BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1401—1404 (1968)

Cleavage Reactions of Alkoxy Radicals Produced by Anodic Oxidation of *t*-Alcohols

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(Received December 7, 1967)

The anodic oxidation of *t*-alcohols in water - dioxane - sodium hydroxide system has been examined. The possibility of production of *t*-alkoxy radicals by anodic oxidation of *t*-alcohols in the electrolytic system was found. The relative ease of bond scission of the intermediate *t*-alkoxy radical was determined by quantitative analysis of the mixture of ketones produced. The relative rates of cleavage decrease in the order: allyl>*sec*-butyl>isopropyl>ethyl>*n*-propyl>*n*-butyl>*n*-pentyl>isobutyl>methyl. The hyperconjugative effect of β-hydrogen and effect of double bond at β-position to the rate enhancement of cleavage reaction was confirmed.

The two typical reactions of *t*-alkoxy radicals are, in general, i) hydrogen abstraction to form alcohols and ii) fragmentation to ketone and alkyl radical.[1,2] The cleavage reaction of *t*-alkoxy radical to form ketone and alkyl radical has been extensively investigated.[3-9] There are three ways of bond scission for an *t*-alkoxy radical theoretically (Eq. (1)).

$$R_1R_2R_3CO\cdot \to \left\{\begin{array}{l} R_1\cdot + R_2COR_3 \\ R_2\cdot + R_1COR_3 \\ R_3\cdot + R_1COR_2 \end{array}\right\} \quad (1)$$

The relative rates of formation of alkyl radicals can be determined if one can estimate quantitatively the amount of ketones and of alkyl radicals which are produced from the fragmentation of *t*-alkoxy radical. By such an idea the relative ease of cleavage reactions has been determined from 1) the redox reaction between alkyl hydroperoxides and reducing metal ion,[4] 2) the thermolysis of dialkyl peroxides,[4] 3) the oxidation of alcohols with Co(III),[5] and 4) the photolytic decomposition of alkyl hypochlorites.[6,8,9]

In this study we examined the possibility of production of *t*-alkoxy radicals by anodic oxidation of *t*-alcohols and intended to obtain a quantitative measure of the relative ease of cleavage reaction in the absence of the oxidising metallic cation or halogen radical, especially at low temperature. Using platinum electrodes the electrolytic oxidation of *t*-alcohols were conducted in a solvent system: dioxane - water - sodium hydroxide.

Results and Discussion

The synthetic methods of *t*-alcohols: R_1R_2PhCOH (R_1, R_2=alkyl, Ph=phenyl) used in this study and their physical constants are described in experimental part (Table 4). The reaction mixture resulted from electrolysis of *t*-alcohols in the dioxane-water - sodium hydroxide system, was extracted by ether and analysed by g.l.p.c. technique. Since it was confirmed by preliminary experiments that the expected ketones were produced efficiently at anode by electrolysis of *t*-alcohols if one used the dioxane - water - sodium hydroxide system as a solvent (80—90% of theoretical yields for ketones in 10—15 hr) and no successive reaction of the ketones was observed in this electrolytic system, the further reactions were conducted as it was described in experimental part. The yields of ketones obtained from the anodic oxidations of *t*-alcohols are given in Table 1. The values given in Table 1 are average of the values obtained by several runs (3—5 times) for an *t*-alcohol. The probable error was lower than 5%. Gaseous products corresponding to the respective runs are given in Table 2.

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[1] J. H. Raley, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 88 (1948); F. F. Rust, F. H. Seubold and W. H. Vaughan, *ibid.*, **70**, 95 (1948); J. H. Raley, F. F. Rust and W. H. Vaughan, *ibid.*, **70**, 1336 (1948); E. R. Bell, F. F. Rust and W. E. Vaughan, *ibid.*, **72**, 337 (1950); M. G. Evans, *Discussions Faraday Soc.*, **10**, 1 (1951).

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[3] A. L. Williams, E. A. Oberright and J. W. Brooks, *J. Am. Chem. Soc.*, **78**, 1190 (1956).

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[7] C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108, 6113 (1960); **83**, 3877 (1961).

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TABLE 1. ANODIC OXIDATION OF *t*-ALCOHOLS : R_1R_2PhCOH

Run	R_1	R_2	R_1COPh	R_2COPh	R_2/R_1
1	C_2H_5	i-C_3H_7	60%	$\sim$1%	$\sim$60
2	C_2H_5	n-C_3H_7	35	53	0.66
3	C_2H_5	s-C_4H_9	85	$\sim$1	$\sim$85
4	C_2H_5	n-C_4H_9	35	57	0.62
5	C_2H_5	i-C_4H_9	25	57	0.44
6	C_2H_5	n-C_5H_{11}	32	56	0.57
7	i-C_3H_7	s-C_4H_9	50	33	1.50
8	n-C_3H_7	n-C_4H_9	31	47	0.66
9	C_2H_5	CH_3	$\sim$1	67	$\sim$0.01
10	C_2H_5	$-CH_2CH{=}CH_2$	71	0	∞
11	i-C_3H_7	$-CH_2CH{=}CH_2$	58	6.3*	9.0

Solvent : dioxane : water = 10 : 4

* Contained 3.1% of *n*-propyl phenyl ketone

TABLE 2. COMPOSITIONS OF GASEOUS PRODUCTS

Run	R_1	R_2	Components of gaseous products
1	C_2H_5	i-C_3H_7	C_3H_6
2	C_2H_5	n-C_3H_7	C_2H_4, C_3H_6, n-C_4H_{10}, n-C_5H_{12}
3	C_2H_5	s-C_4H_9	C_2H_4, n-C_4H_{10}, 1-C_4H_8, 2-C_4H_8
4	C_2H_5	n-C_4H_9	C_2H_4, n-C_4H_{10}, 1-C_4H_8, 2-C_4H_8, i-C_4H_8
5	C_2H_5	i-C_4H_9	C_2H_4, n-C_4H_{10}, i-C_4H_8
9	C_2H_5	CH_3	C_2H_4, n-C_4H_{10}

TABLE 3. RELATIVE RATES OF CLEAVAGE OF ALKYL RADICALS FROM *t*-ALKOXY RADICALS AT 25—35°C

Radicals		$CH_2CH{=}CH_2$	s-C_4H_9	i-C_3H_7	C_2H_5	n-C_3H_7	n-C_4H_9	n-C_5H_{11}	i-C_4H_9	CH_3
Relative rates		$\sim$540 a)	$\sim$85 $\sim$90 b)	$\sim$60 $\sim$57 c)	1.0	0.66 0.93 d)	0.62 0.45 e)	0.57	0.44	$\sim$0.01
	Ref. *		64		1.0	0.63—0.74	0.59—0.72		0.47—0.57	0.005
	Ref. **				1.0	0.65	0.43			0.003
	Ref. ***				1.0	0.34	0.28		0.1	0.01

a) from runs 1 and 11, b) from runs 1 and 7, c) from runs 3 and 7, d) from runs 4 and 8, e) from runs 2 and 8.

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The components of gaseous products could be identified by g.l.p.c. technique, but the amounts of each component could not be determined quantitatively, because the gaseous products produced at electrodes contained a large amount of hydrogen and oxygen which were the invariable products of electrolysis in an aqueous solvent.

Although an ambiguity remains in the anodic oxidation of *t*-alcohols, generation of *t*-alkoxy radical at anode and consequently the ejection of an alkyl radical from *t*-alkoxy radical can be deduced from the results given in Table 1 and Table 2; the high yields of ketones and generation of dimerization product of the ejected alkyl radical are indicative for the generation of *t*-alkoxy radical at anode (Eq. (2)).[*2]

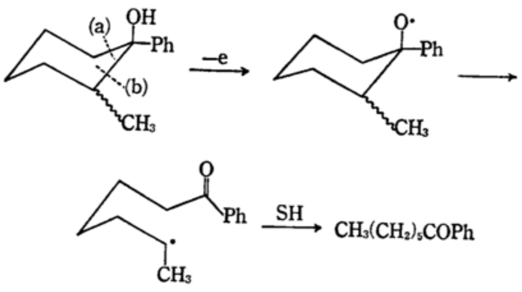
[*2] There is a possibility of the anodic oxidation of *t*-alkoxy radical to *t*-alkoxy cation which produces ketone and alkyl cation. However, *t*-alkoxy cation which would be formed, should decompose to produce aliphatic ketone and phenol:

$$R_1R_2PhCO\cdot \xrightarrow{-e} R_1R_2PhCO^+ \xrightarrow[(H_2O)]{} R_1R_2CO + PhOH$$

because the alkoxy cation is a well established intermediate of the acid catalysed decomposition of aralkyl hydroperoxides. For example, α,α-dimethylbenzyl hydroperoxide decomposes to acetone and phenol (M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950)). Since none of phenolic product nor aliphatic ketone could be detected as the reaction product, such a possibility of the anoidic oxidation of *t*-alkoxy cation can be ignored.

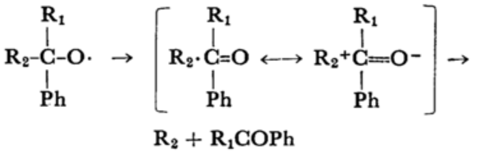
$$\left.\begin{array}{l} \mathrm{R_1R_2PhCOH} \xrightarrow{-e} \mathrm{R_1R_2PhCO\cdot} + \mathrm{H^+} \\ \mathrm{R_1R_2PhCO\cdot}\; -\!\begin{cases}\xrightarrow{k_1} \mathrm{R_2COPh} + \mathrm{R_1\cdot} \\ \xrightarrow[k_2]{} \mathrm{R_1COPh} + \mathrm{R_2\cdot}\end{cases} \\ \mathrm{R_1\cdot} + \mathrm{R_2\cdot}\; -\!\begin{cases}\longrightarrow \mathrm{R_1R_1} + \mathrm{R_2R_2} + \mathrm{R_1R_2} \\ \longrightarrow \mathrm{R_1H} + \mathrm{R_2H} + \text{olefins}\end{cases}\end{array}\right\} \qquad (2)$$

Since the hydrogen abstraction from solvent by *t*-alkoxy radical which is another main reaction of it, produces the starting material in this reaction, such a way of stabilization of *t*-alkoxy radical can be neglected from the consideration. Assuming the relative amounts of ketones are equal to the relative ease of fragmentation of an alkyl moiety from *t*-alkoxy radical; $k_1/k_2=\mathrm{R_2COPh}/\mathrm{R_1COPh}$, a trend of the relative ease of cleavage can be deduced, which is shown in Table 3 with the values obtained from the other reactions by several investigators. Thus, the trend of the relative ease of cleavage reaction deduced from the results of the anodic oxidation of *t*-alcohols coincides qualitatively with the results which are obtained from the other different type of reactions. It has been generally accepted that the predominant cleavage is that which forms the largest alkyl radical; qualitatively, the relative ease of ejection of an alkyl radical from *t*-alkoxy radical decreases in the order: *tertiary > secondary > primary*, but recently have presented the facts which are inconsistent with this conception from the study of dissociation energy of alkanes by electron impact[10] and from the study of photolytic decomposition of alkyl hypohalites.[9] Bacha and Kochi have shown that the relative rates of cleavage decreases in the order which is shown in Table 3; ethyl > γ,γ-dimethylbutyl > *n*-propyl, *n*-butyl > isobutyl > neopentyl ≫ methyl, from the study of photolytic decomposition of various *t*-alkyl hypochlorites, and have proposed that the most important factor which determines the relative rate of ejection of an alkyl radical from *t*-alkoxy radical is the hyperconjugative effect of β-hydrogen of a departing alkyl radical for the stabilization of transcient stage of bond scission.[9] Our results obtained from the anodic oxidation of *t*-alcohols seem to substantiate the conception presented by Bacha and Kochi. In order to examine further this problem, 1-phenyl-2-methyl-cyclohexanol which is considered to be relatively strain free compound, has electrolysed in the dioxane - water - sodium hydroxide system. If the bond scission occurred at (a), the number of β-hydrogen is two. If the bond scission occurred at (b), then the number of β-hydrogen is five. Actually, *n*-hexyl phenyl ketone which indicates the bond scission at (b), was the sole product as the ketonic product; this shows the importance of the hyperconjugative effect of β-hydrogen (Eq. (3)).



SH: solvent (3)

In addition to the effect of the number of β-hydrogen, a prominent rate enhancement for the bond scission by double bond at β-position can be found from the results of runs 10 and 11. Such an effect of double bond for the rate enhancement as well as the effect of β-hydrogen suggests that a stabilization of the polarized transcient stage for the bond scission is predominant factor (Eq. (4)).



$$\mathrm{R_2}\text{-}\underset{\mathrm{Ph}}{\overset{\mathrm{R_1}}{\mathrm{C}}}\text{-}\mathrm{O\cdot} \rightarrow \left[\mathrm{R_2\cdot}\underset{\mathrm{Ph}}{\overset{\mathrm{R_1}}{\mathrm{C}}}{=}\mathrm{O} \longleftrightarrow \mathrm{R_2{}^{+}}\underset{\mathrm{Ph}}{\overset{\mathrm{R_1}}{\mathrm{C}}}{=\!=}\mathrm{O^-}\right] \rightarrow$$
$$\mathrm{R_2} + \mathrm{R_1COPh} \qquad (4)$$

The importance of the polarized transient stage has already pointed out by Bacha and Kochi as to the rate enhancement by β-hydrogen.[9] We can find ample evidences for such an importance of polar effects to the radical reactions.[11] Effects of ring size and ring strain are also shown to be a determining factor of the relative ease of ejection of an alkyl radical from the parent alkoxy radical.[8]

Experimental

Preparation of Alcohols. The tertiary alcohols were prepared by the Grignard procedure from phenyl bromide and corresponding ketones and were purified by vacuum distillation until to obtain materials giving a single spot *via* thin layer chromatography. Physical constants of *t*-alcohols found are shown in Table 4.

Anodic Oxidation and Quantitative Analysis of Reaction Mixtures. A typical anodic oxidation of *t*-alcohol was conducted as following; 1.00 g of an *t*-alcohol and 20 mg of sodium hydroxide were dissolved into a mixture of 10 m*l* of dioxane and 4 m*l* of water. The solution was electrolysed in a 100 cylindrical flask with two parallel platinum plates as electrodes (surface area: 2.0×1.5 cm², distance between electrodes: 0.2 cm, electric potential between electrodes: 10—20 V, current: 0.3—0.5 A). A violent evolution of gaseous product at anode could be observed. The temperature of the solution was held at 25—35°C by cooling with water. After electrolysis was continued for about ten

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TABLE 4. PHYSICAL CONSTANTS OF *t*-ALCOHOLS: R_1R_2PhCOH

	R_1	R_2	Bp (°C)	Press (mmHg)
1	C_2H_5	i-C_3H_7	128—129	20
2	C_2H_5	n-C_3H_7	125—127	20
3	C_2H_5	s-C_4H_9	123—125	16
4	C_2H_5	n-C_4H_9	82—84	3
5	C_2H_5	i-C_4H_9	106—110	15
6	C_2H_5	n-C_5H_{11}	105—110	4
7	i-C_3H_7	s-C_4H_9	100—105	4
8	n-C_3H_7	n-C_4H_9	127	16
9	C_2H_5	CH_3	100—101	15
10	C_2H_5	$-CH_2CH{=}CH_2$	110	17
11	i-C_3H_7	$-CH_2CH{=}CH_2$	118—124	17

hours, the reaction mixture was treated with ether, dried with anhydrous sodium sulfate, and quantitatively analysed by g.l.p.c. techniques. Identifications of products were carried out by the comparison of the retention time of each component on chromatogram with authentic samples. The columns used for analyses of the ketones were calibrated with standard solutions at the same time under the same condition. Bromobenzene was used as an inner standard sample. From the ratio of peak areas (ketone to bromobenzene), the amount of each component could be determined. The gas chromatographic columns for the determination of ketonic components are following; (1) 200 cm Apiezon-L on Cerite (80—100 mesh), (2) 200 cm TG-3000 on Certie (80—100 mesh), (3) 300cm High Vacuum Grease on Cerite (80—100 mesh), Carrier gas: H_2 at 150—200°C. The gas chromatographic column for the identification of gaseous products was a 200 cm column of β,β'-oxydipropionitrile on Cerite, carrier gas: H_2 at 25°C.