alkenes. Trapped hole levels (I_{S^+}. and/or V_{Zn} center) on their surface have been proposed to play an essential role in the photoisomerization. To our knowledge, this is the first example that reveals a crucial role of the surface states of the semiconductor. Further investigations on reactions related with surface states are in progress.
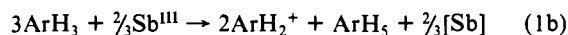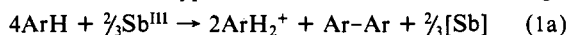
Bonded vs. Nonbonded Electron Transfers in Molten Salts: Characterization and Rates of Formation of the Radical Cations and Dications of Phenoxazine and Phenothiazine and Behavior of the M(2,2'-bipyridine)₃²⁺/³⁺ (M = Fe, Ru, Os) Complexes in SbCl₃-Rich Media

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Abstract: The electrochemical and homogeneous oxidations of phenoxazine (POZ) and phenothiazine (PTZ) to their highly persistent radical cations, POZ⁺· and PTZ⁺·, and dications, POZ²⁺ and PTZ²⁺, were studied in anhydrous SbCl₃–AlCl₃–BPCl (BPCl = *N*-(1-butyl)pyridinium chloride) mixtures with formal compositions close to neutral, i.e., 60–20–20 m/o at 23–27 °C. The progress of these oxidations was followed by fast optical spectroscopy. The cations and dications were found to be persistent (no loss of nitrogenic protons) up to 150 °C. ESR spectra of the radical cations were exceptionally well-resolved and allowed the first determination of all of the hyperfine constants. ¹H NMR spectra of the dications, measured in SbCl₃–AlCl₃ melts, are the first to be reported. The M(bpy)₃^{ν+} (bpy = 2,2'-bipyridine; M = Ru, Fe, Os; ν = 2, 3) complex ions, used as homogeneous single electron transfer (SET) agents, were found to be robust and their SETs were facile in these media. In basic media (AlCl₃/BPCl < 1), the electrochemical oxidations of POZ and PTZ were nernstian SET processes, and homogeneous oxidations by Os(bpy)₃³⁺ and Sb(V) were fast nonbonded (outer-sphere) SET processes. In acidic media (AlCl₃/BPCl > 1), the oxidizing potential of solvent Sb(III) is greatly enhanced and these media spontaneously oxidize POZ, PTZ, and Os(bpy)₃²⁺ The oxidation of Os(bpy)₃²⁺ by Sb(III) proved to be very slow, and this was attributed to the formation of a reactive intermediate containing mononuclear Sb(II). This factor probably also contributed to the very slow rates at which Sb(III) was found to oxidize POZ and PTZ. However, the presence of another rate inhibiting factor was demonstrated by the slow rates at which Ru(bpy)₃³⁺ oxidized POZ and PTZ in acidic melts. This was attributed to the formation of heteroaromatic–solvent complexes with N–Sb bonds. Thus, oxidations of heteroaromatics by Sb(III) were bonded (inner-sphere) processes. In acidic media the homogeneous oxidations of POZ⁺· and PTZ⁺· to POZ²⁺ and PTZ²⁺ by Sb(V) were slow reactions whose rates were inhibited by radical cation–solvent complexation involving the formation of chalcogen–Sb bonds.

Molten, anhydrous SbCl₃ (mp 73 °C) is an associated molecular liquid[2] that has proven to be an especially effective hydrogen transfer catalyst for dissolved arenes.[3] When AlCl₃ is added to SbCl₃, the weak oxidizing power of Sb(III) is substantially enhanced and hydrogen transfer may be accompanied by oxidation leading to some unusual types of reactions such as the following:[4]

$$4ArH + \frac{2}{3}Sb^{III} \rightarrow 2ArH_2^+ + Ar-Ar + \frac{2}{3}[Sb] \quad (1a)$$

$$3ArH_3 + \frac{2}{3}Sb^{III} \rightarrow 2ArH_2^+ + ArH_5 + \frac{2}{3}[Sb] \quad (1b)$$

where ArH is an arene, ArH₃ and ArH₅ are hydroarenes, Ar–Ar is a condensed arene, ArH₂⁺ is an arenium ion, and [Sb] represents soluble lower oxidation state species of antimony.[5,6] The stability of the arenium ion in these otherwise aprotic media is noteworthy. The added AlCl₃ enhances the oxidizing power of Sb(III) by acting indirectly as an acceptor for chloride ions released during reduction as described below.[7,8]

It has been proposed that a key step in many of the above reactions is single electron transfer (SET) from an oxidizable substrate to Sb(III)[3,4] and the present investigation provides a closer look at such reactions. In most of the measurements re-

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(6) Upon hydrolysis the lower oxidation state species of antimony disproportionate to form metal and Sb(III).

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ported here the medium consisted of $SbCl_3$ containing about 2 M N-(1-butyl)pyridinium tetrachloroaluminate (BPAlCl$_4$), formed in situ by adding BPCl and AlCl$_3$ to SbCl$_3$. These electrolyte solutions retain essential redox properties of SbCl$_3$ (see below) and are liquid at 25 °C.[9,10] The latter property allowed us to study reactions at a lower thermal activation than would have been possible in neat SbCl$_3$. Furthermore, since the reactions we shall be considering involve ions at low concentrations, the presence of 2 M BPAlCl$_4$ is useful in maintaining a high and nearly constant ionic strength.

The oxidizable substrates used in the present investigation were the heteroaromatics 10H-phenothiazine (PTZ) and 10H-phenoxazine (POZ) and the tris(2,2'-bipyridine)osmium(II) complex ion (Os[bpy]$_3^{2+}$), while the complexes Fe(bpy)$_3^{2+/3+}$ and Ru-

POZ   PTZ
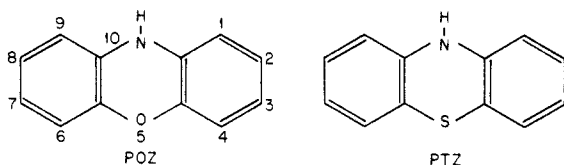
(bpy)$_3^{2+/3+}$ were used as special purpose oxidants and reductants. On the basis of prior studies it appeared that PTZ and POZ would complex with Sb(III) in media with excess AlCl$_3$[11] and thus provide examples of bonded (inner-sphere) oxidation by the medium, while a complex of the M(bpy)$^{2+}$ type would not complex and would provide an example of outer-sphere (nonbonded) oxidation.[12,13] Our results are in accord with this expectation. Moreover, as we shall show, these oxidizable substrates also have other properties that make them especially good reactants, namely: They are oxidized by Sb(III) in acidic media containing a small excess of AlCl$_3$ relative to BPCl to give SET products (PTZ$^+$·, POZ$^+$·, and Os[bpy]$_3^{3+}$) that are very persistent (high kinetic stability) over substantial time periods so that these SET reactions are not complicated by down stream chemistry. In media containing a small excess of BPCl relative to AlCl$_3$, they are not oxidized by Sb(III) but they can be oxidized in a controlled way

(9) Properties of these electrolyte solutions are described in the following: (a) Chapman, D. M.; Smith, G. P.; Sørlie, M.; Petrovic, C.; Mamantov, G. *J. Electrochem. Soc.* **1984**, *131*, 1609. (b) Zingg, S. P.; Dworkin, A. S.; Sørlie, M.; Chapman, D. M.; Buchanan, A. C., III; Smith, G. P. *J. Electrochem. Soc.* **1984**, *131*, 1602.

(10) The saturated SbCl$_3$ electrode, described in the Experimental Section, is the reference for all potentials in SbCl$_3$–AlCl$_3$–BPCl media given here and in ref 9a.

(11) (a) Evidence for complexation between amines and SbCl$_2^+$·nSbCl$_3$ in molten SbCl$_3$ is provided by Bauer and Beck[11c,d] and Johnson and Baughan.[11e] Some of Johnson and Baughan's examples are questionable because of the probable oxidation of the amine by SbCl$_3$, but aniline and pyridine should be valid examples. (b) The crystal structure of the aniline–SbCl$_3$ complex shows a N–Sb bond.[11f] (c) Bauer, D.; Beck, J. P. *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *32*, 21. (d) Bauer, D.; Beck, J. P. *Collect. Czech. Chem. Commun.* **1971**, *36*, 323. (e) Johnson, P. V.; Baughan, E. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1958. (f) Hulme, R.; Mullen, D.; Scruton, J. C. *Acta Crystallogr., Sect. A* **1969**, *25S*, 171.

(12) The M(bpy)$_3^{r+}$ (M = Fe, Ru, Os; ν = 2, 3) ions in many media, both protic and aprotic, are stable, nonlabile complexes (when not photoactivated) that have distinctive visible spectra, undergo rapid SET reactions, and form reversible 3+/2+ redox couples that are relatively insensitive to the nature of the solvent. See, e.g.: (a) McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 135. (b) Sahami, S.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 2511. (c) Fergusson, J. E.; Harris, G. M. *J. Chem. Soc. A* **1966**, 1293. (d) Bryant, G. M.; Fergusson, J. E. *Aust. J. Chem.* **1971**, *24*, 275. (e) Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *60*, 1. (f) Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542. (g) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309. (h) Chum, H. L.; Rock, M.; Rabockai, T. *Inorg. Chim. Acta* **1981**, *54*, L221. (i) Chum, H. L.; Koran, D.; Osteryoung, R. A. *Inorg. Chem.* **1981**, *20*, 3304. (j) Braddock, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 3158. (k) Staniewicz, R. J.; Sympson, R. F.; Hendricker, D. G. *Inorg. Chem.* **1977**, *16*, 2166. (l) Bryant, G. M.; Fergusson, J. E.; Powell, H. K. J. *Aust. J. Chem.* **1971**, *24*, 257. (m) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593. (n) Ford-Smith, M. H.; Sutin, N. *J. Am. Chem. Soc.* **1961**, *83*, 1830. (o) Burstall, F. H.; Dwyer, F. P.; Gyarfas, E. C. *J. Chem. Soc.* **1950**, 953.

(13) For a discussion of the theory of SET reactions applied to organic systems (including the Marcus theory), see: Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

Table I. Cyclic Voltammetric Parameters for PTZ and POZ at 26 ± 1 °C[a]

species concn, mM medium	ν, mV s^{-1}	$\|E_p^a - E_{p/2}^a\|$, mV	$\|E_p^c - E_{p/2}^c\|$, mV	ΔE_p, mV	$E_{1/2}$,[a] mV
POZ	10	56	55	63	155
1.97	20	60	55	63	155
60–19–21	50	60	55	65	157
	100	58	59	60	155
	200	60	63	75	157
	500	60	60	75	157
PTZ	20	55	58	55	122
1.74	50	55	58	55	122
60–19–21	100	58	58	58	125
	200	60	58	65	132
	500	70	63	80	142
POZ$^+$·	10	65	54	65	1120
6.60	20	62	55	62	1117
60–22–18	50	63	55	64	1119
	100	62	58	67	1119
	200	62	60	73	1120
	500	63	62	75	1122
PTZ$^+$·	5	54	47	61	916
9.07	10	56	48	61	916
60–22–18	20	56	50	63	915
	50	58	51	65	916
	100	58	52	68	918
	200	60	54	72	920

[a] Potentials relative to saturated SbCl$_3$ electrode.

either anodically or with added oxidants to give stable SET products.

The persistence of PTZ$^+$· and POZ$^+$· in aprotic SbCl$_3$-rich media was somewhat surprising, but even more unexpected was our discovery that the dications, PTZ^{2+} and POZ^{2+}, are also quite persistent even at temperatures well over 100 °C.[14] We took advantage of this circumstance to measure their ^{1}H NMR spectra for the first time.

The oxidizing power of SbCl$_3$ is very sensitive to the presence of excess chloride ion donors and acceptors and in the current research this factor was controlled by controlling the relative amounts of BPCl and AlCl$_3$ added to SbCl$_3$. In particular, the formal compositions of media used here were 60 m/o SbCl$_3$, 20 + x m/o AlCl$_3$ (−1 ≥ x ≥ +2), balance BPCl. These will be designated by the numerical triads 60–(20 + x)–(20 − x), e.g., the limiting compositions were 60–19–21 (x = −1) and 60–22–18 (x = +2). In media for which x < 0, the chloride ions from the excess BPCl form complexes by bridging pairs of SbCl$_3$ molecules. We denote these as Cl$^-$·2SbCl$_3$. These are Lewis bases relative to SbCl$_3$ and solutions for which x < 0 will be referred to as being basic. Likewise, when x > 0, excess AlCl$_3$ reacts with SbCl$_3$ to form AlCl$_4^-$ and a chloride-deficient entity that we denote SbCl$_2^+$·nSbCl$_3$. Such solutions are referred to as being acidic. In basic 60–19–21 media $E°'$ of the Sb^{III}/Sb couple at 27 °C relative to the saturated SbCl$_3$ electrode[10] is 0.02 V. As the AlCl$_3$/BPCl mole ratio is increased, $E°'$ rises in the form of a steep titration curve centered about the neutral composition, 60–20–20, and reaches 0.41 V for acidic 60–21–19 mixtures and 0.44 V for 60–22–18 mixtures.[9a] The anodic limit in these media is provided by the irreversible oxidation of Sb(III) to Sb(V) at about 0.8 V in 60–19–21 and 1.7 V in 60–22–18.

The Results and Discussion section is divided into three parts. The first two parts provide detailed characterizations of the radical

(14) (a) For a review of phenoxazine chemistry, see: Ionescu, M.; Mantsch, H. *Adv. Heterocycl. Chem.* **1967**, *8*, 83. (b) For a review of phenothiazine chemistry, see: Bodea, C.; Silberg, I. *Adv. Heterocycl. Chem.* **1968**, *9*, 321. (c) In most media PTZ^{2+} readily deprotonates or reacts with nucleophiles. Long-term stability, comparable to that reported here, has only been observed in 96% H$_2$SO$_4$[14d] and liquid SO$_2$ at −40 °C.[14e] (d) Shine, H. J.; Mach, E. E. *J. Org. Chem.* **1965**, *30*, 2130. (e) Tinker, L. A.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 2316. (f) There appears to be no recent literature on POZ^{2+}, but we do not expect it to be much more stable than PTZ^{2+} in most media.
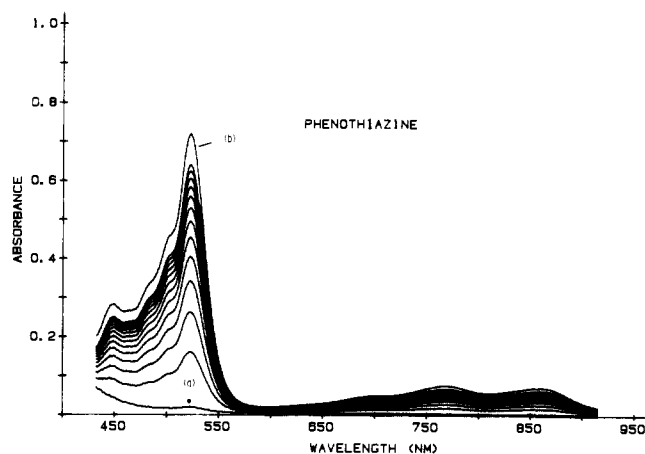
Figure 1. Spectra measurea every 120 s during a 3000-s electrolysis at 0.60 V of 0.60 mM PTZ in 60-19-21: (a) initial (pre-electrolysis) spectrum; (b) after 3000 s of electrolysis. Intermediate spectra: 120-, 240-, ..., 1500-s electrolysis. Spectra not shown: 1620-, 1740-, ..., 2880-s electrolysis. Reticulated vitreous carbon OTE. Cell path length 0.10 cm.

cations and dications of POZ and PTZ and of the $M(bpy)_3{}^{2+/3+}$ complexes. These are a prelude to the third and final part in which the phenomenology of homogeneous electron transfer reactions is described and possible mechanistic origins of the observed behavior are discussed.

Results and Discussion

Characterization of Phenothiazine and Phenoxazine in SbCl₃-Rich Media.
PTZ and POZ dissolve readily in basic 60-19-21 media, and cyclic voltammograms of these solutions were measured at glassy carbon electrodes. Table I lists cyclic voltammetric (CV) parameters, where $\Delta E_p = E_p{}^a - E_p{}^c$ is the difference between the anodic and cathodic peak potentials, $|E_p - E_{p/2}|$ is the magnitude of the difference between the peak and half-peak potentials, $E_{1/2}{}^a = E_{p/2}{}^a + 1.09RT/nF$,[15] and v is the scan rate. For one-electron nernstian processes the theoretical values of $|E_p - E_{p/2}|$ and ΔE_p are 56[16a] and 59 mV,[15] respectively. The observed increases in ΔE_p at the highest scan rates are attributed to incompletely compensated solution resistance (see Experimental Section). We conclude that in basic 60-19-21 media PTZ and POZ underwent fast and reversible one-electron oxidations to give their radical cations, $PTZ^+\cdot$ and $POZ^+\cdot$, that were unreactive on a voltammetric time scale. For PTZ and POZ $i_p{}^a/V^{1/2}$ was constant, indicative of simple diffusion controlled electrode reactions.

Spectroelectrochemistry (SE) provided further evidence that $PTZ^+\cdot$ and $POZ^+\cdot$ were the products of anodic oxidation and quantified their kinetic stabilities over periods of 1-4 h. Controlled potential electrolyses of PTZ and POZ at optically transparent electrodes (OTE) in basic 60-19-21 media were carried out at 0.60 V and spectrometrically monitored in the visible and near-infrared wavelength regions with results described below.

Spectra measured during the electrolysis of PTZ are shown in Figure 1. Absorption bands that appeared during electrolysis occurred at 447, 480, 500, 522 ($\epsilon = 11.6 \pm 0.1 \times 10^3$ M⁻¹ cm⁻¹), 697, 766, and 859 nm. The molar absorptivity was calculated from spectra measured after exhaustive electrolysis and after complete chemical oxidation, described below. A comparison of this spectrum with that of $PTZ^+\cdot$ in other media is summarized in Table II. The $PTZ^+\cdot$ radical cations were electroreduced for 60 min and converted quantitatively to molecular PTZ as evidenced by the disappearance of $PTZ^+\cdot$ bands. A second oxidative electrolysis was then performed, and the difference between a spectrum measured 50 min into the second oxidative electrolysis and one measured 50 min into the first oxidative electrolysis was

Table II. Strongest Bands in Visible Absorption Spectra of PTZ and POZ Cations

species	medium	λ, nm (10^{-3} ε, M⁻¹ cm⁻¹)	ref
$POZ^+\cdot$	MeCN	529 (14.1)	17
	MeCN	525	18
	EtOH	535	19
	60-19-21	547 (18.0)	a
	60-21-19	547 (18.0)	a
$PTZ^+\cdot$	H_2SO_4, 96%	515	14d
	MeCN	516 (6.92)	20
	MeCN	515 (10.3)	21
	MeCN	513 (7.45)	18
	MeCN	517 (8.7)	17
	60-19-21	522 (11.6)	a
	60-22-18	522 (11.6)	a
POZ^{2+}	$H_2O_2 + H_2SO_4$, 96%	460	22
	60-22-18	487 (25.3)	a
PTZ^{2+}	H_2SO_4, 96%	455	14d
	60-22-18	480 (15.9)	a

^{a} This work.

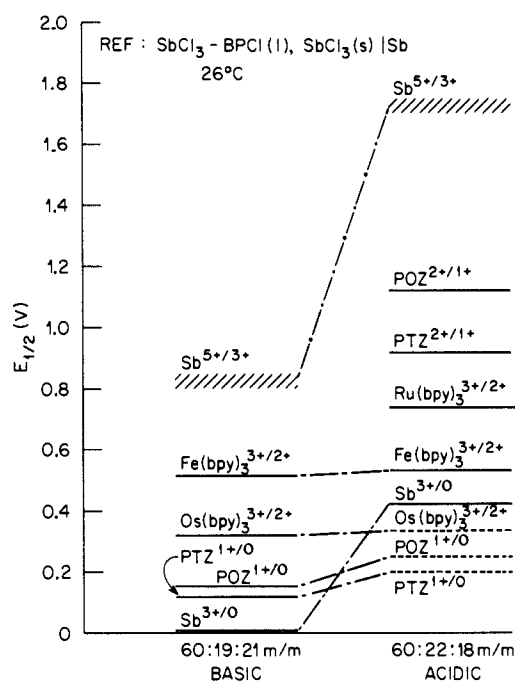**Figure 2.** Potentials of redox couples in representative basic and acidic SbCl₃-AlCl₃-BPCl media. Values for $Sb^{3+/0}$ and $Sb^{5+/3+}$ from ref 6a. Values for $POZ^{1+/0}$, $PTZ^{1+/0}$, and $Os(bpy)_3{}^{3+/2+}$ in acidic media are estimates as described in text.

equal to zero within experimental error at all wavelengths. Thus, there was no perceptible loss of $PTZ^+\cdot$ during these electrolyses.

A SE study of POZ gave results similar to those for PTZ. Absorption bands of the oxidized product occurred at 506, 547 ($\epsilon = 18.0 \pm 0.7 \times 10^3$ M⁻¹ cm⁻¹), 627, 662, 704, and 797 nm. A comparison of the coordinates of the most prominent band with those reported for $POZ^+\cdot$ in MeCN and EtOH is summarized in Table II. Changes in the spectra during repeated oxidation-reduction cycles indicated a loss in radical cation concentration of less than 1.5% in 1 h.

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(19) Gegiou, D.; Huber, J. R.; Weiss, K. *J. Am. Chem. Soc.* **1970**, *92*, 5058.

(20) Hanson, P.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 264.

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Table III. ESR Parameters for POZ$^{+\cdot}$ in Various Media

parameter	medium				
	1^a	2^b	3^c	4^d	5^e
a_1 (a_{NH})	8.45	8.53	8.58	8.64	9.02
a_2 (a_N)	7.69	7.76	7.76	7.90	7.83
a_3 ($a_H^{3,7}$)	3.14	3.17	3.17	3.39	3.27
a_4 ($a_H^{1,9}$)	1.41	1.42	1.42	1.70	1.61
a_5 ($a_H^{4,6}$)	0.64	0.64	0.64	0.72	0.44
a_6 ($a_H^{2,8}$)	0.64	0.64	0.64	0.34	0.66
g				2.0032	
a_{NH}/a_N	1.10	1.10	1.11	1.09	1.15
X	23.80	24.01			
$2a_2 + a_1$	23.83	24.05	24.10	24.44	24.68
spectral width	35.46	35.81			
weighted sum of a_i	35.49	35.79	35.84	36.74	36.84
line width, mG	50	50	50	150	90

^{a}SbCl$_3$, 130 °C, this work. ^{b}60-22-18, 130 °C, this work. ^{c}60-22-18, 90 °C, this work. ^{d}3:1 H$_2$O/H$_2$SO$_4$, -40 °C.[24] ^{e}H$_2$SO$_4$/CH$_3$NO$_2$, -40 °C.[25]

Although POZ and PTZ form stable solutions in basic 60-19-21 media, they are oxidized by Sb(III) in acidic 60-22-18 media. This was demonstrated by using optical spectroscopy to measure the concentration of POZ$^{+\cdot}$ and PTZ$^{+\cdot}$ in such solutions as functions of time and by the recovery of antimony metal following hydrolysis.[6] The complete oxidation of ~0.5 mM PTZ at 30 °C required more than 15 min, and the resulting radical cations were relatively stable (3% loss in 24 h). The oxidation of POZ under similar conditions was even slower with only 74% oxidized in 21 h. At longer times the POZ radical cations decayed faster than they were formed. We shall examine this temporal behavior in more detail below but for the moment it is sufficient to note that the $E^{o\prime}$ values for the PTZ$^{+\cdot}$/PTZ and POZ$^{+\cdot}$/POZ couples in acidic media must be less than $E^{o\prime}$ for the Sb^{III}/Sb couple in 60-22-18 media, namely, 0.44 V.[9a,23] As a matter of convenience we assemble these values of $E^{o\prime}$ in Figure 2 together with other values that will be discussed later.

In order to eliminate any vestage of doubt about the identification of the oxidized products and to obtain further information on their interactions with SbCl$_3$-rich solvents, we measured their ESR spectra in 60-22-18 media at 20-150 °C and in molten SbCl$_3$ at 90-150 °C. An example of the spectrum of POZ$^{+\cdot}$ is shown in Figure 3. ESR parameters are listed in Tables III and IV. The ESR signals did not change perceptibly over 5 h at 130 °C, and the linewidths were decidedly narrower than those reported when using conventional solvents as noted in the tables. This enhanced resolution had a large effect on line shapes and intensities so that a visual comparison with previously published spectra is not simple.

The spectra were analyzed with the aid of the relations $X = 2a_N + a_{NH}$,[18] $a_{NH}/a_N \simeq 1.12 \pm 0.04$[28] and the fact that the spectral width equalled the properly weighted sum of the coupling constants,[29a] where X is the separation (in gauss) defined in Figure
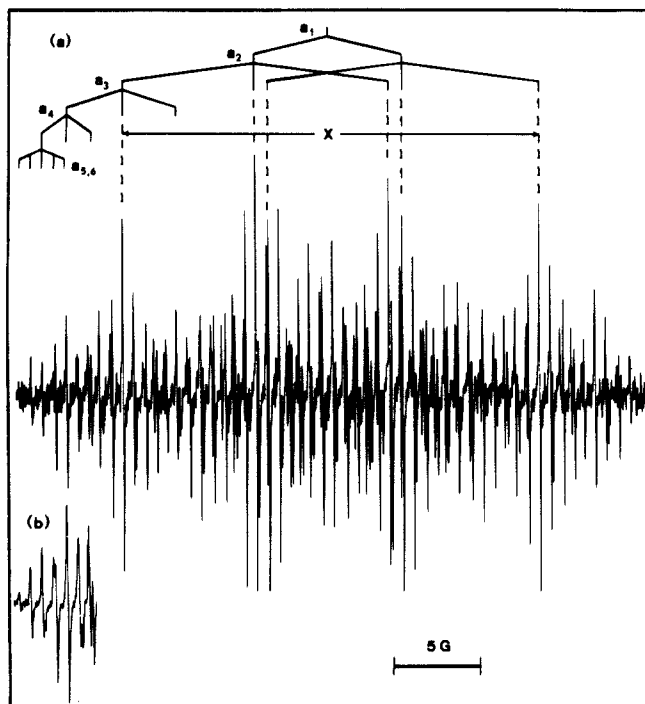

Figure 3. ESR spectrum of POZ$^{+\cdot}$ in SbCl$_3$ at 130 °C: (a) mod. amp., 8 mG; (b) improved S/N, mod. amp., 125 mG.

3 and a_N and a_{NH} are the nitrogen and nitrogenic proton coupling constants, respectively. The hyperfine coupling constants obtained were assigned by comparison of their magnitude to those previously reported and to those calculated from spin densities obtained by molecular orbital (MO) treatments.[27f] The assignments of the two smallest couplings for PTZ$^{+\cdot}$ were somewhat ambiguous, since the amount of calculated spin density at carbons 4 and 6 compared to that at carbons 2 and 8 depended on the MO treatment employed. According to Hückel calculations the spin density at carbons 2 and 8 is greater than that at carbons 4 and 6, while McLachlan and PPP-UHF-SCF calculations give the opposite result.[27f] The assignments in Table IV are based on the calculations of the latter two MO treatments, so that coupling constants of H$_{4,6}$ are greater than those of H$_{2,8}$.

ESR spectra of the radical cations in SbCl$_3$ were obtained over the temperature range 90-150 °C and in 60-22-18 melts over the range 20-150 °C. The spectra in the ternary melts were quite asymmetric, with the asymmetry decreasing with temperature. Spectra measured on the solutions in neat SbCl$_3$ above 90 °C displayed very little asymmetry. The viscosity of the acidic ternary melt (3.5 cP at 100 °C^{9a}) is roughly twice as large as that of SbCl$_3$ (1.84 cP at 99 °C[30]), and thus the asymmetry is probably the result of slow molecular tumbling and a concomitant anisotropy in the hyperfine and g tensors for the radical cations.[29b] The hyperfine coupling constants were only mildly temperature sensitive.

It will be noted from Tables III and IV that the hyperfine coupling constants measured in SbCl$_3$-based media are significantly smaller than those reported for other media (in particular see the weighted sum of a_i). We attribute this reduction to complexation of the radical cations through their chalcogen atoms (S or O) to solvent antimony atoms. This complexation should polarize unpaired spin density in the π system toward the chalcogen nuclei, the principal isotopes of which are nonmagnetic, and away from the other nuclei. Since the magnitude of the hyperfine interaction in π systems is expected to be proportional to the unpaired spin density at magnetic nuclei,[29c] the proposed complexation should reduce the coupling constants. The fact that the

(22) Kehrmann, F.; Sandoz, M. *Ber. Dtsch. Chem. Ges.* **1917**, *50*, 1667.

(23) The fact that the reduced form of Sb in acidic melts consists of dissolved lower oxidation states rather than the metal has only a small effect on the redox potential because the formal, equilibrium solubility of the metal in these media is quite small.

(24) Lhoste, J.-M.; Tonnard, F. *J. Chim. Phys. Phys.-Chim. Biol.* **1966**, *63*, 678.

(25) Sullivan, P. D.; Bolton, J. R. *J. Magn. Reson.* **1969**, *1*, 356.

(26) Gilbert, B. C.; Hanson, P.; Norman, R. O. C.; Sutcliffe, B. T. *J. Chem. Soc., Chem. Commun.* **1966**, 161.

(27) The electronic structures of PTZ, POZ, and their radical cations have been extensively studied and are described in the following: (a) Karreman, G.; Isenberg, I.; Szent-Györgyi, A. *Science* **1959**, *130*, 1191. (b) Pullman, B. J.; Pullman, A. *Biochim. Biophys. Acta* **1959**, *35*, 535. (c) Orloff, M. K.; Fits, D. D. *Biochim. Biophys. Acta* **1961**, *47*, 596. (d) Kamiya, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1589. (e) Domelsmith, L. N.; Munchausen, L. L.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 6506. (f) Chiu, M. F.; Gilbert, B. C.; Hanson, P. *J. Chem. Soc. B* **1970**, 1700. (g) Haink, H. J.; Huber, J. R. *Chem. Ber.* **1975**, *108*, 1118. (h) Bloor, J. E.; Gilson, B. R.; Haas, R. J.; Zinkle, C. C. *J. Med. Chem.* **1970**, *13*, 922.

(28) This relation was determined from ESR spectra of POZ$^{+\cdot}$ and PTZ$^{+\cdot}$ in the literature. See Tables III and IV.

(29) Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance: Elementary Theory and Practical Applications"; McGraw-Hill: New York, 1972: (a) Chapter 4, (b) Chapter 7, (c) Chapters 5 and 6.

(30) Baughan, E. C. In "The Chemistry of Nonaqueous Solvents"; Lagowski, J. J., Ed.; Academic Press: New York, 1976; Vol. IV, Chapter 5.

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Table IV. ESR Parameters for PTZ[+]· in Various Media

parameter	solvent							
	1[a]	2[b]	3[c]	4[d]	5[e]	6[f]	7[g]	8[h]
a_1 (a_{NH})	6.89	7.05	6.97	7.32	7.41	7.36	7.50	7.29
a_2 (a_N)	6.22	6.37	6.34	6.52	6.41	6.52	6.50	6.34
a_3 ($a_H^{3,7}$)	2.42	2.45	2.46	2.58	2.50	2.58	2.59	2.49
a_4 ($a_H^{1,9}$)	1.02	1.04	1.03	1.29	1.19	1.23	1.23	1.13
a_5 ($a_H^{4,6}$)	0.65	0.64	0.64	0.40	0.49	0.46	0.46	0.50
a_6 ($a_H^{2,8}$)	0.45	0.45	0.42	0.46	0.49	0.46	0.46	0.50
g				2.0050		2.0051	2.0053	2.0053
a_{NH}/a_N	1.11	1.11	1.10	1.2	1.16	1.13	1.15	1.15
X	19.39	19.74	19.69					
$2a_2 + a_1$	19.33	19.79	19.65	20.36	20.23	20.40	20.50	19.97
spectral width	28.32	29.00	28.77					
weighted sum of a_i	28.41	28.95	28.75	29.82	29.57	29.86	29.98	29.21
line width, mG	75	75	75	150	90	600	90	180

[a] $SbCl_3$, 130 °C, this work. [b] 60-22-18, 130 °C, this work. [c] 60-22-18, 90 °C, this work. [d] 3:1 H_2O/H_2SO_4, -40 °C.[24] [e] H_2SO_4/CH_3NO_2, -40 °C.[25] [f] (PTZ[+]·)ClO_4^- in MeCN.[26] [g] MeCN/H_2SO_4, -40 °C.[27f] [h] $CH_3NO_2/AlCl_3$, -40 °C.[27f]

ratio of the weighted sum of the coupling constants for PTZ[+]· to those for POZ[+]· is less than unity with a virtually constant value (0.806 ± 0.006) for all media for which data are available is in accord with MO calculations[27f] which indicate that the sulfur atom carries more spin density than does the oxygen atom as a result of the participation of sulfur d orbitals in the π system[27c] and further supports this view. Finally, the supposition that the chalcogen atoms in the radical cations are electron donors is supported by gas-phase photoelectron spectra[27e] from which it was concluded that although the HOMO of neutral PTZ contains a predominant contribution from nitrogen lone-pair electrons, the HOMO of PTZ[+]· has a predominant contribution from sulfur lone-pair electrons.

In acidic $SbCl_3$–$AlCl_3$–BPCl media PTZ[+]· and POZ[+]· were anodically oxidized to the dications PTZ[2+] and POZ[2+], which proved to be relatively stable. These assertions are based on the combined and mutually supportive results of CV, SE, and ^{1}H NMR investigations. The CV parameters, given in Table I, demonstrated that even at very low scan rates there was no indication of the instability of the product. (The electrode was initially conditioned at about +0.6 V in order to ensure complete oxidation to the radical cation.)

SE studies in acidic $SbCl_3$–$AlCl_3$–BPCl media were carried out in order to obtain further evidence that the oxidation products were the dications of PTZ and POZ and in order to evaluate their stabilities for time periods greater than those afforded by CV measurements. After conditioning the OTE at +0.65 V for 10 min the first spectrum, shown in Figure 4, of the solution confirmed that the oxidation to POZ[+]· was complete. Prominent spectral features observed during subsequent electrolysis at 1.4 V were an isosbestic point at 521 nm, indicative of the presence of only two absorbing species, the appearance of an absorption maximum at 487 nm (ϵ = 25.3 ± 1.0 × 10³ M⁻¹ cm⁻¹), weak, overlapping bands in the 600–850 nm region, and a shoulder at 435 nm. We assign these bands to POZ[2+]. There are very few data in the literature with which to compare this spectrum. However, in a very early investigation[22] the absorption spectrum of what was postulated to be POZ[2+] in H_2O_2–H_2SO_4 had a maximum at 460 nm, which presumably corresponds to the band maximum we observe at 487 nm (see Table II). Electrolysis at 1.4 V to give POZ[2+] was complete in 40 min. It was then reduced at 0.6 V for 40 min to give POZ[+]· and then reoxidized. To within experimental error, the difference between a spectrum measured at the start of the second oxidative electrolysis and one measured at the start of the first oxidative electrolysis gave no evidence of decomposition products.

A SE study of the oxidation of PTZ[+]· gave the following results. The initial spectrum showed that oxidation of PTZ to PTZ[+]· by Sb(III) was complete prior to electrolysis. Spectral features observed during electrolysis were isosbestic points at 507, 559, and 726 nm and the appearance of absorption bands at 480 (ϵ = 15.9 ± 0.5 × 10³ M⁻¹ cm⁻¹), 588, 644, and 700 nm. The profile of the product spectrum was closely similar to those of spectra
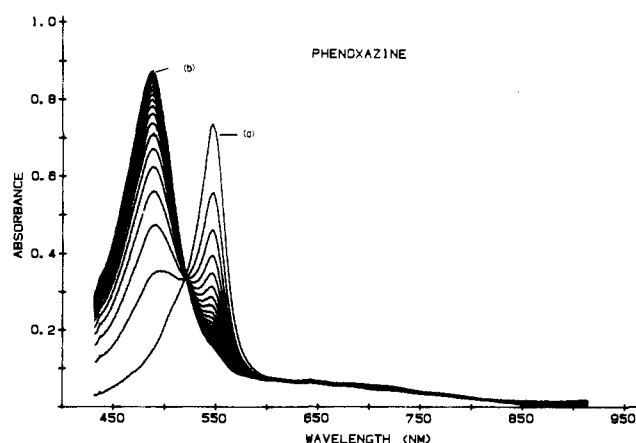
Figure 4. Spectra measured every 120 s during a 2400-s electrolysis at 1.4 V of 0.57 mM POZ[+]· in 60-22-18: (a) initial (pre-electrolysis) spectrum; (b) after 2400 s. Reticulated vitreous carbon OTE. Cell path length 0.10 cm.

previously attributed to PTZ[2+] [14d] and 10-methyl-PTZ[2+] [31] in 96% H_2SO_4. (See, also, Table II.) Spectra obtained during repeated oxidation-reduction cycles gave no evidence of loss of either PTZ[+]· or PTZ[2+] during 40 min. These SE results demonstrate the unreactivity over prolonged periods of time of the oxidized forms of POZ[+]· and PTZ[+]·, assigned as POZ[2+] and PTZ[2+].

Direct evidence that the N–H bond remained intact when the radical cations were oxidized was provided by ^{1}H NMR measurements in which $SbCl_3$–10 m/o $AlCl_3$ was used as the solvent. Solutions of POZ and PTZ in this medium were oxidized at 80 °C by an excess of added $SbCl_5$. The optical spectra of dilute solutions prepared in this way showed that the oxidation products were the same as those obtained by the anodic oxidations in $SbCl_3$–$AlCl_3$–BPCl media at ambient temperatures as described above. ^{1}H NMR spectra were measured for more concentrated solutions (~0.1 M). For PTZ[2+] two major peaks were observed at 9.02 and 9.23 ppm (8 protons) that were assigned to the aryl protons, and a broad peak was observed at 15.04 ppm (1 proton) that was assigned to the nitrogenic proton. For POZ[2+] the aryl protons appeared as a broad singlet at 9.08 ppm while the nitrogenic proton appeared as a very broad resonance at 14.3 ppm.[32] The weighted chemical shifts, δ_{av} ($\delta_{av} = \sum_i n_i \delta_i / \sum_i n_i$, where n_i is

(31) Shine, H. J.; Thompson, D. R.; Veneziani, C. *J. Heterocycl. Chem.* **1967**, *4*, 517.

(32) (a) In organic solvents the ^{1}H-NMR resonances of neutral POZ are broader than those of PTZ. See: Sharpless, N. E.; Bradley, R. B.; Ferretti, J. A. *Org. Magn. Res.* **1974**, *6*, 115. (b) Additional possible causes of line broadening for the POZ[2+] spectrum are electron exchange between POZ[2+] and a trace of POZ[+]· and proton exchange between POZ[2+] and a trace of phenoxazinium ions formed by deprotonation of POZ[2+]. See: Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 4086.

Table V. Voltammetric Parameters for $M(bpy)_3^{2+/3+}$ Couples in $SbCl_3–AlCl_3–BPCl$ Media at 25 ± 2 °C[a]

species	ν, mV s^{-1}	E_p^c, mV	E_p^a, mV	ΔE_p, mV	i_p^c/i_p^a	$E^{\circ\prime}$, mV basic	$E^{\circ\prime}$, mV acidic
$Ru(bpy)_3^{2+}$	5	707	765	58	1.0		736
	10	706	765	59	1.0		735
	20	705	767	62	1.0		736
	50	705	767	62	0.99		736
	100	702	769	67	1.0		735
	200	700	770	70	1.0		735
	500	698	775	77	0.99		737
	1000	694	780	86			737
$Fe(bpy)_3^{2+}$	5	485	546	61		516	531
	10	485	546	61		516	530
	20	485	546	61		516	530
	50	484	546	62		515	529
	100	484	547	63		516	529
	200	484	548	64		517	527
	500	483	553	70		518	528
$Os(bpy)_3^{2+}$	5	350	290	60	1.0	320	
	10	350	290	60	0.98	320	
	20	351	290	61	1.0	320	
	50	350	290	60	0.97	320	
	100	351	289	62	1.0	320	
	200	353	288	65	0.98	320	
	500	355	286	69	0.97	320	
	1000	355	283	72		319	

[a] Potentials relative to saturated $SbCl_3$ electrode.

the number of protons resonating at δ_i), were 9.7 and 9.8 ppm for POZ^{2+} and PTZ^{2+}, respectively. For neutral POZ and PTZ in acetone-d_6, $\delta_{av} = 6.7$ and 6.9 ppm, respectively, with $\delta_{NH} = 7.15$ and 7.77 ppm, respectively.[32a] The charge-induced shifts of the resonances, i.e., $[\delta_{av}(\text{dication}) - \delta_{av}(\text{neutral})]\{9(\text{protons})/2(\text{electrons})\}$, were thus 13.5 and 13.0 ppm per electron for POZ^{2+} and PTZ^{2+}, respectively. For comparison, the ^{1}H NMR charge-induced shifts of a series of arene dipositive ions were found to vary from 2.3 to 14 ppm per electron.[33] Thus, the charge induced shifts for oxidized PTZ and POZ are consistent with the formation of dipositive species and are at the upper end of the induced shifts observed for arene dications. These are the first reported NMR spectra of the dications of PTZ and POZ.

The oxidation potentials for the neutral heteroaromatics, displayed in Table I and Figure 2, lie close together ($\Delta E^{\circ\prime} = 0.03$ V). Hence, the fact that these molecules differ with respect to their chalcogen atoms has only a small effect on the oxidation process. This behavior is consistent with the conclusion, cited above, that the HOMO's on these molecules are largely populated by nitrogen lone-pair electrons. In contrast, the oxidation potentials of the radical cations are substantially separated ($\Delta E^{\circ\prime} = 0.20$ V). This effect is consistent with the conclusion, cited above, that the HOMO's on these radical cations are largely populated by chalcogen lone pairs.

Characterization of Bipyridine Complexes of Fe, Ru, and Os in SbCl$_3$-Rich Media. The $M(bpy)_3^{3+/2+}$ (M = Fe, Ru, Os) couples were electrochemically characterized by CV and double potential-step coulometry (DPSC) or chronocoulometry (CC) at glassy carbon electrodes in SbCl$_3$–AlCl$_3$–BPCl media, and CV parameters are listed in Table V, where ν, E_p^c, E_p^a, and ΔE_p have the same meaning as in Table I, i_p^c/i_p^a is the ratio of cathodic to anodic peak currents, and the formal potential $E^{\circ\prime} = (E_p^a + E_p^c)/2$. Values of the latter are listed separately for basic 60–19–21 and acidic 60–22–18 media and are also displayed in Figure 2.

The electrochemical windows in the SbCl$_3$–AlCl$_3$–BPCl media, fixed by the respective potentials at which Sb(III) is oxidized and reduced, are quite sensitive to the acidity of the solvent as illustrated in Figure 2. This behavior is responsible in part for the interesting redox and catalytic properties of these media but it also places restrictions on which electrochemical properties could and could not be measured for each solute couple. Thus, $E^{\circ\prime}$ for

the $Ru(bpy)_3^{3+/2+}$ couple could only be measured in acidic media because in basic media it was very near the anodic Sb^V/Sb^{III} limit, while the $Os(bpy)_3^{3+/2+}$ couple could only be measured in basic media because in acidic media it lay below the cathodic Sb^{III}/Sb^0 limit. Likewise, current ratios for the iron complexes could not be measured because of the close proximity of the voltammetric wave to the cathodic limit for acidic media and to the anodic limit for basic media.

As shown in Table V, the experimental values of ΔE_p are close to the theoretical value of 59 mV[15] for a one-electron nernstian process at 26 °C except at the highest scan rates, in which case the deviations are plausibly attributed to incompletely compensated solution resistance (see Experimental Section). Likewise, the peak current ratios, where they could be measured, are unity to within experimental error. Confirmation of the reversibility of the $Ru(bpy)_3^{3+/2+}$ couple was provided by DPSC. For pulse widths of 2, 5, and 10 s the average value of $Q_{2\tau}/Q_\tau$ was 0.423 ± 0.025 as compared to the theoretical value of 0.414 for a one-electron nernstian process.[16b] These results show that the $M(bpy)_3^{3+/2+}$ couples fulfill electrochemical criteria for reversible one-electron processes and that the products are stable on a voltammetric time scale. Furthermore, the three couples provide a graded series of potentials in SbCl$_3$–AlCl$_3$–BPCl media that proved useful in investigating homogeneous redox reactions in these media.

As shown in Table V, the formal potential of the $Fe(bpy)_3^{3+/2+}$ couple changed only by a very small amount, 14 mV, in going from the basic to the acidic medium, and a part of this small change is probably due to the junction potential. We assume that the potentials of the other complex ion couples are likewise insensitive to the acidity of these SbCl$_3$-rich media and on this basis we estimate that the formal potential of the $Os(bpy)_3^{3+/2+}$ couple in acidic media is about 0.33 V, that is, about 0.01 V greater than in basic media. This value is displayed in Figure 2 as a dashed line. (Spectroscopic evidence presented below shows that Os-$(bpy)_3^{3+}$ is the stable product of the oxidation of $Os(bpy)_3^{2+}$ by Sb(III) in acidic media.) This relative insensitivity of the formal potentials of these complexes to these changes in Lewis acidity is in line with the properties of these complexes in other media. Thus, Sahami and Osteryoung[12b] found that the formal potentials of the $Ru(bpy)_3^{3+/2+}$ and $Fe(bpy)_3^{3+/2+}$ couples in AlCl$_3$–BPCl mixtures at 40 °C showed relatively modest positive shifts with increasing Lewis acidity over a much wider range than that provided by our media.

(33) Brouwer, D. M.; van Doorn, J. A. *Recl. Trav. Chim. Pays-Bás* **1972**, *91*, 1110.

Table VI. Coordinates of Strongest Bands in Visible Spectra of Bipyridine Complexes

complex	medium	λ, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})	ref
Ru(bpy)$_3^{2+}$	60–22–18	454 (14.7 ± 0.2)	*a*
	AlCl$_3$–BPCl	454 (14.0 ± 0.7)	12b
	acetonitrile	450 (14.0)	12k
	1 M HClO$_4$	453 (13.8)	12l
Ru(bpy)$_3^{3+}$	60–22–18	431 (2.25 ± 0.10)	*a*
	AlCl$_3$–BPCl	424 (3.20 ± 0.16)	12b
	H$_2$O/Ce^{4+}	418 (~3.0)	12d
Fe(bpy)$_3^{2+}$	60–19–21	527 (10.0 ± 0.3)	*a*
	AlCl$_3$–BPCl	523 (8.7 ± 0.4)	12b
	acetonitrile	520 (8.24)	12m
	H$_2$O	522 (8.65)	12n
Fe(bpy)$_3^{3+}$	60–19–21	643 (0.35 ± 0.05)	*a*
	AlCl$_3$–BPCl	627 (0.38 ± 0.02)	12b
	acetonitrile	608 (0.261)	12m
	conc H$_2$SO$_4$	617 (0.320)	12n
	H$_2$O/Cl$_2$	613 (0.289)	12d
Os(bpy)$_3^{2+}$	60–19–21	484 (13.6 ± 0.5)	*a*
	H$_2$O	477 (13.7)	12o
Os(bpy)$_3^{3+}$	60–19–21	575 (0.80 ± 0.05)	*a*
	3 N HCl	563 (0.585)	12d

a This work.

Diffusion coefficients (D) were calculated from the slopes of i_p vs. $v^{1/2}$ plots from CV measurements[16c] and Q vs. $t^{1/2}$ plots from chronocoulometric (CC) measurements.[16d] Average values of $10^7 D$ (cm^2 s^{-1}) were as follows: In 60–22–18 media, Ru(bpy)$_3^{2+}$ 1.37 (CV), 1.37 (CC); Ru(bpy)$_3^{3+}$ 1.30 (CV), 1.46 (CC); Fe(bpy)$_3^{3+}$ 1.26 (CV). In 60–19–21 media, Fe(bpy)$_3^{2+}$ 1.42 (CV), 1.26 (CC); Os(bpy)$_3^{2+}$, 1.27 (CV) 1.38 (CC). Stokes–Einstein radii (r_{SE}) were calculated from the Stokes–Einstein (S–E) formula[34a] $r_{SE} = kT/(6\pi\eta D)$ where kT has its usual meaning and η is the viscosity of the solvent (22.8 cP[9a] at 25 °C). All of these r_{SE} values lie in the range 0.66–0.76 nm and show no statistically significant trends with respect to the identity of the ion or the acidity of the medium. They are within experimental uncertainty of the value 0.70 nm, which is the crystallographic radius (r_c) of all of these complexes.[35] Acetonitrile, like SbCl$_3$, is a dipolar solvent and a prior measurement of D for Fe(bpy)$_3^{2+}$ in this medium gave $r_{SE} = 0.68$.[12h] Because of the approximate nature of the S–E relation,[34b] we do not wish to overly stress these data; nevertheless, the fact that r_{SE} has virtually the same value in both acidic and basic SbCl$_3$–AlCl$_3$–BPCl media and also in acetonitrile suggests that the M(bpy)$_3^{n+}$ complexes are solvated in similar ways in all

(34) (a) Derivations of the S–E relation are given in ref 34c,d. (b) The S–E relation is strictly applicable only to the diffusion of large, spherical molecules in solvents composed of very much smaller molecules. As the size of the diffusing species approaches that of the solvent molecules, the S–E relation becomes increasingly less accurate in ways that depend on the nature of the diffusing species and the solvent. Edward (ref 34c) gives numerous examples for neutral molecules diffusing in molecular liquids, while Bockris and Reddy (ref 34d) give introductions to the more complicated situations provided by the diffusion of ions in dipolar solvents and totally ionized liquids. Judging from data for the diffusion of approximately spherical molecules in carbon tetrachloride and water,[34c] deviations from the S–E relation do not become substantial until the radii of the diffusing molecules are significantly smaller than 0.7 nm. For smaller molecules, there is a systematic deviation that can be approximately corrected by reducing the numerical factor 6 in the S–E equation to smaller values as the molecular size decreases. Thus, for example, McLaughlin[34e] found that by using 4 instead of 6 in the S–E one obtained an improved but still quite approximate correlation for self-diffusion data for small molecules (radii <0.3 nm). (c) Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261. (d) Bockris, J. O'M.; Reddy, A. K. N. "Modern Electrochemistry"; Plenum: New York, 1970; Vol. 1, pp 379–381 and 550–553. (e) McLaughlin, E. *Trans. Faraday Soc.* **1959**, 28. (f) Recent D values (see ref 12b) for Ru(bpy)$_3^{2+}$ and Fe(bpy)$_3^{2+}$ in ionic liquids formed by mixing AlCl$_3$ and BPCl yield unreasonably small r_{SE} values when substituted into the standard S–E relation (numerical factor = 6) but yield r_{SE} values that approximate r_c when McLaughlin's modified S–E equation (see ref 34e) is used (numerical factor = 4). In view of the above discussion we find this behavior puzzling. Possibly it has something to do with the properties of completely ionized liquids.

(35) Powers, M. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 1785.

Table VII. Results of SCM Experiments

expt no.	substrate oxidant medium	product	time, s	amt, %	$\Delta E^{0\prime}$, V
i	POZ Sb(V) 60–19–21	POZ$^+$·	10	100	~0.6
ii	PTZ Sb(V) 60–19–21	PTZ$^+$·	10	100	~0.7
iii	POZ Os(bpy)$_3^{3+}$ 60–19–21	POZ$^+$·	10	100	0.18
iv	Fe(bpy)$_3^{2+}$ Ru(bpy)$_3^{3+}$ 60–21.1–18.9	Fe(bpy)$_3^{3+}$	16	100	0.22
v	Ru(bpy)$_3^{2+}$ Sb(V) 60–22–18	Ru(bpy)$_3^{3+}$	10	100	~0.9
vi	Os(bpy)$_3^{2+}$ Sb(III) 60–20.8–19.2	Os(bpy)$_3^{3+}$	3 600 17 900	50 90	~0.1
vii	POZ Sb(III) 60–21.2–18.8	POZ$^+$·	10 180 870	2.3 3.7 7.0	~0.2
viii	PTZ Sb(III) 60–21.2–18.8	PTZ$^+$·	10 180 870	28 59 72	~0.2
ix	POZ Sb(III) + Ru(bpy)$_3^{3+}$ 60–21–19	POZ$^+$·	10 600 86 400	64^a 65 92	~0.5
x	PTZ Sb(III) + Ru(bpy)$_3^{3+}$ 60–21.1–18.9	PTZ$^+$·	11 600 1 860	75^a 97 100	~0.5
xi	POZ Sb(III) + Sb(V) 60–20.5–19.5	POZ$^+$· POZ^{2+} POZ$^+$· POZ^{2+} POZ$^+$· POZ^{2+}	15 150 2 700 	84^b 12 50 50 3 97	~1.5 ~0.6
xii	PTZ Sb(III) + Sb(V) 60–20.4–19.6	PTZ$^+$· PTZ^{2+} PTZ$^+$· PTZ^{2+}	16 1 620 	16^b 84 0 100	~1.5 ~0.7

^{a} With respect to Ru(bpy)$_3^{3+}$. ^{b} With respect to Sb(V).

these media, and the fact that r_{SE} approximates r_c supports the view that there is no inner-sphere bonding between SbCl$_3$ and the metal atoms.[34f]

Optical absorption spectroscopy and SE were used to confirm the identities of the dipositive complexes and their tripositive oxidation products in SbCl$_3$–AlCl$_3$–BPCl media and to give additional information about their stabilities. The tripositive complexes were prepared by oxidizing solutions of the dipositive ions with Sb(V), generated anodically. Coordinates of the strongest band maxima in each spectrum are listed in Table VI together with their values in other media. The spectra for the solutions of these complexes in SbCl$_3$–AlCl$_3$–BPCl were the same in all essential respects as those for dipositive complexes[12b–d,g,l–o] and tripositive complexes[12b–d] in other solvents and crystalline compounds.

Solutions of the two ruthenium complexes in acidic 60–22–18 media at 25 °C were very stable; their spectra were unchanged after 72 h. Solutions of the two osmium complexes in basic 60–19–21 media showed virtually no decomposition for some hours but very slowly decomposed over long time periods; in particular, Os(bpy)$_3^{2+}$ decomposed 2% in 96 h while Os(bpy)$_3^{3+}$ decomposed

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26% in 120 h. Although the $Fe(bpy)_3^{2+}$ complex in acidic 60–22–18 media at 25 °C showed virtually no decomposition for 6 h, it decomposed 30% in the following 42 h. The $Fe(bpy)_3^{3+}$ complex was not observed over such extended periods but at 25 °C in basic 60–19–21 media no decomposition was detected after 1 h. When solutions of these complex ions in $SbCl_3$–$AlCl_3$–BPCl media were alternately electrooxidized and reduced at an OTE for periods of 2 h at 25 °C, the spectra behaved in the ways expected for stable systems composed of only the $M(bpy)_3^{2+}$ and $M(bpy)_3^{3+}$ ions, without any sign of decomposition. Well-defined isosbestic points occurred and at the end of each oxidation–reduction cycle the final spectrum had the same absorptivity as the initial spectrum.

Homogeneous Oxidation of POZ and PTZ. The homogeneous oxidation of POZ and PTZ was studied under the clean conditions provided by a sealed-cell mixing (SCM) technique, namely, solutions of substrate and oxidant were, respectively, contained in two arms of a small cell sealed-off under purified argon. By rotating the cell these solutions could be mixed and the mixture delivered into an optical cuvette where the subsequent progress of reaction could be monitored by a fast optical spectrometer. The time required for homogeneous mixing was, typically, 10 s. This SCM technique provided a simple means of studying relatively slow reactions with minimal danger of environmental contamination. Table VII summarizes representative results from SCM experiments for which the compositions of the starting solutions are listed in the Experimental Section. The compositions of the $SbCl_3$–$AlCl_3$–BPCl media after mixing are listed in Table VII while the formal concentrations of the substrates after mixing generally lay in the range 0.2–2 mM and temperatures were in the range 23–27 °C. The column headed $\Delta E^{\circ\prime}$ provides a measure of the exergonicity of each reaction in terms of the differences in $E^{\circ\prime}$ values of the redox couples of the two reactants. For $\Delta E^{\circ\prime}$ values marked with $\sim$, one or both of the constituent $E^{\circ\prime}$ values were estimated on bases described above. For experiments in which the temporal progress of the reactions could be measured, attempts to fit the data to simple schemes were not successful.

In experiments i–v, reaction was complete within the mixing time of 10–16 s. In the remaining experiments the reactions were very slow and we report only a few data selected from up to 30 spectra per experiment with each spectrum measured in $\sim$0.2 s. In experiments vi–viii the oxidant was Sb(III), alone, while in experiments ix–xii there was an additional oxidant, substantially stronger than Sb(III), viz-, $Ru(bpy)_3^{3+}$ or Sb(V), whose $E^{\circ\prime}$ values exceeded that of Sb(III) by 0.3 and 1.3 V, respectively. In experiments ix and x, the concentrations of $Ru(bpy)_3^{3+}$, its reduction product $Ru(bpy)_3^{2+}$, and the radical cation oxidation products could be separately monitored and the concentration of $Ru(bpy)_3^{2+}$ equaled the concentration of radical cation throughout as required by stoichiometry. In experiments xi and xii, Sb(V) was a very powerful oxidant, much stronger in these acidic melts than in basic melts, and it oxidized the heteroaromatics virtually completely to a mixture of their radical cations and dications within the mixing time. Thereafter, the oxidation of radical cations to dications proceeded at a very slow pace. In these experiments Sb(V) did not absorb in the visible range whereas the radical cations and dications gave intense and easily distinguished peaks.

There are substantial reasons for supposing that the bipyridine complexes used in the present investigation are facile SET agents and are not responsible for slow reaction rates reported here. These reasons include the results of studies of these complexes in other liquid media[12] together with our studies of their properties in $SbCl_3$–$AlCl_3$–BPCl melts including their reversible electrochemistry, the rapid oxidations of the heteroaromatics in basic melts by $Os(bpy)_3^{3+}$ (experiment iii) and Sb(V) (experiments i and ii), the rapid oxidation of $Fe(bpy)_3^{2+}$ by $Ru(bpy)_3^{3+}$ in an acidic melt (experiment iv), and the rapid oxidation of $Ru(bpy)_3^{2+}$ by Sb(V) in an acidic melt (experiment v). Thus, we ascribe the slow oxidation of $Os(bpy)_3^{2+}$ by Sb(III) in an acidic melt (experiment vi) to slow processes in the reduction of antimony. The stable forms of reduced antimony in $SbCl_3$–$AlCl_3$ melts have Sb–Sb bonds and the simplest of these species is Cl_2Sb–$SbCl_2$.[5,8a] Hence,

a SET reaction between $Os(bpy)_3^{2+}$ and Sb(III) will yield an unstable entity containing mononuclear Sb(II), such as $SbCl_2\cdot$. This unstable Sb(II) is produced in a reaction with a driving force of only $\sim$0.1 V and, hence, should be present at a very low concentration so that subsequent reactions to form stable species, such as Cl_2Sb–$SbCl_2$, and reactions yielding larger, polynuclear cluster ions should be slow.

In MeCN POZ and PTZ are facile electron transfer agents as demonstrated by the following data: The rate constants for the self-exchange reaction of these heteroaromatics (PXZ + $PXZ^+\cdot \rightleftharpoons PXZ^+\cdot$ + PXZ) have values slightly in excess of 10^9 M^{-1} s^{-1} and are in reasonable agreement with the Marcus theory for outer-sphere electron transfer.[36] These large values imply a low activation barrier for electron removal. In addition, studies of the oxidations of POZ and PTZ by aquo-Fe(III) and aquo-Ce(IV) ions in MeCN at 25 °C indicate bimolecular rate constants in excess of 10^6 M^{-1} s^{-1}.[37] As these results show, the nonbonded oxidations of these heteroaromatics by facile oxidants are much too fast to be observed by our SCM technique. Plausibly, their rapid homogeneous oxidations in basic 60–19–21 melts (experiments i–iii) were of this type.

The very slow oxidations of POZ and PTZ in acidic melts, whether by Sb(III) or Sb(III) aided by $Ru(bpy)_3^{3+}$ (experiments vii–x), contrast markedly with their rapid oxidations in basic melts. The slow oxidations by Sb(III) might be attributed, at least in part, to the slow reduction kinetics of antimony (see above). However, their continued slow oxidations in the presence of excess $Ru(bpy)_3^{3+}$ suggests the intervention of an additional rate-inhibiting factor. A conspicuous possibility is the formation preferentially in acidic melts of complexes with N–Sb bonds, e.g.

$$PXZ + SbCl_2^+\cdot nSbCl_3 \rightleftharpoons (PXZ\cdot SbCl_2)^+ + nSbCl_3 \quad (2)$$
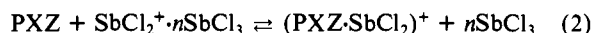
In this reaction the concentration of $SbCl_2^+\cdot nSbCl_3$ is controlled by the self-ionization of $SbCl_3$, viz.

$$(3 + n)SbCl_3 \rightleftharpoons SbCl_2^+\cdot nSbCl_3 + Cl^-\cdot 2SbCl_3 \quad (3)$$
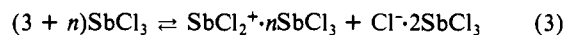
The ion product constant (K_i) for eq 3 is very small for neat $SbCl_3$ at elevated temperatures[38a] and is likely to remain small for our ternary melts at ambient temperatures. Thus the concentration of $SbCl_2^+\cdot nSbCl_3$ is very sensitive to the $AlCl_3$/BPCl ratio in such a way that in acidic melts eq 2 will shift in favor of $(PXZ\cdot SbCl_2)^+$ complexes while the uncomplexed molecules would be favored in basic melts.[38b] A prior investigation has shown that some amines in $SbCl_3$ at elevated temperatures form complexes as in eq 2 while others appeared not to form such complexes and the reason for this difference was not clear.[11c,d,39] The complexation constants for those that did form complexes were generally large enough to drive reactions like eq 2 very far to the right in acidic melts. Assuming that POZ and PTZ form ionic complexes with N–Sb bonds, their rates of oxidation should be slow for the following reasons: In the absence of $Ru(bpy)_3^{3+}$, these complexes will oxidize by a bonded (inner-sphere) mechanism, thus

$$(PXZ\cdot SbCl_2)^+ \rightleftharpoons PXZ^+\cdot + SbCl_2\cdot \quad (4)$$
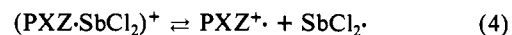
which will be inhibited both by the formation of the energetic Sb(II) intermediate and by the fact that N–Sb bond breaking must pass through an energetic metastable state such as that postulated for the oxidation of PTZ by the methoxyaryldiazonium ion.[40] When $Ru(bpy)_3^{3+}$ is present as an added oxidant, the N–Sb bond must still be broken because the $PXZ^+\cdot$ product no longer has a lone pair on N with which to form a stable N–Sb bond. (See the

(36) Kowert, B. A.; Marcoux, L.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 5538.

(37) Kemp, T. J.; Moore, P.; Quick, G. R. *J. Chem. Soc., Perkin Trans.* 2 **1980**, 291.

(38) (a) For neat $SbCl_3$ at 99 °C, reported values of pK_i, obtained by different methods, are 7.8[7a] and $\geq$10.5.[50] (b) We were unable to study $(PXZ\cdot SbCl_2)^+$ formation by optical spectroscopy because of interference from solvent absorption.

(39) Neutral complexes with $SbCl_3$ are also possible but we expect these to be weakly bound and constitute a solvation effect.

(40) Bisson, J. M.; Hanson, P.; Slocum, D. *J. Chem. Soc., Perkin Trans.* 2 **1978**, 1331.

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above discussion of electronic structure of PXZ[+]· in connection with ESR spectra.) In this case, of course, oxidation of uncomplexed POZ or PTZ, present in equilibrium with their ionic complexes, should be fast. However, if the concentration of these uncomplexed molecules is extremely small (large complexation constant) or if the reverse reaction in eq 2 is a slow reaction, the overall rate of oxidation of the heteroaromatics in acidic melts will be slow.[41]

The above assumptions rationalize in a simple way the temporal course of experiments ix and x. In these experiments a basic solution of heteroaromatic was mixed with an acidic solution of $Ru(bpy)_3^{3+}$ so that during the mixing period uncomplexed heteroaromatics were simultaneously being oxidized by $Ru(bpy)_3^{3+}$ and complexed by $SbCl_2^+ \cdot nSbCl_3$. Although we have supposed that the rate constant for this oxidation was decidedly greater than that for the forward reaction in eq 2, the latter reaction was competitive because the concentration of $SbCl_2^+ \cdot nSbCl_3$ was so much greater than that of $Ru(bpy)_3^{3+}$. Thus at the end of the mixing period the heteroaromatic was partially but not completely oxidized and, thereafter, unoxidized heteroaromatic was present almost entirely in its oxidation-resistant, complexed form.

Thus far we have ignored the likelihood that POZ and PTZ are complexed by $SbCl_2^+$ at their chalcogen atoms (O and S, respectively) as well as their N atoms. In oxidations to radical cations, the chalcogen–Sb bond is not broken. In fact, the ESR spectra of the radical cations imply the presence of such bonds (see above). On the other hand, when the radical cations are oxidized to dications, as in experiments xi and xii, we presume that these bonds are broken because in PXZ[2+] the chalcogen has lost a lone pair. Such bond breaking should have kinetic consequences analogous to those for N–Sb bond breaking when neutrals are oxidized to radical cations. The rapidity of the initial oxidation of the doubly complexed heteroaromatics to singly complexed radical cations is plausibly accounted for by the extremely exergonic character of these reactions (~ 1.5 V). Thereafter, the much less exergonic oxidation of singly complexed radical cations to uncomplexed dications took place at an observable rate. Although the reduction steps for Sb(V) are unknown,[42] it is unlikely that these were in any way rate controlling in view of the speed with which Sb(V) was reduced by $Ru(bpy)_3^{2+}$ in an acidic melt (experiment v).[44]

Experimental Section

Materials. The synthesis of BPCl, the purification of $SbCl_3$, $AlCl_3$, and BPCl, and preparation of their liquid mixtures have been described.[9b] $SbCl_5$ (Alfa, Ultrapure), $[Ru(bpy)_3]Cl_2$ (Pfaltz and Bauer, anhydrous), and $[Fe(bpy)_3](ClO_4)_2$ (Pfaltz and Bauer, anhydrous) were used as received. $[Os(bpy)_3](ClO_4)_2 \cdot H_2O$ was prepared from K_2OsCl_6 (Pfaltz and Bauer) and 2,2'-bipyridine (Pfaltz and Bauer) as described in the literature.[12a] Purity of the product was verified by VIS spectroscopy ($\epsilon_{478} = 13.7 \times 10^3$ M^{-1} cm^{-1}, aq[12b]). POZ (Aldrich, 97%) was twice fractionally sublimed in vacuo with the center cut retained. PTZ (Aldrich, 98%) was thrice recrystallized from benzene and twice sublimed in vacuo. Purities of POZ and PTZ were confirmed by HPLC and GC.

Solutions. Material transfers, weighing, and the preparation of solvents and solutions was done in gloveboxes under Ar that was continuously circulated through a purification train (H_2O and $O_2 < 1$ ppm, each).

Solutions of $M(bpy)_3^{3+}$, M = Ru, Fe, Os, in liquid $SbCl_3$–$AlCl_3$–BPCl were prepared by oxidation of solutions of the corresponding dipositive complexes with accurately weighed amounts of solutions of Sb(V) in

media of the same composition. The latter solutions were prepared by coulometric electrolysis of the solvent. Dilute solutions of these complexes in $SbCl_3$–$AlCl_3$–BPCl were prepared by mixing accurately weighed amounts of more concentrated stock solutions (10–20 mg) with accurately weighed amounts of solvent (5–10 g).

Solutions of PTZ and POZ in 60-22-18 media, used for preliminary observations of their slow rates of oxidation, were prepared as follows: Stock solutions of PTZ and POZ (~ 10 mM) were prepared in 60-19-21 media, and aliquots (~ 0.05 mL) were added to sufficient 60-22-18 media (~ 1 mL) so that the composition of the final solvent composition was close to 60-22-18. These acidic solutions were stirred at 30 $\pm$ 1 °C in the glovebox, and samples were removed from time to time for analysis by optical absorption.

Compositions of solutions mixed in SCM experiments were as follows, where the quantity of solute (if any) is in μmol, the quantity of solvent is in mL, and mw = mixed with: (i) 1.42 POZ, 1.00 (60-19-21) mw 7.06 Sb(V) (electrolysis of Sb(III)), 1.00 (60-19-21). (ii) 1.54 PTZ, 1.00 (60-19-21) mw 7.06 Sb(V) (electrolysis of Sb(III)), 1.00 (60-19-21). (iii) 0.39 POZ, 0.70 (60-19-21) mw 0.45 $Os(bpy)_3^{3+}$, 0.70 (60-19-21). (iv) 0.63 $Fe(bpy)_3^{2+}$, 0.45 (60-19-21) mw 0.70 $Ru(bpy)_3^{3+}$, 1.00 (60-22-18). (v) 4.90 $Ru(bpy)_3^{2+}$, 0.50 (60-22-18) mw 2.65 Sb(V) (electrolysis of Sb(III)), 1.00 (60-22-18). (vi) 1.39 $Os(bpy)_3^{2+}$, 0.70 (60-19-21) mw 1.00 (60-22-18). (vii) 0.60 POZ, 0.50 (60-19-21) mw 1.50 (60-22-18). (viii) 1.92 PTZ, 0.50 (60-19-21) mw 1.50 (60-22-18). (ix) 0.75 POZ, 0.50 (60-19-21) mw 0.79 $Ru(bpy)_3^{3+}$, 1.00 (60-22-18). (x) 0.73 PTZ, 0.50 (60-19-21) mw 0.86 $Ru(bpy)_3^{3+}$, 1.10 (60-22-18). (xi) 0.79 POZ, 1.00 (60-19-21) mw 6.40 $SbCl_5$, 1.05 (60-22-18). (xii) 2.03 PTZ, 0.70 (60-19-21) mw 7.76 Sb(V) (electrolysis of Sb(III)), 1.50 (60-21-19).

Concentrations of solutions in $SbCl_3$–$AlCl_3$–BPCl media were determined from the weight of the solvent and its density.[9a]

Electrochemical Measurements. Cells used for CV, CC, DPSC, and SE have been described previously.[43] The reference electrodes consisted of Sb rods immersed in a $SbCl_3$–BPCl mixture saturated with $SbCl_3$ and separated from the main electrolyte by an alumina frit.[9a] This is referred to as the saturated $SbCl_3$ electrode. Instrumentation consisted of an EG&G PAR Model 174A polarographic analyzer, a Model 173 potentiostat/galvanostat, and a Model 175 waveform generator. Data were recorded with either a Hewlett-Packard Model 7045A X-Y recorder or a Nicolet Model 2090-III digital storage oscilloscope.

For the CV, CC, and DPSC measurements, instrumental compensation for solution resistance was employed. The glassy carbon working electrodes were positioned as close as possible (<5 mm) to the reference electrode. The uncompensated resistances (R_u) at ~ 25 °C were estimated by applying a 50-mV potential step to the working electrode, immersed in pure solvent, measuring the maximum value of the current response and calculating R_u with $R_u \simeq 50$ mV/I. With no resistance compensation, R_u was ~ 430 Ω, while with maximum compensation R_u was ~ 50–100 Ω.

Time-Resolved Optical Spectroscopy. Absorption spectra for SE and SCM experiments were measured as follows: Radiation from a 10-W tungsten/quartz/halogen lamp was filtered with neutral-density filters to control intensity and a long-pass filter to eliminate second-order light. A cropped image of the filament was focused at the center of the optical cell and then focused on the entrance slit (0.025 mm) of a flat-field, 0.32-m spectrograph (Instruments SA, Inc. Model HR-320S, 152.5 grooves mm^{-1} grating) to which was attached a linear diode array detector (EG&G PAR Model 1412 Reticon) operated by a EG&G PAR Model 1412 detector controller. This detector provided 1022 optical channels over a spectral window 505 nm wide at a resolution of 0.5 nm. In some instances measurements were extended into the ultraviolet region down to the UV cutoff of the solvent (~ 340 nm) with a 50-W D_2 lamp. The operation of the detector and the reduction of data were under the programmed control of a EG&G PAR OMA-2 system processor (Model 1215) in such a way that spectra could be taken at programmed time intervals initiated by a trigger signal.

For the spectra reported here, the time used to measure a spectrum, including signal integration to improve S/N, was negligibly small (~ 60 ms). The spectra were corrected for dark current, and lamp intensity drift errors were negligible (<0.005 absorbance units). Two optical references were used in SE measurements; one was the spectrum of the solution prior to electrolysis while the other contained only corrections for light losses at the OTE and due to reflections at the cell windows. For the SCM experiments the reference was a solvent-filled silica cuvette. Wavelength calibration and resolution verification were performed with Hg, Ne, Ar, and Xe lamps.

Sealed-Cell Mixing Technique. The SCM technique was used to measure the temporal evolution of absorption spectra during oxidation reactions initiated by mixing a solution of a reactant with a solution of an oxidant.

(41) Note that the reported division of amines into complexing and noncomplexing classes can be rationalized in terms of fast vs. slow complexation kinetics.

(42) (a) Studies of solutions of $SbCl_5$ in molten $SbCl_3$ indicate strong interactions between the two but leave unresolved the question of what molecular species might be formed except, possibly, in basic melts for which the data suggest $SbCl_6^-$. See the following. (b) Jander, G.; Swart, K.-H. *Z. Anorg. Allg. Chem.* **1959,** *299,* 252. (c) Jander, G.; Swart, K.-H. *Z. Anorg. Allg. Chem.* **1959,** *301,* 54. (d) Badoz-Lambling, J.; Bauer, D.; Texer, P. *Anal. Lett.* **1969,** *2,* 411.

(43) Sørlie, M.; Smith, G. P.; Norvell, V. E.; Mamantov, G.; Klatt, L. N. *J. Electrochem. Soc.* **1981,** *128,* 333.

(44) We attribute the reversibility of heterogeneous (electrochemical) oxidations of PXZ and PXZ[+]· in acidic melts to a catalytic role of the electrode surface in bond breaking.
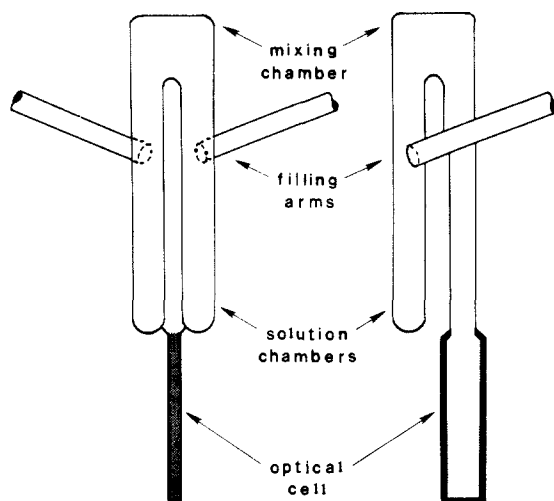
Figure 5. Cell used in the SCM method. The silica cuvette is joined by a graded seal to borosilicate glass.

The cell is shown in Figure 5. In a glovebox solutions of the two reactants in $SbCl_3$-$AlCl_3$-BPCl media were added by syringes into the two solution chambers and the filling arms were sealed off on a vacuum line under $\sim$0.8 atm of purified argon. Inversion and shaking of the cell mixed the two solutions and a second inversion directed the liquid into the cuvette.

Magnetic Resonance. ESR experiments were carried out with a Va-

rian Model E-109 spectrometer equipped with a Model E-257 variable temperature accessory. The temperature of the sample was controlled by means of a convective flow of heated N_2 and was constant to ± 1 °C. The spectrometer operated at a nominal microwave frequency of 9.102 GHz, and spectra were measured with use of 100-kHz field modulation and a scan rate of $\sim$1 G min^{-1}. Hyperfine coupling constants were accurate to ± 0.03 G. Sample tubes and their preparation have been described.[7c] Substrate concentrations were in the range 0.1-1 mM.

^{1}H NMR measurements were made with a Nicolet NT-200 FT spectrometer at 200.17 MHz on solutions of $\sim$0.1 M. The chemical shifts were referenced externally to $(CH_3)_4NCl$ (δ 3.12) in molten $SbCl_3$, which was itself referenced to $(CH_3)_4Si$ in the melt. The dications of POZ and PTZ were generated chemically for NMR measurements by oxidation with an excess of $SbCl_5$ in $SbCl_3$-10 m/m $AlCl_3$.

Supplementary Material Available: Figures showing spectra measured during electrolysis of POZ in 60-19-21 melt, ESR spectrum of PTZ$^+$· in $SbCl_3$, spectra measured during electrolysis of PTZ$^+$· in 60-22-18 melt, and spectra of $M(bpy)_3^{2+}$ and $M(bpy)_3^{3+}$ complexes in $SbCl_3$-$AlCl_3$-BPCl melts (5 pages). Ordering information is given on any current masthead page.

An in Situ Infrared Spectroscopic Investigation of the Role of Ethylidyne in the Ethylene Hydrogenation Reaction on Pd/Al₂O₃

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Abstract: Transmission infrared spectroscopy and kinetic techniques have been used to monitor surface ethylidyne ($\geqslant CCH_3$) concentrations in situ during ethylene hydrogenation reactions on Pd/Al_2O_3 surfaces. For 1:1 mixtures of reactant C_2H_4 and H_2, there is no formation of surface ethylidyne during the ethylene hydrogenation; for reactant mixtures where C_2H_4 is in excess of H_2, the buildup of surface ethylidyne concentration with time is dependent on the amount of excess C_2H_4. Using ^{13}C-labeled ethylidyne, it has been shown that ethylidyne formation and hydrogenation rates are 2 to 3 orders of magnitude slower than ethylene hydrogenation rates. Finally, ethylene hydrogenation rates have been measured on surfaces both with and without preadsorbed ethylidyne and are the same for both. This suggests that ethylidyne is a spectator species not essential to ethylene hydrogenation and that the proposed ethylidene species (on Pt(111)), proceeding from the ethylidyne species, is not a necessary species in the hydrogenation mechanism for ethylene on the typical Pd/Al_2O_3 catalytic surfaces employed in this study.

I. Introduction

The catalyzed ethylene hydrogenation reaction

$$C_2H_4(g) + H_2(g) \xrightarrow{\text{catalyst}} C_2H_6(g)$$
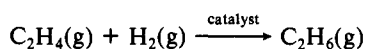
is perhaps one of the most studied classical catalytic reactions and has been the subject of numerous reviews and papers.[1,2] Mechanisms have been proposed for this reaction as early as 1934

by Horiuti and Polanyi[3] (associative mechanism) and in 1938 by Farkas and Farkas[4] (dissociative mechanism). These basic mechanisms have been altered in many ways by various workers through the years (see ref 1 and 2). Despite this large number of studies, there is not a consensus of opinion as to the actual mechanism for C_2H_4 hydrogenation by the platinum group metals.

Very recently, there has been a proposal of a new mechanism in the ethylene hydrogenation reaction by Zaera and Somorjai[5] and in a more generalized scheme by Thomson and Webb.[6] This

(1) Horiuti, J.; Miyahara, K. "Hydrogenation of Ethylene on Metallic Catalysts"; Government Printing Office: Washington, D.C., 1968; NBS-NSRDS No. 13.

(2) Little, L. H. "Infrared Spectra of Adsorbed Species"; Academic: London, 1966; Chapter 5.

(3) Horiuti, J.; Polanyi, M. *Trans. Faraday Soc.* **1934**, *30*, 1164.

(4) Farkas, A.; Farkas, L. *J. Am. Chem. Soc.* **1938**, *60*, 22.

(5) Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 2288.