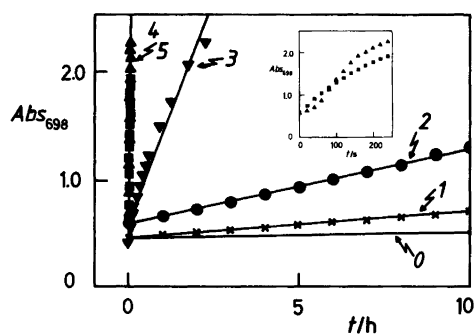
Fig. 2. Time development of Abs_{698} (representing [DMTMA$^{·+}$]) under different light conditions in a solution of 0.4 mM DMTMA in dichloromethane/TFA (3/2, v/v) at 25 ± 1 °C, degassed by Ar if not otherwise stated. 0, darkness; 1, semi-darkness; 2, semi-darkness, bubbled with O_2; 3, diffuse daylight; 4 (squares), "sun lamp"; 5 (triangles), "sun lamp", bubbled with O_2. Lines represent least-squares computed d[Abs]/dt (see Table 1). Insert: Curves 4 (squares) and 5 (triangles) on a time-scale of min.

Fig. 3. Time development of Abs_{698} (representing [DMTMA$^{·+}$]) of a solution of 0.4 mM DMTMA in neat TFA or mixtures of TFA with a cosolvent (ratio cosolvent/TFA was 3/2, v/v) under irradiation by a 300 W sun lamp. Circles, CCl_4 (average of two runs); crosses, acetonitrile; squares, dichloromethane; triangles, neat TFA. Lines represent least-squares computed d[Abs]/dt (see Table 1).

maximum. The disappearing maximum at 540 nm is due to the protonated form of DMTMA. Curve 2 shows the result of a run where the initial solution had been bubbled with oxygen before the start. This reaction is clearly faster, although not drastically so. On the other hand, an Ar-degassed solution that had been kept in complete darkness between measurements showed a significantly lower rate of production of DMTMA$^{·+}$ (curve 0). The rate constant was $\approx 2 \times 10^{-4}$ min^{-1}, corresponding to a second-order rate constant for reaction with TFA of $\approx 10^{-6}$ M^{-1} s^{-1}.

Irradiation of the quartz cuvette with diffuse daylight brought about a drastic increase in the rate of production of DMTMA$^{·+}$ (curve 3) and even higher rates were obtained by irradiation with the unfocussed light from a 300 W 'sun lamp' at a fixed distance of 15 cm (curves 4 and 5, see also the insert for the runs with the 300 W lamp). An even higher rate was obtained in CCl_4/TFA (3/2, v/v) (Fig. 3). In this solvent the radical cation was unstable whereas it was stable in dichloromethane/TFA. This presumably explains why d[Abs]/dt appears to be greater in dichloromethane than in carbon tetrachloride under conditions of low light intensity. In acetonitrile/TFA (3/2, v/v) very little net radical cation production was seen; again the radical cation was not stable (rate constant of decay ≈ 0.1 min^{-1} at 25 °C) so that its formation may be balanced by its decay.

The runs reported in Figs. 2 and 3 and a few others are summarized quantitatively by the values of d[Abs]/dt (dt = 200 s) for the main reaction period of the reactions in Table 1. The possibility of catalytic action of light was checked in CCl_4/TFA (3/2) by irradiation (sun lamp) of a fresh solution for 150 s, followed by a repetitive scan (20×0.5 min) in semi-darkness. This resulted in a d[Abs]/dt of 0.02, significantly larger than that (0.005) of an identical solution exposed to the conditions of a repetitive scan with a period of 0.5 min. By use of filtered light, it was found that the range of wavelengths responsible for excitation was below 430 nm.
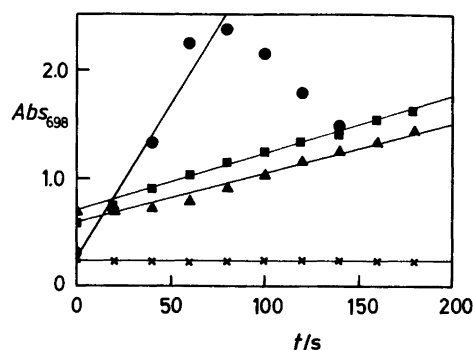
Two other substrates, N-methylphenothiazine ($E°$ = 0.94 V vs. NHE) and tris(4-methoxyphenyl)amine ($E°$ = 0.76 V vs. NHE) were dissolved in TFA and sealed in EPR tubes after being degassed with argon. They were kept in the dark and monitored intermittently by EPR spectroscopy. The very slow build-up of the corresponding radical cations followed first-order kinetics with rate constants $\approx 4 \times 10^{-7}$ and 2×10^{-7} M^{-1} s^{-1}, respectively.

Thus it appears that TFA can oxidize substrates with $E° < 1$ V in thermal electron transfer reactions. These are extremely slow for the three substrates included here, but faster for substrates such of ferrocene ($E°$ = 0.60 V vs. NHE) and decamethylferrocene ($E°$ = 0.16 V vs. NHE). However, photochemical production, even in rather diffuse

Table 1. Values of d[Abs]/dt (t taken to be 200 s) for the reactions of Figs. 2 and 3 and a few others.

Light source	Cosolvent (3/2 v/v)	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
Spectrophotometer light[d]	CH_2Cl_2	Ar	0.11
Spectrophotometer light[d]	CCl_4	Ar	0.05
Semi-darkness[e]	CH_2Cl_2	Ar	0.0015
Semi-darkness[e]	CH_2Cl_2	O_2	0.004
Semi-darkness[e]	CCl_4	Ar	<0.001
Darkness	CH_2Cl_2	Ar	0.0003

[a]300 W 'sun lamp' (Osram ULTRAVITALUX) at a distance of 15 cm. [b]Near a north-facing window. [c]Conventional ceiling neon light. [d]In spectrophotometer cell housing, shutter open, semi-dark room. [e]In spectrophotometer (HP-8452A) cell housing, shutter closed between measurements, semi-dark room.

daylight, of radical cations is much more efficient and extends to substrates as difficult to oxidize as perylene[10f,i] ($E° = 1.30$ V vs. NHE), thianthrene[10a,b] ($E° = 1.52$ V vs. NHE) and pyrene[10f,i] ($E° = 1.60$ V vs. NHE). Oxygen does affect both the thermal and photochemical reaction but to a relatively small extent.

Our studies have demonstrated that great care must be exercised in the use of TFA as a medium for organic reactions in view of its excellent electron-accepting properties with respect to photo-excited species.[14] Carbon tetrachloride/TFA should be even worse because of the additional effect of the similarly strong electron acceptor, CCl_4.[15] Many radical cations and/or radical cation dependent phenomena that have been observed in TFA-containing solvents are presumably derived from the incursion of photochemistry.

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