2,4,4,6-Tetrabromocyclohexa-2,4-dienone: a New Electron Acceptor in the Photosensitized Oxidation of Unsaturated Substrates

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2,4,4,6-Tetrabromocyclohexa-2,4-dienone, usually used as a mild and selective brominating agent, acts as an electron acceptor in the sensitized photo-oxygenation of several unsaturated substrates; a mechanism is proposed.

Quenching of singlet excited sensitizers, such as 9,10-dicyanoanthracene, DCA [E^{red} = −0.98 V *vs.* standard calomel electrode (s.c.e.); ΔE_{0-0} = 2.90 eV], and 2,6,9,10-tetracyanoanthracene, TCA (E^{red} = −0.45 V *vs.* s.c.e.; ΔE_{0-0} = 2.94 eV), by electron donors D leads to a primary geminate radical ion pair of singlet multiplicity. In a polar medium, diffusion can lead to solvent-separated radical ions. Competing with this diffusion process is the reverse electron-transfer process to give the reactants in the ground state. The reduction of molecular oxygen by the DCA⁻ radical anion to the superoxide anion not only produces an oxygen species more reactive than molecular oxygen but also avoids, or at least reduces, the back electron-transfer process. In contrast, in the TCA systems, where for thermodynamic reasons the superoxide anion cannot be formed, the reverse electron-transfer process prevails over the reaction of the intermediate

radical cation D + with molecular oxygen, with the consequent low conversion of starting materials into products.[1]
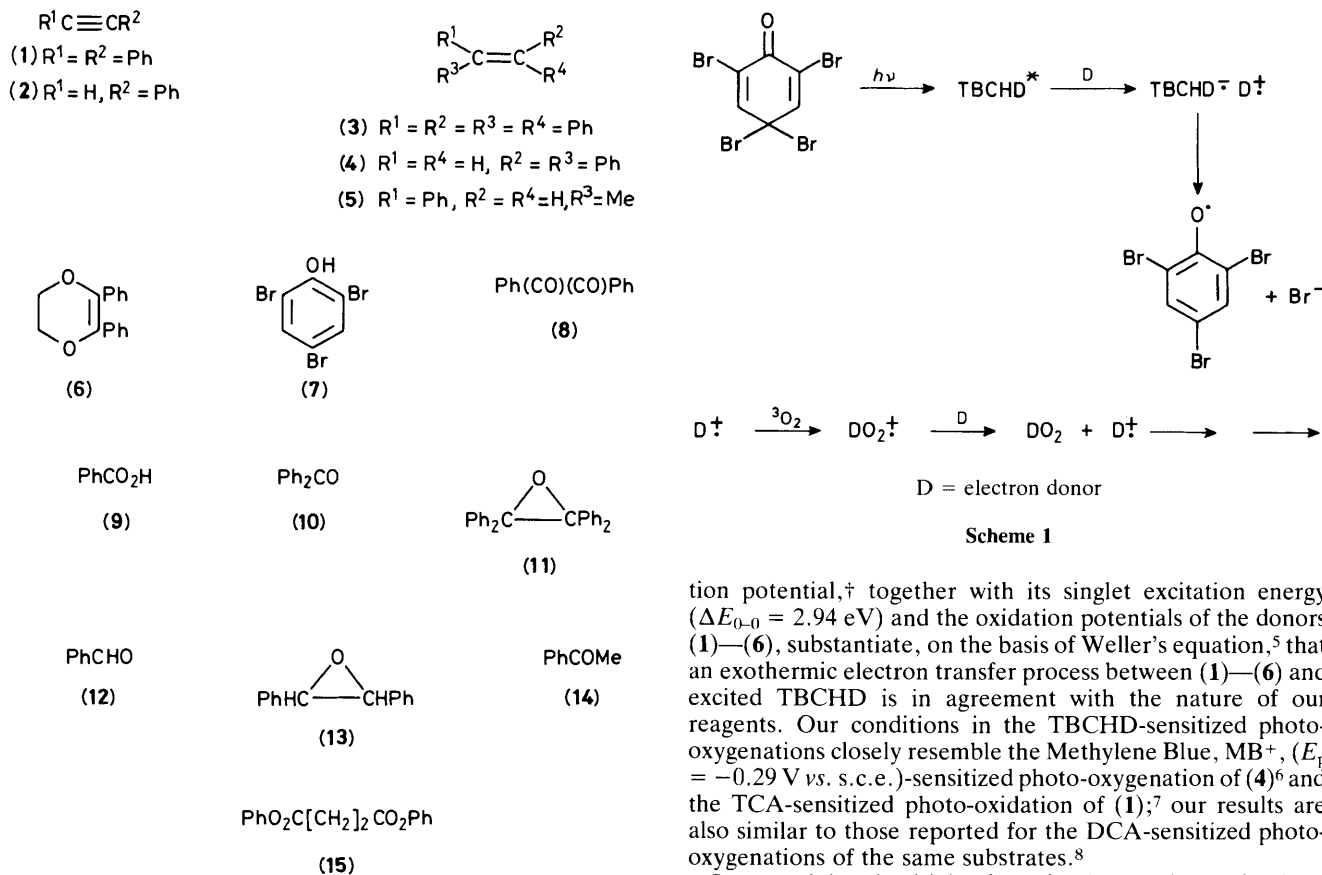
Therefore the main aims in photosensitized electron transfer oxidation experiments are to prolong the lifetime of the intermediate radical cation maximizing the cage-escape efficiency and to liberate the radical cation species from the radical ion pair, thus allowing its reaction with molecular oxygen. We have studied the photosensitized oxidation of several unsaturated substrates such as diphenylacetylene (1), phenylacetylene (2), tetraphenylethylene (3), *trans*-stilbene (4), α-methylstyrene (5), and 2,3-diphenyldihydro-1,4-dioxine (6) as induced by 2,4,4,6-tetrabromocyclohexa-2,4-dienone, TBCHD, usually used as a mild and selective brominating reagent.[2]

Typical experimental conditions are as follows: oxygen-saturated, dry acetonitrile solutions of the substrates (1)—(6)

Table 1

Substrate	E^{ox}/V	Irradiating wavelength(λ/nm)	[(7)]/M	ΔG/eV	Time/h	Products (% yield)[e]
(1)[i]	1.47[a]	300[b]		-1.82	18	(8)(42%),(9)(30%)[f,g]
(1)	1.47	300	8×10^{-3}		10	(8)(70%),(9)(17%)[g]
(2)	2[a]	300		-1.29	9	(9)(70%)
(2)	2		8×10^{-3}		5	(9)(80%)
(3)	1.33[a]	360[c]		-1.96	15	(10)(37%),[g](11)(12%)
(4)	1.51	360		-1.78	18	(12)(48%),[g](13)(36%), (8)(10%),(9)(6%)
(4)	1.51	360	8×10^{-3}		12	(12)(55%),(13)(30%),(8)(9%),(9)(6%)
(5)	1.62	360		-1.67	16	(14)(75%)
(6)[i]	0.928[a]	400[d]		-2.36	2	(15)(70%),(8)(20%)[h]

[a] From cyclic voltammetry see refs. 8, 10. [b] Pyrex filter. [c] Naphthalene–iso-octane, 2.56 g in 20 ml solution. [d] 27 g of $CuSO_4 \cdot 5H_2O$, 30 g of $NaNO_2$, and 50 ml of conc. ammonia diluted with water to 1 l. [e] Yields based on the products isolated by column chromatography on silica gel, eluant hexane–diethyl ether, 5:1 v/v. [f] A small amount of phenyl benzoate is also observed. [g] As two moles of (9), (10), and (12) result from the substrates (1), (3), and (4), % yields are expressed as [(product/2 × substrate)] × 100. [h] Minor quantities of 2-phenyl-2-benzoyl-1,3-dioxolane and 1,6-diphenyl-2,5,7,10-tetraoxobicyclo[4.4.0]decane are also observed. Characterization by comparison with authentic samples; see ref. 13. [i] The reactions with added tetrabutylammonium bromide (10^{-4}—10^{-3} M) are not quenched.

Scheme 1

$R^1 C \equiv CR^2$

(1) $R^1 = R^2 = Ph$

(2) $R^1 = H, R^2 = Ph$

(3) $R^1 = R^2 = R^3 = R^4 = Ph$

(4) $R^1 = R^4 = H, R^2 = R^3 = Ph$

(5) $R^1 = Ph, R^2 = R^4 = H, R^3 = Me$

(6)

(7)

Ph(CO)(CO)Ph

(8)

$PhCO_2H$ (9)

Ph_2CO (10)

Ph_2C——CPh_2 (O) (11)

PhCHO (12)

PhHC——CHPh (O) (13)

PhCOMe (14)

$PhO_2C[CH_2]_2 CO_2Ph$ (15)

D = electron donor

(10^{-2} M) in the presence of TBCHD (5×10^{-4} M) are irradiated at 10 °C with a 700 W mercury lamp, through a filter so that only the electron acceptor absorbs light. The products, isolated by column chromatography on silica gel, have been identified by their spectral properties and by comparison with authentic commercial and/or synthesized samples (Table 1).

Cyclic voltammetric experiments on TBCHD show that it is reducible, through an irreversible process, at $E_p = 0.29$ V vs. s.c.e. at a Pt electrode in MeCN containing tetrabutylammonium tetrafluoroborate (10^{-1} M). This exceedingly low reduc-

tion potential,† together with its singlet excitation energy ($\Delta E_{0-0} = 2.94$ eV) and the oxidation potentials of the donors (1)—(6), substantiate, on the basis of Weller's equation,[5] that an exothermic electron transfer process between (1)—(6) and excited TBCHD is in agreement with the nature of our reagents. Our conditions in the TBCHD-sensitized photo-oxygenations closely resemble the Methylene Blue, MB^+, ($E_p = -0.29$ V vs. s.c.e.)-sensitized photo-oxygenation of (4)[6] and the TCA-sensitized photo-oxidation of (1);[7] our results are also similar to those reported for the DCA-sensitized photo-oxygenations of the same substrates.[8]

In our opinion the driving force for the reaction under these conditions is the aromatization of the TBCHD$\bar{\cdot}$ radical anion into tribromophenoxyl radical and bromide anion. This process avoids, or at least reduces, the back electron-transfer, allowing the free radical cations to combine with molecular oxygen, affording the reaction products through a radical

† Tetrachlorobenzoquinone, TCB, with a similar cyclohexadiene structure, and N-bromosuccinimide, NBS, with comparable reactivity in respect to our reagent, show low reduction potentials: ($E^{red}TCB\bar{\cdot}/TCB = -0.02$ V vs. s.c.e.) (ref. 3); ($E^{red}NBS\bar{\cdot}/NBS = -0.03$ V vs. s.c.e.) (ref. 4).

cation chain mechanism (Scheme 1). The cyclic voltammo-gram of TBCHD‡ and other experimental evidence supports this mechanism. In agreement with Foote's proposal,[8a] no *reaction takes* place in the absence of the electron acceptor and/or oxygen. The involvement of the superoxide anion and/or singlet oxygen has been excluded since the reactions are not quenched in the presence of benzoquinone,[9] an excellent superoxide anion trap, and, with the exception of (6),[10] none of the substrates reacts with singlet oxygen to any extent. The involvement of the radical cations in the process has been shown by quenching the photo-oxygenation of (1) with p-dimethoxybenzene (10^{-3} M), a substrate with a lower oxidation potential than (1). Preliminary experimental data on the TBCHD-sensitized photo-oxygenations of (1)—(3) in the presence of 2,4,6-tribromophenol (7) (8×10^{-3} M) show an appreciable enhancement of the reaction rate (see Table 1). These results support the proposed mechanism, with (7) acting both as an acid and as a nucleophile.[7] As can be seen from Table 1 all the substrates undergo electron transfer spontaneously, including (2), which has an oxidation potential > 2 V $vs.$ s.c.e., making it unreactive in the DCA- and TCA-sensitized photo-oxygenations.[8b]

The intermediate species formed during the reactions, such as radical cations, 1,2-dioxine from acetylenes, and 1,2-dioxetane from alkenes and dioxine, have not been charac-terized by ^{1}H n.m.r. spectroscopy and chemiluminescence, since the low temperature TBCHD sensitization fails to yield detectable intermediates.

The double action of TBCHD, as an electron acceptor and as a mild brominating agent, can be demonstrated, since the thermal reactions of (1) and/or (4) in acetonitrile solution with two equivalents of TBCHD slowly afford 1,2-dibromo-1,2-diphenylethylene§ and *meso*-dibromostilbene, respective-

ly.¶ It can be concluded that the TBCHD-sensitized photo-oxygenations of several unsaturated substrates occur *via* an electron-transfer process in which, dismissing the formation of superoxide anion, the oxygenated products arise from the reactions of the intermediate radical cations with molecular oxygen, through a radical cation chain mechanism.

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‡ The oxidation waves at $E_p = 0.67$ V and $E_p = 0.93$ V result from the oxidation of the bromide anion (ref. 4).

§ The i.r. spectrum and m.p. 211 °C are identical to those of a pure sample prepared by bromination of (1) in CHCl₃ (ref. 11).

¶ The i.r. spectrum and m.p. 241 °C are identical to those of a pure sample, prepared as in ref. 12.