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ELECTROOXIDATION OF ALCOHOLS USING A NEW DOUBLE MEDIATORY SYSTEM[1]

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The electrochemical oxidation of alcohols was accomplished by using a double mediatory system in which both alkyl methyl sulfide and bromine act in concert as mediators.

There has been much mechanistic and synthetic interest in indirect electrochemical reactions using mediators,[2] though only few organic mediators have been exploited so far.[3] One of our interests in the indirect anodic oxidation has been directed toward the development of new mediators or redox systems which leads to accomplishment of oxidation of organic compounds at lower anode potentials than those necessary for direct electrooxidation of the substrates. We have previously reported that thioanisole is an efficient mediator in the electrochemical transformation of alcohols to the corresponding ketones as shown in Fig 1,[4] in which a redox system consisting of thioanisole and its cationic active species ($Ph\overset{+\cdot}{S}CH_3$ or $Ph\overset{++}{S}CH_3$) intervenes between the anode and alcohols. This system may be called a single mediatory system.

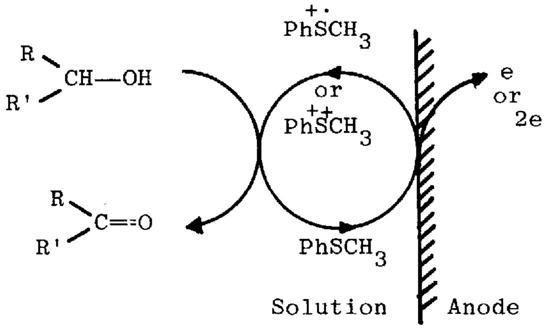


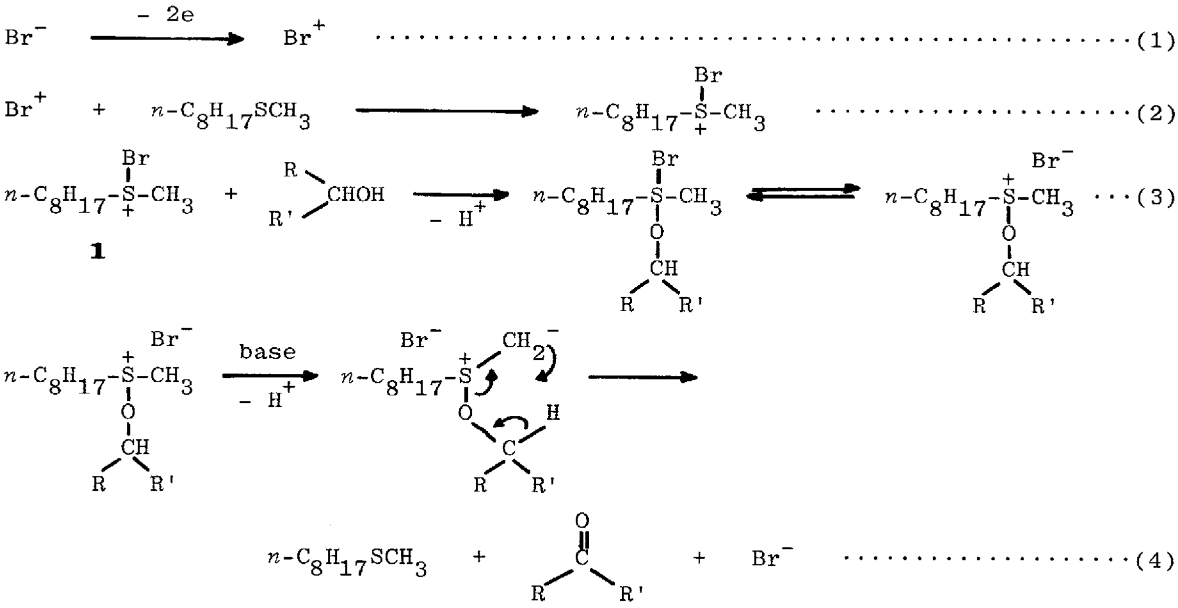
Fig. 1.

Although the oxidation peak potential of thioanisole (1.60 V *vs.* SCE) is sufficiently lower than that of alcohols, we have been interested in other mediators which make the oxidation of alcohols feasible at further lower potential.

In the present study, we have found a new mediatory system in which both alkyl methyl sulfide and bromine act in concert as mediators.

The anodic oxidation of secondary alcohols was carried out in a similar manner to our previously reported method[4] except that tetraethylammonium bromide was used as a supporting electrolyte instead of tetraethylammonium *p*-toluenesulfonate. Results obtained using *n*-octyl methyl sulfide as a mediator are shown in Table I in which yields are reasonable, while the same mediator gave a rather poor yield when tetraethylammonium *p*-toluenesulfonate was used as a supporting electrolyte (run 2), indicating that this sulfide barely worked as a mediator in the absence of bromide ion.

The reaction mechanism is assumably as follows (eqs. 1—4), though it is not conclusive yet.

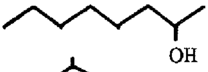
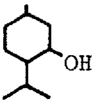
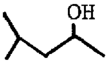
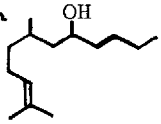
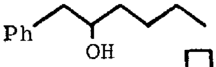
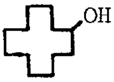


The reaction may be initiated by the oxidation of bromide ion (Br^-) to bromonium ion (Br^+), since the oxidation potential of Br^- to Br^+ (E_p, 1.1 V *vs.* SCE)[5] is sufficiently lower than that of *n*-octyl methyl sulfide (E_p, 1.93 V *vs.* SCE).[5] The sulfonium ion intermediate (**1**) formed from *n*-octyl methyl sulfide and bromonium ion reacts with alcohols in the similar way to those proposed in the chemical oxidation of alcohols by means of dimethyl sulfide and halogens.[6] The regenerated sulfide and bromide ion can play again the role of mediators.

The regeneration of mediators is clearly shown in Table II, in which the yield of ketone is 480% based on mediators when one tenth equivalent of mediators is used.

The concept of this new electrooxidation system can be depicted as shown in Fig. 2, which may be called a double mediatory system. Using this double mediatory system, the anode potential necessary for oxidation of alcohols can clearly be lowered below that in single mediatory system.

Table I. Electrochemical Oxidation of Alcohols Using *n*-Octyl Methyl Sulfide and Tetraethylammonium Bromide.[a]

Run	Alcohol	[Alcohol]/[n-$C_8H_{17}SCH_3$][b]	Passed Electricity (*F*/mol)	Yield of Ketone (%)
1		1/1	10	85
2		1/1	10	25[c]
3		2/1	10	69
4		1/1	10	71
5		2/1	10	72 (82)[d]
6		2/1	5	41 (77)[d]
7		2/1	5	49 (94)[d]
8		2/1	10	51 (93)[d]

a) The reaction conditions are as follows: Solvent; dry benzonitrile (5 ml), supporting electrolyte; tetraethylammonium bromide (5 mmol), alcohol; 5 mmol, base; 2,6-lutidine (2.5 mmol), cathode; carbon, anode; Pt, apparatus; undivided cell.

b) The molar ratio of alcohols to *n*-octyl methyl sulfide.

c) Tetraethylammonium *p*-toluenesulfonate was used as a supporting electrolyte instead of tetraethylammonium bromide.

d) The yields on the basis of the consumed alcohols are shown in parentheses.

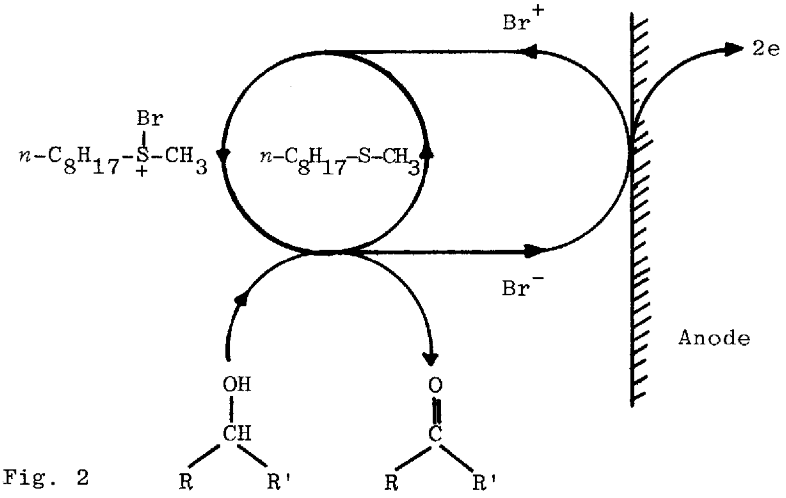


Fig. 2

Table II. Electrochemical Oxidation of 2-Octanol Using Various Equivalents of *n*-Octyl Methyl Sulfide and Tetraethylammonium Bromide (Et_4NBr).[a]

Molar Ratio			Yield of 2-Octanone (%)			Recovered Sulfide (%)
2-Octanol	n-$C_8H_{17}SCH_3$	Et_4NBr				
1	1	1	81[b]	81[d]	81[e]	43
1	1/2	1/2	63[b] (93)[c]	126[d]	126[e]	45
1	1/4	1/2	39[b] (98)[c]	156[d]	78[e]	61
1	1/10	1/10	48[b] (96)[c]	480[d]	480[e]	70

a) The reaction conditions are as follows: Solvent; dry benzonitrile (5 ml), alcohol; 5 mmol, 2,6-lutidine; 2.5 mmol.
b) Based on alcohol.
c) The yields in parentheses are based on the consumed alcohol.
d) Based on *n*-octyl methyl sulfide.
e) Based on tetraethylammonium bromide.

References and Notes

1) Electroorganic Chemistry 44.

2) M. M. Baizer, "Organic Electrochemistry," Marcel Dekker, Inc., New York, 1973, Section G, p. 805.

3) a) W. Schmidt and E. Steckhan, *J. Electroanal. Chem.*, **101**, 123 (1979).
   b) W. Schmidt and E. Steckhan, *Angew. Chem. Int. Ed. Engl.*, **17**, 673 (1978).
   c) H. Lund and J. Simonet, *J. Electroanal. Chem.*, **65**, 205 (1975).
   d) J. W. Sease and R. C. Reed, *Tetrahedron Lett.*, **1975**, 393.

4) T. Shono, Y. Matsumura, M. Mizoguchi, and J. Hayashi, *Tetrahedron Lett.*, **1979**, 3861.

5) The oxidation peak potential was measured under the following conditions: Solvent; dry acetonitrile, supporting electrolyte; tetraethylammonium *p*-toluenesulfonate (0.1 M), concentration of sulfide; 1×10^{-2} M, scanning rate; 100 mV/s.

6) E. J. Corey and C. V. Kim, *J. Am. Chem. Soc.*, **94**, 7586 (1972).

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