CHEMISTRY LETTERS, pp. 1727-1730, 1986.

Effects of Oxygen on Cyclic Voltammetry of Olefins. A Diagnostic Tool for Elucidating the Reactivity of Olefin Radical Cations with Molecular Oxygen

Masahiro TSUCHIYA, Ryoichi AKABA,† Shin AIHARA,
Hirochika SAKURAGI,* and Katsumi TOKUMARU
Department of Chemistry, University of Tsukuba,
Sakura-mura, Ibaraki 305

The oxidation currents of olefins were measured under cyclic voltammetry conditions in the absence and presence of oxygen. Under oxygen the currents decreased to different extents depending on the structure of olefins. The mechanism of the oxygen effect are discussed in connection with elucidation of the reactivity of olefin radical cations with molecular oxygen.

Cyclic voltammetry (CV) has been employed to determine electrochemical redox potentials of various compounds and to examine behavior of their radical ions.1) The CV measurements are usually carried out under an inert gas to avoid eventual interference of oxygen. However, during the course of an investigation of oxygenation of olefins through electron transfer processes,2) we have found that on application of oxidative CV potentials to some olefins in solution the oxidation current decreases under oxygen compared to that under inert gases, and that this effect is significantly varied, from highly remarkable to nil, depending upon the structure of substrates. Accordingly, the oxygen effect can be used as a diagnostic tool for evaluating the reactivity of olefin cation radicals with molecular oxygen.3)

A typical example of the oxygen effect is shown in Fig. 1 for cyclic voltammograms of 2,3-dimethyl-2-butene (DMB, 2×10^{-3} mol dm^{-3}) taken with a scan rate of 100 mV s^{-1} in acetonitrile containing tetrabutylammonium perchlorate (TBAP, 0.1 mol dm^{-3}) as a supporting electrolyte at ambient temperature under argon and oxygen;4) in the latter case the oxidation current was dramatically reduced compared with that in the former case. An exploratory investigation was made on the oxygen effect on the cyclic voltammogram for a variety of olefins. The ratios of CV peak currents (R_{Ip}) under argon and oxygen were determined under similar conditions to those employed for DMB, and are summarized in Table 1.

Inspection of Table 1 indicates that the oxygen effect is associated with the number and positions of methyl groups on the double bond. The most pronounced effect was observed on the olefins bearing geminal dimethyl groups on the olefinic

---

† Present address: Department of Chemistry, Gunma Technical College, Toriba-machi, Maebashi, Gunma 371.

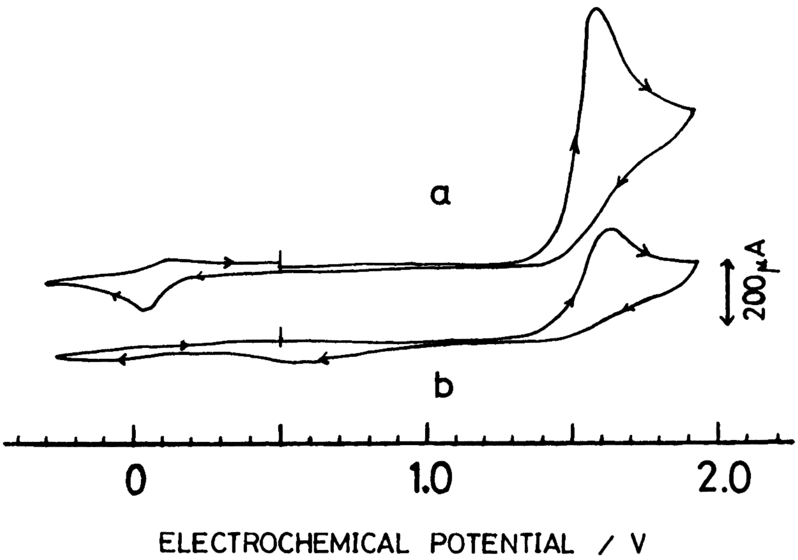
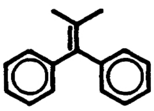
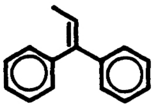
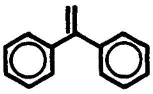
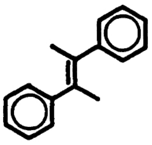
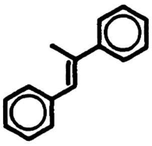
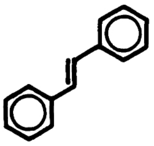
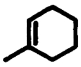
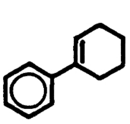
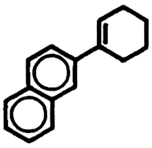
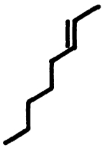


Fig. 1. Cyclic voltammograms of DMB under argon (a) and oxygen (b).

carbon such as DMB and 1,1-diphenyl-2-methylpropene,[5)] and a moderate effect was exerted on 2-methyl-2-butene and 1-methylcyclohexene, which contain a structure equivalent to geminal dimethyl groups. However, among aromatic olefins, none of such oxygen effects were observed on 1,1-diphenylethene and (E)-1,2-diphenylethene (trans-stilbene) which have only phenyl groups as substituents on the double bond. It is also of interest that no oxygen effect was observed on (E)-

Table 1. Oxygen effect upon cyclic voltammograms of olefins[a)]

Olefin								
E_{ox}/V [b)]	1.62	1.73	1.85	1.57	1.52	1.42	1.90	
R_{Ip} [c)]	2.0	1.0	1.0	1.0	1.0	1.0	1.2	
Olefin								
E_{ox}/V [b)]	1.87	1.59	1.49	1.59	2.36	1.59	1.95	2.40
R_{Ip} [c)]	1.7	1.4	1.3	1.0	1.0	1.8	1.5	1.0

a) Cyclic voltammograms were obtained at 100 mV s^{-1} scan rate. b) Peak potentials vs. SCE. c) Peak current ratios, Ip(argon)/Ip(oxygen).

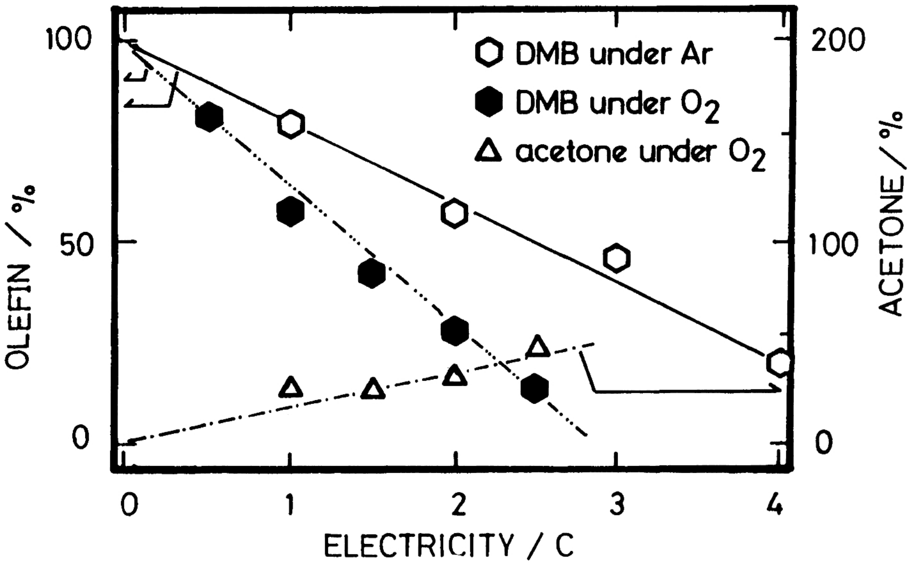
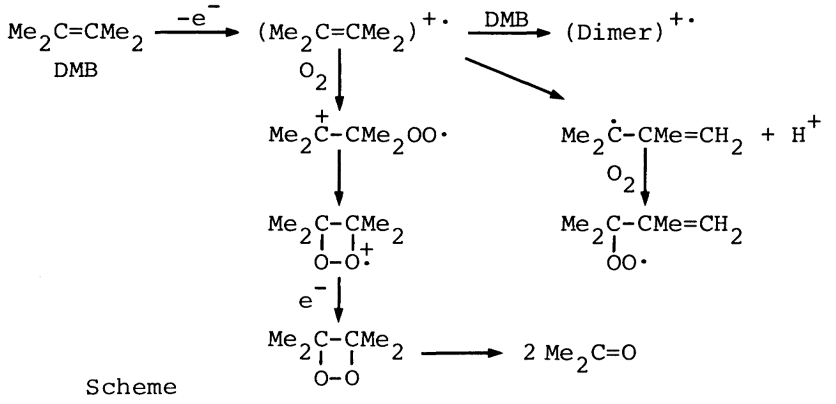


Fig. 2. Plot of the amounts of DMB remained and acetone formed vs. the quantity of electricity passed in anodic oxidation of DMB under argon and oxygen.

2,3-diphenyl-2-butene, an isomer of 1,1-diphenyl-2-methylpropene, and isomeric 1,1- and 1,2-diphenylpropenes, which carry at most one methyl group on the olefinic carbon. Among 1-methyl-, 1-aryl-, and unsubstituted cyclohexenes, the effect was reduced in the same order. However, no oxygen effect was exerted upon α-pinene in spite of the presence of a methyl group on the double bond. For alicyclic olefins, the effect was diminished with decreasing methyl groups on the olefinic carbons.

The observed effect is understood in terms of the reactions of molecular oxygen with the radical cations resulting from electrode oxidation and/or neutral free radicals derived therefrom. These reactions would suppress their subsequent electrode oxidation which might proceed in the absence of oxygen.

Product and coulometry studies support the above mechanism. Controlled potential electrolysis of DMB (1.5×10^{-3} mol dm^{-3}) was carried out at 1.7 V vs. SCE in acetonitrile with TBAP as a supporting electrolyte (0.1 mol dm^{-3}) in the absence and presence of oxygen.[6)] Under oxygen acetone was produced as the main product in a yield of 0.46 mol/mol DMB consumed. The amounts of DMB and acetone



Scheme

in the solution are plotted as a function of the quantity of electricity passed through the solution in Fig. 2. This figure indicates that the electrochemical oxidation proceeds as a nearly one-electron process under argon, but as a nearly half-electron process under oxygen. These results suggest that DMB radical cations react with oxygen to give peroxyalkyl radical cations (which correspond to dioxetane radical cations), which either react with DMB or receive an electron from the electrode at the applied potential[7,8] to give an unstable dioxetane affording acetone finally.[9]

As we will report elsewhere,[5] 1,1-diphenyl-2-methylpropene gives, upon anodic oxidation under oxygen, benzophenone and acetone through the reaction of the corresponding radical cation with oxygen.

The oxygen effect might be different in nature among the compounds. However, it is certain that the presence of methyl groups, particularly of geminal dimethyl groups, on the olefinic carbons increases the reactivity of olefin radical cations with oxygen and also facilitates deprotonation of the radical cations to give allylic radicals which react further with oxygen.

Finally, it is worthwhile to note that the above effect of oxygen which has been hitherto overlooked should be noticed on the measurement of CV and, furthermore, is useful for an understanding of the reactivity of the radical cations with oxygen.

References

1) For example, V. D. Parker, Adv. Phys. Org. Chem., 19, 131 (1983); J. M. Saveant, Acc. Chem. Res., 13, 323 (1980).

2) R. Akaba, H. Sakuragi, and K. Tokumaru, Tetrahedron Lett., 25, 665 (1984); R. Akaba, H. Sakuragi, and K. Tokumaru, Chem. Lett., 1984, 1677; K. Onodera, G. Furusawa, M. Kojima, M. Tsuchiya, S. Aihara, R. Akaba, H. Sakuragi, and K. Tokumaru, Tetrahedron, 41, 2215 (1985).

3) S. F. Nelsen and R. Akaba, J. Am. Chem. Soc., 103, 2096 (1981); E. L. Clennan, W. Simmons, and I. W. Almgren, ibid., 103, 2098 (1981); W. Ando, Y. Kabe, and T. Takata, ibid., 104, 7314 (1982); Y. Kabe, T. Takata, K. Ueno, and W. Ando, ibid., 106, 8175 (1984).

4) Cyclic voltammetry was carried out using a three compartment cell system with a platinum disc, a platinum wire, and an SCE as a working, a counter, and a reference electrode, respectively.

5) R. Akaba, S. Aihara, H. Sakuragi, and K. Tokumaru, unpublished resutlts.

6) The electrolysis was performed in a two compartment cell with platinum gauzes as a working and a counter electrode. DMB (42 mg, 0.05 mmol) was dissolved in 40 ml of 0.1 mol dm^{-3} TBAP acetonitrile solution.

7) S. W. Feldberg and L. Jeftic, J. Phys. Chem., 76, 2439 (1972).

8) As an example, the oxidation potential of a dioxetane of adamantylideneadamantane has been reported as 2.25 V vs. SCE: S. F. Nelsen, D. L. Kapp, F. Gerson, and J. Lopez, J. Am. Chem. Soc., 108, 1027 (1986).

9) More detailed discussion will be described elsewhere.

(Received July 15, 1986)