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A SPECIES REACTIVE WITH NITRATE ORGANIC SUBSTRATES IS GENERATED BY ANODIC OXIDATION OF PERCHLORATES IN ACETONITRILE

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The reaction of a solution obtained by anodic oxidation of tetraethylammonium perchlorate in MeCN with 5,7,4'-trimethoxyflavanone or 7-methoxycoumarin afforded a chlorinated derivative 1 and the nitrated derivatives 2, 3, and 4, or 6-nitro-7-methoxycoumarin.

KEYWORDS —— anodic oxidation; tetraethylammonium perchlorate; acetonitrile; flavanone; coumarin; nitration

It is known that ammonium perchlorates used widely as electrolytes undergo electrochemical oxidation in non-aqueous solvents at high oxidation potential (ca. 2.0 V vs. SCE in MeCN).[1)] Although a few explanations of the anodic oxidation processes of perchlorates have been proposed, [2)]a generally acceptable principle has not yet appeared.

We report here the generation of a fairly stable species active to nitrate organic substrates by the anodic oxidation of perchlorates in MeCN which provides evidence on the fate of ammonium perchlorates by anodic oxidation.

Electrolysis of a 0.2 M solution (50 ml) of the perchlorate Et_4NClO_4 (TEAP) in MeCN[3)] was carried out using a two-compartment cell dividing to the anode and cathode (both 6 cm^2 platinum plate electrodes) with a commercially available porous porcelain cup (rough ceramic cup) under a constant current of 300 mA (3.5-4.5 V vs. Ag-AgCl) and ice-water cooling for 60 min, using a Hokuto Denko HA 3001 Potentio-Galvanostat (Fig. 1). During the course of electrolysis, the anodic solution changed from colorless to pale yellow and then colorless, and the cathodic irreversible wave at $E_{1/2}$1.15 V vs. SCE in the cyclic voltammogram (CV) increased in proportion to electrolysis time. Also amine Et_3N was produced at the cathode and oxygen evolved from the anode. The solution finaly obtained at the anode column was strongly acidic with a rest potential of ca. 1.5 V vs. SCE. The resulting solution was titrated with $Fe(bpy)_3(ClO_4)_3$ (E = 1.1 V vs. SCE). That is, when the solution was electrolyzed for 20 min it oxidized 1 mM of the complex. When electrolyzed for 60 min it consumed 3 mM of the complex. The latter solution was stable at room temperature for several hours, as indicated by titration. The same solution with a high rest potential was obtained by the similar electrolysis of $HClO_4$ solution instead of TEAP in MeCN.

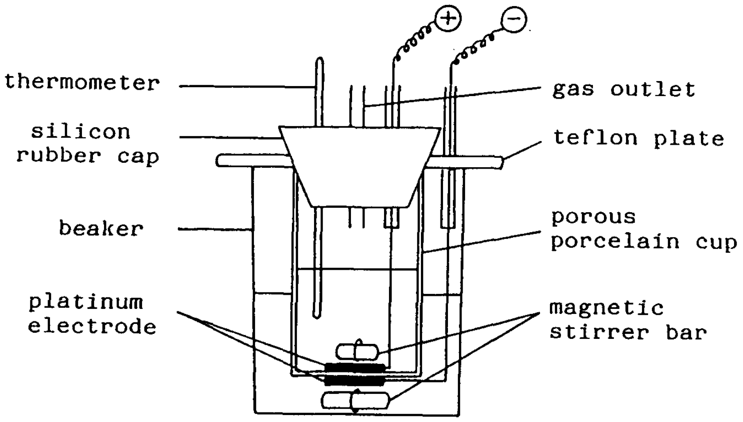

Fig. 1. Two Compartment Cell for the Electrolytic Oxidation

The reactivities of the resulting solution with organic substrates were subsequently investigated because of its high oxidation potency.

The reaction of 5,7,4'-trimethoxyflavanone (314 mg, 1 mmol) with the solution of 0.2 M TEAP in MeCN (50 ml) electrolyzed for 60 min afforded four products, namely, 8-chloro-5,7,4'-trimethoxyflavanone (1), 6-chloro-3'-nitro-5,7,4'-trimethoxyflavanone (2), 3'-nitro-5,7,4'-trimethoxyflavanone (3), and 8-chloro-3'-nitro-5,7,4'-trimethoxyflavanone (4) in yields of 6.9%, 2.6%, 25.9%, and 12%, respectively.[4)] The formation of the nitro derivatives such as 2, 3, and 4 was a surprising result. The similar reaction with 7-methoxycoumarin also gave a nitro derivative, 6-nitro-7-methoxycoumarin as a sole product in 80.5% yield.

The structures of the products derived from the trimethoxyflavanone were assigned by the following spectroscopic analysis. A position of chlorination in the product 1 was established to be C-8 by analysis of $^{13}C-^{1}H$ long range couplings of the ^{13}C-NMR as follows. Carbon signals at 161.0 and 160.7 ppm appeared each as a doublet-quartet (Fig. 2 A) coupled with an aromatic proton and three protons of the methoxy group. When the aromatic proton was irradiated, each carbon signal appeared as a quartet (Fig. 2 B). The signals at 161.0 and 160.7 ppm are assignable to C-7 and C-5, respectively, by comparison with the corresponding carbon signals (166.0 ppm, doublet-quartet and 162.4 ppm, doublet-doublet-quartet) of the starting material. The carbon signal at C-4' (159.9 ppm) appeared as a multiplet of a triplet-triplet-quartet coupled with the protons at C-2', C-3', C-5', and C-6', and the three protons of the methoxy group. Further, the carbon signal at C-9 appeared at 159.2 ppm, a singlet, although it was a doublet coupled with the proton at C-8 in the starting material. Thus, it appears that the position of the chlorine atom in 1 should be at C-8.

The ^{1}H-NMR and mass spectra of the products 2 and 4 showed that they are isomers of each other at the substitution position of the chlorine atom either at C-6 or C-8, since their mass spectra had the same fragment peaks at m/z 241 and 214, and the signals of their ^{1}H-NMR spectra showed a difference only at 6.42 ppm in 2 and 6.19 ppm in 4. The signal at 6.19 ppm in 4 is assignable to

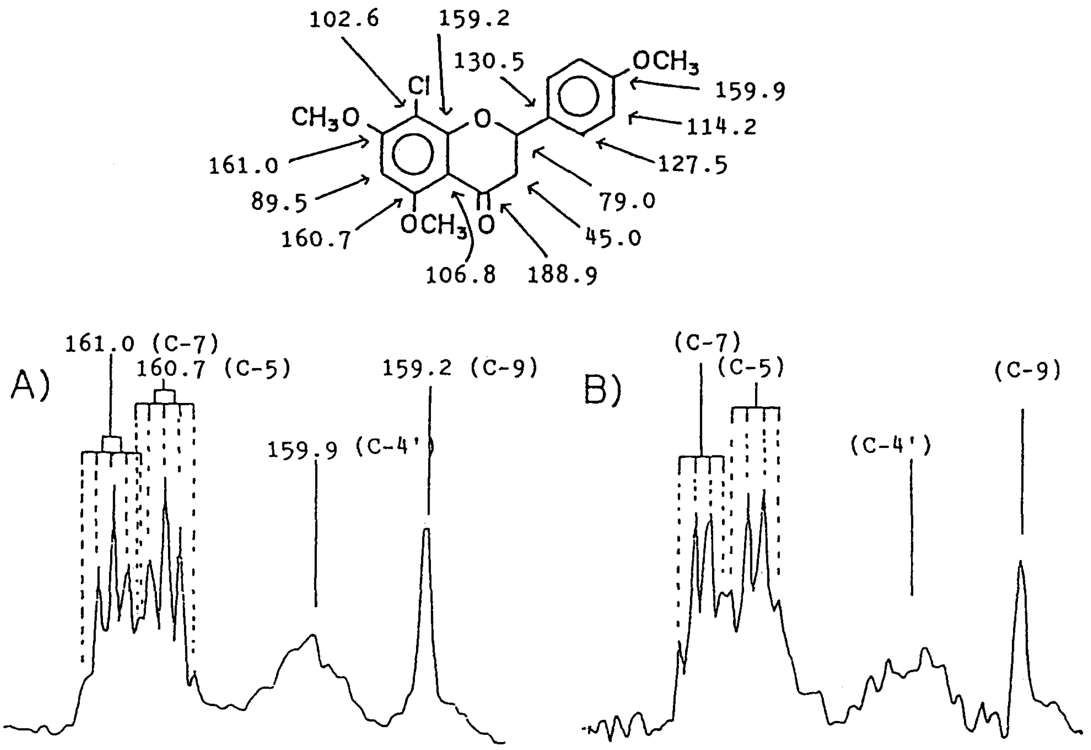

Fig. 2. ^{13}C-NMR and ^{13}C-^{1}H Long Range Coupling Spectra of 8-Chloro-5,7,4'-trimethoxyflavanone (1)

C-6 H by the comparison with the corresponding signal of 1. Thus, the structure of 4 was assigned as an 8-chloro-3'-nitro derivative and the isomer 2 as a 6-chloro-3'-nitro derivative of the flavanone.

These results show that the electrolyzed anodic solution contains some species which react with chlorinate and nitrate organic substrates. Apparently the species which chlorinates the organic substrate is formed in the solution, since the exhaustive oxidation of perchlorate may result in some reactive molecule for chlorination through the oxidative degradation of perchloric ions. On the other hand, the production of the species reactive with nitrate organic substrates is suprising. The nitrogen source of the active species may be derived from the nitrogen of MeCN and not from the ammonium nitrogen, since the same reactive solution was obtained on electrolysis of $HClO_4$ MeCN solution. And the oxygen source in the active species may originate from the decomposition of the $HClO_4$ radical or its degradation products, since fluoroborate did not produce the active species by the electrolysis. And ClO_2, a degradation product, may not be involved in the production of the active species since the electrolysis of ClO_2 MeCN solution under the same conditions did not produce the same reactive solution.

Although several species reactive with nitration, such as $MeCO_2NO_2$ and $MeC(Cl)_2NO_2$ etc., can be expected, these compounds are excluded by the following evidence. (a) $MeCO_2NO_2$ is excluded because reaction of cyclohexene with the electrolyzed solution did not afford any addition product; (b) $MeC(Cl)_2NO_2$ may not be responsible because its MeCN solution has neither as high a rest potential as the electrolyzed solution nor is it reactive to nitrate organic substrates in acidic condition.

Therefore, we can not specify the active species for nitration at the present time, but the high rest potential of the obtained electrolyzed solution may depend on the active species and not Cl_2 or ClO_2 since their rest potentials are very low.

REFERENCES AND NOTES

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3) MeCN was purified according to the procedure reported by J. F. Coetzee, Pure Appl. Chem., 13, 429 (1966), and the supporting electrolytes purchased from Tokyo Kasei Co. Ltd. were used.

4) 8-Chloro-5,7,4'-trimethoxyflavanone (1), mp 183-185°C. IR (nujol) cm^{-1} : 1665, 1605, 1585, and 1518; ^1H-NMR($CDCl_3$) δ: 2.88 (1H, dd, J= 16.36 and 3.42 Hz, C-3 Hb), 3.04 (1H, dd, J= 16.36 and 11.96 Hz, C-3 Ha), 3.82 (3H, s, OMe), 3.94 (3H, s, OMe), 3.97 (3H, s, OMe), 5.47 (1H, dd, J= 11.96 and 3.42 Hz, C-2 H), 6.16 (1H, s, C-6 H), 6.94 (2H, d, J= 8.79 Hz, C-3' and C-5' H), 7.42 (2H, d, J= 8.79 Hz, C-2' and C-6' H); MS m/z: 348 and 214.

6-Chloro-3'-nitro-5,7,4'-trimethoxyflavanone (2), mp 230-232°C. IR (nujol) cm^{-1}: 1673, 1590, and 1530; ^1H-NMR ($CDCl_3$) δ: 2.84 (1H, dd, J= 16.6 and 3.42 Hz, C-3 Hb), 2.99 (1H, dd, J= 16.6 and 12.45 Hz, C-3 Ha), 3.92 (3H, s, OMe), 3.93 (3H, s, OMe), 3.99 (3H, s, OMe), 5.43 (1H, dd, J= 12.45 and 3.42 Hz, C-2 H), 6.42 (1H, s, C-8 H), 7.14 (1H, d, J= 8.79 Hz, C-5' H), 7.59 (1H, dd, J= 8.79 and 2.2 Hz, C-6' H), 8.0 (1H, d, J= 2.2 Hz, C-2' H); MS m/z: 393, 241, and 214.

3'-Nitro-5,7,4'-trimethoxyflavanone (3), mp 190-192°C. IR (nujol) cm^{-1} : 1662, 1607, 1576, and 1530; ^1H-NMR ($CDCl_3$) δ: 2.82 (1H, dd, J= 16.36 and 3.42 Hz, C-3 Hb), 2.98 (1H, dd, J= 16.36 and 12.45 Hz, C-3 Ha), 3.84 (3H, s, OMe), 3.90 (3H, s, OMe), 3.99 (3H, s, OMe), 5.41 (1H, dd, J= 12.45 and 3.42 Hz, C-2 H), 6.12 (1H, d, J= 2.4 Hz, C-6 H), 6.16 (1H, d, J= 2.4 Hz, C-8 H), 7.14 (1H, d, J= 8.79, C-5' H), 7.61 (1H, dd, J= 8.79 and 2.44 Hz, C-6' H), 8.02 (1H, d, J= 2.44 Hz, C-2' H); MS m/z: 359, 207, and 180.

8-Chloro-3'-nitro-5,7,4'-trimethoxyflavanone (4), mp 248-249.5°C. IR (nujol) cm^{-1}: 1660, 1621, 1600, 1575, and 1525; ^1H-NMR ($CDCl_3$) δ: 2.89 (1H, dd, J= 1636 and 4.4 Hz, C-3 Hb), 2.98 (1H, dd, J= 16.36 and 10.98 Hz, C-3 Ha), 3.92 (3H, s, OMe), 3.97 (6H, s, 2 x OMe), 5.49 (1H, dd, J= 10.99 and 4.39 Hz, C-2 H), 6.19 (1H, s, C-6 H), 7.14 (1H, d, J= 8.79 Hz, C-5' H), 7.66 (1H, dd, J= 8.79 and 2.2 Hz, C-6' H), 7.96 (1H, d, J= 2.2 Hz, C-2' H); MS m/z: 393, 241, and 214.

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