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Electrochemical Oxidation of Olefins Using *N*-Hydroxyphthalimide as a Mediator

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Electrochemical oxidation of olefins using *N*-hydroxyphthalimide as a mediator was studied. Allylic methylene and allylic methine groups were oxidized to give the corresponding enones, while allylic methyl groups were not readily oxidized except for those of 2,3-dimethyl-2-butene. The product distribution was similar to that observed in free radical autoxidation of olefins. A possible mechanism of the oxidation is proposed.

Keywords——anodic oxidation; mediator; olefin; *N*-hydroxyphthalimide; α,β-unsaturated ketone; glassy-carbon electrode; phthalimide *N*-oxyl

Sensitized photochemical oxidation and chemical oxidation using metal hypochlorite and hydrogen peroxide (ClO^-/H_2O_2) of olefins have been studied extensively, and the reactive oxidant in both oxidations was suggested to be singlet oxygen.[1] The product distributions in these oxidations were reported to be different from those obtained in free-radical oxidations.[2] In unsensitized photooxidation of certain olefins, however, it has been reported that the oxidation proceeds through competing singlet oxygen and radical processes.[3]

The electrochemical oxidation of an isolated double bond requires a high oxidation potential, and in general produces addition products at the double bond carbon. To reduce the oxidation potential, various inorganic mediators have been utilized.[4] We have shown that *N*-hydroxyphthalimide (NHPI) is an excellent mediator for electrochemical oxidations of alcohols and other organic compounds.[5] Cyclohexene was shown to be oxidized to 2-cyclohexene-1-one in fairly good yield.

In the present study, the electrochemical oxidation of cyclic and acylic olefins possessing one isolated double bond was studied using NHPI as a mediator, and the product distribution was compared with those obtained by other methods. The olefins were oxidized to enones with a shifted or an unshifted double bond, and the product distribution was found to be close to that in free radical-induced autoxidation of olefins.[2]

Results and Discussion

Cyclic Voltammetry

The olefins in Table I show an irreversible oxidation wave at the indicated potential. The oxidation potentials are less positive with increasing number of alkyl substituents on the double bond carbon. The results indicate that the first electron transfer takes place from the double bond, occurring most easily at the position with higher electron density due to the electron-releasing alkyl substituent.

Controlled Potential Electrolysis

Controlled potential electrolyses of the olefins were performed in the same manner as in

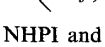
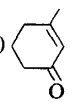
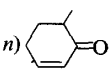
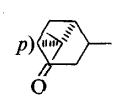
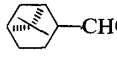
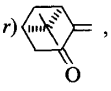
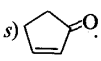
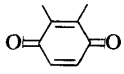
TABLE I. Cyclic Voltammetric Data for Olefins in MeCN–0.1 M $NaClO_4$, 25 °C at a Glassy-Carbon Electrode

Subst. (No.)	E_p [a]	Subst. (No.)	E_p [a]
2 [b]	2.53	**8** [g]	1.88
3 [c]	2.03	**6** [h]	1.67
5 [d]	2.03	**7** [i]	1.52
4 [e]	2.00	**1** [j]	1.45
9 [f]	1.95	**10** [k]	1.45

a) Peak potential in volt *vs.* SCE. *b*) 1-Octene. *c*) *trans*-4-Octene.
d)  . *e*) Cyclohexene. *f*) Cyclopentene. *g*)  , (1*S*)-(−)-β-pinene.
h)  . *i*)  , (1*S*)-(−)-α-pinene. *j*)  . *k*)  .

TABLE II. Results of Electrolysis of Olefins Using NHPI as a Mediator [a]

Subst. (No.)	F/mol [b]	Products (No.)	Yield (%) [c]	Recovered subst. (%)	Recovered NHPI (%)
1	0.9 [d]	**1′** [e]	43	0	5
	0.7 [d,f]		28	25	Trace
2	1.4 [d]	**2′** [g]	7	51	19
3	1.5	**3′** [h]	36	i)	27
	2.0		25	15	26
	2.0		27 [j]	Trace	60 [j]
4	1.5	**4′** [k]	44 [l]	5	50
5	1.5	**5′** [m]	28	i)	23
		5″ [n]	3		
6	1.5	**5′**	39	i)	24
		6′ [o]	3		
7	0.9	**7′** [p]	13	i)	i)
	1.5	**7′**	23	0	i)
		7″ [q]	Trace		
8	0.9	**8′** [r]	12	33	10
		7″	9		
	1.3	**8′**	9	17	10
		7″	8		
9	1.8	**9′** [s]	60	i)	8
10	0.2	**10′** [t]	6	64	i)
	0.8		12	14	i)
	1.5		10	0	i)
10′	1.5	**10″** [u]	v)	0	i)

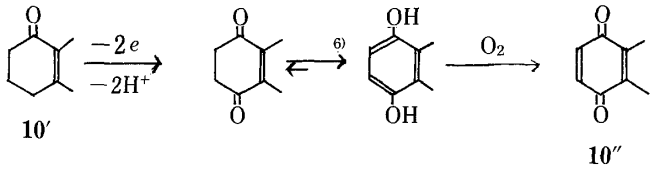
a) 5 mM NHPI and 20 mM substrate were electrolyzed in an undivided cell at room temperature unless otherwise stated. *b*) Electricity passed per mole of substrate. *c*) Based on substrate. *d*) Electrolysis did not proceed further. *e*) HO_2  . *f*) Electrolyzed at 0 °C. *g*) 1-Octene-3-one. *h*) 3-Octene-5-one.
i) Not determined. *j*) 10 mM NHPI and 20 mM **3** were used. *k*)  . *l*) Electrolyzed in a divided cell.
m)  . *n*)  . *o*)  . *p*)  , (1*S*)-(−)-verbenone.
q)  , (1*R*)-(−)-myrtenal. *r*)  , (1*R*)-(+)-pinocarbone.
s)  . *t*)  . *u*)  . *v*) See text.

the previous studies, *i.e.*, using 20 mM substrate, 5 mM NHPI and 5 mM pyridine in 20 ml of acetonitrile containing 0.1 M sodium perchlorate, with a glassy-carbon plate anode at 0.85 V *vs.* saturated calomel electrode (SCE) in an undivided cell, unless otherwise stated.

The amount of electricity that we planned to use was 2 F per mole of olefin, but in some runs, the current dropped nearly to zero before 2 F/mol of electricity had been consumed. As shown in Table II, the main products were enones with a shifted or an unshifted double bond except for the case of **1**, which gave a hydroperoxide with a shifted double bond, **1′**. The yields of enones were higher for the olefins having four allylic protons (**3**, **4**, **6** and **9**) than for those having two (**2**) or three allylic methylene or methine protons (**5**, **7** and **8**), and did not appear to depend on the oxidation potentials of the olefins. Oxidation of an allylic methyl group was negligible (**7**) except in the case of **1**. This is contrary to the results of oxidation by singlet oxygen, which oxidizes an allylic methyl group effectively; compounds with an exocyclic double bond were produced from **7** and **10**.[1] Oxidation of **5** yielded **5′** and **5″** in a ratio of 9 : 1, resulting from the preference for hydrogen abstraction from tertiary rather than secondary allylic carbon. In the oxidation of **6**, the major product **5′** seems to be produced by hydrogen abstraction from the sterically less hindered position. The yields of enones from **7** and **8** are low, especially in the case of **8**. No product derived from the abstraction of bridge-head hydrogen was detected.

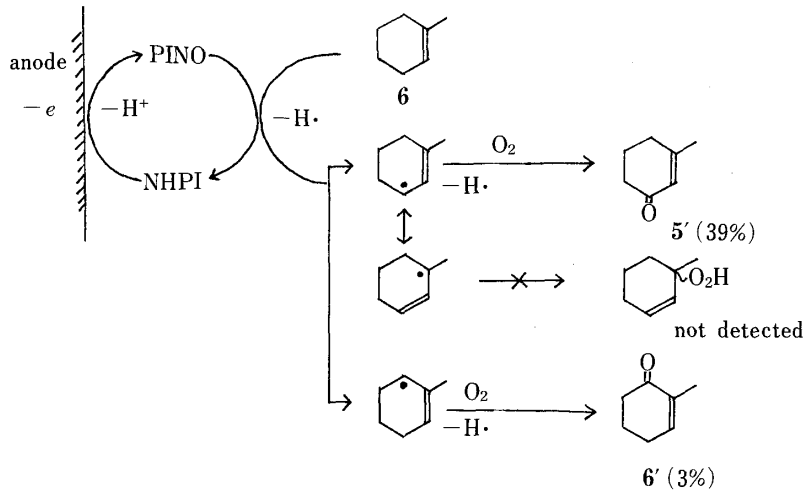
The current decrease observed before the consumption of 2 F/mol based upon the substrate (**1** and **2**) is probably explicable as follows. i) In the case of **1**, a part of the starting olefin may have evaporated off because of its low boiling point, 73 °C; ii) the reactivity of **2** toward electrogenerated phthalimide *N*-oxyl (PINO) is so low that about half of **2** remains unoxidized. When electrolysis of **1** was performed at a lower temperature, 0 °C, the amount of **1** recovered was increased (see Table II), but the amount of electricity consumed and the yield of **1′** decreased.

In the cases of **3**, **4**, **7** and **10** the yields of enones after consumption of a larger amount of electricity are rather lower than those after a lower consumption of electricity. This suggests that a part of the products is further oxidized. In fact, a small amount of 2,3-dimethyl-1,4-benzoquinone (**10″**) was formed by the electrolysis of **10**, as determined by column chromatography. The quinone **10″** was, however, not detected in the solution just after the electrolysis, and it may be formed from 2,3-dimethyl-1,4-hydroquinone during the work-up of the electrolysed solution, as follows.



The cell type, divided or undivided, and the kind of supporting electrolyte, $LiClO_4$ or $NaClO_4$, did not affect the yields of **4′** and **9′** significantly. The results shown in Table II reveal no definite relation between the electricity consumed and the amount of enones produced, but, in general, the results suggest that the olefins yielding larger amounts of enones require smaller amounts of electricity to form a given amount of enones.

From the above results, the oxidation route of the olefins is considered to be similar to that proposed for radical-induced autoxidation;[2] *i.e.*, a hydrogen atom is abstracted first by electrogenerated PINO from an allylic carbon to yield an allylic radical, then the resulting species (stabilized by resonance) is attacked by molecular oxygen to yield α,β-unsaturated carbonyl compounds. For example, oxidation of **6** to **5′** or **6″** may occur as follows.



The yields of enones from olefins obtained by the present method, in general, are insufficient from a preparative point of view, though little attempt was made to optimize the conditions. However, as compared with the methods reported[7] for the preparation of **3′** and **9′**, the present method of oxidation is superior, because it is a single-step reaction that is easy to carry under very mild conditions and does not require any dangerous reagent.[2]

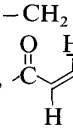
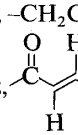
Experimental

Nuclear magnetic resonance (NMR) spectra were recorded on a Hitachi R-20 or R-600 spectrometer with Me_4Si as an internal standard. Infrared (IR) spectra were recorded on a JASCO A-202 spectrophotometer. Gas liquid chromatographic (GLC) analyses were performed on a JEOL JGC-20K instrument. High-performance liquid chromatography (HPLC) was done on a Waters M-600 A instrument equipped with a Shimadzu SPD-2A spectrophotometric detector. Thin layer chromatography (TLC) was performed on Merck aluminum plates (0.2 mm layer of silica gel). Column chromatographies were done on Wakogel C-200 (Wako Pure Chemicals Industries, Ltd.), "Silicic Acid" (Mallinckrodt, Inc.) or "Aluminiumoxid 90 aktiv neutral" (Merck & Co., Inc.).

Apparatus and Procedures——Cyclic Voltammetry: Cyclic voltammetry was performed with a three-electrode system employing a linear scanning unit (Hokuto Denko Co., model HB 101) equipped with a potentiostat (Hokuto Denko Co., model PS-500B). The electrode system consisted of a glassy-carbon indicator electrode (3 mm i.d.), a glassy-carbon counter electrode and a SCE. Measurements were carried out at 25±0.05 °C with a substrate concentration of *ca.* 5 mM and a sweep rate of 0.05 V s^{-1}.

Controlled Potential Electrolysis: Controlled potential electrolysis was carried out with a Hokuto Denko HA 101 potentiostat; the current was recorded on a Toa Dempa EPR-2TB recorder and the quantity of electricity consumed was measured with a Hokuto Denko HF-102 coulombmeter. The electrolyses were generally performed with 20 mM substrate, 5 mM NHPI and equimolar pyridine with respect to NHPI in 20 ml or 100 ml of acetonitrile containing 0.1 M $NaClO_4$ using a divided or an undivided cell with a glassy-carbon plate electrode, at 0.85 V *vs.* SCE. On electrolysis in a divided cell, about twice the amount of pyridine with respect to the substrate was used.

Materials——The starting materials **1**, **2**, **7**, **8** and **9** were purchased from Tokyo Kasei Kogyo Co., Ltd., **4** and **6** were from Wako Pure Chemicals Industries, Ltd., **3** was from Aldlich Chemical Co., and **5** was from Nakarai Chemicals, Ltd. **10** was prepared according to the reported method,[8] bp 137 °C (lit.[8] 135.4—135.9 °C).

Authentic samples of products **4′**, **5′**, **7′**, **7″** and **9′** were purchased from Aldrich Chemical Co. All materials were of reagent (or equivalent) grade and were used as received from the commercial source. Other authentic samples **1′**,[9] **2′**,[10] **3′**,[6a] **5″**,[11] **6′**,[12] **8′**[13] and **10′**,[14] were prepared according to the cited methods. **1′**, bp 49—52 °C/8 mmHg (lit.[9] 53—55 °C/12 mmHg) **2′**, 59—60 °C/16 mmHg, ^{1}H-NMR (in $CDCl_3$) 0.9 (3H, s, Me), 0.8—2.03 (6H, m, $-CH_2\times3$), 2.58 (2H, t, J=7 Hz, $-CH_2CO-$), 5.73 (1H, dd, J=9 and 4.5 Hz, $-CO-C\underline{H}=CH_2$), 6.22 (1H, d, J=4.5 Hz, ), 6.28 (1H, d, J=9 Hz, ) **3′**, bp 82—84 °C/32 mmHg (lit.[6a] 68—72 °C/25 mmHg); the proton nuclear magnetic resonance (^{1}H-NMR) coupling constant, J_{ab}=16 Hz, between two vinyl protons, H_a (6.30 ppm) and H_b (6.80 ppm), indicates that **3′** is *trans* form. **5″**, bp 78—80 °C/37 mmHg (lit.[11] 74—75 °C/24 mmHg) **6′**, bp 84—86 °C/37 mmHg

(lit.[12] 83—85 °C/35 mmHg) **8′**, bp 35 °C/1 mmHg (lit.[13b] 84—86 °C/8 mmHg) **10**, bp 77 °C/8 mmHg (lit.[14] 96 °C/14 mmHg). **10″** was isolated from the electrolyzed solution of **10** by column chromatography; ^{1}H-NMR (in $CDCl_3$) δ: 2.03 (6H, s), 6.71 (2H, s) and IR (KBr) spectroscopic data were in accord with those in the literature.[15]

Products Analysis——The oxidation products **3′**, **7′**, **8′**, **9′**, **10′** and **10″** were isolated from the electrolyzed solution by silica gel thin layer or column chromatography and identified by comparison of spectroscopic (IR and ^{1}H-NMR) data, and GLC and HPLC retention times with those of authentic samples. Unless otherwise specified, all GLC analyses of the products and starting materials that remained unoxidized were done on 2 m × 3 mm i.d. or 3 m × 3 mm i.d. stainless steel columns packed with 10% PEG 20 M on Celite 545 at 100—175 °C. All HPLC analyses were performed using a bonded-phase cartridge C_{18}, Radial-PAK A (Waters Associates, Inc.) with 70% (v/v) aqueous methanol as the eluent. The oxidation products **1′**, **2′**, **4′**, **5′**, **5″**, **6′**, and **7″** were identified and determined by comparison of the GLC and HPLC retention times with those of authentic samples using 5 μl of the solution after electrolysis. NHPI that remained unoxidized was isolated by silica gel column chromatography and determined by HPLC.

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