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13. ABSTRACT *(Maximum 200 words)*

The ESR of electrooxidation products of orthogonally bridged dimers of α,α-coupled thiophene oligomers and spiro-fused phenylene–thiophene mixed oligomers was studied as a function of temperature. ESR measurements on the one-electron oxidation products indicate that the charge remains on a single oligomer unit and does not hop between the two bridged oligomer chains for temperatures up to 300 K. This is evident from the presence of hyperfine structure in ESR spectra for the dimers of short-chain oligomers and the small temperature-dependent line broadening for longer chain spiro dimers, characteristic of a low-energy process such as the paramagnetic site moving along the oligomer chain length. The activation energy for a paramagnetic center moving along the oligomer chain length has been estimated at $<100\ \mathrm{cm}^{-1}$. The incorporation of phenylene into the oligomer unit shifts oxidation potentials anodic and also inhibits the mobility of the polaron along the π-conjugated oligomer segment. Evidence for formation of π–π dimers in solutions of 7-mT has also been obtained.

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The ESR Characterization of Oligomeric Thiophene Materials

by

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The ESR Characterization of Oligomeric Thiophene Materials

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Abstract

The ESR of electro-oxidation products of orthogonally bridged dimers of α,α-coupled thiophene oligomers and spiro-fused phenylene-thiophene mixed oligomers was studied as a function of temperature. ESR measurements on the one electron oxidation products indicate that the charge remains on a single oligomer unit and does not hop between the two bridged oligomer chains for temperatures up to 300K. This is evident from the presence of hyperfine structure in ESR spectra for the dimers of short chain oligomers and the small temperature dependent line broadening for longer chain spiro dimers, characteristic of a low energy process such as the paramagnetic site moving along the oligomer chain length. The activation energy for a paramagnetic center moving along the oligomer chain length has been estimated at $<100\ \mathrm{cm}^{-1}$. The incorporation of phenylene into the oligomer unit shifts oxidation potentials anodic and also inhibits the mobility of the polaron along the π-conjugated oligomer segment. Evidence for formation of π-π dimers in solutions of 7-mT has also been obtained.

Introduction

The applications of conducting polymers, such as polyacetylene,[1] polypyrole,[2] polyaniline,[3] and polythiophene[4] range from batteries,[1] display devices,[5] to molecular wires[6] useful in the creation of molecular electronic devices.[7]

Understanding the electrochemistry is critical to the successful utilization of these materials, and has been the subject of some controversy. For example, oxidized films of polythiophene have been reported to produce curious wave shapes and processes, some of which have been attributed to mechanical properties of the polymers.[8] Ultimately, the understanding of the properties of the polymers is limited by the inability to obtain well-characterized polymers.[8] Consequently, the electrochemical examination of well-defined soluble thiophene oligomers has been done.[9-10] However, here the reactivity of the oxidized species for short chain oligomers (n=1-3), has limited detailed description of these species.[11] Most recently, α,α-coupled thiophene oligomers (n=2-8) with terminal $Si(CH_3)_3$ groups, were used to prevent dimerization of the oxidized (chemical and electrochemical) products.[12] Subsequently, two stepwise oxidations have been observed for the n=2-8 thiophene oligomers in methylene chloride at room temperature. The determination of the optical absorption spectra for the oxidized products enabled assignment of the electronic transitions.

The ESR of the oxidized oligomeric thiophene at room temperature was first reported by Garnier and coworkers[9-10] and produces an exchange narrowed Lorentzian signal at low doping concentrations for the n=6 species. Most recently Miller and coworkers[13-15] examined the ESR of the oxidation products of the n=2,3 thiophene oligomers in which oxidative polymerization at the terminal positions was blocked by CH_3 or SCH_3 groups. Electrogenerated one electron oxidation samples produced a strong structured ESR signal at room temperature, but lowering the temperature to -20°C reversibly reduced the intensity of the ESR signal. This behavior was attributed to a monomer-dimer (π electron) equilibrium.

The current temperature dependent ESR study was motivated by the 1988 publication of Aviram[16] in which he proposes that the monoxidized orthogonal dimer of π-conjugated thiophene oligomers could be used as a "molecular switch." Subsequently, the synthesis of two types of π-σ-π molecules, orthogonally bridged through carbon or silicon was accomplished by one of us.[17-19] Earlier, one of the authors and his group had detailed the intramolecular hopping of an electron from one orthogonal π ligand to another (eqns 1,2) in the paramagnetic reduction products of $[Ru(bpy)_3]^{2+}$ and other tris diimine Ru(II) complexes.[20-24]

$$[Ru(bpy)_3]^{2+} + e^- \longrightarrow [Ru(bpy^-)\,(bpy)_2]^+ \qquad (1)$$

$$[Ru(bpy^-)(bpy')_2]^+ \longrightarrow [Ru(bpy'^-)(bpy)_2]^+ \qquad (2)$$

Key to the determination of the energy barrier for electron hopping (Note that the prime (') simply labels the distinct bpy rings of the complex) between the orthogonal bipyridyl rings was the measurement and interpretation of a temperature dependent ESR line broadening for the electrochemically generated paramagnetic species. Here we report the solution, temperature dependent ESR for the paramagnetic oxidized thiophene oligomers to determine if thermal electron hopping between the two orthogonal halves of the oxidized dimers does occur. Activation energies for various temperature dependent processes are determined.

Experimental

Preparations of compounds 7-mT, C-II, C-VI, S-III, and S-VII (see Figure 1) have been described previously.[17-19] Solvents (HPLC grade) and reagents were obtained from Aldrich Chemical Co. unless otherwise specified. Tetrahydrofuran (THF, Burdick and Jackson) was distilled under vacuum from a solution of sodium/benzophenone. Acetonitrile (MeCN) and dichloromethane (CH_2Cl_2) were refluxed over calcium hydride for several hours and distilled under vacuum. Tetrabutylammonium hexafluorophosphate (TBAH) was recrystallized three times from methanol and dried under vacuum. Anhydrous ferric chloride ($FeCl_3$) was used as received.

All electrochemical measurements and ESR sample preparations were conducted in a dry nitrogen atmosphere (Vacuum Atmospheres glovebox equipped with Dri-train O_2/H_2O removal system). The cyclic voltammetry experiments were performed with a potentiostat/galvanostat EG&G model 273 and recorded on an X-Y IBM recorder. The working, counter and reference electrodes were a 0.5 cm^2 Pt disk, a gold wire and an SCE double junction containing the electrolyte, respectively. The in situ ESR electrochemical cell was composed of a quartz tube containing Pt wire working, counter and pseudo reference electrodes. The counter electrode was separated from the working and reference electrodes by a teflon sleeve and a porous VYCOR disk. No iR compensation was used in electrochemical measurements.

Chemically generated oxidation products were prepared by a method similar to that used by Fichou.[10,26-27] Oxidations were done by successive additions of 2:1 stoichiometric amounts of fresh $FeCl_3/CH_2Cl_2$ solutions to the analyte/CH_2Cl_2 solutions. In CH_2Cl_2, ferric chloride has been shown to undergo the reaction:

$$e^- + 2FeCl_3 \rightarrow FeCl_2 + FeCl_4^- \quad (3)$$

with $E_{1/2}$ ~ 1.22 V (vs SCE).[10,12] Ferric chloride readily oxidizes the compounds under study except C-II which has a very anodic first oxidation potential. Sample concentrations were on the order of 10^{-4} M for electrochemical and chemical oxidations. Electrochemical preparation of the oxidized sample resulted in coulometry data that could not be rationalized, therefore the chemically oxidized samples were used for the temperature dependent ESR data.

Chemically oxidized UV-VIS-NIR samples were prepared in a quartz cell and spectra were recorded immediately using a Perkin-Elmer UV-VIS-NIR Lambda 9 spectrophotometer at room temperature. Successive oxidation products were generated through the addition of another two equivalents of ferric chloride.

Electron spin resonance spectra (X-Band) were obtained with a Bruker ESP 300 ESR spectrometer equipped with a Bruker VT-4111 variable temperature unit. ESR measurements at 77K were obtained using a quartz dewar sample holder. The klystron was tuned to a microwave frequency of 9.44-9.78 GHz. Microwave power ranged from 0.200 - 12.6 mW. The modulation amplitude selected was no greater than 25% of the signal peak-to-peak width. The microwave power remained constant during individual variable temperature experiments. Solid materials in solution ESR samples of electrochemically generated oxidation products were separated from solution by gravity filtration through a fine porosity glass disk. Solid ESR samples were obtained by either gravity filtration or evaporation of solvent.

Chemically generated oxidation samples were pipetted directly from the reaction container into the sample tube without modification.

Results and Discussion

I. Electrochemistry

Results of cyclic voltammetry measurements are given in Table 1 and representative voltammograms are shown in Figures 2-3. The cyclic voltammetry of 7-mT in CH_2Cl_2 has been reported previously.[27] We have measured the voltammetry in various other solvents and found that the potential of first oxidation of 7-mT is not solvent dependent. Voltammetry of 7-mT reveals only one reversible oxidation wave followed by a large increase in the anodic current. The anodic wave for the first oxidation may partially overlap with the wave for the large increase in anodic current. The appearance of waves for a second oxidation process was only observed for measurements in the CH_2Cl_2/MeCN solvent system. Electrolysis of 7-mT at a potential on the rise of the first anodic wave (+0.810 V (SCE)) produced a dark insoluble product. This potential was chosen to minimize the process responsible for the large increase in anodic current.

Voltammetry for the orthogonally bridged silicon compounds has been described previously.[28] The oxidation potentials for these bridged dimers (S-III and S-VII) are similar to the monomer thiophene oligomer. Two oxidation processes similar to those observed in 7-mT are evident in these voltammograms. As with the monomer oligomers the oxidation potential increases with decreasing chain length. Electrolysis in 0.1M TBAH/CH_2Cl_2 produces the soluble green (S-VII) or blue (S-III) one electron oxidation products. The one electron oxidation product of S-III is short lived and dimerizes.

Voltammetry of the phenylene-thiophene spiro bridged dimers show oxidation potentials more anodic than the silicon bridged analog. The first oxidation potentials of C-II and C-VI are more anodic than those of S-III and S-VII, respectively, therefore the biphenylene shifts potentials anodic. The voltammogram of C-II shows waves for only the first one electron oxidation process within the solvent potential window, while two are evident for C-VI. The first oxidation product of C-VI appears to be stable although $\Delta E \sim 120$ mV indicates irreversibility and the second oxidation wave is difficult to interpret since it is buried in the discharge current of the solvent. Results indicate that oxidation products of the phenylene-thiophene spiro fused dimers are more stable than those of the silicon bridged analogs. The one electron oxidation products of C-II and C-VI are soluble in CH_2Cl_2 and are blue and green, respectively.

II. UV-VIS-NIR

Absorption spectra for the neutral and oxidized forms of 7-mT, S-III and S-VII have been described previously.[27-28] Spectra for the successive oxidation products of C-VI are shown in figure 4. The spectra show a decrease in the π-π^* transition band at ~800 nm and the appearance of bands at longer wavelength with increased oxidation. The position of the π-π^* band for C-VI is close to that obtained for S-VII. The spectra for the neutral, one, and two electron oxidation products of 7-mT show a decrease in the π-π^* band at 800 nm, the appearance of a band at 1688 nm for the one electron product and the appearance of a band at 1256 nm for the dication. The absorption spectrum of the dication of S-VII shows an increase in the band at ~1650 nm, a decrease in the intensity of the band at

~800 nm, and very little indication of a band at 1250 nm. These data suggest that the two electron oxidation product of S-VII is a bis species with a positive charge on each of the two thiophene oligomer units. Spectra were recorded immediately following addition of the oxidizing agent, $FeCl_3$. Since the spectra for C-VI are similar to those for S-VII, except that the longer wavelength bands are broad and not discernible, the charge distribution in oxidized products of C-VI is likely to be similar to that of S-VII. Absorption spectra for C-VI indicate the two electron oxidation product is a bis dication, as is that of $(S\text{-}VII)^{2+}$. Spectra for the oxidized forms of C-II could not be studied since C-II is not oxidized by $FeCl_3$ in CH_2Cl_2.

III. ESR Measurements

Because of the obvious complications observed in the cylic voltammetry and coulometry experiments for the electrochemically produced sample, ESR are reported only for the chemically oxidized samples and one electron in situ electrochemical/ESR measurements. Odd electron oxidation products of 7-mT, C-VI, and S-VII gave similar ESR spectra (with respect to linewidth and g value). The ESR line is a narrow S=1/2 Lorentzian shape with no hyperfine structure and $g = 2.005$ (see Figure 5 and Table 2). The narrow line is a result of motional narrowing due to mobility of the polaron along the conjugated oligomer.[29] The only notable distinction between these ESR spectra is the peak-to-peak linewidth at a given temperature. The Dysonian lineshape characteristic of a conducting species[30,31] is not observed for the solid oxidized thiophene as have been observed for solid oxidized thiophene oligomers,[25] polyacetylene,[32] and polythiophene.[9] The lack of evidence of conduction would indicate that intermolecular charge transfer between oligomer chains is a slow or a minor process. The absence of conductivity in solution is expected due to the short oligomer chain length and dilute hole concentrations. The absence of the Dysonian ESR line shape in solid samples of 7-mT indicates that intermolecular charge transfer is also minimal in these powdered samples.

Even electron oxidation products of 7-mT, C-VI, and S-VII produced no or very weak ESR signals which were similar to those obtained for the odd electron products. In a few instances an ESR signal was obtained for the two electron oxidation products of S-VII and C-VI, but over a period of several minutes the signal disappeared unlike the long lived one electron oxidation product. In the preparation of dications of S-VII and C-VI, it was noted that the solution is initially blue, but turns to green in a few minutes. The solution remains green similar in color to the one electron oxidized state even after the signal is lost. If the two electron oxidized sample was reduced to a one electron oxidized state, an increase in ESR signal intensity would be expected with the characteristics of the intense one electron oxidation product ESR signal. These data suggest that the dications of S-VII and C-VI are diamagnetic and have the charge localized on a single oligomer unit of the orthogonally bridged dimers. Since these data conflict with the UV-VIS-NIR data, it must be assumed that either the diamagnetic product is favored thermodynamically or another quenching process is involved. The π-π association of the bis-dications similar to that proposed by Miller et al.[13-15] and discussed below for 7-mT may be an alternative explanation to the loss in signal intensity.

The temperature dependent ESR linewidth data obtained was fit to an Arrhenius equation. The results of this data analysis are given in Table 2 and Arrhenius plots are shown in Figures 6-8. These studies were performed to probe the energy barrier for the positively charged center (polaron) mobility process in the various molecules. If the movement of the polarons is controlled by a thermally activated process then the energy barrier for this process may be calculated from the Arrhenius equation.[20] The activation energy required for a polaron to move along the oligothiophene chain may be calculated from the data obtained for 7-mT since this is the only process available for a polaron in this molecule. Any difference in the activation energy of 7-mT vs. the bridged species must be due to either a perturbation to the oligothiophene chain or a second process, such as, crossing the bridging linkage or intramolecular hole hopping between the orthogonal chains.

The activation energy values for the one electron oxidation samples of 7-mT and S-VII are slightly lower than that of C-VI. Since E_a values much greater than 100 cm^{-1} are expected for charge transfer between the orthogonal halves of the bridged dimers, these low values are more likely for the process of the polaron moving along the individual oligomer chain. The activation energies given in Table 2 may be an upper limit to the true value since the peak-to-peak linewidth variations measured were very near the lower limit of detection. An estimate of the uncertainty in the activation energies of approximately 40-50 cm^{-1} is based on the uncertainty in selecting the exact linewidth peak positions. These small activation energies for polaron mobility along the oligomer chain although slightly greater, compare well to the 8 cm^{-1} value obtained for polyacetylene.[30]

The temperature dependent line broadening (no hyperfine structure) for the longer chain dimer oligomers (single chain and two chain) is evidence for a thermal process while the occurrence of hyperfine structure for the C-II (generated directly in the ESR cavity) indicates that for this short chain dimer, the hole produced by oxidation is delocalized on a single thiophene ring as found for a typical organic π radical. Since the activation energy for the single chain thiophene and the bridged (two chain) dimers have comparable activation energies, the process in both single chain oligomers and dimer chain thiophene must be the same, i.e. a polaron moving along a single thiophene strand. The polaron hopping between strands for the dimer oligomeric thiophenes must require a much larger activation energy. For the reduced Ru(diimine) complexes, the thermal barrier to electron hopping between orthogonal π electron ligand is measured to be ~1000 cm^{-1}. Such a magnitude barrier (1000 cm^{-1}) to the hopping between the orthogonal halves of the dimer would be consistent with the molecular electronic switch proposed by Aviram.[16]

To obtain a measure of the upper limit of the barrier to polaron hopping in the bridged dimer species, two types of experiments were attempted. The first experiments involved an effort to increase the measurement temperatures above room temperature to activate any larger energy process that is present. The solubility of the bridged dimers and solvent volatility limitations prevented a successful conclusion of this effort. The second experiment involved a structural perturbation that would favor the bridge hopping process. Earlier we noted that Miller and coworkers reported the ESR of the one electron oxidation for the thiophene trimer. The significant feature of their results is the occurrence of a broad structured (hfs) signal, indicating that the trimer is not long enough to permit the charge transport process that typically produces the motionally narrowed line for conducting polymers and oligomers. Therefore, we were motivated to examine the ESR spectra of the oxidized dimers of the trimer species. In situ ESR/electrolysis measurements for S-III did not produce an ESR signal but, measurements for C-II produced an ESR signal with hyperfine structure. The presence of hyperfine structure indicates a large barrier to charge transport across the dimer linkage of the two halves of this linkage.

The activation energy obtained for (S-VII)$^{+3}$ (the three electron oxidation species) is 63 cm^{-1}, lower than the barrier for the one electron species, while that obtained for (C-VI)$^{+3}$ is 153 cm^{-1}, a value greater than that for the one electron process. However, in both C-VI and S-VII, the activation energy determined for the one and three electron oxidation species are not very different if the error limits are noted. This is the result expected if the two halves of the orthogonally bridged dimers are noninteracting in both the one and three electron products. The increase in the magnitude of the value of the three electron oxidation product (vs. the one electron) obtained for C-VI may result from the presence of the biphenylene. The biphenylene shifts the oxidation potential anodic relative to the potential of the silicon bridged species.

Multiple electron oxidation samples of S-VII and C-VI were examined at 77K over the range 50-4000 Gauss in an effort to find evidence for the triplet state. No indication of a triplet state was found.

Signal intensity vs. temperature data for the one electron oxidation products of 7-mT, C-VI and S-VII are shown in Figure 10. The signal intensity for oxidized 7-mT is shown to decrease with decreasing temperature while the signal intensity of C-VI and S-VII does not. This suggests that the 7-mT forms a dimer and is consistent with the results of Miller and coworkers for the thiophene trimer.[13-15] The orthogonally bridged C-VI and S-VII are bulky and cannot form the π-π dimers as do the thiophene oligomers. The ESR signal intensity vs. temperature data is reversible upon temperature cycling.

Conclusions

We have shown that the π-σ-π thiophene materials studied can be oxidized and an ESR signal is found for the odd electron oxidation products. The ESR line is motionally narrowed as a result of polaron migration along the π-conjugated oligomer chain, with an activation energy of less than 100 cm^{-1}. When this migration is inhibited in the orthogonally bridged oligomer C-II, hyperfine structure is observed, indicating a large potential barrier, possibly above 1000 cm^{-1}, to the intramolecular charge transfer from oligomer to oligomer unit. The mono-oxidation product of 7-mT reversibly forms π-π dimers with decreasing temperature while this is not observed for C-VI or S-VII. The diamagnetic dication species is either thermodynamically favored over the bis-dication or another ESR signal quenching process such as the π-π association, mentioned above, occurs in C-VI and S-VII.

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References

1) MacDiarmid, A. G.; Mu, S-L; Somasiri, N. L.; Wu, W., Mol. Cryst. Liq. Cryst. 121, 187 (1985).

2) Diaz, A. F.; Kanzawa, K. K.; Gardini, J. P., J. Chem. Soc. Chem. Comm. 1979, 635.

3) Diaz, A. F.; Logan, J. A., J. Eletroanal. Chem. 111, 111 (1980).

4) Diaz, A. F., Chemica Scripta 17, 142 (1981).

5) Nguyen, M. R.; Dao, L. H., J. Electrochem. Soc. 136, 2123 (1989).

6) MacDiarmid, A.; Heeger, A., Ch. 20 In Molecular Electronic Devices, Vol. 1 (F. L. Carter ed.) Dekker, N.Y. 1992.

7) Tourillon, G. and Garnier, F., J. Electroanal. Chem. 161, 51 (1984).

8) Aviram, A., J. Am. Chem. Soc. 110, 5687 (1988).

9) Tourillon, G.; Gourier, D.; Garnier, P.; Vivien, D., J. Phys. Chem. 88, 1049 (1984).

10) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F., Synth. Met. 39, 243 (1990).

11) Gourier, D.; Tourillon, G., J. Phys. Chem. 90, 5561 (1986).

12) Guay, J.; Kasai, P.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L.; Chem. Mater., 4, 1097 (1992).

13) Zinger, B.; Mann, K.; Hill, M.; Miller, L., Chem. Mater. 4, 1113 (1992).

14) Hill, M.; Penneau, J-F.; Zinger, B.; Mann, K.; Miller, L., Chem. Mater. 4, 1106 (1992).

15) Hill, M.; Mann, K.; Miller, L.; Penneau, J-F., J. Am. Chem. Soc. 114, 2728 (1992).

16) Aviram, A., J. Am. Chem. Soc. 110, 5657 (1988).

17) Tour, J. M.; Wu, R.: Macromol. 25, 1901 (1992).

18) Tour, J. M.; Wu, R.; Schumm, J., J. Am. Chem Soc. 112, 5662 (1990).

19) Tour, J. M.; Wu, R.; Schumm, J., J. Am. Chem. Soc. 113, 7064 (1991).

20) Motten, A.; Hanck, K.; DeArmond, M. K., Chem. Phys. Lett. 79, 541 (1981).

21) Morris, D.; Hanck,K.; DeArmond, M. K., J. Am. Chem. Soc. 105, 3032 (1983).

22) Gex, J.; DeArmond, M. K.; Hanck, K., J. Phys Chem. 91, 251 (1987).

23) Gex, J.; DeArmond, M. K.; Hanck, K., Inorg. Chem. 25, 3[illegible] 1987).

24) DeArmond, M. K.; Hanck, K., Proceedings of CompCon '84', 28th IEEEComputer Society International Conference, Feb. 1984.

25) Fichou, D.; Xu, B.; Horowitz, G.; Garnier, F., Synth. Met. 41, 463 (1991).

26) Fichou, D.; Horowitz, G.; Garnier, F., Synth. Met. 39, 125 (1990).

27) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M., Submitted to J. Am. Chem. Soc.

28) Guay, J.; Kasi, P.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L., Chem. Mater. In press.

29) Weinberger, B.; Ehrenfreund, E.; Pron, A.; Heeger, A.; MacDiarmid, A., J. Phys. Chem. 72(9) , 4749 (198?).

30) Goldberg, I.; Crowe, H.; Newman, P.; Heeger, A.; MacDiarmid, A., J. Phys. Chem. 70(3), 1132 (1979).

31) Feher, G. and Kip, A., Phys. Rev. 98(2) 337 (1955).

32) Dyson, F., Phys. Rev. 98(2) 349, (1955).

Table 1. Summary of cyclic voltametry results.

Table 2. Summary of ESR results.

Figure 1. Structures of molecules studied.

Figure 2. Cyclic Voltammogram of C-II (9×10^{-5} M) at Pt electrode in 0.1 M Bu_4NBF_4/CH_2Cl_2 solution (Sweep rate = 50 mV/s).

Figure 3. Cyclic Voltammogram of C-VI (7×10^{-5} M) at Pt electrode in 0.1 M Bu_4NBF_4/CH_2Cl_2 solution (Sweep rate = 50 mV/s).

Figure 4. UV-VIS-NIR absorbance spectra of neutral and oxidized C-VI in CH_2Cl_2 (5×10^{-6} M) at room temperature.

Figure 5. Solution ESR spectrum of chemically generated one electron oxidation product of 7-mT in CH_2Cl_2 at 295K.

Figure 6. Arrhenius activation energy plot for 7-mT.

Figure 7. Arrhenius activation energy plot for S-VII.

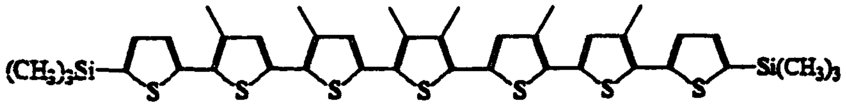
Figure 8. Arrhenius activation energy plot for C-VI.

Figure 9. Solution ESR spectrum of in situ electrolysis of C-II in 0.1 M Bu_4NPF_6/CH_2Cl_2 at room temperature.

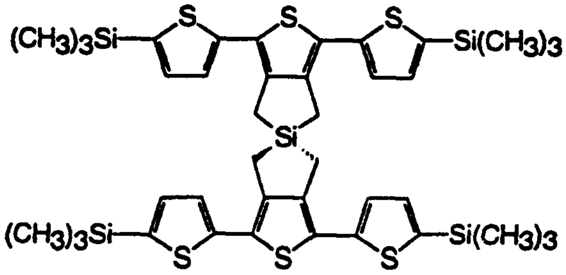
Figure 10. Plot of ESR signal intensity vs. temperature.

Compound	E_{pa1},E_{pa2} (V vs. SCE)	ΔE_p(mV)	Reference
ferrocene	0.64	70	28
7-mT	0.87, 1.05	90, 190	28
S-III	1.17, 1.53	150, –	28
S-VII	0.78, 1.10	70, –	28
C-II	1.4		
C-VI	1.1, 1.6	120, –	

Comound	Oxidation	Phase	g	ΔH_{p-p}	Temp. Range (K)	E_a (cm^{-1})
7-mT*	1e$^-$	Solid	2.005	1.4-1.8	120-297	48
7-mT	1e$^-$	Sol'n	2.005	3.7-5.4	180-295	114
C-VI	1e$^-$	Sol'n	2.005	3.2-5.2	180-297	113
C-VI	3e$^-$	Sol'n	2.005	4.0-6.2	180-294	153
S-VII	1e$^-$	Sol'n	2.005	3.8-4.7	180-291	83
S-VII	3e$^-$	Sol'n	2.005	4.1-5.0	180-296	63



7-mT



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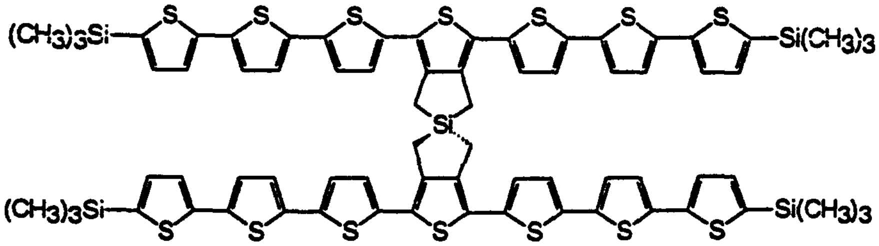
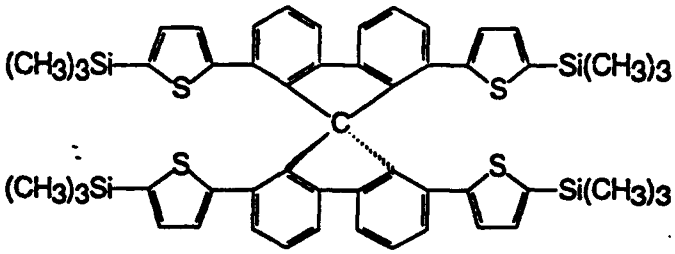
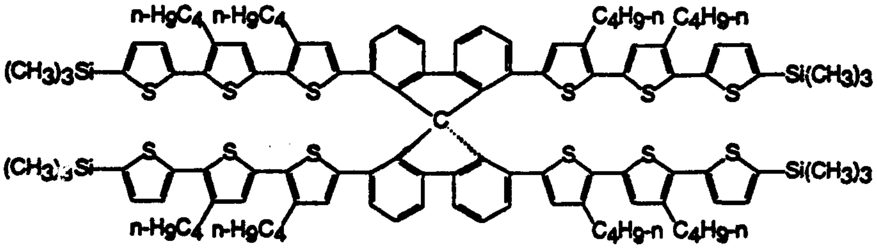


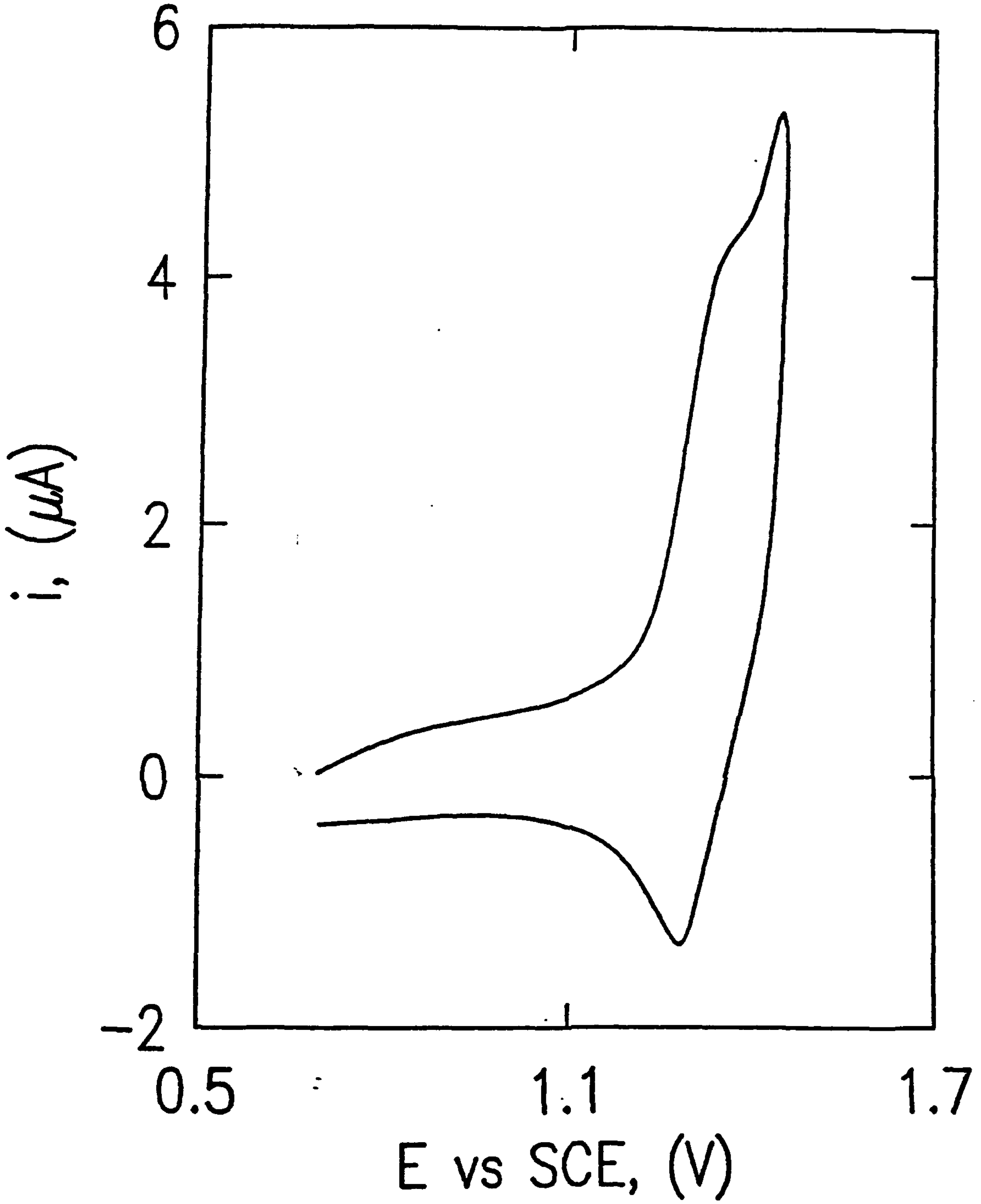
S-VII

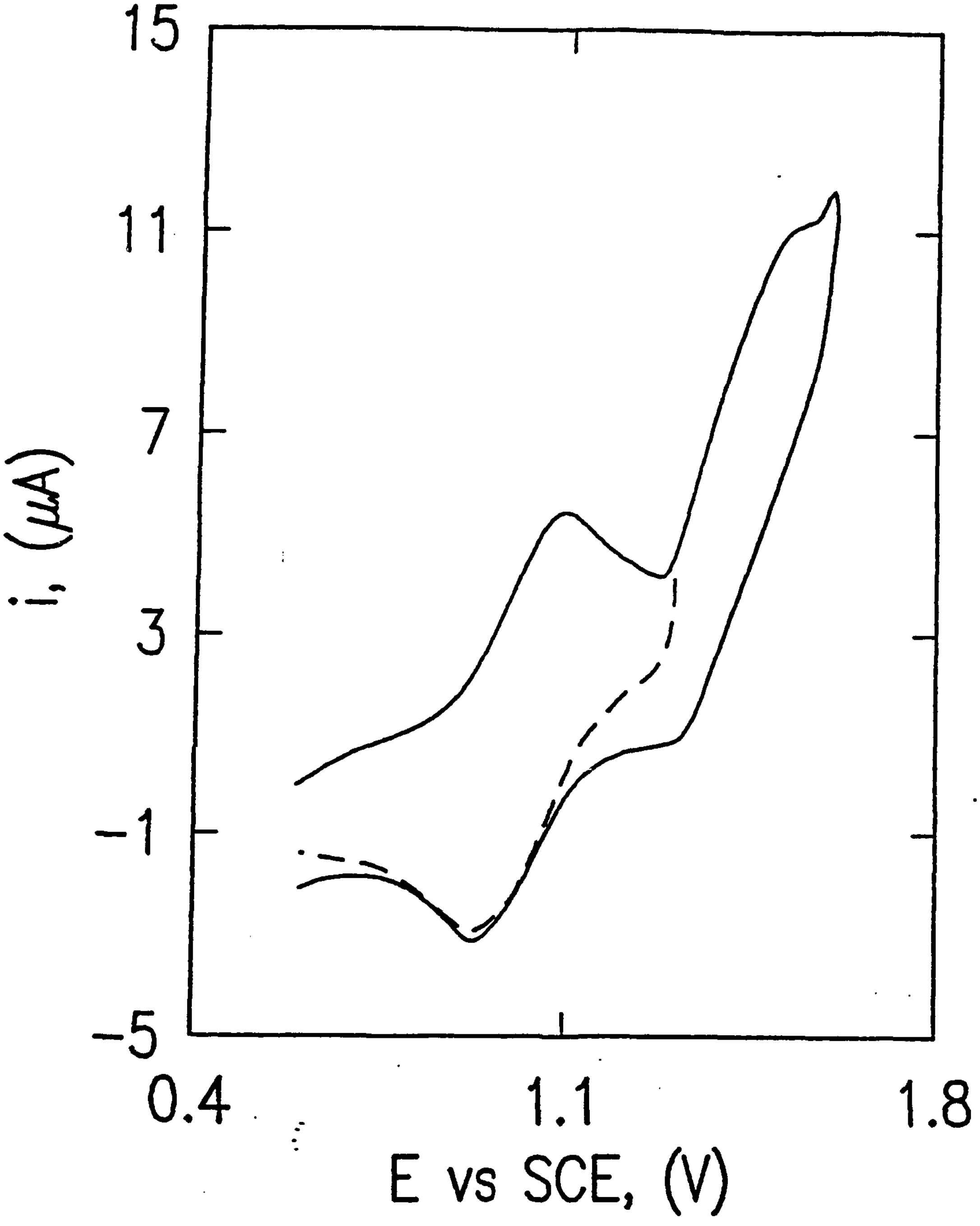


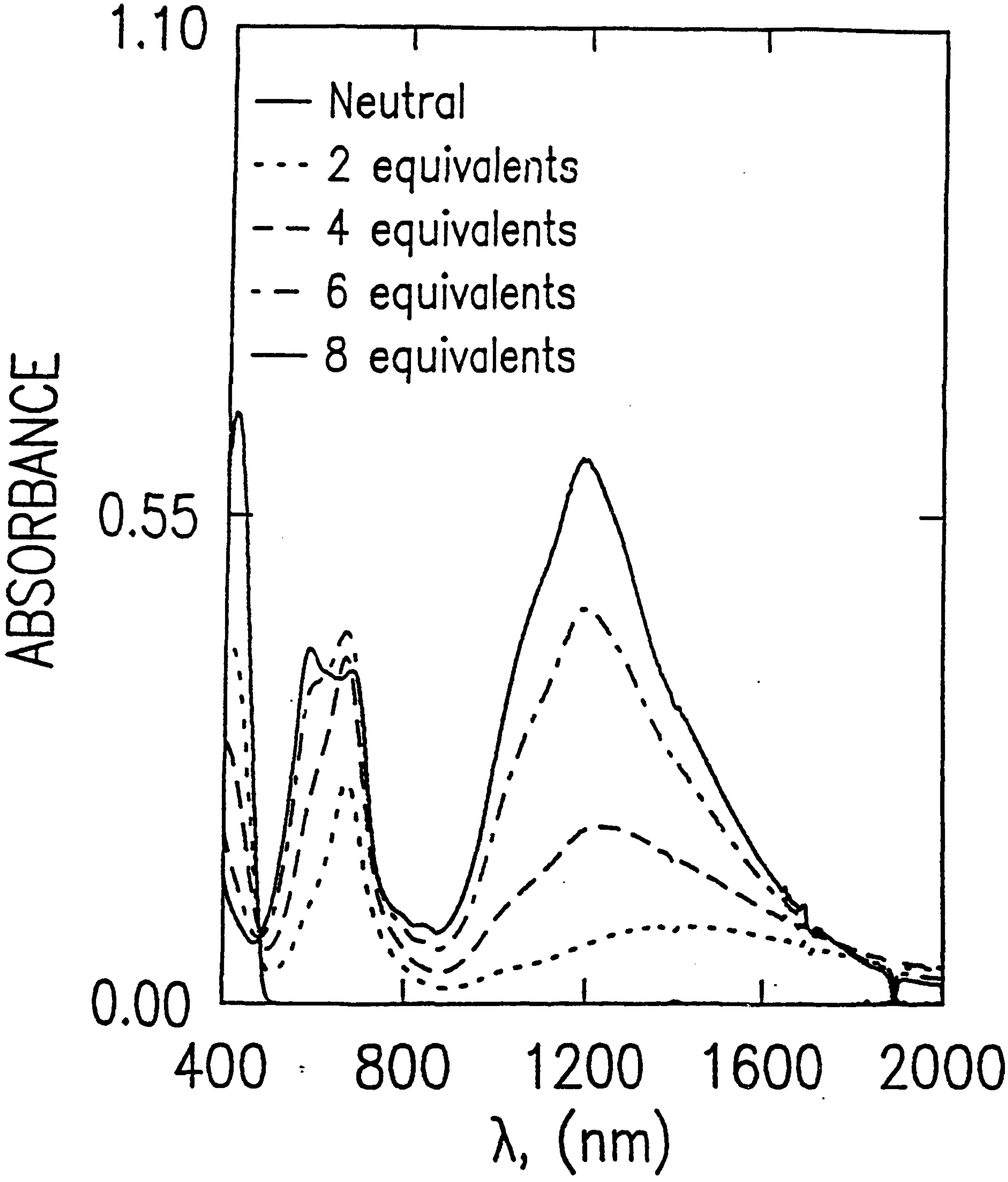
C-II

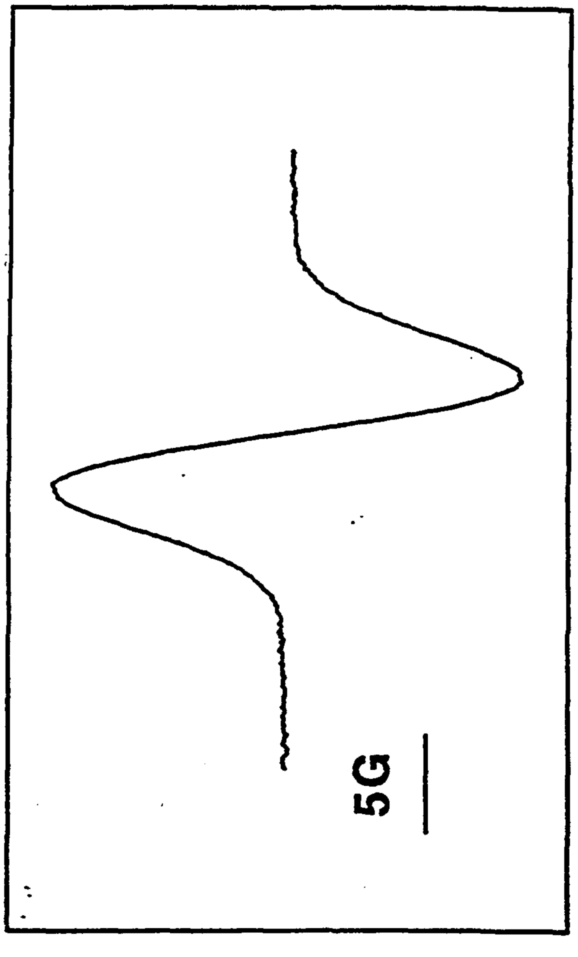


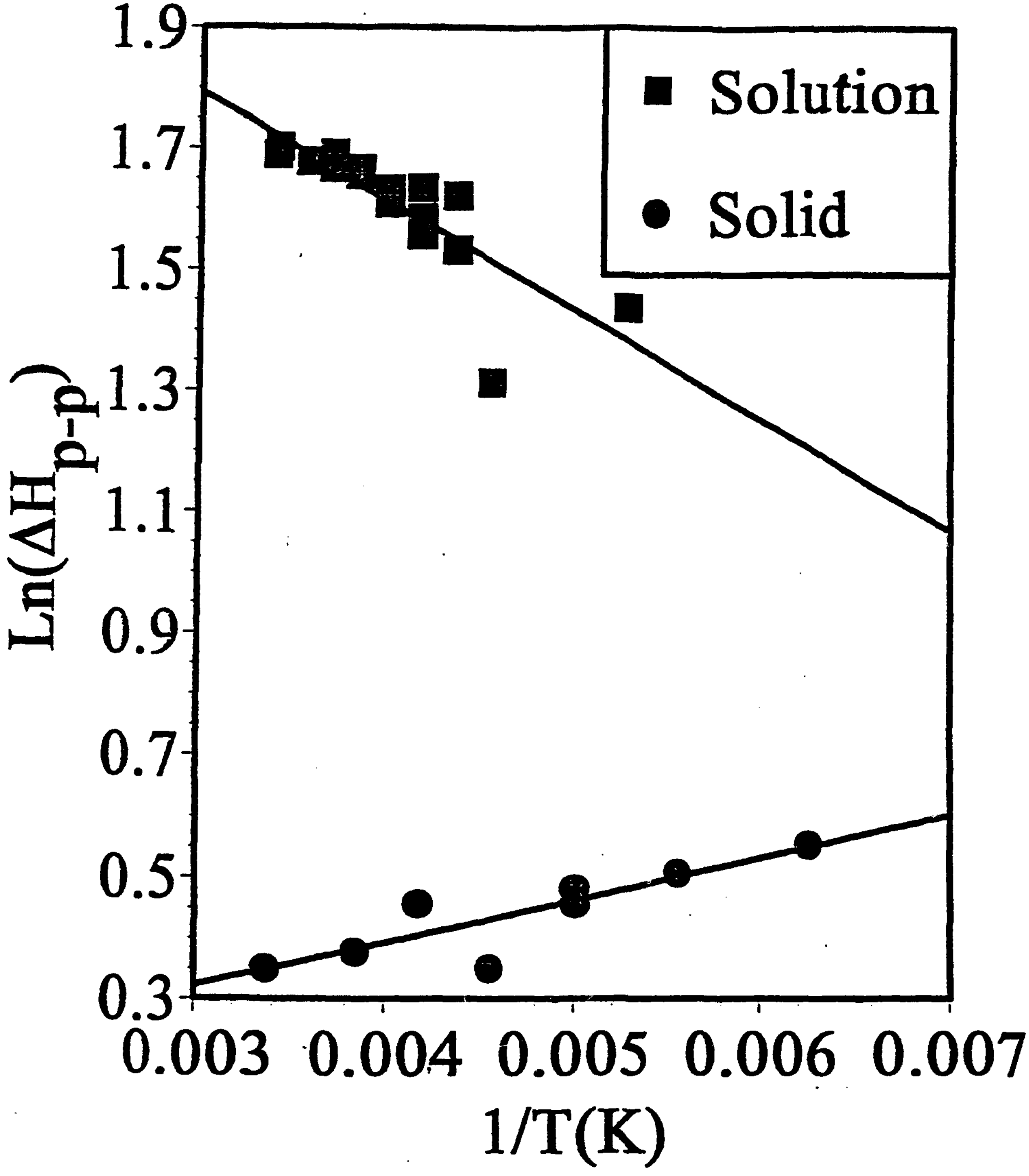
C-VI

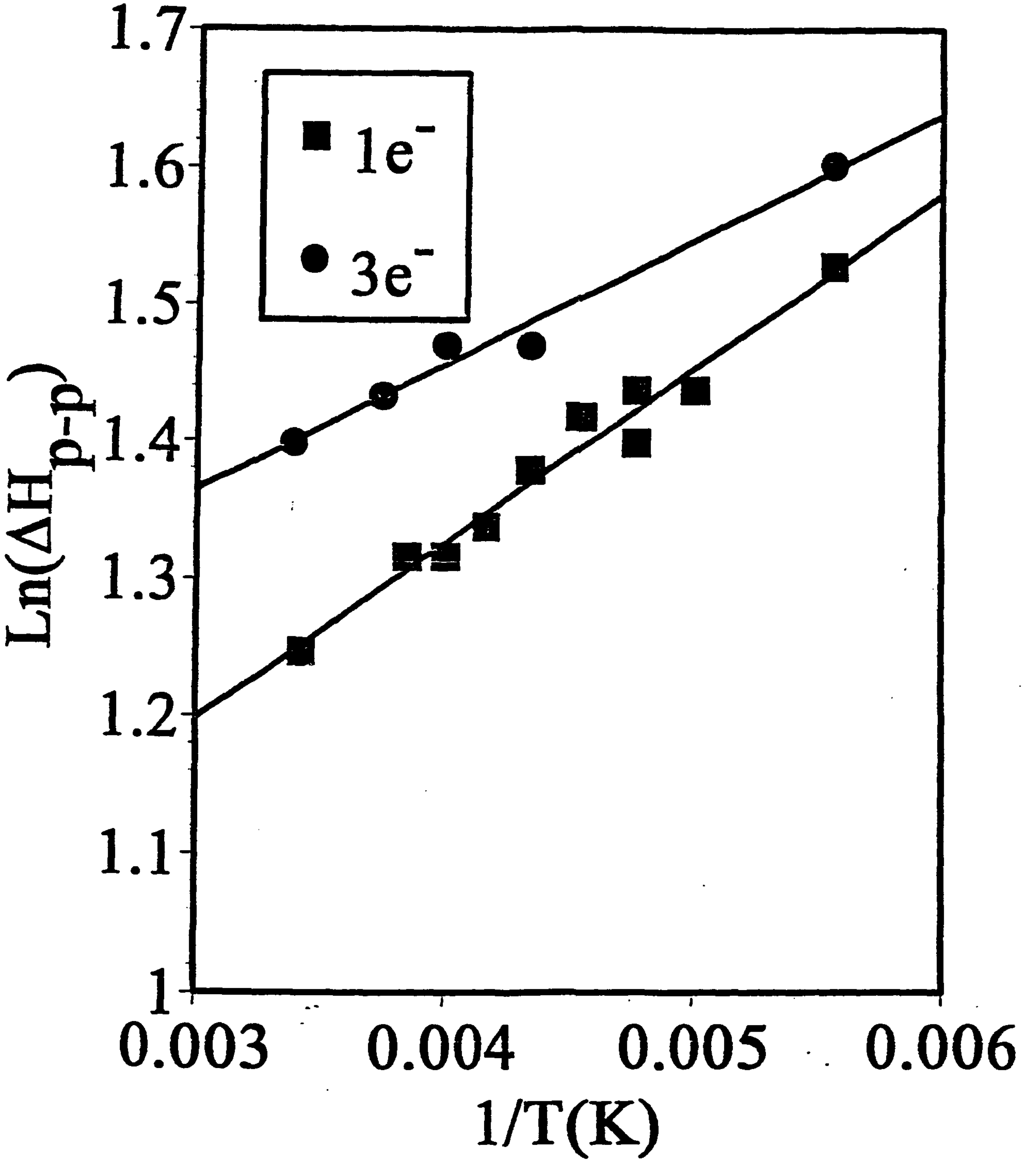

6
4
2
0
−2
i, (μA)
0.5
1.1
1.7
E vs SCE, (V)


15
11
7
3
-1
-5
i, (μA)
0.4
1.1
1.8
E vs SCE, (V)

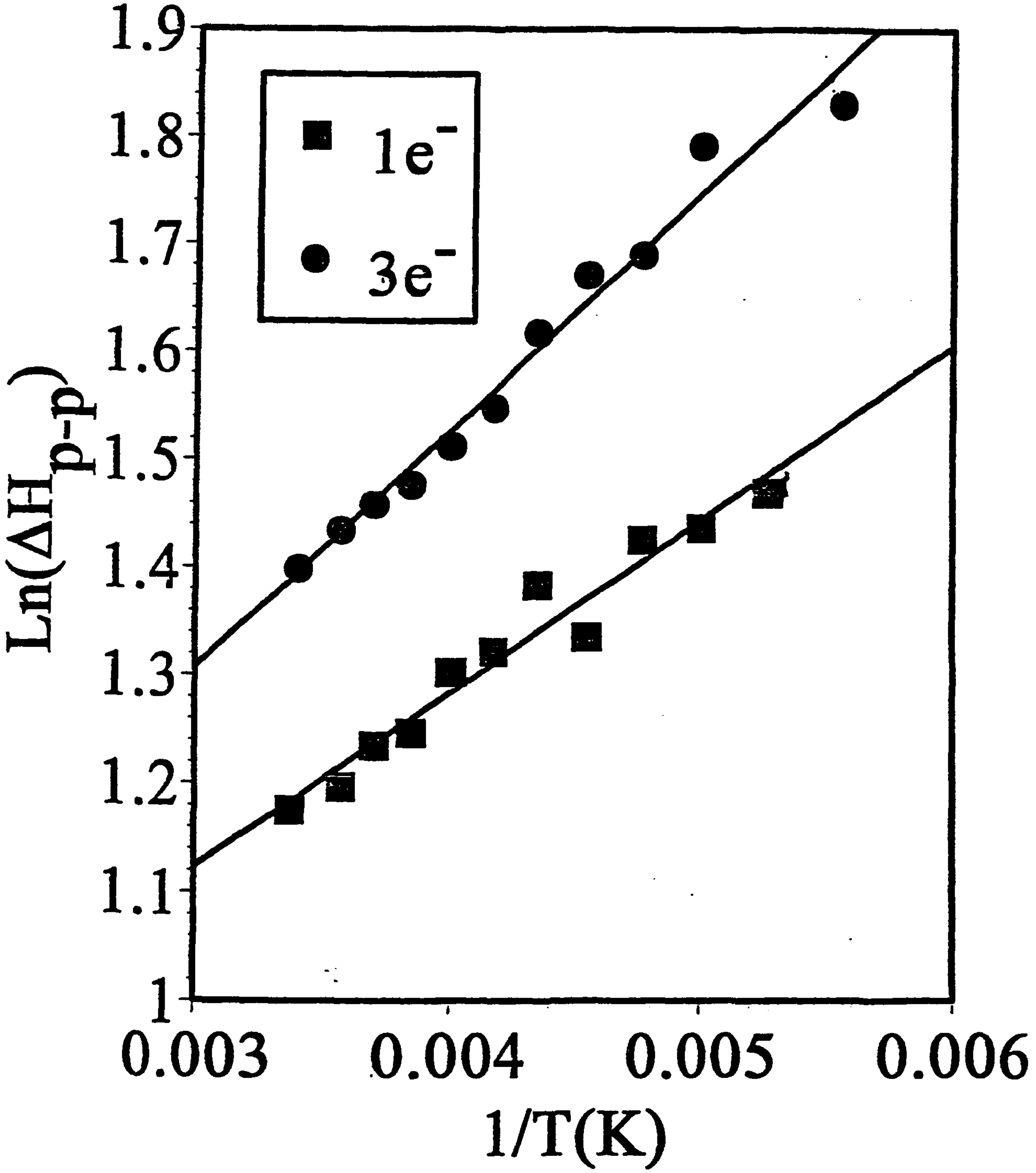

1.10
0.55
0.00
ABSORBANCE
Neutral
2 equivalents
4 equivalents
6 equivalents
8 equivalents
400
800
1200
1600
2000
λ, (nm)

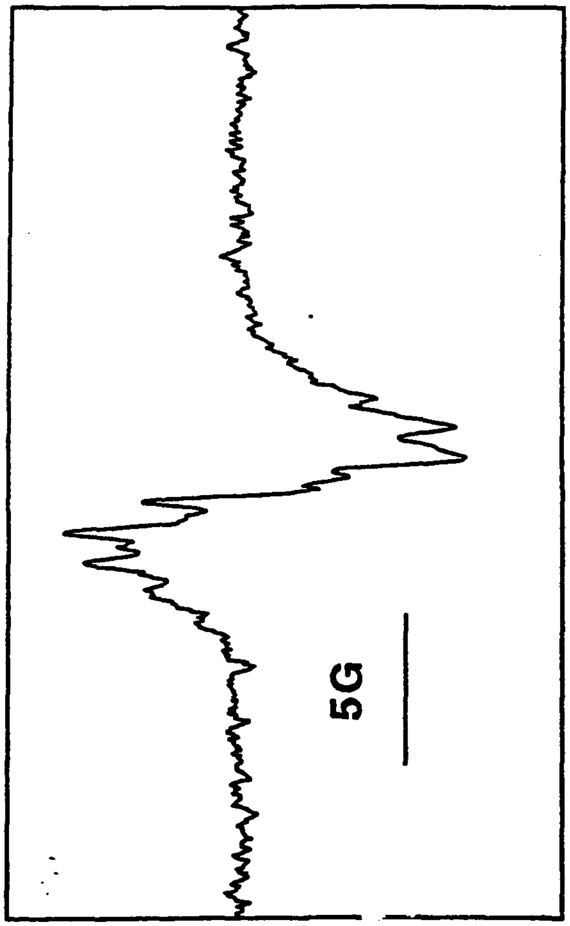

5G

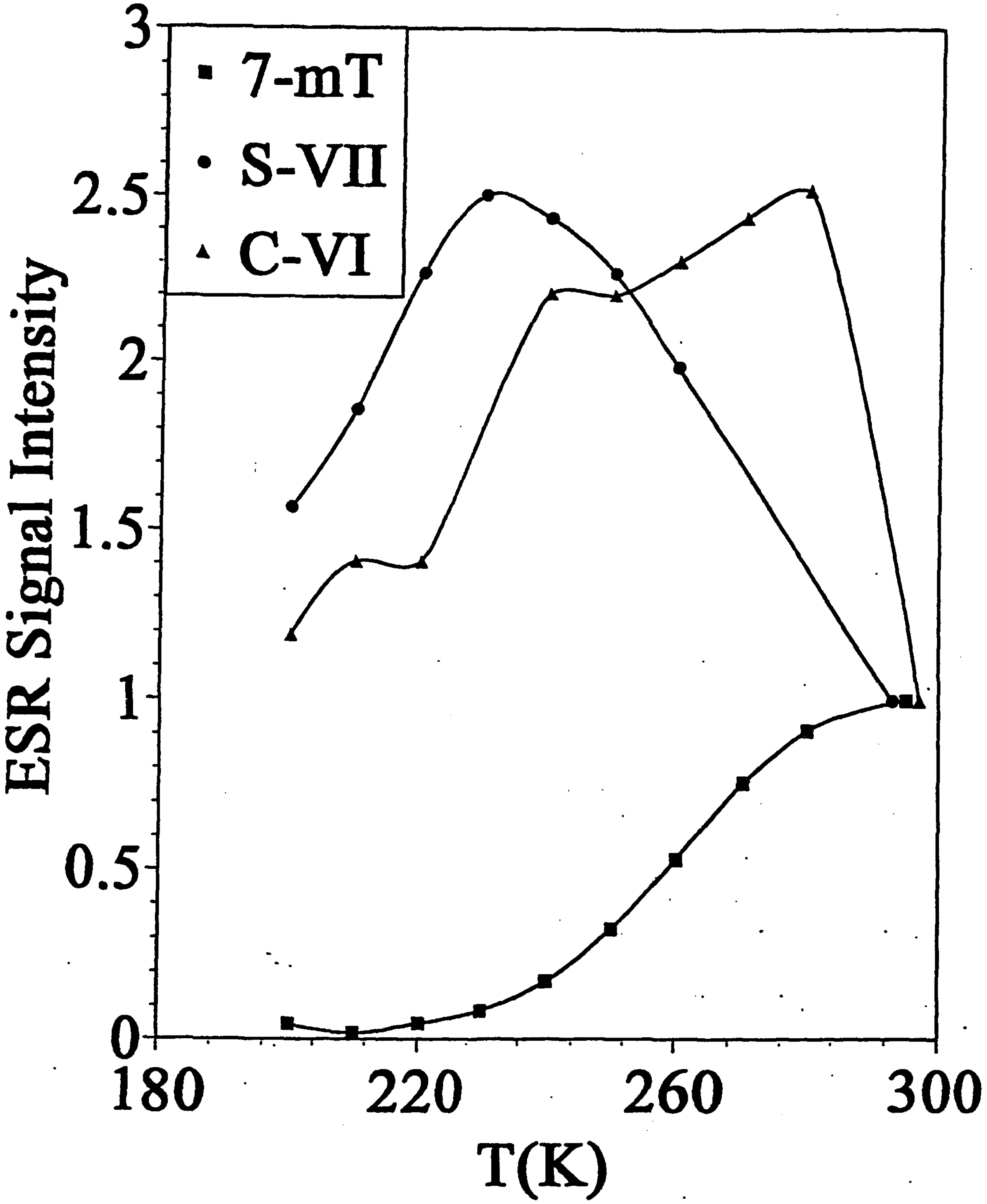

1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
0.3
$\mathrm{Ln}(\Delta H_{p\text{-}p})$
■ Solution
● Solid
0.003
0.004
0.005
0.006
0.007
1/T(K)



1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.003
0.004
0.005
0.006
Ln(ΔH_{p-p})
1/T(K)
■ $1e^-$
● $3e^-$


1e⁻
3e⁻
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.003
0.004
0.005
0.006
1/T(K)
Ln(ΔH_{p-p})


5G


3
2.5
2
1.5
1
0.5
0
180
220
260
300
ESR Signal Intensity
T(K)
■ 7-mT
● S-VII
▲ C-VI