cm^{-1}; nmr (CCl$_4$) δ 4.10 (1 H, d of d of d, $J_{1,2} = 4$ Hz, $J_{2,3n} = 5$ Hz, $J_{2,3x} = 10$ Hz, CHOH), 2.60 (1 H, singlet, OH), 0.9–2.3 (14 H, complex band) ppm.

# Effects of Base Association and Strength upon Base-Promoted Syn Eliminations

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Abstract: Primary deuterium isotope effects and Hammett ρ values for syn E2 reactions of *trans*-2-arylcyclopentyl tosylates promoted by associated and dissociated alkoxide ion bases have been determined. More carbanionic transition states are observed for a dissociated base than the corresponding associated base. Transition states with greater carbanionic character and C$_\beta$–H bond rupture are found for a stronger dissociated alkoxide ion base in an alcoholic solvent of lower polarity.

Base association has been postulated to facilitate transition states for base-promoted syn eliminations by allowing simultaneous coordination of the counterion with the base and leaving group as depicted in **1**, where X is the leaving group, B is the base, and M
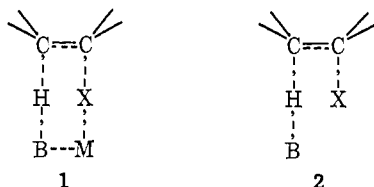
is the counterion.[2,3] In order to assess transition-state differences for syn eliminations induced by (a) *associated* and *dissociated* alkoxide base species, **1** and **2**, respectively, and (b) *dissociated* alkoxide ion bases of varying strength, the following investigation was conducted.

Results and Discussion

Reactions of *trans*-2-arylcyclopentyl tosylates **3**, with
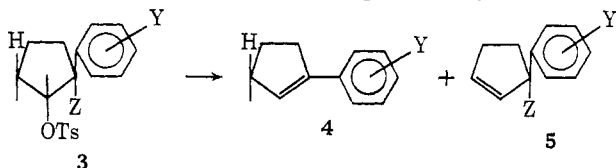
	Y	Z
a	H	H
b	H	D
c	m-Cl	H
d	p-Cl	H
e	m-Me	H
f	p-Me	H
g	p-OMe	H

various bases produce 1-arylcyclopentene **4**, by activated syn elimination and 3-arylcyclopentene, **5**, by unactivated anti elimination.[4-6] Formation of **5** by unactivated syn elimination is unimportant.[6] Since rates of anti elimination producing **5** should be insensitive to variation of Y[7] or substitution of deuterium for hydrogen at Z in **3**, relative rates of formation of **4** may be determined with reference to the internal standard **5** by product analysis.

Associated and Dissociated Alkoxide Ion Bases. The relative proportions of **4a** and **5a** obtained from reactions of **3a** with 0.10 M t-BuOK–t-BuOH in the absence and presence of two crown ethers[8] are presented in Table I. Addition of the strong potassium ion

Table I. Effect of **6** and **7** upon the Relative Proportions of Isomeric Phenylcyclopentenes Formed in Reactions of 0.025 M **3a** with 0.10 M t-BuOK–t-BuOH at 50.0°

Crown ether	[Crown ether], M	Total phenylcyclopentenes, % 1-Phenyl-cyclopentene	3-Phenyl-cyclopentene
		89.2 ± 0.5^a	10.8 ± 0.5
6	0.031	46.5 ± 0.3^a	53.5 ± 0.3
6	0.049	33.0 ± 0.2^a	67.0 ± 0.2
6	0.10	$30.1 \pm 0.7^{a,b}$	69.9 ± 0.7
6	0.17	29.5 ± 0.3^a	70.5 ± 0.3
6	0.22	30.8 ± 0.4^a	69.2 ± 0.4
7	0.10	90.7 ± 0.4^a	9.3 ± 0.4

^{a} Standard deviation from repetitive analysis of product mixture. ^{b} Average of values from three runs conducted by three different investigators.

(1) Address correspondence to this author at the Department of Research Grants and Awards, American Chemical Society.

(2) J. Sicher, *Angew. Chem., Int. Ed. Engl.*, **11**, 200 (1972), and references cited therein.

(3) R. A. Bartsch and K. E. Wiegers, *Tetrahedron Lett.*, 3819 (1972).

(4) C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Amer. Chem Soc.*, **87**, 2421 (1965).

(5) P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2240 (1972).

(6) P. Beltrame, A. Ceccon, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2315 (1972).

(7) Rates of formation of **5** in reactions of **3a** and **3f** with t-BuOK–t-BuOH^4 are the same within experimental error.

(8) Macrocyclic polyethers. For a review, see C. H. Pederson and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).
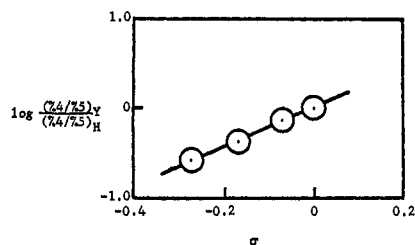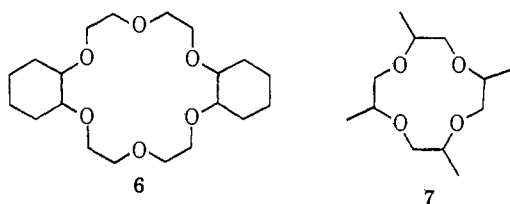
Figure 1. Hammett correlation for reactions of **3** with *t*-BuOK–*t*-BuOH.

complexing agent[8] dicyclohexyl-18-crown-6, **6**, produces marked diminution of the syn elimination product proportion until approximately equimolar concentrations of *t*-BuOK and **6** are attained. However, the

6   **7**

presence of equimolar tetramethyl-12-crown-4, **7**, for which the crown ether cavity is too small to accommodate potassium ions,[8] has no significant effect. Thus, the changes in olefin proportions resulting from addition of **6** may be attributed specifically to potassium ion complexation. These results corroborate the proposal[3] that associated *t*-BuOK[9] is the effective base species for syn eliminations from **3a** promoted by *t*-BuOK–*t*-BuOH. Whereas, in the presence of equimolar **6**, dissociated ions[9] are the active base.

In order to probe transition-state differences for syn eliminations involving associated and dissociated *tert*-butoxide ion bases, primary deuterium isotope effects[10] and the influence of substituents in the β-phenyl group upon relative reaction rates were determined. The relative proportions of **4a–g** and **5a–g** formed in reactions of **3a–g** with 0.10 *M* *t*-BuOK–*t*-BuOH in the absence[11] and presence of 0.10 *M* **6** are recorded in Table II. Control experiments (Experimental Section) demonstrated negligible solvolytic elimination and the stability of olefinic products to reaction conditions.

Calculated primary deuterium isotope effects and ρ values from Hammett correlations (Figures 1 and 2) for syn elimination are displayed in Table III. The k_H/k_D values, in combination with earlier evidence,[4] establish a normal, concerted E2 mechanism for these reactions.[12] Addition of **6** has little apparent effect upon k_H/k_D, but produces a significantly increased ρ.

Change from an associated to a dissociated base for syn eliminations from **3** should result in a stronger base

(9) In the absence of specific evidence regarding the actual base species present, we shall refer to contact ion pairs and aggregates of contact ion pairs as the associated species and to free ions and separated ion pairs as the dissociated base.

(10) For a review of isotope effect studies in elimination reactions, see A. Fry, *Chem. Soc. Rev.*, **1**, 163 (1972).

(11) Reactions of **3c,d** with *t*-BuOK–*t*-BuOH produced only **4c,d**[4] and therefore were not useful for this study.

(12) Much higher values of k_H/k_D and lower ρ values are reported for syn eliminations from cyclopentyl derivatives which proceed *via* carbanion intermediate mechanisms; see F. G. Bordwell, K. C. Yee, and A. C. Knipe, *J. Amer. Chem. Soc.*, **92**, 5945 (1970); F. G. Bordwell, M. M. Vestling, and K. C. Yee, *ibid.*, **92**, 5950 (1970); F. G. Bordwell, J. Weinstock, and T. F. Sullivan, *ibid.*, **93**, 4728 (1971).
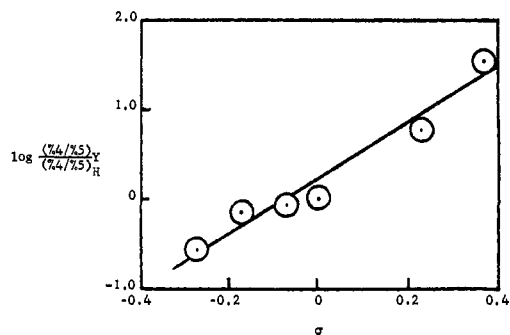

Figure 2. Hammett correlation for reactions of **3** with 6-*t*-BuOK–*t*-BuOH.

Table II. Relative Proportions of Isomeric Arylcyclopentenes Formed in Reactions of 0.025 *M* **3a–g** with 0.10 *M* *t*-BuOK–*t*-BuOH at 50.0° in Absence and Presence of 0.10 *M* **6**

| | | **6** | Total arylcyclopentenes, % | |
Y	Z	present	1-Aryl-cyclopentene	3-Aryl-cyclopentene
H	H	No	89.8 ± 0.9[a–c]	10.2 ± 0.9
H	D	No	62.5 ± 0.3[c,d]	37.5 ± 0.3
m-Me	H	No	86.1 ± 0.5[c]	13.9 ± 0.5
p-Me	H	No	76.8 ± 2.4[c,e]	23.2 ± 2.4
p-OMe	H	No	68.2 ± 0.8[c]	31.8 ± 0.8
m-Cl	H	Yes	93.9 ± 0.5[c]	6.1 ± 0.5
p-Cl	H	Yes	72.5 ± 0.7[c]	27.5 ± 0.7
H	H	Yes	30.1 ± 0.7[c,f]	69.9 ± 0.7
H	D	Yes	7.8 ± 0.3[c]	92.2 ± 0.3
m-Me	H	Yes	26.0 ± 0.5[c]	74.0 ± 0.5
p-Me	H	Yes	23.3 ± 1.0[b,c]	76.7 ± 1.0
p-OMe	H	Yes	10.0 ± 1.0[c]	90.0 ± 1.0

[a] Reference 4 reports 91% 1-arylcyclopentene. [b] Average of two runs. [c] Standard deviation from repetitive analysis of product mixture(s). [d] Reference 4 reports 70% 1-arylcyclopentene. [e] Reference 4 reports 82% 1-arylcyclopentene. [f] Average of three runs.

Table III. Primary Deuterium Isotope Effects and Hammett ρ Values for Reactions of **3a–g** with *t*-BuOK–*t*-BuOH in the Absence and Presence of **6**

Base–solvent	k_H/k_D	ρ (r^a)
t-BuOK–*t*-BuOH	5.3[b,c]	+2.2[d] (0.997)
t-BuOK–*t*-BuOH–**6**	5.1[b]	+3.1[e] (0.977)

[a] Correlation coefficient. [b] Estimated uncertainty = ±0.4. [c] Reference 4 reports k_H/k_D = 5.6 and ρ = +2.8 for a somewhat different set of substituents. [d] Average deviation of points from the line is 0.017. [e] Average deviation of points from the line is 0.14.

but a poorer leaving group. For anti eliminations from β-phenylethyl compounds, stronger bases[13] and poorer leaving groups[14a] lead to transition states with greater carbanion character. The k_H/k_D values reported in Table III indicate that relative transition-state force constants for the O···H and H···C$_\beta$ bonds are quite similar for the dissociated and associated bases.[15] Therefore, the more carbanionic transition states observed with the dissociated base apparently result from a dominant leaving group effect.

(13) S. Alunni and E. Baciocci, *Tetrahedron Lett.*, 4665 (1973).

(14) W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions," Wiley-Interscience, New York, N. Y., 1973: (a) Chapter 2; (b) p 28.

(15) This conclusion is made somewhat less certain by the double-valued nature of the primary deuterium isotope effect[16] and the possibility of nonlinear C$_\beta$···H···O transition states.[17]

(16) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(17) R. A. More O'Ferrall, *J. Chem. Soc. B.*, 785 (1970).

Dissociated Alkoxide Ion Bases of Varying Strength.
Relative percentages of **4a–g** and **5a–g** observed in reactions in **3a–g** with 6-*n*-BuOK-*n*-BuOH and of **3a,b** with 6-*s*-BuOK-*s*-BuOH are displayed in Table IV.

Table IV. Relative Proportions of Arylcyclopentenes[a,b] Formed in Reactions of 0.025 *M* **3a–g** with 0.10 *M* *n*-BuOK-*n*-BuOH and 0.10 *M* **6** and of 0.025 *M* **3a,b** with 0.10 *M* *sec*-BuOK-*sec*-BuOH and 0.10 *M* **6** at 50.0°

R of ROK-ROH	Y	Z	Total arylcyclopentenes, %	
			1-Aryl-cyclopentene	3-Aryl-cyclopentene
n-Bu	*m*-Cl	H	71.8 ± 1.1	28.2 ± 1.1
n-Bu	*p*-Cl	H	66.0 ± 1.1	34.0 ± 1.1
n-Bu	H	H	60.6 ± 2.3	39.4 ± 2.3
n-Bu	H	D	57.0 ± 1.9	43.0 ± 1.9
n-Bu	*m*-Me	H	63.7 ± 2.2	36.3 ± 2.2
n-Bu	*p*-Me	H	62.4 ± 2.1	37.6 ± 2.1
n-Bu	*p*-OMe	H	59.1 ± 2.7	40.9 ± 2.7
sec-Bu	H	H	63.9 ± 0.5	36.1 ± 0.5
sec-Bu	H	D	56.1 ± 0.8	43.9 ± 0.8

[a] Averages of two or more runs. [b] Standard deviations from repetitive analyses of reaction mixtures.

Absence of solvolytic elimination and product isomerization were demonstrated by suitable control experiments (Experimental Section).

Calculated primary deuterium isotope effects for syn eliminations from **3** promoted by three dissociated base–solvent combinations and ρ values from Hammett correlations (Figures 2 and 3) for two dissociated base–solvent systems are presented in Table V. A marked

Table V. Primary Deuterium Isotope Effects and Hammett ρ Values for Reactions of **3** with Various Base–Solvent Systems in the Presence of **6**

Base–solvent	k_H/k_D	ρ (r^a)
n-BuOK-*n*-BuOH	1.2	+0.3[b] (0.899)
sec-BuOK-*sec*-BuOH	1.4	
t-BuOK-*t*-BuOH	5.1	+3.1 (0.977)

[a] Correlation coefficient. [b] Average deviation of points from the line is 0.03.

influence of the base–solvent system upon syn elimination transition-state character is readily evident.

The large variations in k_H/k_D and ρ values necessitate consideration of possible changes of mechanism. Control experiments have ruled out E1 reactions. Furthermore, E1 and E2ip[14b,18] mechanisms seem unlikely in view of the observed positive ρ values.[19] Likewise, the k_H/k_D and ρ values appear to be inconsistent with those reported for E1cb processes.[12] That the eliminations proceed *via* E2 mechanisms therefore seems most reasonable.

The variations in k_H/k_D and ρ may be rationalized within the framework of the variable E2 transition-state theory.[14a,20] According to this theory, wide variations in relative amounts of C_β–H and C_α–leaving group bond breakage and C–C double bond formation exist in transition states for concerted, bimolecular β elimina-
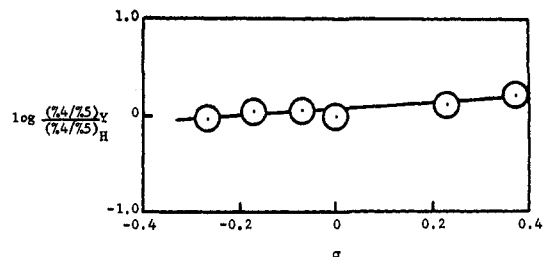
Figure 3. Hammett correlation for reactions of **3** with 6-*n*-BuOK-*n*-BuOH.

tions. Replacement of the dissociated base–solvent system of *tert*-butoxide-*t*-BuOH with *n*-butoxide-*n*-BuOH involves change to a weaker base but a better solvent for a leaving group which bears partial negative charge in the transition state. Both factors should produce transition states with less C_β–H bond rupture, more C_α–leaving group bond cleavage, and a lesser carbanion character.[20,21]

Marked diminution in k_H/k_D and ρ resulting from substitution of *tert*-butoxide-*t*-BuOH by *n*-butoxide-*n*-BuOH (Table V) evinces less carbanionic character and C_β–H bond stretching in syn elimination transition states promoted by a weaker base in a better solvent for anions. The similarity of k_H/k_D values for *n*-butoxide-*n*-BuOH and *sec*-butoxide-*sec*-BuOH when compared with that for *tert*-butoxide-*t*-BuOH indicates a pronounced influence of low polarity solvents upon transition-state character.

These results are in agreement with a recent report of diminished carbanionic character for anti eliminations from β-phenylethyl bromide induced by a weaker oxyanion base in a common solvent.[13] However, the findings are in sharp contrast to the large decrease in k_H/k_D, but moderately enhanced ρ value, observed for anti eliminations[22] from β-phenylethyltrimethylammonium bromides when the base–solvent system was changed from *t*-BuONa-*t*-BuOH to EtONa-EtOH.[23] Since the proton is more than half-transferred in the transition state,[24] greater C_β–H bond stretching and carbanion character were indicated for the weaker base.[24] At present, it is not possible to reconcile the differences between our observations concerning syn eliminations in which the leaving group is initially neutral and this reported anti elimination involving a positively charged leaving group.

Experimental Section

Materials. *trans*-2-Arylcyclopentyl tosylates, **3a–g**, were prepared by DePuy's procedure.[4] Melting points were in close agreement with literature values.[4,19]

1-Arylcyclopentenes, **4a,c–g**, and 3-arylcyclopentenes, **5a,c–g**, were synthesized by the method of DePuy[4] with final purification of liquids by preparative glpc. **4a** had bp 127° (31 mm), lit.[25] 118° (25 mm); **4c** had bp 81–84° (0.4 mm), lit.[4] 81° (0.6 mm); **4d** had mp 73°, lit.[19] 73–74°; **4e** had bp 64–66° (0.4 mm); **4f** had bp 69° (0.3 mm), lit.[4] 76° (0.6 mm); **4g** had bp 50–52° (0.1 mm). **5a** had bp 70–71° (3 mm), lit.[4] 50° (2 mm); **5c** had bp 65° (0.5 mm), lit.[4] 84°

(18) F. G. Bordwell, *Accounts Chem. Res.*, **5**, 374 (1972).

(19) A value of ρ = −1.05 has been reported for the acetolysis of *trans*-2-arylcyclopentyl tosylates at 50°: C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **94**, 5051 (1972).

(20) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, **1**, 225 (1962); *Surv. Progr. Chem.*, **5**, 53 (1969).

(21) For an opposing view, see E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 2915 (1967).

(22) P. J. Smith and A. N. Bourns, *Can. J. Chem.*, **48**, 125 (1970); A. N. Bourns and A. C. Frost, *ibid.*, **48**, 133 (1970).

(23) W. H. Saunders, Jr., D. G. Bushman, and A. F. Cockerill, *J. Amer. Chem. Soc.*, **90**, 1775 (1968).

(24) L. J. Steffa and E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 6149 (1967).

(25) W. H. Tallent, *J. Org. Chem.*, **21**, 862 (1956).

(2 mm); **5d** had bp 65–67° (0.5 mm), lit.[4] 84° (2 mm); **5e** had bp 56–58° (0.3 mm); **5f** had bp 60–63° (0.3 mm), lit.[4] 71° (2 mm); **5g** had bp 74° (0.25 mm.)

Dicyclohexyl-18-crown-6[26] (Aldrich), **6**, was used directly. Reagent grade alcohols were refluxed over and distilled from calcium hydride and then stored under nitrogen.

Solutions of potassium alkoxides in alcohols were prepared by the method of DePuy.[4]

Reaction Procedure. (a) **For 6-*t*-BuOK-*t*-BuOH.** Into a glass-stoppered reaction vessel fashioned from 6-mm glass tubing was weighed 0.05 mmol of **3**. After addition of 1.0 ml of *t*-BuOH to dissolve **3**, 1.0 ml of a solution of 0.20 *M* **6** and 0.20 *M* *t*-BuOK in *t*-BuOH was added. After mixing of the contents, the reaction vessel was placed in a 50.0° constant-temperature bath for 3 hr. The vessels were removed and placed in ice. The vessel contents were quickly thawed with warm water, poured into 5 ml of water, and extracted with 5 ml of 40% diethyl ether–60% pentane. The extracts were analyzed by glpc.

(b) **For *t*-BuOK-*t*-BuOH.** Same procedure as above except for the absence of **6** and a 24-hr reaction period.

(c) **For 6-*n*-BuOK-*n*-BuOH and 6-*sec*-BuOK-*sec*-BuOH.** Same procedure as with 6-*t*-BuOK-*t*-BuOH except solvent was not added to **3** prior to addition of 2 ml of 0.10 *M* **6** and 0.10 *M* base in solvent.

Glpc Separations and Analysis. Preparative glpc purification of **4a,c,e-g** and **5a,c-g** were conducted using a Varian Aerograph A-90P gas chromatograph with a 4 ft × ³/₈ in. column of 15% Carbowax 20M on Chromosorb W.

(26) A mixture of two isomers: H. K. Frensdorf, *J. Amer. Chem. Soc.*, **93**, 4684 (1971).

Analysis of reaction products was performed on a Varian Aerograph 1700 dual column flame ionization gas chromatograph employing 5 ft × ¹/₈ in. columns of 15% Carbowax 20M on Chromosorb P for reactions conducted in *t*-BuOH and 10-ft columns for reactions carried out in other solvents. Molar responses were determined to be: **4a/5a** = 1.12; **4c/5c** = 0.99; **4d/5d** = 1.09; **4e/5e** = 1.11; **4f/5f** = 1.11; **4g/5g** = 0.98.

Control Experiments. Reaction of **3a** with 0.10 *M* **6** in *n*-BuOH and *t*-BuOH under the conditions of the base-promoted reactions produced negligible amounts of phenylcyclopentenes. Absence of product isomerization was demonstrated by treating **3c** with 0.10 *M* 6–0.10 *M* *t*-BuOK-*t*-BuOH and 0.10 *M* 6–0.10 *M* *n*-BuOK-*n*-BuOH at 50.0° for varying reaction periods. Product proportions were invariant with time which demonstrated no isomerization for that product, **5c**, which would be most prone to isomerize.

Calculations. Primary deuterium isotope effects were calculated[27] from the relative proportions of **4a,b** and **5a,b** produced in reactions of **3a,b** with a given base–solvent combination. Hammett ρ values were calculated by computer linear regression least-squares analysis.[28]

(27) M. S. Silver, *J. Amer. Chem. Soc.*, **83**, 3487 (1961).
(28) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

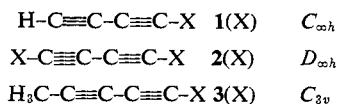# The Photoelectron Spectra of Halodiacetylenes, Dihalodiacetylenes, and Halomethyldiacetylenes

Edgar Heilbronner,* Volker Hornung, John P. Maier, and Else Kloster-Jensen

Contribution from the Physikalisch-Chemisches Institut der Universität Basel, CH-4056 Basel, Switzerland. Received September 25, 1973

Abstract: The photoelectron spectra, excited by HeI radiation, of the halodiacetylenes XC≡CC≡CH, dihalodiacetylenes XC≡CC≡CX, and halomethyldiacetylenes XC≡CC≡CCH₃ with X = Cl, Br, and I are presented. The data afford the determination of the ionization potentials, of spin–orbit coupling (for X = I and Br), and of the discrete vibrational excitation in some of the ionic states. The assignments of the photoelectron bands is discussed in terms of a ZDO LCBO model. It is shown that although the basis orbital parameters as utilized previously in the interpretation of the haloacetylenes XC≡CH and dihaloacetylenes XC≡CY can again reproduce the experimental ionization potentials well, erroneous spin–orbit couplings are predicted. As the magnitude of the spin–orbit coupling is a sensitive probe of the electronic environment and hence of the adequacy of the model, the pitfalls of parametrization to fit ionization potentials alone are illustrated. It is shown that inclusion of antibonding CC π orbitals yields a self-consistent rationalization of the ionization potential and spin–orbit coupling data. The assignment of the bands correlates with the vibrational fine structure observed and the shapes of the Franck–Condon envelopes.

Linear molecules containing heavy atoms, *e.g.*, haloacetylenes, are of special interest in photoelectron (PE) spectroscopy. Not only are their PE spectra of extreme simplicity, but the easily measurable band splits due to spin–orbit coupling yield additional information which makes them an ideal and sensitive probe of the adequacy of simple molecular orbital models.

In Figures 1–3 are shown the HeI PE spectra of the halodiacetylenes **1(X)**, dihalodiacetylenes **2(X)**, and halomethyldiacetylenes **3(X)** with X = Cl, Br, and I.

$$\text{H–C≡C–C≡C–X} \quad \mathbf{1(X)} \quad C_{\infty h}$$
$$\text{X–C≡C–C≡C–X} \quad \mathbf{2(X)} \quad D_{\infty h}$$
$$\text{H}_3\text{C–C≡C–C≡C–X} \quad \mathbf{3(X)} \quad C_{3v}$$

The ionization potential and vibrational excitation data are collected in Tables I–VI.

In the range from 8 to 18 eV the PE spectra of **1(X)** or **2(X)** consist of five or six bands, respectively. Bands 1–3 (**1(X)**) or 1–4 (**2(X)**) are twin π bands corresponding to an ionization process

$$\text{M(X)} + h\nu \longrightarrow \text{M}^+(^2\Psi_j) + e^- \tag{1}$$
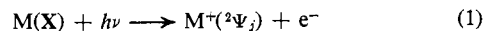
in which the photoelectron e⁻ is ejected from one of the sets of degenerate π orbitals $\psi_j \equiv \pi_\lambda(j)$ of the singlet ground state molecule M(X). (The lower index $\lambda = \pm 1$ of the orbitals $\pi_\lambda(j)$ represents the angular momentum quantum number.) This leaves the radical cation M⁺ in one or the other of the doublet states $^2\Psi_j \equiv$