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Limits to Oxidation of Organic Substrates. SET Oxidative Processes of Commonly Used Solvents as Revealed through the Photochemical Reaction with 1,2,4,5-Benzenetetracarbonitrile

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Abstract: The chemical reactivity upon single electron transfer of some common solvents has been explored. This has been obtained by using photo excited benzene-1,2,4,5-tetracarbonitrile (TCB) as the oxidant. Under this condition acetonitrile, isobutyronitrile, methanol and trifluoroethanol all undergo α-deprotonation from their radical cations giving alkyl radicals which are trapped by $TCB^{-\cdot}$ and yield alkylbenzenetricarbonitriles or products derived from them. The reaction of the two aliphatic nitriles occurs only in the presence of protic additives, and is accompanied by a different fragmentation leading to methyl (or respectively isopropyl) radicals. Trifluoroacetic acid decarboxylates, probably via oxidation of the anion. TCB irradiation in neat methanol (rather than in MeOH-MeCN mixtures) leads to protic addition onto the cyano group, finally giving dicyanoindoles.

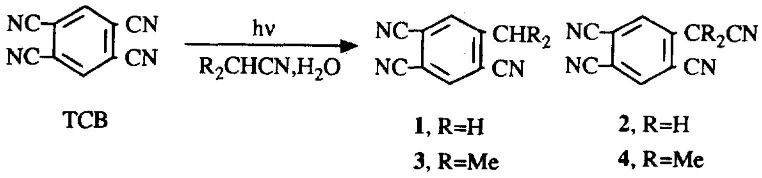
Oxidation of organic substrates, most often through the use of metal oxidants[1] or anodically[2] is an important tool in synthetic chemistry. A reaction resulting in an overall oxidation may involve a variety of mechanisms, e.g. hydrogen abstraction or metal insertion in a C-H bond, but recently there has been an increasing interest in oxidations proceeding via single electron transfer (SET). Due to the need for mutual solubility, such processes are usually carried out in non aqueous solvents. The desirable properties of a solvent for this aim are that it is polar, in order to dissolve the oxidising salt or, in the case of electrochemical experiments, the supporting electrolyte; that its E_{OX} is conveniently high, so that it does not interfere with the desired substrate oxidation; that it is a poor nucleophile, in order to avoid trapping of the cationic species formed in the process (unless this is required in the planned synthesis). Solvents which may serve this purpose are e.g. acetonitrile and trifluoroacetic acid. Obviously, there is an interest in applying such methodologies also to hard to oxidise substrates, and there competitive oxidation of the solvent becomes a problem.

Therefore, it is useful to establish which are the reactions which the solvent may undergo during an oxidative process, in particular via the SET mechanism, since obviously such a reaction could not be avoided under whichever oxidative condition, and this puts a limit to the use of the solvent. For this aim oxidation with inorganic salts or the anodic technique are not well suited, as it is not always easy to understandhow the initial SET step intervenes from the structure of the end products, since these arise from a complex reaction sequence, and furthermore the process is influenced by salts and nucleophiles present. On the other hand, the recently introduced photoinduced SET[3] is better suited for a model study. In this case the excited state of an organic molecule is used as the short-lived oxidant, and thus it is possible to study the oxidation in neat organic solvents. Furthermore, the primary intermediates (radical cations and radicals) are not over-oxidised, due to the extremely low steady state concentration of the oxidant, and are less subject to competing reactions, provided that the photosensitizer is chosen among those having stable and non nucleophilic radical anions. Indeed, previous experience shows that the final products obtained under this condition are logically derived from a direct reaction of the radical cation formed in the first SET step.

Convenient photochemical oxidants meeting these requirements are aromatic nitriles, since their singlet excited states are photophysically well characterised,[3,4] and chemically unreactive (not susceptible e.g. to ionic addition),[5] but are strong oxidants and, since they fluoresce efficiently, interaction with a donor can be monitored by emission quenching. Furthermore, the radical anions formed in the SET step are persistent and non-nucleophilic species.[6] Among the nitriles we chose 1,2,4,5-benzenetetracarbonitrile (TCB), in view of its convenient oxidation potential (see below).

RESULTS

Irradiation in Neat Acetonitrile and Isobutyronitrile and the Effect of Moisture. When a solution of TCB in MeCN purified by passing through an alumina column and refluxing and distilling from CaH_2 was irradiated for 3 h, no appreciable decomposition of the arene took place. When a similar solution containing 0.1% H_2O was irradiated for the same time, TCB was almost completely converted to give two products, the methylbenzenetricarbonitrile **1** and the benzeneacetonitrile **2**, easily identified from their spectroscopic properties (Scheme 1, Table 1). These were both primary photoproducts, as demonstrated both by small-scale experiments at different irradiation times (see Fig. 1a) showing the parallel formation of both compounds, and by separated irradiation of **2** in MeCN. The role of water was explored by monitoring the conversion of TCB to **1** and **2** in the presence of different amounts of water. In every case the two products were formed in a parallel way, but their rate of formation decreased at higher water percentage (see Fig. 1b). The formation of **1** by irradiation of TCB in MeCN had been previously reported,[7] although the role of water had not been pointed out. Commercially available acetonitrile usually contains ca 0.1% H_2O, and under this condition TCB reacts efficiently. We noticed that this photo reaction took place at different rates when solvents from different firms were used, and that simply passing over an alumina column was not sufficient to quench the reaction, but a more rigorous drying method was required (see above).

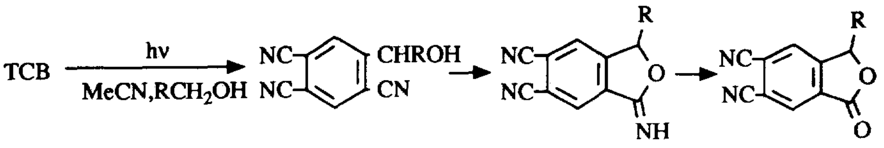


TCB

1, R=H
3, R=Me

2, R=H
4, R=Me

Scheme 1



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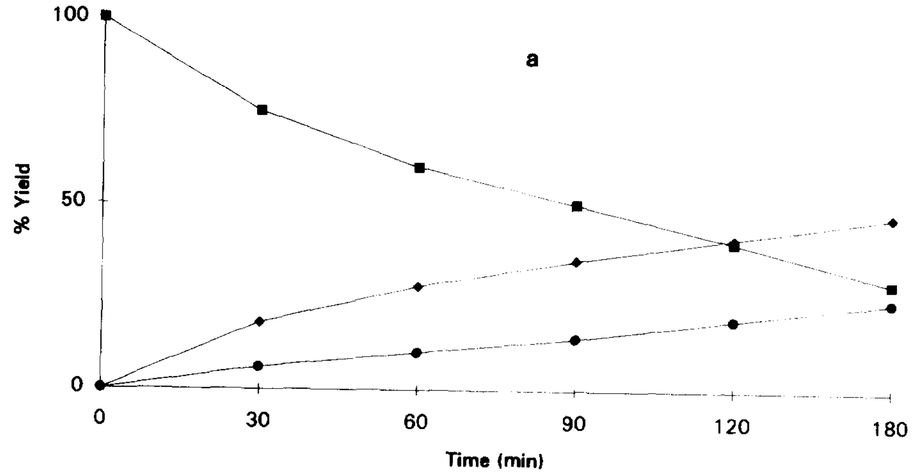
6, R=H
7, R=CF_3

5, R=H

Scheme 2



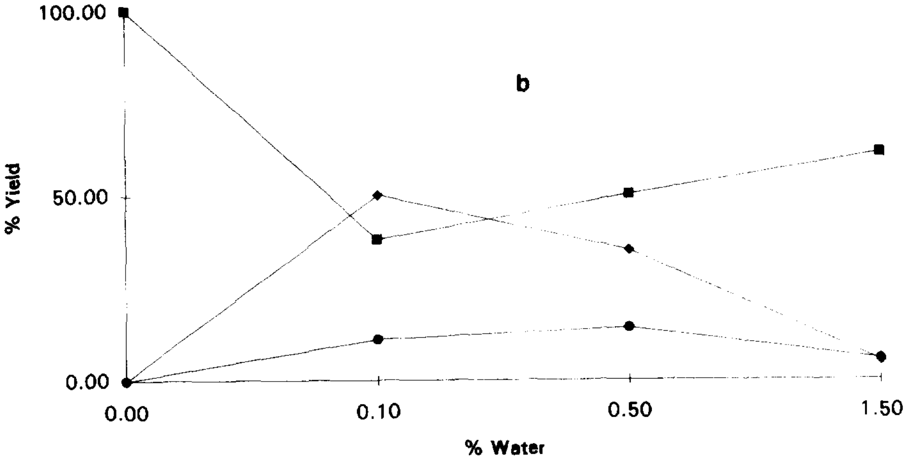


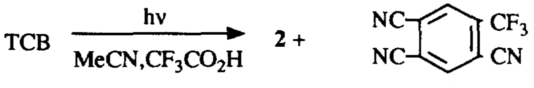
Fig. 1. TCB consumed (squares), products 1 (diamonds) and 2 (circles) formed: a. Time evolution in the presence of 0.5% water. b. After irradiation for 90 min in the presence of various amounts of water.

Irradiation of a solution of TCB in isobutyronitrile (used as received) required several days for consuming the reagent and led again to two benzenetricarbonitriles (products **3** and **4**, the latter one largely predominating). On the other hand, the reaction proceeded in some hours in the presence of 0.5% water. The formation of the two alkylated nitriles had been previously reported, but contrary to what suggested by the previous researchers,[7] **3** was not a product of secondary photolysis of **4**, as checked in a separate experiment irradiating **4**, and in fact both products were formed from TCB in a parallel way, similarly to the acetonitrile case.

Irradiation in Acetonitrile in the presence of Other Protic Additives. Similar irradiation of TCB in the presence of small amounts (0.5 to 1.5%) of methanol followed by chromatography led to the isolation of a single main product, which was identified from its properties as the phthalide **5**; small amounts of products **1** and **2**, as well as minor coloured components which were not identified were also present (see Scheme 2). However, immediate GC and NMR examination of the raw photolysate showed that compound **5** was a minor component at this stage and the main product was a different aromatic compound which slowly converted into **5** both upon standing (with some decomposition) and during chromatography; this was not fully characterised (see Experimental), but analogy with the trifluoroethanol experiment (see below) suggested that it was the iminoether **6**. It was also noted that the irradiated solution became acidic. The rate of the reaction was only slightly affected in the presence of higher MeOH proportions, and the course of the reaction did not change; e.g. compound **5** was again the major product in MeCN-MeOH 5:1 (v/v).

Irradiation in anhydrous MeCN in the presence of 0.5-1.5% trifluoroethanol led to no measurable consumption of the nitrile for several hours, provided that thoroughly dried solvents were used, while in wet (0.1% water) acetonitrile the irradiation of TCB gave products **1** and **2** at about the same rate as in the absence of the alcohol. On the other hand, with 10% CF_3CH_2OH in MeCN the trifluoromethyliminoether **7** (sufficiently stable to be chromatographically purified, even if slowly decomposing in solution) was formed along with the benzotrinitriles **1** and **2** (see Scheme2).

Finally, upon irradiation of TCB in MeCN containing 0.15% trifluoroacetic acid, a rather slow reaction took place, and gave 5-trifluoromethyl-1,2,4-benzenetricarbonitrile (**8**) along with a considerable amount of **2** (see Scheme 3).



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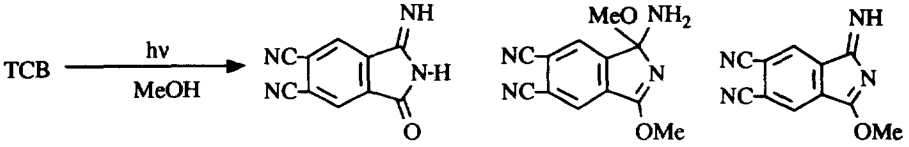
Scheme 3



9 **10** **11**

Scheme 4

Table 1. Isolated products form the irradiation of TCB in various solvents.

Solvent	Irradiation time	%TCB converted	Products (%Yield)
MeCN, anh.	2 d	ca 0	
MeCN, 0.1% H_2O	3 h	82	**1**(55), **2**(45)
i-PrCN	4 d	80	**3**(2), **4**(30)
i-PrCN, 0.5% H_2O	4 h	100	**3**(15), **4**(40)
MeCN, 0.1% MeOH	3 h	92	**1**(6), **2**(5), **5**(60),
MeCN, 20% MeOH	3.5 h	70	**5**(25)
MeCN, 10% CF_3CH_2OH	4 h	54	**1**(tr), **2**(10), **7**(44)
MeCN, 0.15% CF_3CO_2H	14 h	63	**2**(30), **8**(35)
MeOH	6 h	45	**9**(40), **10**(41), **11**(13)

Table 2. Quenching of the TCB fluorescence in acetonitrile.

	K_{SV}, M^{-1}	k_q, $s^{-1}M^{-1}$
MeOH	40	3.7×10^9
H_20	1	1×10^8
CF_3CH_2OH	a	$<<1 \times 10^7$
CF_3CO_2H	a, b	$<<1 \times 10^7$

a. too small to be measured. b. ref.7 has 0.02 M^{-1}

Irradiation in Neat Methanol. The irradiation of TCB in MeOH required a longer time for conversion than in MeCN, and gave a mixture of polar derivatives, which were separated by chromatography and identified from their spectroscopic properties as the isoindole derivatives **9**, **10** and **11** (see Scheme 4). Minor amounts of intensely blue and red-coloured components were also present, but were not identified.

Spectroscopic Experiments. The longest-wavelength absorption of TCB in MeCN was a structured band (λ_{max} at 315 nm) and the, likewise structured, emission band had λ_{max} =334 nm. Water caused a limited quenching, and methanol a much stronger one (Table 2). In neat methanol there was no major change in the absorption spectrum, although the bands were less sharp, and virtually no fluorescence was detected. Trifluoroethanol and trifluoroacetic acid did not appreciably quench the TCB fluorescence in MeCN.

DISCUSSION

The aim of the present study is that of obtaining evidence on the oxidation pathway of some common organic solvents under bona fide SET conditions. Indeed, it can be assumed that such a pathway is followed in the reaction with singlet excited TCB. The alternative possibility of a hydrogen abstraction mechanism, often competitive with metal oxidants, can be discarded since aromatic nitriles are well known to be excellent electron acceptors and not hydrogen abstractors in the excited state, and furthermore the type of products obtained fit well with an electron transfer initiated process (see below). The obvious way to monitor the first step in such a reaction is to measure the fluorescence quenching. A problem arises from the fact that TCB^{1*} is such a powerful oxidant [$E_{red}(TCB^{1*})= E_{red}(TCB) + E_{exc}=3.4$V vs SCE].[3,4] This makes it difficult to devise conditions where *no* SET takes place, i.e. to find a reference zero point. As an example, excited TCB oxidises alkanes,[8] and one has to consider, as it has been done by Tsujimoto at al,[7] the possibility that also MeCN function as a donor.

However, since the emission lifetime of TCB in deaerated MeCN is 10.8 ns,[9a] very similar to that measured for other aromatic nitriles such as benzene-1,4-dicarbonitrile or naphthalene-1,4-dicarbonitrile which have a much lower E_{red} in the excited singlet state,[4, 9b] it appears reasonable to assume that electron transfer in neat MeCN according to eq.1 is inefficient, $k_{et} << 1 \times 10^7\ M^{-1}s^{-1}$

$$TCB^{1*} + MeCN \quad \rightarrow \quad TCB^{-\cdot} + MeCN^{+\cdot} \qquad (1)$$

Indeed, SET is largely endoergonic, since it is known that MeCN has a high IP (12.21 eV,[10a] which would make E_{ox}= 4.84 V vs SCE using the Miller equation for the conversion)[10b], even if a quantitative rationalisation appears improper because of the uncertain IP/E_{ox} relation in this range and because in neat acetonitrile one has static rather than dynamic quenching.

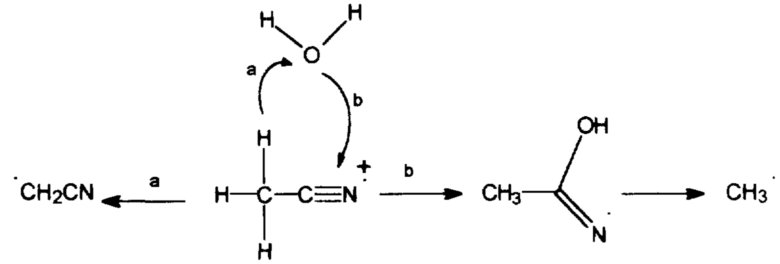
Other solvents such as trifluoroethanol and trifluoroacetic acid do not measurably quench the fluorescence in MeCN solution, and thus electron tranfer occur in these cases at most to the same degree as with MeCN, while with better donors such as MeOH or H_2O quenching in MeCN is well measurable (see Table 2) and thus SET is more efficient than with MeCN.

Our experiments show that in rigorously dried acetonitrile the redox process in eq. 1 leads to no irreversible chemical reaction, and small fraction of radical ions formed according to eq. 1 decay only by back electron transfer regenerating the ground state reagents. On the other hand, in the presence of moisture the irradiation of TCB gives products **1** and **2**. A rationalisation that we first considered for this reaction is that under this condition water is oxidised (SET to TCB^{1*}) and the OH· radicals thus produced abstract hydrogen from the solvent.

$$TCB^{1*} + H_2O \rightarrow \quad TCB^{-\cdot} + H_2O^{+\cdot} \quad \rightarrow \quad OH^{\cdot} + H^{+} \qquad (2)$$

This would explain the formation of compound **2** but not of **1**, however, and apart from this, that such a mechanism does not apply is shown by the decrease of the rate of formation of both compounds **1** and **2** with increasing water content. This is shown in Fig. 1b, where it appears that the optimum condition for the reaction is 0.1% water, where only 5% of singlet TCB is quenched by the additive, while a dramatic drop of the efficiency takes place e.g. at 1.5% water, where *ca* 45% is quenched. The deactivation is probably due to the hydrogen bonding with TCB, analogously to the methanol case (see below).

Thus, the reaction is due to an efficient reaction of water with the small amount of MeCN radical cations formed according to eq.1, not to quenching by water of the excited state (eq.2). As is shown in Scheme 5, this may be envisaged to occur in two ways, viz either through path a where water assists proton transfer from the acetonitrile radical cation, or through path b, where nucleophilic addition to the π bond leads to an iminoether radical expected, like a carboxy radical, to undergo C-C bond fragmentation and to give an alkyl radical.[11] In both cases, the alkyl radicals thus formed are trapped by the TCB radical anion. giving the observed products of ipso alkylation, a reaction observed with several other radicals.[12] It is worthwhile to consider in more detail the mechanism of the radical ion fragmentation.



Scheme 5

It is well known that ionisation brings about a conspicuous bond weakening, and the bond dissociation energy for a given bond in a radical cation

$$R\text{-}X^{+\cdot} \rightarrow R\cdot + X^+ \qquad (3)$$

can be evaluated on the basis of the BDE of the neutral substrate through a thermochemical cycle leading to eq.4

$$BDE(R\text{-}X^{+\cdot}) = BDE(R\text{-}X) - E_{ox}(R\text{-}X) + E_{ox}(X\cdot) \qquad (4)$$

Evaluation of the free energy change for deprotonation of the acetonitrile radical cation can be done in this way, and results, as in analogous cases,[3c,13] to be markedly negative ($\Delta G < -10$ kcal mol^{-1}). This is quite a general property of radical cations, which have been shown to behave as strong C-acids, i.e. $BDE(R\text{-}X^{+\cdot})$ is often a small or negative quantity when X=H, due to the largely negative value of $E_{ox}(H)$.[3c,13]

On the other hand, it has previously been observed with several substrates that deprotonation is relatively slow even if $BDE(R\text{-}H^{+\cdot})$ is negative, so that, when fragmentations of a different electrofugal group from the radical cation (eq.3, $X \neq H$) is possible even with a slightly positive ΔG, this is kinetically favoured over deprotonation.[3c,13] This is due to the fact that detaching a proton from an unpolarized C-H bond requires an extensive internal and external reorganisation and thus involves a more considerable barrier than when a larger and generally more delocalized organic cation is cleaved, and is in accordance with the present finding that, in order to compete with back electron transfer, deprotonation requires assistance by a cosolvent capable to form hydrogen bonds such as water. Likewise, the further characteristics of the reaction are rationalised by this scheme. Thus, the slowness of deprotonation leaves room for a different process, water addition to the π bond, to takes place; on the other hand, when the C-H bond is weaker, as with *i*-PrCN, deprotonation competes more efficiently with addition.

A different situation arises in the presence of methanol. Here the reaction clearly depends on the quenching of singlet TCNB by the additive. The maximum reaction rate (both of TCB consumption and product **5** formation) is optimal at 0.5-1% MeOH where 85-92% of TCB^{1*} is quenched by the alcohol, and decreases somewhat only a much higher MeOH content (e.g. it decreases by 1/3rd with 20% with respect to 1% MeOH, and the reason of this effect is discussed below). The reaction clearly involves deprotonation of the methanol radical cation (eq.5)

$$TCB^{1*} + MeOH \quad \rightarrow \quad TCB^{-\cdot} + MeOH^{+\cdot} \quad \rightarrow \quad {}^{\cdot}CH_2OH \qquad (5)$$

and coupling of the hydroxymethyl radical with $TCB^{-\cdot}$ as above to yield a benzyl alcohol (product **12** in Scheme 2). Since the medium becomes acidic during irradiation, acid-catalysed nucleophilic ring closure[14] to yield the cyclic iminoether **6** takes place directly in the irradiated solution. In turn, this is further hydrolysed to the phthalide **5**, both in solution and during chromatographic work up (Scheme 2).

Thermochemical considerations show that also in this case α-depronation of the radical cation is an exothermic process, and although there is no precedent for such a photosensitised reaction with alcohols, α-deprotonation from aliphatic ethers has been reported.[15] Noteworthy is that C-H deprotonation is favoured over O-H deprotonation not only thermodynamically (see eq.4: the electrofugal group is the proton in both cases, and thus the difference is given by the bond energy in the neutral molecule; thus, the weaker C-H bond is fragmented in preference to the O-H bond) but also kinetically (assistance by hydrogen bonding is obviously afforded by MeOH itself in this case).

Trifluoroethanol does not quench appreciably the TCB fluorescence in MeCN, and indeed SET to TCB^{1*} is expected to be strongly endoergonic. Accordingly, when present in small amounts this additive causes no reaction. When its proportion in the mixed solvents is sufficiently high (10%, see Table 1), CF_3CH_2OH participates to quenching, and SET to TCB, although hardly more efficient than with MeCN, is sufficient to induce α-deprotonation and thus alkylation of TCB (also in this case the higher thermodynamic and kinetic acidity of the C-H bond with respect to the O-H bond is confirmed). Since this alcohol is such a poor donor, SET from MeCN continues to occur, and side-products arising from its oxidation are formed, or at least this holds for the case of **2**, since CF_3CH_2OH is capable of assisting proton transfer through hydrogen bonding, while product 1, the formation of which requires nucleophile addition is, as expected, formed only in traces with this non nucleophilic additive.

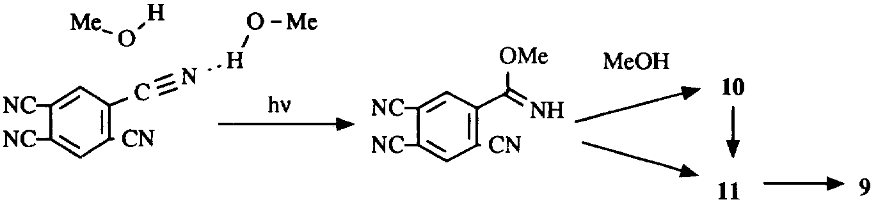
Trifluoroacetic acid is an extremely weak donor. Thus electron transfer quenching of TCB is expected to be negligible, while the possibility of quenching by protonation may be envisaged (eq. 5), in view of the fact that mineral acids do quench the TCB fluorescence.[16]

$$TCB^{1*} + S\text{-}H \quad \rightarrow \quad TCBH^{+} + S^{-} \qquad (6)$$

Actually, the experiment shows that CF_3COOH does not quench the TCB fluorescence appreciably in MeCN (see Table 2). Despite this fact, the reaction occurs at a low concentration of this additive (1.5×10^{-2} M); under this condition, direct quenching of TCB^{1*} either by proton or by electron transfer (viz either similarly to eq.2 or 6) is precluded. The most reasonable possibility is that, due to significant ionisation of this acid in MeCN, the anion may be directly involved in the SET process, and the carboxy radical thus formed undergoes fast decarboxylation, followed by trapping of the trifluoromethyl radical by $TCB^{-\cdot}$ similarly to the previous cases.

$$TCB^{1*} + CF_3COO^- \rightarrow TCB^{-\cdot} + CF_3COO^\cdot \rightarrow CF_3^\cdot \qquad (7)$$

Quenching by the low amount of anion present is slow and leaves room for the formation of product 2 with the mechanism seen above.



Scheme 6

The radical substitution of TCB obtained in MeCN-MeOH does not occur in neat methanol, where nucleophilic addition to the nitrile group is the only reaction detected, and reasonably occurs according to Scheme 6. Product 9 apparently results from partial hydrolysis of compound 11 during chromatographic work-up. The small change in the uv spectrum of TCB in MeOH vs that in MeCN suggests that a weak interaction with the protic solvent occurs already in the ground state, and this must be the key factor, since products 9-11 are the main products only in neat MeOH, and are formed in trace amounts e.g. in 20%MeOH-MeCN. The interaction is expected to be larger in the excited state, which is certainly more basic (see e.g. the quenching by mineral acids). In the case of benzonitrile, previous work had demonstrated that no photoinduced nucleophile addition takes place despite the expected increased basicity of the nitrile group, while in contrast phenylacetylene does undergo ionic addition in the excited state.[5] However, the present experiments show that the additional substitution in TCB activates solvent addition, and this becomes a significant, if unefficient (see the long irradiation time required, Table 1) process. The fact that when the alcohol proportion in the solvent is large TCB becomes increasingly hydrogen-bonded explains that the normal SET pathway is progressively quenched, and a drop of the overall TCB consumption rate (and, more rapidly, of the formation of 5) results by irradiation of MeCN solutions containing large amounts of MeOH (see above).

In conclusion, we have identified the chemistry occurring with some common solvents under condition of single electron tranfer using TCB both as the oxidant and as a trap to reveal the formation of radicals. With methanol, but also with much weaker donors such as trifluoroethanol and aceto- and isobutirronitrile the radical cations are formed, although inefficiently, and undergo α-deprotonation. With the last two solvents, the process occurs only in the presence of water or other protic additives, and is accompanied by a different fragmentation, leading to methyl (or isopropyl) radicals via previous nucleophilic addition to the triple bond. One of the consequences of this work is that MeCN is indeed an excellent solvent for oxidation processes, provided that it is rigorously purified, and a sensitive test of its purity (whether a photochemical reaction of TCB occurs or not) is offered. Although we did not extend the exploration further, it can be safely assumed that other common solvents, e.g. acetamides will also undergo α-deprotonation under such conditions. Another diagnostic reaction is the C-H rather than O-H deprotonation of alcohols when the radical cation is involved. Carboxylic acids on the other hand are decarboxylated.

From the photochemical point of view this work confirms the exceptional oxidising properties of TCB in its singlet excited state and the stability of the corresponding radical anion, which persists during the fragmentation of the substrate radical cation even under protic and acidic conditions, and finally couples with the alkyl radicals formed in the fragmentation.

EXPERIMENTAL

General. 1,2,4,5-Benzenetetracarbonitrile (Aldrich) was used as received. Acetonitrile was anhydrified by passing over an activated alumina column, then refluxing over CaH_2 for 1 day, and finally distilling directly into the reaction vessel. Isobutirronitrile (Aldrich) was used as received. ^1H and ^{13}C spectra were recorded on a Brucker AC 300 MHz spectrometer and chemical shifts are reported downfield form Me_4Si. Uv spectra were measured by means of a Cary 19, fluorescence spectra of a Aminco MPF, and elemental analyses of a Carlo Erba instrument. The course of the photochemical reactions was monitored by glc (methylsilicone column, 25mx0.2mmx0.3μm), with dodecane as the internal standard. Chromatographic separation was obtained on Merk 60 silica gel column eluting with cyclohexane - ethyl acetate mixtures.

Photochemical Reactions. A solution of TCB (25 mg) in the appropriate solvent or solvents mixture (20 mL) in a quartz tube capped with a serum septum was deaerated by flushing with argon for 10 min and irradiated by means of a multilamp apparatus fitted with 6x20W phosphor-coated lamps (center of emission, 320 nm). The contents of 4 such tubes were reunited, the solvent evaporated and the residue chromatographed on silica gel.

Photochemical Products. The benzenetrinitriles **1** and **3** have been previously characterized.[9a] The main characteristics of new products are reported below.

2,4,5-Tricyanobenzeneacetonitrile (2). Mp 95-102°C (Found: C, 69.0; H, 2.1; N, 29.0. Calc. for $C_{11}H_4N_4$: C, 68.74; H, 2.10; N, 29.16); ^1H NMR [$(CD_3)_2CO$] δ 4.5 (s, 2H), 8.4 (s, 1H), 8.65 (s, 1H); ^{13}C NMR [$(CD_3)_2CO$] δ 22.7 (CH_2), 114.2, 114.25, 114.6 (CN), 115.5 (CN), 116.4 (CN), 117.8, 120.0 (CN), 134.7 (CH), 138.3 (CH), 141.3.

α,α-Dimethyl-2,4,5-tricyanobenzeneacetonitrile (4). Mp 138-140°C (Found: C, 70.7; H, 3.7; N, 25.3. Calc. for $C_{13}H_8N_4$: C, 70.89; H, 3.66; N, 25.44); ^1H NMR ($CDCl_3$) δ 2.05 (s, 6H), 8.2 (s, 1H), 8.23 (s, 1H); ^{13}C NMR δ ($CDCl_3$) 26.8 (CH_3), 37.7, 112.9; 113.6; 114.3(CN), 115.7(CN), 116.3 (CN), 120.0, 120.6 (CN), 132.0 (CH), 139.4 (CH), 148.8.

5,6-Dicyano-1(3H)-isobenzofuranone (5). Mp 103-105°C (Found: C, 64.9; H, 2.3; N, 14.5. Calc. for $C_{10}H_4N_2O_2$: C, 65.22; H, 2.19; N, 14.21); ^1H NMR [$(CD_3)_2CO$] δ 5.65 (s, 2H), 8.45 (s, 1H), 8.53 (s, 1H); ^{13}C NMR [$(CD_3)_2CO$] δ 70.4 (CH_2), 115.1 (CN), 115.3 (CN), 116.2, 119.8, 129.6 (CH), 130.4, 130.9 (CH), 152.2, 168.0; MS m/e 184 (17%), 155 (100%). In the raw photolysate the main product shows ^1H NMR [$(CD_3)CO$] δ 5.55 (s, 2H), 8.32 (s, 1H), 8.47 (s, 1H), compatible with the structure of the furanimine **6**.

5,6-Dicyano-3-trifluoromethyl-1(3H)-isobenzofuranimine (7). This compound is not very stable in solution. The sample from chromatographic separation was not recrystallized. ^{1}H NMR [(CD$_3$)$_2$CO] δ 6.4 (q, J=4Hz, 1H), 8.45(s, 1H), 8.55 (s,1H), 9.0 (bs, exch, NH); MS, 251(40%), 183 (100%); ^{13}C NMR [(CD$_3$)CO] δ 79.2 (CH, q, J=30 Hz), 116.0 (CN), 116.1 (CN), 119.7, 120.4, 123.7 (CF$_3$, J=270 Hz), 129.3 (CH), 129.5 (CH), 134.9, 142.3, 160.3; IR (KBr) 3320, 1704, 1175 cm^{-1}.

5-Trifluoromethyl1,2,4-benzenetricarbonitrile ***(8)***. Mp 133-135 °C (Found: C, 54.1; H, 0.9; N, 18.8. Calc. for $C_{10}H_2N_3F_3$: C, 54.31; H, 0.91; N, 19.00); ^{1}H NMR [(CD$_3$)$_2$CO] δ 8.82 (s, 1H), 8.98 (s, 1H); ^{13}C NMR [(CD$_3$)$_2$CO] δ 114.3 (CN), 114.8 (CN), 115.1 (CN), 115.89, 115.92, 121.7 (CF$_3$, J$_{C\text{-}F}$ 272 Hz), 121.8, 133.5 (CH, q, J= 5 Hz), 137.0 (q, J=32 Hz), 141.1 (CH); IR (KBr) 1120 cm^{-1}.

5,6-Dicyano-1,3-isoindolonimine ***(9)***. Mp >290 °C (Found: C, 60.9, H, 2.1; N, 28.2. Calc. for $C_{10}H_4N_4O$: C, 61.22; H, 2.06; N, 28.57); ^{1}H NMR [(CD$_3$)$_2$SO] δ 8.48 (s, 1H), 8.68 (s, 1H), 10.42 (bs, exch, NH), 10.63 (bs, exch, NH); ^{13}C NMR [(CD$_3$)$_2$CO] δ 115.6, 115.7, 115.8, 116.4, 127.1 (CH), 127.7 (CH), 131.8, 132.4, 147.6, 167.2; IR (KBr) 3275, 3043, 1730, 1673 cm^{-1}; MS 196 (100%).

1-Amino-5,6-dicyano-1,3-dimethoxy-(1H)-isoindole ***(10)***. Mp ca 200°C dec (Found: C, 59.9; H, 4.2; N, 23.0. Calc. for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.13); ^{1}H NMR [(CD$_3$)$_2$SO] δ 3.27 (s, 6H), 7.53 (bs, exch, NH$_2$), 8.29 (s, 1H), 8.40 (s, 1H); ^{13}C NMR [(CD$_3$)$_2$SO] δ 51.1 (OCH$_3$), 116.24, 116.26, 116.5 (CN), 116.9 (CN), 117.9, 126.2 (CH), 127.2 (CH), 138.3, 152.0, 160.8; IR(KBr) 3387, 3370, 1672 cm^{-1}; MS (EI) 243 (0.4%), 180 (100%).

5,6-Dicyano-3-methoxy-(1H)-isondolimine (11). Mp > 250°C (Found: C, 62.5; H, 3.1; N, 26.3. Calc.for $C_{11}H_6N_4O$: C, 62.85; H, 2.88; N, 26.66); ^{1}H NMR [(CD$_3$)$_2$SO] δ 3.19 (s, 3H), 7.45 (bs, exch, NH), 8.25 (s, 1H), 8.37 (s, 1H); ^{13}C NMR [(CD$_3$)$_2$SO] δ 50.7 (OCH$_3$), 116.0, 116.1 (CN), 116.5 (CN), 125.9 (CH); 126.9 (CH), 138.0, 138.1; 153.0, 160.3; IR (KBr) 3358, 1699.

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