H_2O=94: 6 (v/v) at the flow rate of 8 ml/min. The elution profile is shown in Fig. 7. As illustrated in Fig. 7, Fr. A-1-2a-1 was identified as ginsenoside-Rh_1 by cochromatography with an authentic sample. No impurities were detected by analytical HPLC.

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Studies on Sulfenanilides. V.[1] Anodic Oxidation of 4′-Substituted 2-Nitrobenzenesulfenanilides at a Reticulated Vitreous Carbon Electrode

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Constant current electrolysis of 4′-substituted 2-nitrobenzenesulfenanilides (4′-OMe (**1a**), 4′-Me (**1b**), 4′-Cl (**1c**), 4′-COOEt (**1d**)) was carried out in acetonitrile containing 0.1 M ethyltributylammonium trifluoromethanesulfonate (ETBT), 1% trifluoroacetic acid, and 1% trifluoroacetic anhydride at a reticulated vitreous carbon (RVC) electrode. The quantity of electricity to be fed into the electrolytic cell was determined from the anodic potential-time curves. The yields of 2,7-disubstituted phenazines (di-OMe (**2a**), di-Me (**2b**), di-Cl (**2c**), di-COOEt (**2d**)) were 56%, 24%, 42%, and 33%, respectively. The RVC anode was found to be useful for preparative electrolysis of **1a**—**d**, since the considerable yields of phenazines were obtained within several minutes without the use of an expensive potentiostat.

Keywords——anodic oxidation; 2-nitrobenzenesulfenanilides; 2,7-disubstituted phenazines; constant current electrolysis; reticulated vitreous carbon; oxidation of sulfenamides; RVC electrode

Reticulated vitreous carbon (RVC) is a glassy carbon with a porous structure having a free void volume of about 97% and a surface area of about 65 cm^2/cm^3.[3] A relatively small piece of it can provide an electrode with a substantial surface area for its low electrical resistance and physically continuous structure. So far, RVC has been used as an optically transparent electrode,[4] a rotated porous carbon disk electrode,[5] and a flow-through electrode in voltammetric analysis.[6] An RVC electrode should be very useful for preparative electrolysis because of the high ratio of the porous electrode surface to solution volume, wide operating voltage range, chemical inertness, high electrical conductivity, and relatively reproducible performance of RVC. Therefore, we have attempted to utilize RVC for the anodic oxidation of 4′-substituted 2-nitrobenzenesulfenanilides (4′-OMe (**1a**), 4′-Me (**1b**), 4′-Cl (**1c**), 4′-COOEt

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[1] Part IV: H. Sayo, K. Mori, and T. Michida, *Chem. Pharm. Bull.*, **27**, 2316 (1979).
[2] Location: *Ikawadani-cho, Tarumi-ku, Kobe 673, Japan.*
[3] Bulletin No. 176, Chemotronics International, Inc., Ann Arbor, Michigan 48104, U.S.A.
[4] V.E. Norvell and G. Manantov, *Anal. Chem.*, **49**, 1470 (1977).
[5] W.J. Blaeded and J. Wang, *Anal. Chem.*, **52**, 76 (1980).
[6] A.N. Strohl and D.J. Curran, *Anal. Chem.*, **51**, 353 (1979); W.J. Blaeded and J. Wang, *ibid.*, **51**, 799 (1979); W.J. Blaeded and Z. Yim, *ibid.*, **52**, 564 (1980).
[7] H. Sayo, K. Mori, and T. Michida, *Chem. Pharm. Bull.*, **27**, 2093 (1979).

(**1d**)). In the previous paper,[7] it was shown that controlled potential electrolysis of **1a**—**c** at a glassy carbon plate anode gave the corresponding 2,7-disubstituted phenazines (di-OMe (**2a**), di-Me (**2b**), di-Cl (**2c**)).

Results

Anodic Potential-Time Curve

It has been reported that the presence of acid is essential for the formation of the phenazines,[8] and that the perchlorate ion acts as an oxidizing agent in the anodic oxidation of **1a**—**c**[7] and complicates the reaction mechanism. Therefore, anodic potential-time curves were obtained from 10 mM solutions of **1a**—**d** in acetonitrile containing 0.1 M ethyltributylammonium trifluoromethanesulfonate (ETBT), 1% trifluoroacetic acid, and 1% trifluoroacetic anhydride at an RVC anode. Trifluoroacetic anhydride was added to the solution in order to reduce the water content of the solution. The electrolytic cell used is illustrated in Fig. 1.

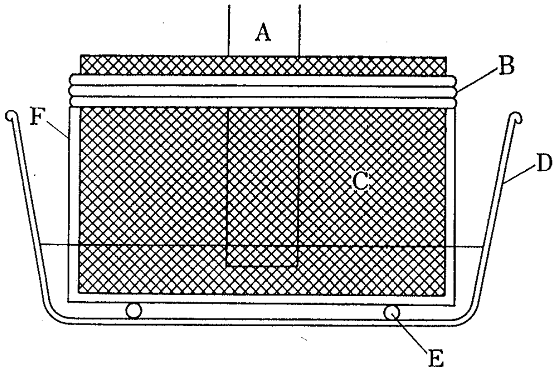

Fig. 1. Electrolytic Cell used for Constant Current Electrolysis

(A) S. C. E., (B) Pt wire, (C) RVC, (D) 18-8 stainless steel box, (E) glass rod, (F) filter paper

When the anodic potential was recorded during the electrolysis of **1c** (10 mM) at a constant current of 0.5 A, the potential increased gradually with time from 1.2 to 1.35 V[9] in about 8 min and rapidly from 1.35 to 1.85 V in the next 4 min. The anodic potential-time curves of **1a**, **1b**, and **1d** showed similar behavior.

Preparative Electrolysis

Electrolysis of **1c** (10 mM) was carried out in acetonitrile containing 0.1 M ETBT, 1% trifluoroacetic acid, and 1% trifluoroacetic anhydride with a constant current of 0.5 A at room temperature in the electrolytic cell shown in Fig. 1. The quantity of electricity to be fed to the cell was varied by changing the duration of electrolysis from 6 min to 14 min. The yield of **2c** increased rapidly with increase in the duration of electrolysis from 17% at 6 min to 42% at 10 min, and then decreased slowly to 36% at 14 min. At electrolysis times longer than about 10 min, only a small amount of unchanged **1c** (less than 2%) was detected in the resulting solution. Therefore, the decrease in the yield of **2c** at longer electrolysis times is

TABLE I. Results of Electrolysis of 4′-Substituted 2-Nitrobenzenesulfenanilides (10 mM) in Acetonitrile[a] with a Constant Current of 0.5 A[b]

Compd. No.	Substituent	Time (sec)	Anodic potential	Yield of Phenazine
1a	4′-OMe	429	0.9 —1.3 V	56%
1b	4′-Me	577	1.05—1.4 V	24%
1c	4′-Cl	600	1.2 —1.6 V	42%
1d	4′-COOEt	662	1.3 —1.5 V	33%

a) The solution contained 0.1 M ETBT, 1% CF_3COOH, and 1% $(CF_3CO)_2O$.
b) The electrolytic cell shown in Fig. 1 was used.

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8) H. Sayo, K. Mori, and T. Michida, *Chem. Pharm. Bull.*, 27, 351 (1979).
9) All potentials were measured against an aqueous saturated calomel electrode (S.C.E.).

considered to be due to oxidation of **2c** formed. The electrolysis time at which the maximal yield of **2c** (42%) was obtained, 10 min, corresponded to the midpoint of the steep rise in the potential-time curve. Thus, the electrolysis of **1a**—**d** was stopped when the anodic potential reached the mid-point of the stteep rise of the potential-time curve. The results of constant current electrolysis carried out in this way are shown in Table I.

Discussion

Since many chemical follow-up reactions which do not participate in the formation of the phenazines are involved in the anodic oxidation of **1a**—**d**,[7] higher yields of the phenazines will be expected if the electrolysis is completed in a short time. The high ratio of the electrode surface to solution volume of an RVC anode permits a considerable reduction in electrolysis time, and hence an RVC anode is expected to be a very powerful tool for the preparative electrolysis of **1a**—**d**. However, it also presents some difficulties. Since there is no way to stir the whole solution during electrolysis with an RVC anode, it is impossible to maintain the potential of the entire surface of the anode at a uniform value. Therefore, if the electrolysis is continued up to the time when the substrate **1a**—**d** is electrolyzed almost completely, a considerable amount of the phenazines formed will be oxidized further at parts of the anode which attain a higher potential than the monitoring part, and hence the yield of the phenazines will decrease.

On the other hand, if the electrolysis is stopped before the phenazines formed are oxidized further, a fairly large amount of unchanged **1a**—**d** remains.

Another characteristic inherent in the use of an RVC anode is a low current density arising from the large surface area of the RVC anode. Because the concentration of protons generated at the surface of an electrode plays an important role in the formation of phenazines, the low current density of the RVC anode will result in a low concentration of protons at the anode surface during the electrolysis, which may cause a decrease in the yield of the phenazines. In fact, the electrolysis of **1a**—**d** at the RVC anode without addition of trifluoroacetic acid gave poor yields. However, this difficulty was largely overcome by addition of the acid, and the phenazines were obtained in satisfactory yields.

In conclusion, the RVC anode was found to be useful for the preparative electrolysis of **1a**—**d**, since considerable yields of the phenazines were obtained within several minutes without the use of an expensive potentiostat.

Experimental

Materials——2-Nitrobenzenesulfenanilides[1,8] and ETBT[7] were prepared as described previously. Acetonitrile was purified as described previously.[10]

Apparatus——RVC with a porosity of 80 pores per inch (RVC 2 × 1-80-s) was obtained from Chemotronics International, Inc. This material was cut into a rectangular brick of approximately 105 × 75 × 50 mm for use as an anode. Electrical contact to the RVC was made by winding a Pt wire around the top end of it. The anode was placed in a box made of Toyo filter paper No. 4. An 18-8 stainless steel box was used as the cathode, and two glass rods were placed between the anode and the cathode in order to prevent short-circuiting of the electrolytic cell. A saturated calomel electrode (S.C.E.) was inserted in a hole bored in the upper center of the anode (Fig. 1). The electrolytic current was fed in from a Shimadzu RDS-3 regulated DC power supply. The potential of the RVC anode was monitored by the use of an electrometer (Hokuto Denko, model HA-104). Anodic potential-time curves were recorded on a Riken Denshi SP-55V recorder. The concentration of unchanged **1a**—**d** in the electrolyzed solution was determined by high speed liquid chromatography as described previously.[7]

Isolation of the Phenazines Obtained by Preparative Electrolysis——a) **1a** (276.7 mg) was subjected to electrolysis in acetonitrile (100 ml) containing 0.1 M ETBT, 1% trifluoroacetic acid, and 1% trifluoroacetic anhydride at room temperature for 429 sec with an electrolytic current of 0.5 A. Na_2CO_3 (10%, 100 ml)

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[10] H. Sayo and A. Morimoto, *Chem. Pharm. Bull.*, **23**, 3114 (1975).

was added to the resulting solution, and the mixture was extracted with benzene. The organic layer was separated and evaporated to dryness under reduced pressure. The residue was extracted with benzene, and the benzene extract was extracted with 10% HCl (200 ml). The HCl solution was made slightly alkaline with 10% NaOH. Yellow crystals separated out; they were filtered off and weighed (46.1 mg). The filtrate was extracted with ether. The ethereal layer was subjected to column chromatography on alumina (Merck art. 1077, 10 g) with benzene as an eluent. The yellow crystals obtained from yellow fractions were identified as **2a** (21.2 mg).

b) **1b** (259.8 mg) was dissolved in the same solution as in (a) and subjected to electrolysis for 577 sec with a current of 0.5 A. The resulting solution was treated according to procedure (a) above. The yellow crystals obtained were identified as **2b** (37.5 mg).

c) **1c** (280.5 mg) was dissolved in the same solution as in (a) and subjected to electrolysis for 600 sec. Solid Na_2CO_3 (1 g) was added to the resulting solution, and the solution was cooled in a refrigerator overnight. Pale yellow crystals separated out; they were filtered off, washed with acetonitrile and then with water and identified as **2c** (51.8 mg).

d) **1d** (319.0 mg) was dissolved in the same solution as in (a) and subjected to electrolysis for 662 sec. The resulting solution was treated according to procedure (c) above. The yellow crystals obtained were identified as **2d** (52.8 mg).