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REACTION OF VINYL- AND PROPENYL-ETHERS WITH TERT-BUTOXYL RADICALS - AN ESR STUDY.

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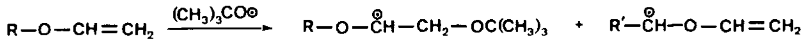
Abstract: Photolytically generated tert-butoxyl radicals react with vinyl- and propenyl ethers by hydrogen abstraction and addition to the double bond; the abstraction/addition ratio and the regioselectivity of addition are interpreted in terms of predominant steric interactions.

For the reaction of tert-butoxyl radicals with alkenes two main pathways are observed: addition to the double bond and abstraction of sufficiently activated hydrogen atoms, preferentially at allylic positions[1-3]. While considerable information exists on the reaction of tert-butoxyl radicals with unsaturated hydrocarbon substrates or alkenes bearing electron-withdrawing groups, less is known about the reaction with electron-rich enol ethers. In the present study we have investigated by ESR spectroscopy the radicals which are produced in the reaction of various vinyl- and propenyl-ethers with photolytically generated tert-butoxyl radicals[4].

Vinyl ethers

Irradiation of $CFCl_3$-solutions of ethyl- (1a), n-butyl- (1b), and phenyl-vinyl-ether (1c) in the presence of di-tert-butylperoxide (DTBP) at -90°C leads to ESR spectra which unambiguously can be assigned to radicals produced by addition of tert-butoxyl radicals to the unsubstituted carbon atom of the double bond (tail addition) and (for 1a, 1b) hydrogen abstraction at the α-oxy-methylene group:



$$R-O-CH=CH_2 \xrightarrow{(CH_3)_3CO\odot} R-O-\overset{\odot}{C}H-CH_2-OC(CH_3)_3 \; + \; R'-\overset{\odot}{C}H-O-CH=CH_2$$

1a: R = Et
1b: R = n-Bu
1c: R = Ph

2a-c

3a: R' = Me
3b: R' = n-Pr

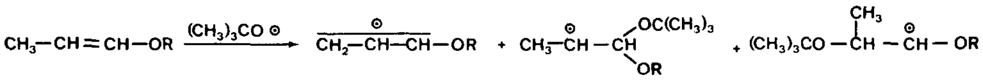
The ESR coupling constants and g-values (Table 1) agree well with literature data for methyl- and ethyl-vinyl ether radicals[5]. A characteristic feature of the ESR spectra of all adduct radicals are the rather broad hyperfine lines (0.05 - 0.1 mT). The approximate concentration ratio of radicals 2a, 3a, and 2b, 3b, respectively, was evaluated from the integrated intensity of the ESR signals. The relative amount of adduct radicals decreases with increasing temperature. Within the resolution of the ESR spectra no radicals could be detected which are expected from addition of tert-butoxyl radicals to the substituted side of the vinyl group (head-addition)[6].

This result is in accordance with both the steric demands of radical addition (unsymmetrical transition state) and dominant SOMO-LUMO interactions of the electrophilic tert-butoxyl radicals and electron-rich double bonds[7,8]. However, a spin-trapping investigation[3] reveals that a small amount of head-adduct radicals is formed in the reaction of ethyl-vinyl-ether or vinyl-acetate with tert-butoxyl radicals at +60°C.

Table 1 - ESR data of radicals from the reaction of tert-butoxyl radicals with vinyl ethers

starting compound	radicals (approx. conc.ratio)	temp. (°C)	g-value	coupling constants (mT)
$C_2H_5\text{-}O\text{-}CH{=}CH_2$	$C_2H_5O\text{-}\overset{\odot}{C}H\text{-}CH_2\text{-}O\text{-}tBu$	-94	2.00318	a = 1.628 (1H)
1a	2a			a = 0.738 (2H)
				a = 0.240 (2H)
	$CH_3\text{-}\overset{\odot}{C}H\text{-}O\text{-}CH{=}CH_2$	-94	2.00311	a = 1.532 (1H)
	3a			a = 2.248 (3H)
				a = 0.014 (1H)
	2a : 3a = 9 : 1			a = 0.123 (3H)
$n\text{-}C_3H_7\text{-}O\text{-}CH{=}CH_2$	$n\text{-}C_3H_7O\text{-}\overset{\odot}{C}H\text{-}CH_2\text{-}O\text{-}tBu$	-94	2.00319	a = 1.616 (1H)
1b	2b			a = 0.730 (2H)
				a = 0.238 (2H)
	$C_2H_5\text{-}\overset{\odot}{C}H\text{-}O\text{-}CH{=}CH_2$	-16	2.00302	a = 1.539 (1H)
	3b			a = 1.973 (2H)
				a = 0.118 (2H)
				a = 0.019 (1H)
	2b : 3b = 8 : 1 (-94°C)			a = 0.062 (2H)
$C_6H_5\text{-}O\text{-}CH{=}CH_2$	$C_6H_5\text{-}O\text{-}\overset{\odot}{C}H\text{-}CH_2\text{-}O\text{-}tBu$	-90	2.00302	a = 1.594 (1H)
1c	2c			a = 0.934 (2H)

Propenyl ethers. Tert-butoxyl radicals normally exhibit a strong preference for allylic hydrogen abstraction over addition to double bonds. However, the ESR spectra obtained during irradiation of $CFCl_3$-solutions of propenyl ethers 4 in the presence of DTBP indicate the formation of the expected allylic radicals 5 accompanied by different adduct radicals 6, 7 (Table 2):



$$CH_3{-}CH{=}CH{-}OR \xrightarrow{(CH_3)_3CO\,\odot} \overline{CH_2{-}\overset{\odot}{C}H{-}CH}{-}OR + CH_3{-}\overset{\odot}{C}H{-}CH{<}^{OC(CH_3)_3}_{OR} + (CH_3)_3CO{-}\overset{CH_3}{\overset{|}{C}H}{-}\overset{\odot}{C}H{-}OR$$

4a-f　5a-f　6a-f　7a-f

a: R = CH_3; cis　b: R = CH_3; trans

c: R = $n\text{-}C_3H_7$; cis　d: R = $n\text{-}C_3H_7$; trans

e: R = $C(CH_3)_3$; cis　f: R = C_6H_5; cis

The formation of adduct radicals, which in some cases by far overrides the hydrogen abstraction, evidently results from a strong interaction of the low-energy SOMO of the tert-butoxyl radical and the high-energy HOMO of the enol ether. By contrast, for electron-deficient propenyl compounds, like crotononitrile, no addition products could be observed by ESR spectroscopy in the reaction with tert-butoxyl radicals[10]. The relative ratios of radicals 5 - 7 strongly depend on the stereochemistry of the double bond and the steric demand of the substituent R. Whereas the trans-propenyl ethers 4b, 4d yield allylic radicals (5b, 5d) and adduct radicals (6b, 6d) in nearly equal amounts, the corresponding cis-propenyl ethers 4a, 4c undergo addition to a much larger extent. This fact most likely has to be attributed to steric interactions in the encounter complex of the reactants. The high sensitivity of the addition step to steric influences is demonstrated by the addition/abstraction ratio of the cis-compounds 4a, 4c, 4e, 4f. Moreover, steric interactions must be responsible for the regioselectivity of addition. For the methyl- and propyl-propenyl ethers 4a - 4d the addition predominantly occurs at the alkoxy-side of the double bond, regardless of the stereochemistry. This is in contrast to the polar effects, predicted by frontier-orbital interactions[7-9]. On the other hand, going to the more space-filling tert-butyl- or phenyl groups in 4e, 4f, the direction of addition reverses to the methyl-side of the double bond. Thus, the regioselectivity of tert-butoxyl-addition to electron-rich double bonds is mostly governed by steric interactions, as in the case of electron-deficient olefins[8,9].

Table 2 - ESR data of radicals from the reaction of tert-butoxyl radicals with propenyl ethers

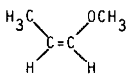
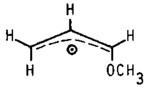
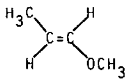
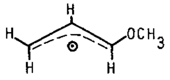
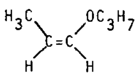
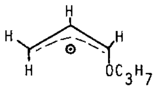
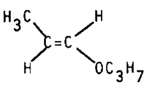
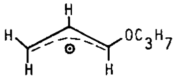
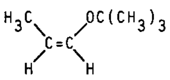
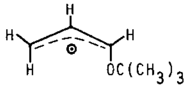
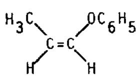
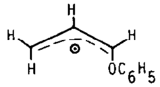
starting compound	radicals (approx. conc.ratio)	temp. (°C)	g-value	coupling constants (mT)
 4a	 5a	-115	2.00305	a = 1.400 (1H) a = 1.359 (1H) a = 1.313 (1H) a = 0.300 (1H) a = 0.115 (3H)
	$H_3C\text{-}\overset{\odot}{C}H\text{-}CH(OCH_3)\text{-}OtBu$ 6a 5a : 6a = 1:45	-115	2.00282	a = 2.243 (1H) a = 2.532 (3H) a = 2.420 (1H)
	$tBuO\text{-}CH(CH_3)\text{-}\overset{\odot}{C}H\text{-}OCH_3$ 7a			see 7b (traces)
 4b	 5b	-105	2.00311	a = 1.415 (1H) a = 1.310 (1H) a = 1.300 (1H) a = 0.349 (1H) a = 0.147 (3H)
	6b = 6a			see above
	$tBuO\text{-}CH(CH_3)\text{-}\overset{\odot}{C}H\text{-}OCH_3$ 7b = 7a 5b : 6b : 7b = 4 : 2 :1	-105	2.0033	a = 1.45 (1H) a = 1.00 (1H) a = 0.16 (3H) a = 0.09 (3H)
 4c	 5c	-96	2.00306	a = 1.375 (1H) a = 1.354 (1H) a = 1.310 (1H) a = 0.299 (1H) a = 0.118 (2H)
	$H_3C\text{-}\overset{\odot}{C}H\text{-}CH(OC_3H_7)\text{-}OtBu$ 6c 5c : 6c = 1 : 9	-96	2.00278	a = 2.212 (1H) a = 2.460 (1H) a = 2.530 (3H)
	$tBuO\text{-}CH(CH_3)\text{-}\overset{\odot}{C}H\text{-}OC_3H_7$ 7c			not analyzed (traces)

Table 2 (continued)

 4d	 5d	-99	2.00311	a = 1.406 (1H) a = 1.298 (1H) a = 1.291 (1H) a = 0.347 (1H) a = 0.160 (2H)
	6d = 6c 5d : 6d = 1 : 1.5			see above
	7d = 7c (traces)			not analyzed
 4e	 5e	-98	2.00307	a = 1.312 (1H) a = 1.376 (2H) a = 0.296 (1H) a = 0.014 (9H)
	$\text{tBuO-CH(CH}_3\text{)-}\overset{\odot}{\text{C}}\text{H-OtBu}$ 6e	-98	2.00316	a = 1.445 (1H) a = 1.094 (1H) a = 0.089 (3H) a = 0.021 (9H)
	5e : 6e = 1 : 1			
 4f	 5f	-91	2.00293	a = 1.352 (1H) a = 1.382 (1H) a = 1.422 (1H) a = 0.320 (1H)
	$\text{tBuO-CH(CH}_3\text{)-}\overset{\odot}{\text{C}}\text{H-OC}_6\text{H}_5$ 6f	-91	2.0032	a = 1.520 (1H) a = 1.200 (1H) a = 0.090 (3H)
	5f : 6f = 1 : 1			

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4) Radical generation: Irradiation of deoxygenated mixtures of enolether, DTBP, and $CFCl_3$ (1:1:1, by volume; 4-mm quartz tubes or 0.7-mm flat flow cell) with the filtered light of a 1-kW Hg/Xe-lamp (Hanovia 977-B1); ESR spectrometer: Bruker ER-420. ESR coupling constants were refined by computer simulation.

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6) The ESR spectra deriving from the vinyl ethers show weak additional signals of an unknown radical, which could not be analyzed, but is unlikely due to head-addition because of its g-value (∿2.0036) and overall width (∿4.5 mT).

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