Isotope Enrichment and Stereochemistry of the Products from the Reaction of Electronically Excited Iodine Monochloride with *cis*- and *trans*-1,2-Dibromoethylene

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Abstract: The reaction of electronically excited iodine monochloride with *cis*- and *trans*-1,2-dibromoethylene has been studied in detail. Selective excitation of $I^{37}Cl$, using a CW dye laser, gave *cis*- and *trans*-1-bromo-2-chloroethylene products containing up to 78.4 and 73.9% ^{37}Cl, respectively. The quantum yield of the two products together was about 30%. The product stereochemistry for the reaction of ICl* with 1,2-dibromoethylene is similar to that of free Cl atoms, but differs from that of the competing dark reaction with ICl. A mechanism for reaction with ICl* giving preferential retention of geometry is proposed.

Introduction

Laser-assisted isotope separation methods have received considerable attention in recent years, and numerous reports have been published exploiting various photophysical and photochemical means for separating the isotopes of several elements.[1] In addition to the separation of isotopes, such studies have often elucidated interesting photochemical phenomena. Several reports on the laser-induced photochemical separation of chlorine isotopes from the reaction of electronically excited iodine monochloride with various organic molecules have been published, both from our laboratory[2-4] and elsewhere.[5] We have given a detailed account of our work on the photochemical reaction of ICl* with bromobenzene,[4] but only preliminary results on the reaction of ICl* with 1,2-dibromoethylene (DBE) have been reported.[2,3] This paper describes further studies of the photochemical reaction of ICl* with DBE and with 1-bromo-2-chloroethylene (BCE). In addition to the enrichments of the products, *cis*- and *trans*-BCE and *cis*- and *trans*-1,2-dichloroethylene (DCE), and their quantum yields, we also report some interesting stereochemical observations. We find that electronically excited iodine monochloride behaves kinetically and stereochemically in a manner similar to a free chlorine atom in the attack on olefins.

Experimental Section

An argon ion laser (Spectra Physics Model 165) pumped Rhodamine 6 G dye laser (Spectra Physics Model 375) was used for the selective excitation of iodine monochloride. The bandwidth of the dye laser was 0.1 Å. The reaction was carried out in a 30-cm long, 5-cm diameter Pyrex vessel which was rinsed several times with methanol and then baked at 110 °C for at least 24 h each time before being used. This treatment was important since otherwise the enrichments were found to be irreproducibile from one run to the next, and quantum yields greater than 1.0 were often obtained, indicating the presence of a chain reaction. Nine identical Pyrex vessels were used for these experiments.

Iodine monochloride was obtained from ICN (K&K) and purified by slow vacuum transfer to a trap cooled to 77 K. The olefins, 1,2-dibromoethylene (Aldrich), 1-bromo-2-chloroethylene (Columbia Organic Chemicals Co.), 1,2-dichloroethylene (Aldrich), and dibromomethane (Aldrich), were purified by gas chromatography (Varian A90-P) on a 10 ft × 0.25 in. column of Carbowax 20M on Chromosorb P (NABW); the cis and trans isomers of DBE, BCE, and DCE were collected separately and identified by retention-time comparison with authentic samples. Anhydrous diethyl ether (MCB), employed as a solvent in some of these experiments, was used without further purification. Isotope analyses were done using either a Varian MAT-44 GC-MS or a Finnigan Model 4000 GC-MS equipped with a data acquisition system.

In a typical experiment, 20 μL of the organic substrate (corresponding to a pressure of 9.6 Torr in the reaction vessel) was vacuum transferred into the reaction cell and collected in a cold finger. ICl, containing ^{35}Cl and ^{37}Cl in natural abundance (75.5% ^{35}Cl and 24.5% ^{37}Cl), was slowly introduced into the cell until the desired pressure was obtained, as measured with a Datametrics capacitance manometer (Model 1173). The cell was then removed from the vacuum line, the cold finger was warmed, and the olefin was expanded into the cell. The mixture was allowed to equilibrate in the dark for 3 min and then irradiated for 60 min at 6053 Å, corresponding to the (18-0) bandhead of the $I^{37}Cl$ A-X system.[6] The wavelength was set each day by taking the absorption spectrum of ICl using a 1-m absorption cell, a 1000-W Hg-Xe lamp (Hanovia), and a 0.75-m spectrometer (SPEX Model 1702). Following irradiation, the reaction mixture from the cell was injected directly into the GC-MS via a gas sampling valve (Carle Model 2018) and the products were separated on a 20 ft × 0.25 in. column of SE-30 on Anachrom ABS. Isotope compositions were obtained from the ratio of peaks with *m/e* 61 and 63 (corresponding to $C_2H_2{}^{35}Cl^+$ and $C_2H_2{}^{37}Cl^+$) and/or *m/e* 140 and 144 (corresponding to $C_2H_2{}^{79}Br^{35}Cl^+$ and $C_2H_2{}^{81}Br^{37}Cl^+$). In the latter case, a simple correction must be made for the relative abundances of ^{79}Br and ^{81}Br to obtain the ^{37}Cl isotope content.[7] The compositions are reported in terms of % ^{37}Cl, i.e., the percentage of the chlorine content of the product molecules that is the ^{37}Cl isotope.

Quantum yield studies utilized a Perkin-Elmer Model 3920 GC equipped with FID, using a Carbowax 20M open tubular capillary column. The procedure is the same as reported previously.[4] In the experiments for measuring quantum yields, a weighed amount of the olefin was vacuum transferred to the cold finger attached to the reaction vessel. Following irradiation, the reaction mixture was collected in an ampule into which a weighed amount of CH_2Br_2, the internal standard, had already been vacuum transferred, and the products were then analyzed on GC.

In all the experiments a cell (Control Laser) containing $I^{35}Cl$ was placed inside the cavity[3] of the dye laser to suppress any radiation at 6053 Å, corresponding to absorption of $I^{35}Cl$. Unless otherwise mentioned, the incident power of the dye laser was 25 ± 2.5 mW as measured with a power meter (Spectra-Physics Model 404).

Results

Dark Reaction. Quantitative measurements of the products from the dark reaction of ICl with *cis*- and *trans*-DBE for 61 min were made at various pressures of ICl. Table I gives the results for ICl at a pressure of 5 Torr. Note that the stereochemistry of the product is found to be largely *opposite* to that of the starting material. Moreover, *trans*-DBE reacts with ICl in the dark at a more rapid rate than does *cis*-DBE. The product yields scale approximately linearly with ICl pressure. As the pressure of ICl was raised, a pink, nonvolatile liquid appeared which was inferred from mass spectrometric analysis to be the addition product $C_2H_2Br_2ICl$. In the dark reaction a very small fraction of the *cis*-DBE was converted to *trans*-DBE and vice versa. No correction has been made for isomerization of the starting material because of the small extent

0002-7863/79/1501-7173$01.00/0

Table I. Product Yields from the Dark Reaction of DBE with ICl[a]

DBE, mol	products, mol[b]
cis-DBE 1.2×10^{-3}	*cis*-BCE 1.0×10^{-6}
	trans-BCE 4.4×10^{-6}
	trans-DBE 3.0×10^{-6}
trans-DBE 1.2×10^{-3}	*cis*-BCE 13.5×10^{-6}
	trans-BCE 1.5×10^{-6}
	cis-DBE 5.9×10^{-6}

[a] At an ICl pressure of 5 Torr and an olefin pressure of ca. 10 Torr for a reaction time of 61 min. [b] ±5%.

Table II. ^{37}Cl Enrichment[a] and Product Mix from Reactions[b] of ICl* with *cis*- and *trans*-DBE

reactant	product	% ^{37}Cl content	product ratio *trans-/cis-*
cis-DBE	*cis*-BCE	59	0.4
	trans-BCE	62	
trans-DBE	*cis*-BCE	29-66	0.7-4.0
	trans-BCE	51-69	

[a] Natural abundance of ^{37}Cl = 24.5%. [b] The reaction conditions are 9.6 Torr of reactant, 0.5 Torr of ICl, 60 min exposure at 6053 Å at ~25 mW power.

Table III. ^{37}Cl Enrichment[a] and Product Mix from Reactions[b] of ICl with *trans*-DBE

date	product	% ^{37}Cl content[c]	product ratio *trans-/cis-*
Jan 29, 1978	*cis*-BCE	52.9	4.0
	trans-BCE	55.4	
Feb 12, 1978	*cis*-BCE	55.5	2.6
	trans-BCE	65.6	
Dec 26, 1977	*cis*-BCE	66.4	2.2
	trans-BCE	68.8	
Dec 27, 1977	*cis*-BCE	41.9	2.0
	trans-BCE	60.2	
Dec 27, 1977	*cis*-BCE	39.4	0.9
	trans-BCE	63.4	
Dec 26, 1977	*cis*-BCE	28.6	0.7
	trans-BCE	51.7	

[a] Natural abundance ^{37}Cl = 24.5%. [b] The reaction conditions are the same as in Table II. [c] ±1%.

Table IV. ^{37}Cl Enrichments in Products from Reaction[a] of ICl* with BCE

reactant	product	% ^{37}Cl content[b]	
cis-BCE	*cis*-DCE	49	(72)
	trans-DCE	50	(75)
trans-BCE	*cis*-DCE	35	(44)
	trans-DCE	48	(71)

[a] The reaction conditions are the same as in Table II. [b] ±1%; corrected value in parentheses; see ref 7.

of conversion. To reduce the effect of dark reaction on the photochemical studies the ICl pressure was set at 0.5 Torr in subsequent runs. At this pressure there is no detectable dark reaction with either *cis*- or *trans*-DBE. However, we do not know whether some dark reactions may be photochemically induced (vide infra).

Quantum Yield. The photochemical reaction of ICl with *cis*-DBE or *trans*-DBE forms in both cases *cis*-BCE and *trans*-BCE products with relatively high yield. At an ICl pressure of 0.5 Torr and with 2.7×10^{-4} mol (ca. 10 Torr) of the starting material, the quantum yields for the formation of *cis*- plus *trans*-DCE are 0.29 ± 0.01 from *cis*-DBE and 0.33 ± 0.01 from *trans*-DBE. In comparison, the quantum yield[4] of chlorobenzene from the reaction of ICl* with bromobenzene under similar conditions was about 0.10.

Stereochemistry and Enrichment of the Photoproducts. A study was made of the relative product ratios and the extent of product isotope enrichment when 9.6 Torr of starting material and 0.5 Torr of ICl were exposed to 6053-Å radiation for 60 min at ~25 mW incident power. Table II lists the ^{37}Cl enrichments and the product mix from *cis*-DBE and from *trans*-DBE. Unlike the dark reaction with ICl, the photochemical reaction of DBE with ICl* gives products that preferentially *retain* the stereochemistry of the starting material.

For reactions with *cis*-DBE, the extent of enrichment and the product ratio were reproducible from run to run and from vessel to vessel to within ±20%. However, as Table III shows, the reactions of *trans*-DBE exhibited much more variability. Examination of Table III shows that, as more *cis*-BCE product is formed relative to *trans*-BCE, the enrichment in the *cis*-BCE decreases, whereas the enrichment in the *trans*-BCE product remains roughly unaffected. These results are consistent with the presence of some nonreproducible (possibly light-induced) reaction that preferentially produces *cis*-BCE which is not isotopically enriched, as from the dark reaction. (As Table I indicates, *trans*-DBE reacts in the dark with ICl more rapidly than does *cis*-DBE and gives predominantly the *cis*-BCE product, although at this pressure no appreciable reaction is observed in the absence of radiation). Efforts to control or to stabilize the extent of this unwanted reaction by cell treatment were not successful. Nevertheless, the ^{37}Cl enrichments obtained in the *cis*- and *trans*-BCE products from *trans*-DBE are comparable to or higher than that obtained[4] in the chlorobenzene product from bromobenzene at the same pressure of ICl.

cis- and *trans*-BCE were also used as reactants and the isotope compositions in the *cis*- and *trans*-DCE products were measured (Table IV). However, the % ^{37}Cl contents obtained from the ratio of the mass fragments 61 and 63 (or 96 and 100) do not reflect the true enrichment obtained from the reaction of ICl*, as one of the two Cl atoms in the DCE product occurs in natural abundance. The enrichments were therefore corrected for this factor,[7] and the corrected values are listed in parentheses in Table IV next to the values obtained directly from the ratio of m/e 63 and 61. Just as the *cis*-BCE product appears less enriched than the *trans*-BCE product from *trans*-DBE, Table IV shows the same behavior for the *cis*- and *trans*-DCE products from *trans*-BCE.

Reaction of Cl Atoms with *cis*- and *trans*-DBE. The photochemical reactions of Cl atoms with *cis*-DBE and *trans*-DBE were also studied. Cl atoms were produced by photodissociating ICl. The reactants were prepared as described previously and exposed for 5 min to the output of an argon ion laser operating on all lines. The results are summarized in Table V. As expected, no isotopic selectivity was observed from the reaction of Cl atoms with *cis*-DBE or with *trans*-DBE. However, the stereochemistry of the products shows overall retention as was the case with ICl*.

Variation of Enrichment with ICl Pressure. The ^{37}Cl enrichment in *cis*- and *trans*-BCE products as a function of ICl pressure was investigated in reactions with *cis*-DBE. In previous work[4] the variation in the ^{37}Cl enrichment of chlorobenzene from the reaction of ICl* with bromobenzene was found to be inversely proportional to the square of the pressure

Table V. Product Mix from Reaction[a] of Cl Atoms with *cis*- and *trans*-DBE

reactant (mol)	product (mol)	product ratio *trans-/cis-*
cis-DBE (2.74×10^{-4})	*cis*-BCE (1.52×10^{-6})	0.4
	trans-BCE (0.54×10^{-6})	
trans-DBE (2.77×10^{-4})	*cis*-BCE (1.37×10^{-6})	1.5
	trans-BCE (1.99×10^{-6})	

[a] Reaction conditions as in Table II, except for excitation source and exposure time.

of ICl. No such simple relationship between the enrichment and the pressure of ICl could be deduced either for *cis*-BCE or for *trans*-BCE products from the *cis*-DBE. However, an overall decrease in the enrichment was observed as the pressure of ICl was increased. Some variation was observed in the enrichments when reactions at the same pressure of ICl were prepared on different days, evidently caused by a cell aging process.

In a previous paper[3] it was reported that, when 10 Torr each of ICl and DBE (cis-trans mixture) were irradiated at 6054 Å, the *trans*-DCE product was found to contain 84.7% ^{37}Cl, based on three separate experiments. In that study a different laser (Control Laser) was used where the bandwidth was 3 Å and the output power was estimated to be ≤8 mW when an I^{35}Cl cell was placed intracavity. In the experiments reported here, we have found the *trans*-DCE to contain only 48.5% ^{37}Cl when 10 Torr of ICl and 9.6 Torr of *cis*-DBE were irradiated. (These enrichments are calculated from the ratio of the mass peaks of the parent ions, *m/e* 96 and 100. Enrichments calculated from fragment mass peaks at *m/e* 61 and 63 also give the same value.) Stuke[8] has also repeated this experiment and reported a 44% ^{37}Cl content of the DCE product (cis and trans mixture).

We have not been able to obtain the high enrichments in *trans*-DCE found earlier, under the present experimental conditions. This difference in enrichment may be partly caused by the different laser bandwidths and different cavity configuration in the two experiments.[7,9] Unknown surface effects may also be an important contributing factor.

Discussion

We have found that *cis*-DBE gives approximately equal enrichment of *cis*- and *trans*-BCE while the photoproducts show preferential retention of stereochemistry (*cis*-BCE > *trans*-BCE). Therefore the photochemical reaction with ICl* must proceed more rapidly than chlorine atom additions or isomerization.[10] Moreover, the contribution from dark reactions (which show the opposite stereochemistry) cannot be of great importance. The reactions of *trans*-DBE show transitions between two regimes. In the first regime, behavior is similar to that of *cis*-DBE. Nearly equal enrichments are found in both photoproducts, and the stereochemistry of the starting material is preferentially retained in the products (*trans*-BCE > *cis*-BCE). Therefore, again, reactions must occur predominantly with ICl*, and chlorine atom and dark reactions are not of great importance. In the second regime the amount of *cis*-BCE is relatively increased while the enrichment in the *cis*-BCE is decreased. Consequently we believe that, although the photochemical reaction still dominates, a reaction, which produces predominantly *cis*-BCE in natural abundance, is contributing. Again, chlorine atoms do not appear to play an important role.

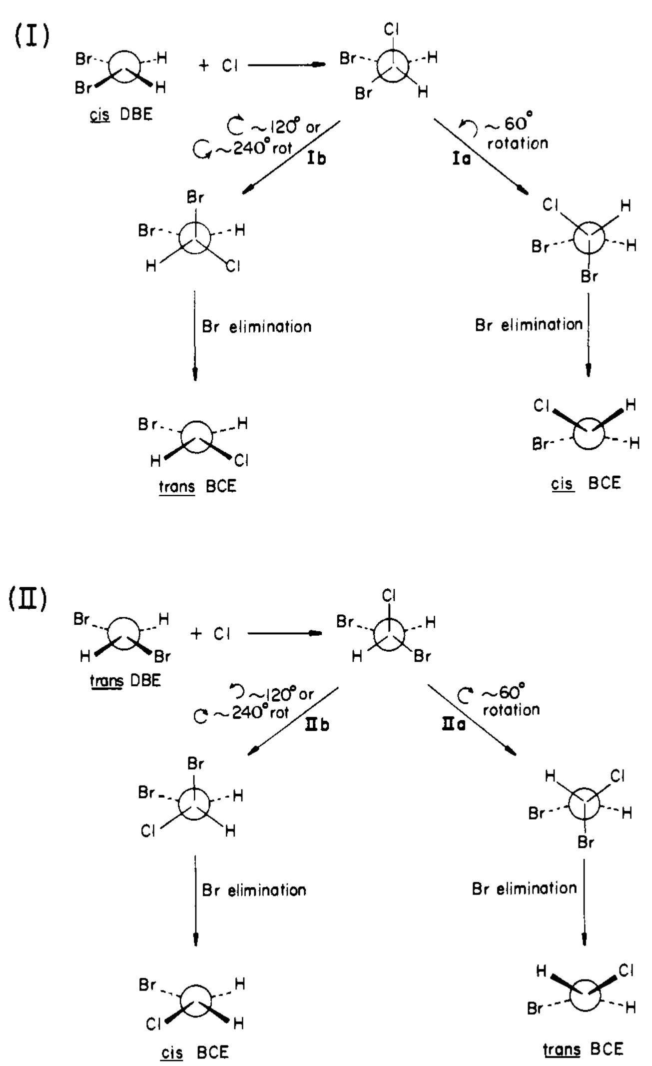

Figure 1. Pathways for reaction of Cl atoms with (I) *cis*-dibromoethylene; (II) *trans*-dibromoethylene.

In summary, our results require that the predominant reaction we have observed is that of organic substrates with excited iodine monochloride (ICl*). The observation of isotopic enrichment precludes major contributions from either dark reactions or chlorine atom reactions. This is further supported by the observation that the photoproduct stereochemistry is opposite to that of the dark reaction. Furthermore, chlorine atom scrambling is precluded by different enrichment and stereochemistry with isomeric starting materials. Finally, decreasing enrichment with increasing ICl pressure is consistent with loss of specificity via energy transfer between I^{37}Cl* and I^{35}Cl.

It has been suggested previously that ICl* behaves kinetically in a manner similar to that of a Cl atom in its reactions with olefins.[4] Indeed our results show similar stereochemical behavior for these two species in their reactions with *cis*- and *trans*-DBE. These reactions occur in a low-pressure regime in which the formation of a C-Cl bond and loss of the C-C π bond leave the resulting radical internally energized. This activated radical must undergo an internal rotation in order to lose a bromine atom at the same time that the π bond is reformed. The high quantum yields with ICl* show that this rotation competes favorably with loss of Cl, and the different stereochemistry from isomeric DBEs shows that loss of Br competes favorably with further rotations.

Figure 1 illustrates a simple model for rationalizing the preference for stereochemistry with retention of geometry. When Cl atoms react with *cis*-DBE, the lower energy pathway

Ia is favored over Ib. In Ia only an H atom passes another H atom in the course of the 60° rotation, whereas in Ib a Br atom passes a Br atom and a Cl atom passes an H atom. Consequently the formation of *cis*-BCE (path Ia) from *cis*-DBE should be kinetically more favorable than that of *trans*-BCE. From the same line of reasoning, in reaction of Cl atoms with *trans*-DBE, the formation of *trans*-BCE is favored over *cis*-BCE; path IIa is preferred over path IIb since the latter involves more unfavorable steric interactions.

ICl* is only 3.2 kcal/mol below its dissociation limit. Thus the $C_2H_2Br_2Cl$ radical formed from ICl* has at least 3.2 kcal/mol less energy than the same radical formed from Cl atoms. (This energy difference may be even greater if the resulting fragments recoil with excess translational energy.) In this regard ICl* is an exceptionally interesting chlorinating agent in that it may be viewed as a source of Cl atoms with negative energy. This may account for the high quantum yields since the intermediate radicals may not have sufficient energy to expel a Cl atom. Furthermore, the lower energy of the radical may accentuate the preference for the stereochemical pathway of lowest energy.

Acknowledgments. We are grateful to the Department of Energy for financial assistance through Grant EY-76-S-03-0326-PA2.

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$$\%\ ^{37}\mathrm{Cl} = \frac{0.505R}{0.505R + 0.495}$$

where $R = m/e$ 144/140. To obtain the "true enrichment" in the DCE product due to the reaction of ICl* with BCE, the following formula was used:

$$\%\ ^{37}\mathrm{Cl} = \frac{5(35.1R - 4.9)}{R + 1}$$

where $R = m/e$ 63/61. See S. Datta, Ph.D. Thesis, Columbia University, New York, N.Y., 1978.

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Conformational Preferences and Electronic Structures of $Ni(C_2H_4)_2$ and $Ni(C_2H_4)_3$

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Abstract: Nonempirical molecular electronic structure theory has been applied to the organometallic systems bis(η^2-ethene)nickel(0) and tris(η^2-ethene)nickel(0). Three types of contracted Gaussian basis sets have been used in conjunction with restricted self-consistent-field theory. The middle basis set may be labeled Ni(14s 9p 6d/10s 6p 3d), C(10s 6p/6s 3p), H(5s/3s) and is perhaps the most complete basis set used to date for an experimentally known organotransition metal complex such as $Ni(C_2H_4)_3$. The chosen basis comes very close to reproducing the exact Hartree–Fock term splittings for the nickel atom. For $Ni(C_2H_4)_2$ the twisted (D_{2d}) and "planar" (D_{2h}) conformations are predicted to lie energetically within 0.1 kcal of each other. For the $Ni(C_2H_4)_3$ complex, however, the planar conformation lies ~24 kcal lower than the upright form. Both of these predictions are in qualitative accord with the earlier semiempirical work of Rösch and Hoffmann. The lowest D_{2h} triplet state of $Ni(C_2H_4)_2$ is of $^3B_{3u}$ symmetry, and a number of other electronic states were also investigated. The ionization potentials of both molecules were predicted and large deviations from Koopmans' theorem were found. Mulliken population analyses are also reported and used to qualitatively discuss the electronic structures.

Introduction

One of the most remarkable organometallic species synthesized in recent years is the tris(η^2-ethene)nickel(0) molecule.[2a] This was the first transition-metal complex prepared in solution with ethylenes alone as its ligands. In 1973 Fischer, Jonas, and Wilke prepared $Ni(C_2H_4)_3$ in a diethyl ether solution, which was found to be pale yellow in color. Upon crystallization from solution at 195 K they obtained colorless needle-shaped crystals. Fischer, Jonas, and Wilke assumed the molecule to have the "planar" D_{3h} structure seen in Figure 1 and reported nuclear magnetic resonance and infrared spectroscopic data consistent with this assumption. More recently the analogous $Pt(C_2H_4)_3$ molecule has been synthesized by Green, Howard, Spencer, and Stone.[2b]

Our attention was first drawn to tris(ethylene)nickel(0) by the excellent theoretical study of Rösch and Hoffmann.[2c] They elucidated the qualitative features of the electronic structures of $Ni(C_2H_4)_n$ for n = 2, 3, and 4, and supported their findings with extended Hückel calculations. Rösch and Hoffmann were able to predict the conformational preferences of both $Ni(C_2H_4)_2$ and $Ni(C_2H_4)_3$. In the first case, they found little preference for the D_{2d} or twisted form (see Figure 2) over the D_{2h} or planar (that is, all four C atoms lie in a plane) geometry.

0002-7863/79/1501-7176$01.00/0