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C-C BOND CLEAVAGE IN THE INTERACTION OF ANTHRAQUINONE TRIPLET WITH TERTIARY ALCOHOLS AND TERTIARY BUTYLBENZENE

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Summary: In the photochemical reaction of anthraquinone triplet with both tertiary alcohols and tert.Bu-benzene in C_6H_6 at $\lambda \geq 334$ nm not only C-H (or O-H) bonds but C-C bonds are also broken, yielding $\dot{C}H_3$, and $R_1\dot{C}(R_2)OH$ (or $C_6H_5\dot{C}(CH_3)_2$) radicals, at room temperature.

Wagner and Puchalski have shown, that in the photochemical interaction of acetophenone triplet (^{T}RO) with 1-phenylethanol (HROH) in C_6H_6 both α-CH and O-H bonds are broken, yielding alkoxy radicals, which may undergo β-scission.[1] At the same time we have *found, that in the reaction of anthraquinone triplet (^{T}Q) with HROH in the same solvent* at $T \geq 333$ K both $\dot{C}H_3$ and $C_6H_5\dot{C}H(OH)$ radicals are formed[2], that is, the photochemical C-C bond cleavage cannot be a result of β-scission of alkoxy radicals exclusively.

In the present work we report results on the photochemical interaction of ^{T}Q with a number of alcohols in C_6H_6 at room temperature in the presence of 2,6-dibromonitrosobenzene (DNB) used as an excellent spin trap for both alkoxy and C-centred radicals.[3,4] Furthermore, products in the photochemical interaction of ^{T}Q with ethylbenzene, cumene and tert.butyl-benzene in the same solvent are also summarized. Measurements have been carried out in the absence of O_2. The incident light intensity was maintanined at 10^{-4} mol photon $l^{-1}s^{-1}$ measured by using potassium ferric oxalate actinometer.[5] Experimental details have been described earlier.[2-5] Deaereated solutions were directly illuminated in the ESR cavity at $\lambda \geq 334$ nm. Nitroxyl radicals detected in the ^{T}Q-alcohol (or aromatic hydrocarbon) systems are listed in Table 1. It can be seen, that in the reaction of ^{T}Q with C_2H_5OH, n-propyl and i-propyl alcohols as well as with ethylbenzene and cumene the α-CH bonds are broken and primary C-centred radicals trapped by DNB, while a number of further radicals were also detected during the photochemical interaction of ^{T}Q with tertiary butyl-benzene or with tertiary alcohols. According to the data of Table 1 not only ^{T}RO (as suggested by Wagner and Puchalski)[1] but also ^{T}Q abstracts hydrogen from OH groups of alcohols, yielding $HR\dot{O}$ (from HROH) or $CH_3C(CH_3)_2\dot{O}$ (from tert.Bu OH).

Furthermore, rupture of C-C bonds was observed in the reaction of ^{T}Q with tert. Bu OH - and cumylalcohol - as well as with tert.butyl-benzene yielding $R_1\dot{C}(R_2)OH$ or $C_6H_5\dot{C}(CH_3)_2$ as well as $\dot{C}H_3$ radicals. The energy of the lowest triplet state of Q is 62.5 kcal/mol,[5] that is, the T-T energy transfer from the lowest triplet state of Q to the triplet states of tertiary alcohols and tert.butyl-benzene would be substantially endothermic.[6,7]

It has been suggested, that the Norrish type I cleavage occurs in a two photon reaction at room temperature.[8,9] Reexcitation by absorption of a second photon leads to

Table 1

Nitroxyl radicals obtained by spin trapping of free radical intermediates by 2,6-dibromonitrosobenzene in the photochemical interaction of anthraquinone triplet with alcohols and aromatics in C_6H_6 at 298 K in the absence of oxygen.
$[Q]_0 = 10^{-3}$ M, $[DNB] = 7 \cdot 10^{-3}$ M, $\lambda \geq 334$ nm, $I_0 = 10^{-4}$ mol photon $l^{-1}s^{-1}$

Alcohol or hydrocarbon	Conc. M	Trapped Radicals	Hfs constans (mT) a_N	a_H
C_2H_5-OH	1	$CH_3\dot{C}HOH$	1.321	0.843
$CH_3CH_2CH_2OH$	1	$CH_2CH_2\dot{C}HOH$	1.32	0.68
$CH_3CH(CH_3)OH$	1	$\underset{\cdot}{(}CH_3)_2COH$	1.34	-
		$\underset{\cdot}{C}H_2-R_1$	1.316	0.92 ± 0.2
$(CH_3)_3C-OH$	1	CH_3	1.32	1.21
		$(CH_3)_3\underset{\cdot}{C}O^{\cdot}$	2.65	-
		$(CH_3)_{\cdot 2}COH$	1.32	-
$C_6H_5CH_2CH_3$	1	$C_6H_5\underset{\cdot}{C}HCH_3$	1.30	0.54
$C_6H_5C(CH_3)_2-H$	1	$C_6H_5\underset{\cdot}{C}(CH_3)_2$	1.38	-
$C_6H_5C(CH_3)_2OH$	1	$C_6H_5C(CH_3)OH$	1.38	-
		$R_2-\dot{C}H_{\cdot 2}$	1.32	0.89
$C_6H_5C(CH_3)_3$	1	$C_6H_5C(CH_3)_2$	1.30	-
$C_6H_5CH(CH_3)OH$	1	$C_6H_5\underset{\cdot}{C}H(CH_3)\dot{O}$	2.7 ± 0.2	-
		$C_6H_5CH(OH)$	1.334	0.68

the upper triplet state possessing more than sufficient energy to facilitate the bond cleavage. Due to the energy requirements of the photochemical interaction of ${}^{T}Q$ with tertiary alcohols, as well as with tert.Bu-benzene a two photon process[6,7] cannot be excluded at room temperature. It is worth mentioning, that at low temperature (77 K) the C-C bond cleavage of tert.Bu-alcohol has been supported by Terenin et al[6,7] in the reaction of a number of various triplets with this alcohol.

References

1. P.J.Wagner,A.E.Puchalski,*J.Am.Chem.Soc.*,1980,*102*,7140
2. G.Móger,A.Rockenbauer,P.Simon,*Radiochem.Radioanal.Lett.*,1980,*42*,407
3. A.Rockenbauer,L.Sümegi,G.Móger,P.Simon,M.Azori,M.Győr,*Tetrahedron Lett.*,1978,*50*, 5057
4. A.Rockenbauer,S.A.Abdel-Monem,G.Móger,L.Sümegi,*J.Mol.Struct.*,1978,*46*,169
5. G.Móger,D.Gál,*Ber.Bunsenges.Phys.Chem.*,1989,*93*,575
6. A.Terenin,*Photochemistry of Dyes (in Russian) "Nauka" Moscow*,1967
7. A.Terenin,V.Rylkov,V.Khoglomorov,*Photochem.Photobiol.*,1966,*5*,43
8. W.G.McGimpsey,I.C.Scaiano,*J.Am.Chem.Soc.*,1989,*111*,335,ibid.,1987,*109*,2179
9. L.I.Johnston,I.C.Scaiano,*J.Am.Chem.Soc.*,1987,*109*,5487

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