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Alkyl Radicals from *t*-Butyl Esters through Photoinduced Electron Transfer

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Abstract. Alkyl radicals are obtained under mild conditions from 1,2,4,5-benzenetetracarbonitrile SET photosensitized fragmentation of *t*-butyl esters. The same process occurs with undissociated carboxylic acids.

The Kolbe oxidation of the salts of carboxylic acids (eq.1) is known to have a photochemical parallel,[1] following either electron ejection upon direct irradiation[2,3] or electron transfer to a photosensitizer (eqs 2,3).[4]

$$\text{R-CO}_2^- \xrightarrow{-e} \text{R-CO}_2\cdot \longrightarrow \text{R}\cdot \qquad (1)$$

$$\text{PhCH}_2\text{CO}_2^- \xrightarrow{h\nu} \text{PhCH}_2\text{CO}_2\cdot + e_{aq} \longrightarrow \text{PhCH}_2\cdot \qquad (2)$$

$$\text{A}^* + \text{R-CO}_2^- \longrightarrow \text{A}^{-\cdot} + \text{R-CO}_2\cdot \longrightarrow \text{R}\cdot \qquad (3)$$

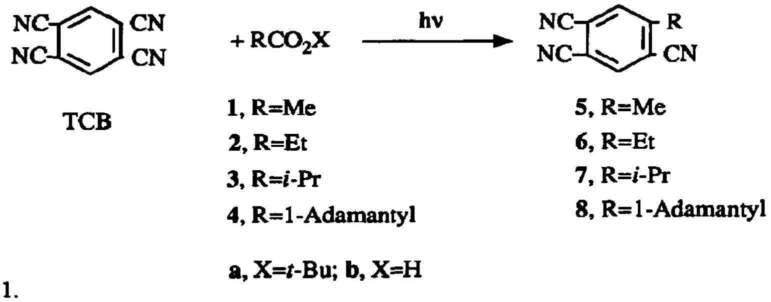
Most reported photodecarboxylations involve α-aryl,[1-4] α-thio,[4,5] α-oxo[6] derivatives and similar relatively easily oxidized acids. However, recent reports include decarboxylation of unsubstituted fatty acids induced by photochemical electron transfer (PET), with either 10-methylacridinium salts[7] or 1,2,4,5-benzenetetracarbonitrile (TCB)[8] as the sensitizer; in the first case, the carboxylate anion is involved, in the latter one it has been proposed that the undissociated acid is oxidized. This is an interesting proposal, and we thought that, if this is correct, it should be possible to extend the reaction to functional derivativatives of acids containing an electrofugal group different from the proton (eq.4, X≠H).

$$\text{A}^* + \text{RCO}_2\text{X} \longrightarrow \text{A}^{-\cdot} + \text{RCO}_2\text{X}^{+\cdot} \longrightarrow \text{RCO}_2\cdot \longrightarrow \text{R}\cdot \qquad (4)$$

In the frame of our continuing interest in new methods for the generation of radicals via PET reactions,[9] we presently report the successfull obtention of radicals from the *t*-butyl esters of aliphatic acids via TCB photosensitization, as well as data supporting the fragmentation mechanism of both acids and esters.

Irradiation of acetonitrile solutions of TCB in the presence of the *t*-butyl esters **1a-3a** (1 M) resulted in the formation of the alkyltricyanobenzenes **5-7** as the only aromatic products (isolated yields 25 to 60%, Scheme 1).[10] Thus, PET induced decomposition of esters according to eq.4 (X=*t*-Bu) was a viable path, and the alkyl radicals were trapped by $\text{TCB}^{-\cdot}$, following the general mechanism of PET alkylation of aromatics (Scheme 2, see the discussion below).[11] Repetition of the reaction with the corresponding acids (**1b-3b**) gave the same products, as previously reported.[8]

In order to define the mechanism of the sensitized decarboxylation, further experiments were carried out. As it appears in Table 1, both the esters and the acids quenched the fluorescence of TCB. We tested that a mineral acid (HClO_4) quenched the TCB fluorescence diffusion controlled (K_{SV} 136 M^{-1}). Quantum yields were measured (Table 1), and in the case of **2a** and **2b** it was observed that double reciprocal plots for the reaction quantum yield vs substrate concentration gave K_{SV} values rather close to those obtained from the fluorescence measurements, thus confirming that singlet excited TCB is the reactive state. Irradiation of TCB with adamantanecarboxylic acid gave the alkylated derivative **8** (50%).[12]



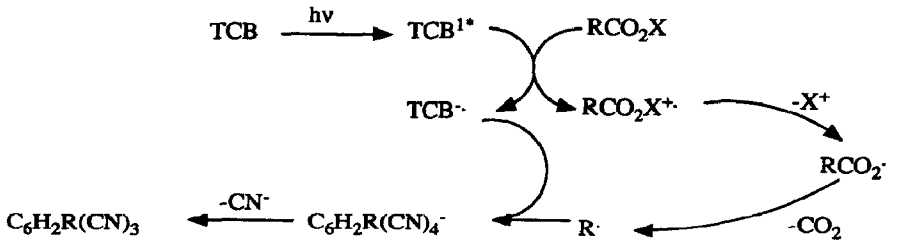
Scheme 1.

As detailed below, these data allow the conclusion that the TCB singlet excited state sensitizes the decarboxylation of both esters and acids, and that in the latter case the undissociated acid rather than the carboxylate anion is involved, and furthermore that electron rather than proton transfer is implied (eq.6 rather than eqs 3 or 5).

$$A^* + RCO_2H \longrightarrow AH^+ + RCO_2^- \qquad (5)$$

$$A^* + RCO_2H \longrightarrow A^{-\cdot} + RCO_2H^{+\cdot} \qquad (6)$$

Thus, 1) although TCB^{1*} is certainly more basic that the ground state, and indeed its emission is efficiently quenched by mineral acid, the dissociation of carboxylic acid in MeCN is too low for significant quenching of this short lived state (τ_S 10.8ns).[10b] 2) The quenching by the esters is similar to the quenching by the acids, confirming that the proton has no role. 3) Adamantanecarboxylic acid (**4b**), which is more easily oxidized than **1b**-**3b** but is not a stronger acid quench the TCB fluorescence near to diffusion controlled, indcating electron rather than proton transfer. 4) The calculated ΔG for electron transfer to singlet excited TCB is near to zero for acids and esters, and is markedly negative for **4b** (Table 1).



Scheme 2

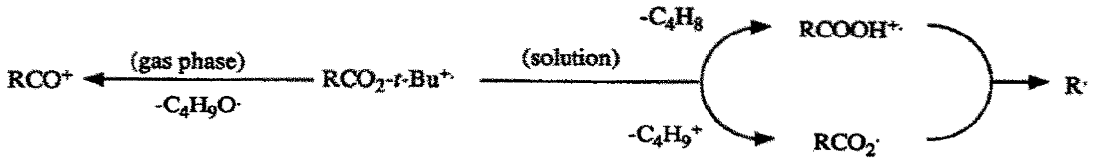
As for the following course of the reaction, the key step is obviously decomposition of the radical cations. It is unlikely that TCB$^{-\cdot}$ plays any role, since the radical anions of aromatic nitriles have been demonstrated to be strongly stabilized species and poor nucleophiles.[13] The relatively high quantum yield observed for TCB alkylation implies that fragmentation of both types of radical cations, viz deprotonation in the case of the acids (the solvent is the proton acceptor) and loss of the *t*-butyl group with the esters, is sufficiently fast to compete with back electron transfer. In the latter case, fragmentation may involve either a six-centered intramolecular hydrogen transfer, which would give the acid radical cation as above, or direct C-O bond cleavage liberating the *t*-butyl cation which then deprotonates (Scheme 3). If the first mechanism would apply, than a similar fragmentation (loss of isobutene) would be probably observed also in the mass spectrum. This is not the case, however (the acyl cation is the most abundant fragment in the spectrum of of *t*-butyl esters, with C(=O)-O rather than CO_2-R cleavage; on the other hand the chemistry of radical ions in solution is often different from the gas phase). A further support for this view comes from consideration of the relevant thermochemical cycles. These showed that the ΔG for fragmentation of the radical cation is largely negative not only for acids, but also for *t*-butyl esters, eqs.7,8.[14]

$$RCO_2H^{+\cdot} \rightarrow RCO_2\cdot + H^+ \quad \Delta G = -18\ \text{kcal mol}^{-1} \qquad (7)$$

$$RCO_2\text{-}t\text{-}Bu^{+\cdot} \rightarrow RCO_2\cdot + t\text{-}Bu^+ \qquad \Delta G = -9\ \text{kcal mol}^{-1} \qquad (8)$$

The final steps, fragmentation of the carboxy radicals, addition of the thus formed alkyl radicals to TCB^{-} and cyanide loss follow previously well documented paths (Scheme 2).[11]

These findings demonstrate once again the versatility of photoinduced SET and radical cation fragmentation for the generation of radicals from unconventional substrates under exceptionally mild conditions. The results with the *t*-butyl esters extend the oxidation to cases for which there is no precedent via electrochemistry or reaction with inorganic oxidants. Radicalic elimination of a *t*-butoxycarbonyl group may find use in synthesis.



Scheme 3

Table 1. Quenching constants of the TCB fluorescence (K_{sv}), calculated ΔG for electron transfer to TCB^{1*}, quantum yield of TCB alkylation in the presence of acids and *t*-butyl esters.

Substrate	K_{sv} mol^{-1}	ΔG_{et} eV	Φ(0.1M)	Φ_{lim}[a]	K_{sv}[a] mol^{-1}
1a	4.3	-0.15	0.12		
2a	7.3		0.11	0.23	10
3a	25.6		0.11		
1b	1.6	+0.19	0.22		
2b	4.3	+0.06	0.12	0.24	9
3b	7.6		0.15		
4b	124	-0.72			

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a. from doubly reciprocal plots of quantum yield of TCB alkylation vs donor concentration.

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12. ^{1}H NMR ($CDCl_3$) δ 1.8 (m, 6H), 2.2 (s, 6H), 2.25 (s, 3H), 7.98 (s, 1H), 8.07 (s, 1H)

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14. The bond dissociation energy for the radical cations is calculated through the formula $\Delta G(RX^{+\cdot}) = \Delta G(RX) + \Delta G_{ox}(X\cdot) - \Delta G_{ox}(RX)$, see ref.9. Where no solution phase redox parameters are available, IP are used. Unfortunately, this introduces a large uncertainity in the calculated values. Values used: AcOH, IP 10.87 eV; AcOMe, IP 10.50 eV; *t*-Bu·, ΔG_{ox} 0.09 V vs SCE, see Wayner, D.D.M.; McPhee,D.J.;Griller,D. *J.Am.Chem.Soc.*, 1988, *110*, 132.

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