the lowest ionic diabatic potential near the surface. Therefore, most of the neutral flux is lost at the initial (outer) crossing of the neutral and lowest ionic diabatic potentials. Since the ionic states do not significantly couple, this ionic flux remains in the lowest ionic channel until it crosses the neutral potential on the outward path. As a consequence, most of the change in probability on the outward path will again be in P_2 and P_3 at the outer crossing. When the collision energy increases, this description becomes less accurate. The neutral flux which survives the initial crossing generally increases as the collision energy increases. As this neutral flux increases, including the extra ionic channel should become more important in determining the final values of the total electron-transfer probability. However, for the energy range used here, the extra ionic channel does little to increase P^{ion}. This suggests that including a third ionic channel would have practically no affect on P^{ion} at these energies.

The most noticeable effect of the extra ionic channel is that it gives rise to much slower oscillations in P_2 and P^{ion}. An analysis of these oscillations clearly shows that they can be attributed to the topological similarity of the two ionic channels. Since there is a continuous set of energy levels for a metallic surface, it is doubtful whether these slower oscillations are physically real. Of interest would be to move the ionic potentials closer to each other. This would give a better description of the continuum of surface states and provide information about how close the ionic potentials have to be in order for the extra ionic channel to play a significant role. The rapid oscillations present in the two-state results are simply a consequence of having a neutral and ionic pathway and could therefore be physically significant. Moving the ionic potentials closer to each other could give some insight into this possibility too.

Including the extra ionic channel does not improve the disagreement between theory and experiment at the lowest energies. We feel that this is most likely due to confining the transferred electron to the metal cluster. In reality, the transferred electron can travel many lattice spacings away from the collision zone during the course of the collision. This suggests that the ionic potentials of the initial and final stages of the reaction may not be the same. It would be of interest to define a realistic prescription based on the duration of the collision that would allow these ionic potentials to change during the collision. This will be the subject of future work.

Acknowledgment. The financial support of the Office of Naval Research, the National Science Foundation, the IBM Corporation, and the Camille and Henry Dreyfus Foundation is gratefully acknowledged.

Registry No. Na, 7440-23-5; W, 7440-33-7.

Matrix Absorption Spectra of the Radicals Formed by the Addition of Hydrogen Atoms to Phenylacetylene

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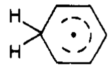
Codeposition of hydrogen atoms from a blind discharge with phenylacetylene in argon at 20 K gave two new products with absorptions at 314.4, 474.7 nm and 346.9, 614.4 nm, respectively. These bands exhibited different photolysis behavior and are grouped accordingly. The former pair agree with assignments to α-styryl radical from radiolysis experiments, and the latter pair are assigned to the radical formed by hydrogen atom addition to the aromatic ring. Deuterium substitution at all positions aids in vibronic assignment of the sharp 346.9-nm band system. The strong electron-withdrawing and conjugating ability of the ethynyl group stabilizes the cyclohexadienyl radical product. Complementary results were obtained from the reactions of styrene and 1-phenylpropyne with H atoms. These experiments provide information on the relative reactivity of unsaturated substituents and the aromatic ring toward free radical addition.

Introduction

Although electrophilic aromatic substitution has been widely studied, free radical addition to aromatic rings has received far less attention.[1] In particular, the addition of hydrogen atoms to benzene to form the cyclohexadienyl (C_6H_7) radical (**1**) occurs in radiolysis of benzene solutions and glasses[2-6] or cyclohexadiene[7] and in matrix photolysis experiments with benzene[8] and the radical product has been characterized by ESR and UV-vis absorption spectra. Much less is known about H atom addition to substituted benzenes; radiolysis of the solute in methanol glasses[2,9] and H atom addition in matrix experiments with toluene, xylene, and ethylbenzene[10-12] have led to substituted cyclohexadienyl radical absorption spectra. In the case of styrene and phenylacetylene in methanol glasses, irradiation effected H addition to the substituent to give α-methylbenzyl or 1-phenylethyl (**2**) and α-styryl (**3**) radicals, respectively, which were characterized by absorption spectra.[2] In matrix photoionization experiments with styrene and



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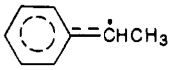

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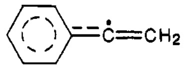

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phenylacetylene, parent cations were the major products; however, two weaker sets of minor product absorptions were observed with each precursor which provided evidence for H atom addition free radicals.[13-15] In these cases, H atoms can, in principle, add to the unsaturated substituent or to the aromatic ring, and the following matrix study was performed to seek information on these two different free radical products.

Although benzyl and substituted benzyl radicals have been studied extensively,[10-12,16-19] the α-styryl radical (3) has received less attention presumably owing to difficulty of preparation. This radical has been characterized as a linear π-radical ($Ph—C═CH_2$) by ESR studies of the $Ph—CBr═CH_2$ reaction with sodium;[20] subsequent ESR studies of phenylacetylene radiolysis products have supported this description.[21,22] Visible thermoluminescence from phenylacetylene solutions subjected to γ-radiolysis has been ascribed to α-styryl radicals.[23,24] The present matrix study relates the emission and ultraviolet absorption spectra of this interesting π-radical.

Experimental Section

The cryogenic and vacuum equipment have been discussed in detail previously.[25] Matrix samples were prepared by codepositing argon-diluted phenylacetylene mixtures (Ar/phenylacetylene = 100–500/1) at 2 mmol/h onto a 20 K sapphire plate with a similar quantity of a hydrogen or deuterium in argon (Ar/H_2 = 20–100/1) mixture passing through an "L"-shaped discharge tube for periods of 2–4 h. The discharge, excited by a 100-W microwave diathermy unit, was positioned so that none of the resonance radiation would illuminate the condensing sample. Following matrix sample preparation, UV–vis spectra were recorded on a Cary 17 spectrophotometer between 800 and 300 nm both before and after standard glass filtered mercury arc (BH-6-1) photolyses.

Phenylacetylene-h_6 (PA), 1-phenylpropyne (PP), and styrene (Aldrich) and phenylacetylene-d_5 (Merck Sharp and Dohme) were degassed by several freeze–thaw while pumping cycles and used without further purification. Phenylacetylene-d_1 was prepared by stirring phenylacetylene-h_6 with excess NaOD in D_2O at room temperature for 24 h. The deuteriated product was decanted from the aqueous layer and dried with anhydrous $MgSO_4$; the extent of deuteriation was checked by NMR. Phenylacetylene-d_6 was prepared in the same manner using phenylacetylene-d_5.

Results

Phenylacetylene. In the earlier matrix photoionization study with phenylacetylene, a sharp structured absorption system beginning at 346.8 nm exhibited very different photochemical behavior from the parent cation.[14] Similar more concentrated experiments also gave a weak, broad 314-nm absorption, which photolyzed when irradiated by ultraviolet light.[15] When these vacuum-UV photolysis experiments were repeated with H_2 added to the argon gas flowing through the discharge tube, the 314- and 346.8-nm band yields increased markedly, parent cation bands decreased, and very sharp, weak absorptions appeared at 515, 568, and 627 nm that are characteristic of the hydrogen open-discharge system. The present experiments employed the blind discharge of a H_2–argon stream without vacuum-UV radiation impinging on the sample as a source of H atoms for reaction with phenylacetylene during codeposition in excess argon at 20 K. The

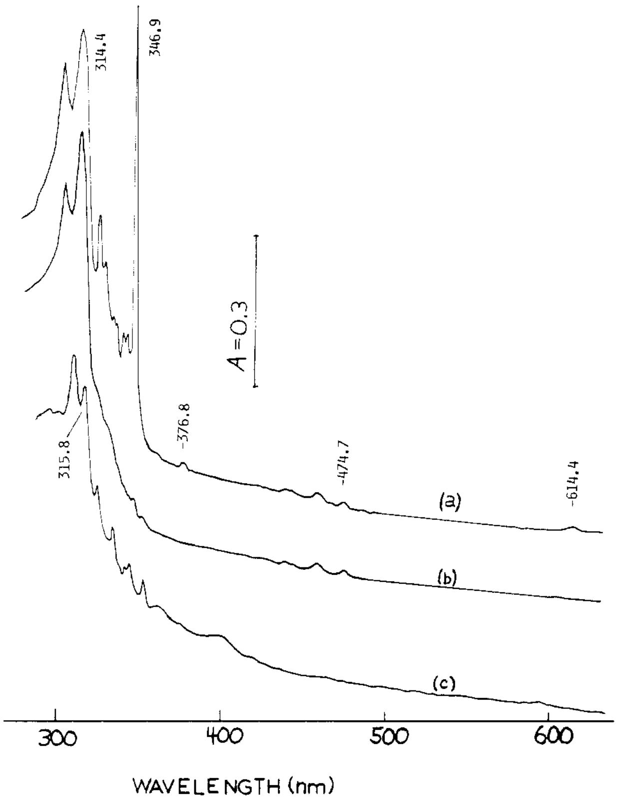

Figure 1. Absorption spectra in the visible and near-ultraviolet for argon–phenylacetylene = 200/1 sample codeposited at 20 K with argon/H_2 = 20/1 sample flowing through a blind discharge: (a) sample codeposited for 3 h, (b) spectrum after 290–1000-nm photolysis for 15 min, (c) spectrum after 220–1000-nm photolysis for 15 min.

TABLE I: Product Absorptions Observed after Codeposition of Phenylacetylene with H Atoms in Excess Argon

absorption, nm		
PA-h_6	PA-d_5	assignments[a]
614.4	612	echd origin
474.7	472.5	α-styryl origin
458.4 (750)[b]	457.5 (700)	ν = 750 cm^{-1}
444.0 (1460)	451.5 (980)	ν = 1460 cm^{-1}
439.5 (1680)		ν = 1680 cm^{-1}
376.8	376.2	styrene + H
361.8	361.2	styrene + H
346.9	346.0	echd origin
342.8	342.0	ν = 340 cm^{-1}
340.3	339.5	ν = 550 cm^{-1}
335.7	336.2	ν = 840 cm^{-1}
333.8	332.2	ν = 930 cm^{-1}
329.0	328.7	ν = 1520 cm^{-1}
325.3	324.6	ν = 1905 cm^{-1}
314.4	312.4	α-styryl
303.4	303.5	
	299.2	
Photolysis Product Absorptions		
352.5	350.5	unidentified
344.5	342.5	unidentified
333	332	unidentified
324	323	unidentified
315.8	315.0	α-methylbenzyl
309.2	308.2	unidentified

[a] Ethynylcyclohexadienyl radical = echd; vibrational intervals for hydrogen radical. [b] Vibrational interval.

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TABLE II: Ethynylcyclohexadienyl Radical Absorptions Observed after Codeposition of H or D Atoms with Phenylacetylene Isotopes in Excess Argon at 20 K[a]

absorption, cm^{-1}		assignt[a]
Ph—C≡C—H + H	Ph—C≡C—H + D	
28825 ± 5	28840 ± 5	origin
345 ± 10	355 ± 10	β(C—C—H)
570	570	ring def
970	(920)[b]	ring breathing
1140	1140	β(C—H)
1570	1570	ν(C=C)
1915	1915	ν(C≡C)
Ph—C≡C—D + H		
28870 ± 5		
250 ± 10		
570		
970		
1130		
1570		
1850		
Ph-d_5—C≡C—H + H	Ph-d_5—C≡C—H + D	
28905 ± 5	28920 ± 5	origin
340 ± 10	345 ± 10	
550	550	
840	860	β(C—D)
930	—	
1520	1520	
1905	1905	
Ph-d_5—C≡C—D + H	Ph-d_5—C≡C—D + D	
28945 ± 5	28965 ± 5	origin
250 ± 10	265 ± 10	
560	560	
860	850	
—	—	
1530	(1520)[b]	
1860	1855	

[a] First band is electronic origin; successive intervals are vibrational fundamentals. [b] Uncertain due to overlapping impurity.

spectrum, illustrated in Figure 1a for Ar/PA = 200/1 and 5% H_2 in argon, shows strong, broad absorptions at 303.4 and 314.4 nm (A = 0.5), the strong, sharp band system beginning at 346.9 nm ($A \sim 1.0$), weaker band systems at 376.8, 474.7, and 614 nm, and no parent cation absorption at 579 nm. The sample was irradiated by filtered light from the high-pressure mercury arc, and more spectra were recorded; 380–1000-nm radiation had little effect, but 340–1000-nm light substantially reduced the weak 376.8- and 361.8-nm bands and slightly decreased the strong 346.9-nm system. Pyrex photolysis (290–1000 nm) destroyed the 346.9-, 376.8-, and 614-nm band systems and decreased the 314.4- and 474.7-nm band systems by 10%, as shown in Figure 1b. A final 220-nm irradiation destroyed the 314.4- and 474.7-nm systems, produced new bands, also given in Table I, and revealed a sharp new 315.8-nm band, as shown in Figure 1c. The latter band has been identified previously as α-methylbenzyl (**2**) radical.[12] A similar experiment was run with Ar/PA = 600/1 and 1% H_2 in argon, and the 346.9- and 614-nm systems were 40% and the 314.4- and 474.4-nm systems were 20% of their absorbances in Figure 1a. The structured 346.9-nm band system from this experiment is shown in Figure 2a.

Deuterium substitution was done first by replacing H_2 in the argon stream with D_2. Small reproducible blue shifts were measured for the sharp band progression, which is illustrated in Figure 2b. The sharp origin bands (fwhm = 100 cm^{-1}) can be measured on an expanded scale to ±5-cm^{-1} accuracy. No deuterium shifts were found for other product absorptions. Similarly, the codeposition of discharged H_2 with PA-d_1 shifted only the sharp band system, shown in Figure 2c. The sharp, weak 337.9-nm band is due to NH in solid argon,[26,27] which shifts to 337.5 nm with discharged D_2 and appears as a variable impurity in these experiments. Table II gives the sharp band origin positions and the vibronic intervals from their origin; the first and last intervals show measurable d_1 substitution effects.

TABLE III: Product Absorptions Observed after Codeposition of Styrene with H Atoms in Excess Argon

absorption, nm	assignment
706	vinylcyclohexadienyl origin
377.7	vinylcyclohexadienyl origin
371.8	ν = 430 cm^{-1}
362.2	ν = 1140 cm^{-1}
356.6	ν = 1550 cm^{-1}
346.9	ethynylcyclohexadienyl origin
315.8	α-methylbenzyl
310.4	ν = 550 cm^{-1}
306.4	ν = 970 cm^{-1}
304.3	ν = 1190 cm^{-1}
302.7	ν = 1370 cm^{-1}
301.5	ν = 1500 cm^{-1}
297.6	ν = 2 × 965 cm^{-1}

TABLE IV: Product Absorptions Observed after Codeposition of 1-Phenylpropyne and H Atoms in Excess Argon

absorption, nm	assignment
348.6	propynylcyclohexadienyl origin
341.9	ν = 560 cm^{-1}
335.2	ν = 1140 cm^{-1}
330.7	ν = 1550 cm^{-1}
325.6	ν = 2020 cm^{-1}
314.4	β-methyl-α-styryl
310.5	

Phenylacetylene-d_5 and PA-d_6 were used in similar experiments, and small blue shifts were found for the PA-d_5 origin bands, as listed in Table I. Spectra for the sharp band systems are illustrated in Figure 2, and the intervals are given in Table II. Although the sharp system origin bandwidth was unchanged (100 cm^{-1}) on d_5 substitution, the 314.4-nm bandwidth (400 cm^{-1}) was halved (shifted to 312.4 nm, bandwidth 200 cm^{-1}). Photolysis in the d_5 studies matched that described above. In the PA-d_6 + H_2 discharge experiment, 320–1000-nm irradiation virtually destroyed the 346-, 376-, and 612-nm band systems without affecting the 312- and 472-nm systems; photolysis at 220–1000 nm, however, destroyed the latter and produced new bands, given in Table I. The 315.0-nm band is clearly due to the $C_6D_5CHCDH_2$ radical.

The hydrogen discharge experiments, in general, gave larger product band absorbances than corresponding D_2 experiments, which presumably arises from easier dissociation of H_2 as compared to D_2.

Styrene. Since styrene can be formed by the addition of two H atoms to phenylacetylene, several similar experiments were done with styrene and H atoms from the blind discharge. As expected, the major product gave a sharp band system beginning at 315.8 nm due to α-methylbenzyl radical.[12] Sharp weaker bands were observed at 377.7 (A = 0.18), 371.8 (A = 0.03), 362.2 (A = 0.08), and 356.6 nm (A = 0.025) with sharp resolved satellites 1.3–1.6 nm to the blue; the 346.9-nm (A = 0.08) system and a weak 706-nm (A = 0.008) band were detected. Photolysis at 370–460 nm halved the 377.7-, 362.1-, and 356.6-nm band systems and the 706-nm band and had no effect on the 346.9- and 315.8-nm band systems. A similar experiment with styrene and D atoms gave the same bands within measurement error, and 340–1000-nm photolysis virtually destroyed the 377.7-nm system and decreased the 346.9-nm system as in PA studies. Product bands in styrene + H atom experiments are collected in Table III.

1-Phenylpropyne. Two hydrogen discharge experiments were done with 1-phenylpropyne, and a product spectrum is shown in Figure 3a. The total product yield is less than in corresponding phenylacetylene studies. The sharp band origin shifted to 348.6 nm (twice the bandwidth, fwhm = 200 cm^{-1}, and half the absorbance of comparable PA experiments), and weak broad bands were observed at 314.4 and 310.5 nm, as listed in Table IV. Photolysis at 340–1000 nm reduced only the 348.6-nm band

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(27) Miller, J. C.; Andrews, L. *J. Chem. Phys.* **1979**, *71*, 5276.

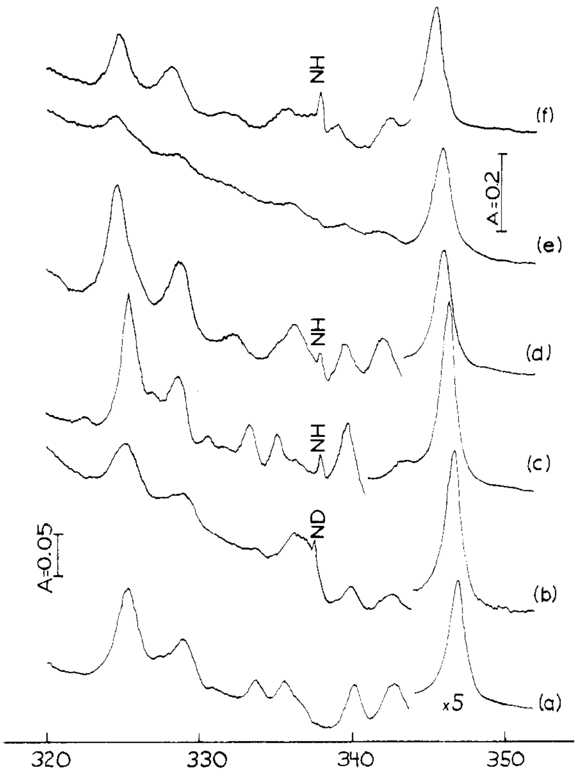


Figure 2. Absorption spectra in the 320–350-nm region for isotopic phenylacetylene samples codeposited with discharged H_2 or D_2 in excess argon: (a) Ph-C_2H + H, (b) Ph-C_2H + D, (c) Ph-C_2D + H, (d) Ph-d_5-C_2H + H, (e) Ph-d_5-C_2H + D, (f) Ph-d_5-C_2D + H. The origin band in all but (e) must be expanded ×5 to be on the same scale as the other spectra.

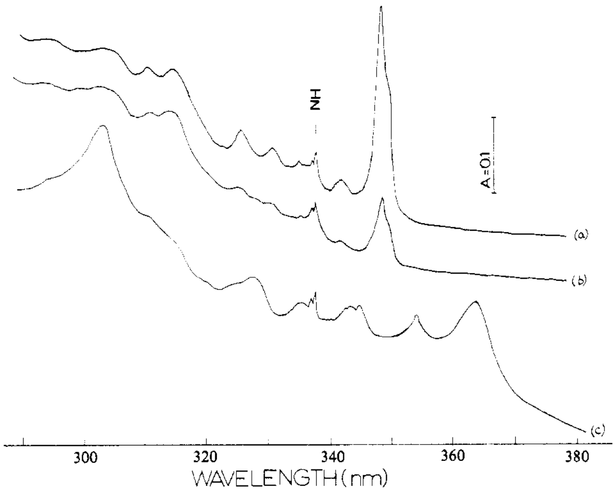
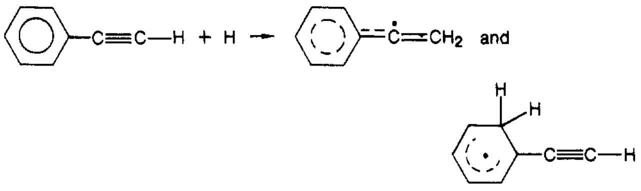


Figure 3. Absorption spectra in the near-ultraviolet for argon/phenylpropyne = 200/1 codeposited at 20 K with Ar/H_2 = 50/1 sample flowing through blind discharge: (a) sample codeposited for 4 h, (b) spectrum after 340–1000-nm photolysis for 30 min, (c) spectrum after 220–1000-nm photolysis for 30 min.

system (Figure 3b), and a similar 290–1000-nm irradiation destroyed the 348.6-nm system without affecting the 314.4- and 310.5-nm bands. Final 220–1000-nm irradiation (Figure 3c) destroyed the latter bands and produced a strong band at 303.0 nm, a band system beginning at 363.0 nm, and weak bands at 478, 508, and 515 nm. The strong 303.0- and 363.0-nm bands were observed in previous mercury arc photolysis experiments with phenylpropyne and electron traps.[28] Several blank argon/phenylpropyne samples were irradiated at 220–1000 nm, and the latter bands were again observed with the same relative intensities.

SCHEME I



These bands are due to the 3-phenylpropargyl radical (Ph—C≡C—CH_2) produced by detachment of H from the methyl substituent, which will be discussed in a future report.

Discussion

The new free radical species produced from each precursor will be identified.

Phenylacetylene. The phenylacetylene + H atom codeposition experiments (Figure 1) exhibit two strong absorption band systems (314.4 and 346.9 nm) with associated weaker band systems (474.7 and 614.4 nm, respectively) which are due to two different reaction products. The photolysis studies clearly associate the 614.4- and 346.9-nm band systems and separate them from the associated 474.7- and 314.4-nm band systems. The weak 376.8- and 361.8-nm bands were much stronger in the styrene experiments to be discussed later.

Two previous observations indicate that the 474.7- and 314.4-nm band systems are due to the α-styryl radical (**3**) formed by H atom addition to the β-carbon of phenylacetylene (Scheme I). First, the 314.4- and 303.4-nm bands are similar in profile to 320- and 315-nm bands of α-styryl radical in irradiated methanol glass; the latter bands were attributed to α-styryl radical produced by phenylacetylene anion abstracting a proton from methanol following radiolysis.[2] Second, the 474.7-nm absorption origin agrees with the first emission band at 474 nm for α-styryl radical in hydrocarbon glass produced again by radiolysis.[23] Several ESR studies have characterized α-styryl radical as a π-radical (linear Ph—C=CH_2)[20-22] like benzyl radical, which has electronic absorption origins at 457.4 and 310.5 nm in solid argon.[10] The close comparison between benzyl (Ph-CH_2) and α-styryl radical is therefore obvious. The band positions and relative intensities argue for the same electronic assignments in C_{2v} symmetry, namely, the 474.7-nm band as $1^2A_2 \leftarrow 1^2B_2$ and the 314.4-nm band as $2^2A_2 \leftarrow 1^2B_2$. Finally, there is no conclusive evidence here for H atom addition to the α-carbon of phenylacetylene to give the σ-type β-styryl radical, although the unidentified bands produced by photolysis (Table I) might include absorptions for this σ-radical.

Unlike benzyl radical, which can be produced by 220–1000-nm photolysis of toluene,[10] α-styryl radical is photodissociated by this radiation (Figure 1), which presumably involves detachment or rearrangement of one β-hydrogen atom. This explains the failure of Baches et al.[24] to produce α-styryl radical using photodissociation of HI as a source of H atoms. In the present work H atoms from a blind discharge flow around a bend and react directly with phenylacetylene on codeposition in the absence of radiation.

The strong 346.9- and weak 614.4-nm bands are due to a different C_8H_7 free radical formed in the PA + H reaction (Scheme I). These two bands have similar relative intensity and are shifted to slightly longer wavelengths than 316- and 559-nm bands[3] assigned to the cyclohexadienyl radical, **1**. The extensive vibronic structure and deuterium substitution provide keys to identification of this new radical. The data in Table II show vibrational levels and zero-point energy shifts in the origin band that provide diagnostic information. First, the added H and the acetylide H are not equivalent in the new species (in contrast to α-styryl, **3**) since the origin and spacings are different for Ph—C≡C—H + D and Ph—C≡C—D + H radicals (Table II). The largest vibrational interval, 1915 cm^{-1}, shows a small d_5 shift (10 ± 10 cm^{-1}) and a larger d_1 shift (60 ± 10 cm^{-1}), and it falls below the 2120-cm^{-1} ν(C≡C) fundamental of the precursor[29] molecule but not as low as the 1630-cm^{-1} ν(C=C) fundamental of styrene.[30]

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(28) Kelsall, B. J.; Andrews, L. *J. Chem. Phys.* **1982**, *76*, 5005.

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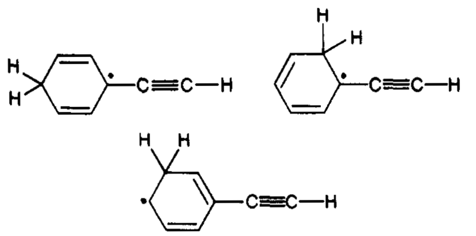
SCHEME II

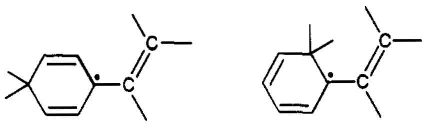


This vibrational interval indicates *partial triple bond* character for the substituent group and therefore shows that the new hydrogen adds to the ring, giving a cyclohexadienyl type radical. The ν(C≡C) mode exhibits a 140-cm^{-1} red shift on alkyne-d_1, substitution in the PA precursor,[29] but this new radical exhibits a corresponding shift of only 60 ± 10 cm^{-1}. This change may be due to a difference in coupling between the ν(CC—H) and ν(C≡C) modes, which provides evidence for a nonlinear C≡C—H subgroup in this substituted cyclohexadienyl radical. The fact that the Ph—C≡C—D + H species exhibits a larger zero-point energy blue shift (45 ± 5 cm^{-1}) than the Ph—C≡C—H + D species (15 ± 5 cm^{-1}) shows that the added C-H vibration is reduced less in the excited state than the PhC$_2$-H vibration. This demonstrates that the added hydrogen is considerably different from the alkyne hydrogen and again shows that this hydrogen must be added to the ring, which is represented in Scheme II by a number of Lewis structures. Spin density calculations for cyclohexadienyl radical (**1**) show a concentration at the ortho and para positions,[3] and these positions can be stabilized by the electron-withdrawing -C≡C—H group. We obviously cannot determine whether the H atom is added ortho or para or both, but the stabilizing -C≡C—H group would not be as effective for meta substitution. The ortho addition product has the advantage of π-conjugation for the tertiary radical. Simple HMO calculations suggest that the ortho form is slightly more stable.

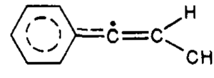
Other vibrational intervals in Table II provide information on this ethynylcyclohexadienyl radical. The 1570-cm^{-1} interval, which shifts to 1520 cm^{-1} upon d_5 substitution, is in the ν(C=C) stretching region (1575 cm^{-1} for 1,3-cyclohexadiene, CHD),[31] and the 1570-cm^{-1} band is assigned accordingly. The 1140-cm^{-1} band, which shifts to about 850 cm^{-1} on d_5 substitution, is clearly due to a ring C-H bending mode like ν_7 for PA at 1175 cm^{-1} and ν_7 for CHD at 1150 cm^{-1}.[29,31] The 970-cm^{-1} interval shifts to 930 cm^{-1} with d_5 substitution, which is appropriate for a ring breathing mode (998 cm^{-1} for PA, 945 cm^{-1} for CHD).[29,31] The 570-cm^{-1} band is due to a ring deformation mode as the small d_5 and nil d_1 shifts indicate; this mode is substituent sensitive since the analogous styrene compound presents instead a 430-cm^{-1} interval. The 350 ± 10 cm^{-1} interval is most interesting, as no counterpart was observed in the spectra of PA and CHD. This band shows a d_1 shift to 255 ± 10 cm^{-1} and no d_5 dependence; hence, it must primarily involve a motion of the acetylide hydrogen. Since C≡C—H bending modes for this collinear subunit in PA occur higher at 649 and 613 cm^{-1}, the low 350-cm^{-1} bending interval might be a consequence of π-delocalization and broadening the C≡C—H bending potential function in the out-of-plane direction.

Styrene. Like phenylacetylene, H atom addition to styrene gave two product band systems, but unlike PA, the more stable 315.8-nm band system dominated by a factor of 5 the photosensitive 377.8-nm band. The 315.8-nm band system was produced in large yield from UV photolysis of ethylbenzene and assigned[12] to α-methylbenzyl radical, **2**. The present observation reinforces that assignment. The weaker photosensitive band system at 377.8 nm exhibits vibronic intervals of 430, 1140, and 1550 cm^{-1}. The latter two agree with intervals in the PA experiments, giving the cyclohexadienyl type radical shown in Scheme II. The 430-cm^{-1} interval is near a bending mode for styrene,[30] and it should be assigned accordingly. The 377.8-nm band system and the associated very weak 706-nm band are believed to be due to a vinyl-substituted cyclohexadienyl type radical represented in Scheme III. The small yield of ethynylcyclohexadienyl radical observed in styrene experiments is, perhaps at first, surprising; however, molecular hydrogen elimination from the species in Scheme III may occur on formation owing to the unusual stability of the product in Scheme II. The α-styryl radical was not detected in the present or earlier[13] styrene experiments.

SCHEME III



1-Phenylpropyne. The H atom addition experiments with PP (Figure 3) gave two band systems, like PA, but the photosensitive 348.6-nm band system was clearly favored over the more stable 314.4-nm band. Analogy with the PA experiments indicates that the broad, weak 314.4- and 310.5-nm bands are due to β-methyl-α-styryl radical, **4**, formed by H atom addition to the triple bond. The first band is not sharp enough to detect a methyl substitution dependence. The markedly reduced yield of β-methyl-α-styryl radical suggests that approach of a hydrogen atom to the triple bond is sterically hindered by the methyl group. On the other band, the photosensitive product yield was comparable for PA and PP, and vibrational intervals were similar for the photosensitive product bands. For PP the ν(C≡C) mode[32] is 2267 cm^{-1} and the largest vibronic interval at 2020 cm^{-1} falls below by a slightly larger amount than the analogous PA product. The 1550-, 1140-, and 560-cm^{-1} intervals are assigned to ν(C=C) stretching, C-H bending, and ring deformation modes as in the PA product. The absence of a 350-cm^{-1} vibronic interval is noted. The photosensitive band system is therefore assigned to the propynylcyclohexadienyl radical formed by hydrogen atom addition to the aromatic ring analogous to the structures presented in Scheme II (with CH$_3$ substitution for the ethyne hydrogen).



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Trends in Reactivity and Bonding. It is of interest to compare the reactivity of the three compounds studied here with that of benzene[8] and ethylbenzene[12] toward hydrogen atoms in similar blind discharge experiments and to relate this to hydrogen atom reactions in solution.[33] It is clear, based on absorption band areas, that hydrogen atoms add to the -C≡C—H and -CH=CH$_2$ groups in preference to the aromatic ring. This is consistent with relative reactivities of benzene and ethylene toward methyl radical addition.[34] Considering, however, only the absorptions due to the substituted cyclohexadienyl radicals, the PA yield exceeds ethylbenzene and benzene, respectively, but the styrene yield falls still lower. The latter is probably due to a strong preference for addition to the vinyl group, but the former appears to be due to stabilization of the cyclohexadienyl radical by the more strongly electron withdrawing ethynyl substituent. Unfortunately, solution studies of reactivity have apparently not been done with PA for comparison. The ethynyl-substituted cyclohexadienyl radical is an unusually stable substituted cyclohexadienyl radical, which may involve conjugation of the -C≡CH group with the ring. The vinyl group in styrene, on the other hand, does not delocalize the radical spin density as well as the acetylide group in phenylacetylene. One difference between PA and PP is also striking—the α-styryl radical yield is markedly less with PP. The C≡C—CH$_3$ skeletal framework must bend to add hydrogen to the β-carbon to give

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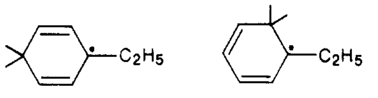
the β-methyl-α-styryl radical, and this must reduce the rate markedly from the C≡C—H case. In contrast, the ethynyl- and propynylcyclohexadienyl radical origin band yields were comparable as expected for H addition to the aromatic rings in each case. Replacing the ethynyl hydrogen with CH_3 and C_2H_5 gave a small red shift in the alkynylcyclohexadienyl radical electronic origin bands.[14]

Finally, these studies provide information on substituent effects in free radical addition to aromatic systems. In the case of ethylbenzene and benzene, the 317.3-nm ethylcyclohexadienyl radical origin was broader (fwhm = 260 cm^{-1}) and stronger (A = 0.21) than the 310.2-nm origin for cyclohexadienyl radical (fwhm ~ 130 cm^{-1}, A = 0.05). Two noteworthy points arise from these observations. First, the H atom addition yield is substantially higher with ethylbenzene than benzene; this is surely due to the enhanced stability of the tertiary radical product with ethylbenzene (**5**) over the secondary cyclohexadienyl radical with benzene (**1**), which is consistent with rate factors from solution studies.[33] Second, the increased line width for the ethylbenzene product may be due to a mixture of para and ortho tertiary radical isomers.



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The ethyl substituent clearly stabilizes the cyclohexadienyl radical, but not as much as the electron-withdrawing -C≡C—H group.

Conclusions

Reactions of H atoms from a blind discharge with phenylacetylene in argon gave two new free radical products with different photochemical behavior which were identified from matrix absorption spectra. The first, α-styryl radical, results from H addition to the β-carbon of the alkyne substituent, and the second, ethynylcyclohexadienyl radical, results from H addition to the aromatic ring. Deuterium substitution at all positions facilitates identification and vibronic assignment for the latter radical. The increasing yields of cyclohexadienyl radicals in benzene, ethylbenzene, and phenylacetylene experiments show that the strongly electron withdrawing ethynyl group stabilizes the cyclohexadienyl radical better than the ethyl group, which in turn gives a tertiary radical that is more stable than unsubstituted cyclohexadienyl. Finally, these studies are an important source of information on substituent effects in free radical addition to aromatic systems.

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Registry No. **1**, 15819-51-9; **3**, 34089-70-8; H, 12385-13-6; phenylacetylene, 536-74-3; styrene, 100-42-5; 1-phenylpropyne, 673-32-5.

Ground- and Excited ($3s^13p^1$)-State Reactivity of Mg with HF: A Theoretical ab Initio SCF-CI Study

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Model potential energy surfaces (PES's) have been calculated (ab initio 631 G* and 631 G** + CI) for the following reactions of Mg (^1S, ^3P, and ^1P) with HF: (1) Mg + HF → MgF + H ($C_{\infty v}$); (2) Mg + HF → MgH + F ($C_{\infty v}$); (3) Mg + HF → HMgF (C_s). Reaction 2 appears to be very unlikely, even from excited Mg. Triplet ^3P Mg could yield (1) and (3) with a low efficiency; the singlet PES of (2), arising from ^1P Mg, is attractive and exhibits a minimum. This path thus is presumably greatly favored. From the GS, the insertion reaction (3) is the most likely to occur. The various approaches and the topology of the PES are briefly discussed by using correlation and perturbation MO arguments.

Introduction

The reactivity of metal atoms with small covalent molecules, either in the gas phase or in matrices at low temperature, has stimulated many experimental and theoretical studies.

The Mg + H_2 system has been recently studied by sophisticated methods.[1] In a previous paper[2] dealing with this system, we explored a complete set of model reaction paths (ab initio SCF + CI) and we emphasized the easy C_{2v} side-on approach of ^1P Mg, with formation of a $^1B_2$ exciplex initially proposed by Jordan et al.[1c]

We will now report the results of calculations relative to the Mg + HF system. This system, as far as we know, has not yet been investigated experimentally, and HF has been chosen as the simplest strongly dissymmetrical diatomic molecule. Our goal is to discuss the differences of reactivity brought about by this dissymmetry: for this purpose, we have limited ourselves to the three following model reactions, in the ^1S (ground state) and the ^3P and ^1P excited states of the Mg atom:

$$\text{Mg} + \text{F–H} \rightarrow \text{MgF} + \text{H} \quad (C_{\infty v}) \qquad (1)$$

$$\text{Mg} + \text{H–F} \rightarrow \text{MgH} + \text{F} \quad (C_{\infty v}) \qquad (2)$$

$$\text{Mg} + \text{H–F} \rightarrow \text{H–Mg–F} \quad (C_s) \qquad (3)$$

The potential energy surfaces (PES's) relative to reaction 1 in the ground state (GS) have been recently investigated by Paniagua et al.[3] Moreover, Dykstra et al. studied the thermal insertion of Mg with HF and other related species such as CH_3F and CH_3Cl.[4] Nevertheless, no theoretical study has been published concerning either the excited-state reactivity of Mg or the possible competition of reactions 1–3 in the GS, although (2) is unexpected

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