193 nm Excimer laser photochemistry of benzene in argon matrices

Jorge L. Laboy and Bruce S. Ault[†]

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221 (USA)

Abstract

Reactions of C_6H_6 and C_6D_6 after 193 nm excimer laser irradiation have been studied by the trapping of products into an argon matrix at 14 K. IR spectroscopy was used to identify the product species; most were known species arising from either isomerization or fragmentation. The ratio of isomerization product to fragmentation product was seen to vary as a function of sample concentration. Addition of Cl_2 as an electron trap to aid in cation formation led to a number of chlorinated benzene species as well as biphenyl. A set of bands was also observed that could be photobleached by a mercury arc lamp; these bands may be due either to $C_6H_6^+$ or to the σ complex $C_6H_6Cl^+$. Parallel experiments with C_6D_6 were conducted in support of these observations.

1. Introduction

The photochemistry of benzene and related aromatic compounds represents a fascinating area for experimental and theoretical study. Early studies [1] found that excitation of the $^1B_{1u}$ (S_2) state in the gas phase produces C_2H_2 as the primary product. Shorter wavelength excitation led to additional products through both isomerization and fragmentation [2]. Irradiation of liquid C_6H_6 over the 165–200 nm range yielded primarily the isomers[††] fulvene, Dewar benzene and benzvalene, with additional minor products [3]. As a result of these many studies, Nakashima and Yoshimara [4, 5] have proposed a hot molecule mechanism for the production of fulvene, involving initial excitation of the S_2 state followed by rapid conversion to highly vibrationally excited S_0 and then isomerization. Recent studies include collision-free molecular beam work [6], where radicals were the principal products, vacuum UV irradiation of C_6H_6 in argon matrices [7] and 254 nm Hg arc irradiation of C_6H_6 in low temperature matrices [8]. From all these studies it is clear that the product distribution is a strong function of the medium and experimental conditions.

The benzene radical cation $C_6H_6^+$ has been studied extensively as well, following exposure to ionizing radiation. Gamma radiolysis of benzene in glassy solids produced $C_6H_6^+$, with identification and characterization by UV spectroscopy [9]. Exposure of argon matrices containing C_6H_6 and an electron trap (CCl_4 or Cl_2) to argon resonance radiation led to UV spectroscopic identification of $C_6H_6^+$ as well as the dimer cation $(C_6H_6)_2^+$ and several radical products [10, 11]. Despite these successes, no IR spectra of $C_6H_6^+$ have been reported.

Previous studies [12, 13] in this laboratory have coupled an excimer laser operating at 193 nm with the matrix isolation technique for the generation, isolation and IR spectroscopic characterization of neutral and charged intermediate species. In particular, two-photon ionization of a stable precursor, CCl_4, has been observed. Application of this approach to argon matrices containing C_6H_6 would have the potential to form a range of products, including the $C_6H_6^+$ radical cation, with subsequent observation by IR spectroscopy. Consequently, a study was undertaken to isolate and identify the products arising from the 193 nm irradiation of Ar/C_6H_6 and Ar/C_6D_6 samples during deposition on a cryogenic surface.

2. Experimental details

The experiments in this study were carried out in conventional matrix isolation equipment that

---

[†]Author to whom correspondence should be addressed.

[††]Systematic names for the various benzene isomers are: 5-methylene-1,3-cyclopentadiene (fulvene), tricyclo[3.1.0.0^{2,6}]hex-3-ene (benzvalene), bicyclo[2.2.0]hexa-2,5-diene (Dewarbenzene), tetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane (prismane).

has been described elsewhere [14, 15]. Benzene (Baker and Adams), C_6D_6 (Aldrich, 99.5% D) and CCl_4 (MCB) were introduced into the vacuum line as the vapor above the liquid and purified by freeze–pump–thaw cycles at 77 K. Cl_2 was introduced into the vacuum line from a lecture bottle and purified in a similar manner. Argon, the matrix gas in all the experiments, was used without further purification. Samples were diluted to the desired ratio with argon and deposited on the 14 K cold window for 20–24 h before final spectra were recorded from 400 to 4000 cm^{-1} on a Mattson Cygnus Fourier transform IR spectrometer at 1 cm^{-1} resolution.

Two arrangements were initially used for laser irradiation. In the first (in situ), after the sample had been deposited, the cold window was rotated by 45°, allowing exposure to the laser through a Suprasil window. After the sample had been irradiated for 1–2 h, the window was rotated back into the beam of the IR spectrometer and additional spectra were recorded. In the second arrangement the cold window was rotated at the beginning of the experiment and irradiation was concurrent with deposition. In both arrangements irradiation was done using a Lambda Physik EMG 103 MSC excimer laser with a repetition rate of 5 Hz and a pulse energy of up to 200 mJ. A number of matrices were subsequently irradiated with the full light of an H_2O-filtered, medium pressure Hg arc after laser irradiation and initial scans were collected.

3. Results

Prior to any irradiation experiments, blank experiments were carried out for each of the parent species. The spectra obtained in these experiments were in good agreement with literature spectra [16–19].

When a number of samples of Ar/C_6H_6 and Ar/C_6D_6 over a range of concentrations were deposited and irradiated in situ, no new bands were observed. Additionally, when samples of Ar/C_6H_6/CCl_4 or Ar/C_6H_6/Cl_2 were deposited and irradiated in situ, no new product bands were detected. By comparison, irradiation during deposition led to substantial product formation in each experiment. Therefore only experiments involving irradiation during deposition were pursued and all the results reported below came from experiments employing irradiation during deposition.

3.1. C_6H_6, C_6D_6

A number of samples of Ar/C_6H_6 were subjected to 193 nm excimer laser irradiation during deposition, with sample concentrations ranging from 250:1 to 2000:1. In each experiment a large number of product absorptions were seen; these are listed in Tables 1 and 2 for experiments with Ar/C_6H_6 = 250, 1000 and 2000. It is noteworthy that

TABLE 1. Product bands and assignments following excimer laser irradiation of a sample of Ar/C_6H_6 = 250 in argon matrices[a]

Band (cm^{-1})	Absorbance	Assignment[b]
3340	0.077	$H(C\equiv C)_2H$
3331	0.187	$H(C\equiv C)_3H$
3324	0.314	$H(C\equiv C)_3H/CH_3CCH$
3320	0.313	CH_3CCH
3263	0.065	$(C_2H_2)_2$
3137	0.071	Fulvene
3116	0.155	Fulvene
1857	0.097	Fulvene
1853	0.233	Fulvene
1488	0.422	Fulvene
1486	0.352	Fulvene
1342	0.778	Fulvene
1334	0.169	Fulvene
1312	0.174	Benzvalene
1269	0.146	Dewar benzene
1165	0.079	Benzvalene
1135	0.049	Dewar benzene
1089	0.293	Benzvalene
1080	0.288	Fulvene
948	0.306	Fulvene/prismane
926	1.198	Fulvene/Dewar benzene
915	0.214	Benzvalene
908	0.166	Fulvene
894	0.427	Fulvene
824	0.072	Dewar benzene
811	0.195	Benzvalene
797	0.102	Fulvene/prismane
794	0.242	Dewar benzene
792	0.178	Dewar benzene
770	1.626	Fulvene
747	0.154	Benzvalene/$(C_2H_2)_2$
742	0.933	Benzvalene
735	0.184	Benzyne
708	0.093	Phenyl, C_6H_5
670	0.250	Prismane
643	0.217	CH_3CCH
639	0.275	CH_3CCH
636	0.323	CH_3CCH
629	0.134	$H(C\equiv C)_2H/CH_3CCH$
615	1.293	Fulvene/CH_3CCH
609	0.175	Fulvene
605	0.158	Fulvene
507	0.115	Benzvalene
504	0.072	Benzvalene
490	0.053	Fulvene
469	0.098	Benzyne

[a]Samples were irradiated during deposition.
[b]See text for references used in making assignments.

TABLE 2. Product bands and assignments following excimer laser irradiation of Ar/C₆H₆ samples in argon matrices[a]

Band (cm⁻¹)	Absorbance		Assignment[b]
	Ar/C₆H₆ 1000:1	2000:1	
3340	0.100	0.205	H(C≡C)₂H
3334	0.233	0.324	H(C≡C)₂H
3331	0.233	0.319	H(C≡C)₃H
3329	· · ·	0.402	H(C≡C)₃H
3324	0.683	2.518	H(C≡C)₃H, CH₃CCH
3320	0.450	0.555	CH₃CCH
3312	0.214	0.274	CH₃CCH
3300	0.088	0.176	C₂H₂
3282	0.163	0.310	C₂H₂
3279	0.186	0.356	C₂H₂
3263	0.096	0.197	(C₂H₂)₂
3116	0.038	0.048	Fulvene
1853	0.081	0.036	Fulvene
1488	0.137	0.127	Fulvene
1486	0.092	0.084	Fulvene
1342	0.306	0.219	Fulvene
1334	0.042	0.036	Fulvene
1080	0.068	0.041	Fulvene
948	0.153	...	Fulvene
946	0.153	0.121	C₂H₄
926	0.413	0.250	Fulvene
915	0.139	0.136	Benzvalene
908	0.058	0.042	Fulvene
904	0.058	0.042	Fulvene
894	0.118	0.066	Fulvene
832	0.102	0.094	
770	0.604	0.370	Fulvene
747	0.175	0.241	Benzvalene/(C₂H₂)₂
742	0.256	0.314	Benzvalene
740	0.279	0.342	Benzyne
738	0.302	0.383	Benzyne
735	0.334	0.469	C₂H₂
643	0.257	0.246	CH₃CCH
641	0.353	0.356	CH₃CCH
639	0.364	0.382	CH₃CCH
636	0.359	0.375	CH₃CCH
629	0.447	0.569	H(C≡C)₂H/CH₃CCH
627	0.480	0.606	H(C≡C)₃H
621	0.326	0.354	H(C≡C)₃H
617	0.421	0.339	Fulvene/H(C≡C)₃H
615	0.682	0.514	Fulvene/CH₃CCH
609	0.161	0.181	Fulvene
490	0.073	0.052	Fulvene

[a]Samples were irradiated during deposition.
[b]See text for references used in making assignments.

as increasingly dilute experiments were conducted, some product bands decreased in intensity, others increased and some additional bands appeared. Several of these matrices were then subjected to Hg arc irradiation; no changes in product band intensity were noted.

In a manner very similar to the C₆H₆ experiments, numerous samples of Ar/C₆D₆ over a range of concentrations were subjected to 193 nm excimer

laser irradiation during deposition. In these experiments a large number of product bands were observed as listed in Table 3. These were reproducible from one experiment to the next, although the product bands showed varying intensity dependences on sample concentration. None of these bands coincided with product bands observed in the C₆H₆ experiments above. Again, Hg arc irradiation of these samples resulted in no spectral changes.

3.2. Cl₂, CCl₄ doping experiments

Andrews and coworkers [10, 11] and others have shown that the addition of an electron scavenger in irradiation experiments can enhance ionization processes. Consequently, a number of experiments were conducted with added CCl₄ or Cl₂. When CCl₄ was employed as an electron trap, the only new products observed relative to the undoped experiments were bands known to arise from 193 nm excimer laser irradiation of Ar/CCl₄ samples. In contrast, irradiation of samples of Ar/C₆H₆/Cl₂ with concentrations ranging from 1000:1:1 to 250:1:2 gave quite different results. Several entirely new IR absorptions were noted, while many bands seen in the undoped experiments were not seen in the doped experiments or were present with greatly diminished intensity. In addition, subsequent Hg arc irradiation of these matrices led to significant changes, with certain product bands decreasing in intensity, others increasing and new bands appearing. Table 4 lists all the product bands in these Cl₂-doped experiments and the behavior of each during Hg arc irradiation.

Samples of Ar/C₆D₆/Cl₂ over a wide range of concentrations were also subjected to 193 nm excimer laser irradiation. As in the above experiments, a number of new IR absorptions were observed in these experiments, while a number that were observed in the undoped experiments were greatly decreased in intensity. Table 5 lists the product bands and intensities in five such experiments. Unfortunately, technical difficulties prevented Hg arc irradiation of these latter experiments.

4. Discussion

4.1. Product identification

As is very evident from the tables, a large number of new IR absorptions, some very intense, were observed after 193 nm excimer laser irradiation of Ar/C₆H₆ samples during deposition into argon matrices. Many previous studies have examined

TABLE 3. Product bands and assignments following excimer laser irradiation of Ar/C_6D_6 samples in argon matrices[a]

Band (cm^{-1})	Absorbance				Assignment[f]
	Ar/C_6D_6 250:1	500:1	1000:1	2000:1	
2860	0.158	...	...	...	Group A[d]
2831	0.119	...	...	...	Group A
2607	0.047	0.090	0.115	0.100	CD_3CCD
2601	...	0.134	...	...	CD_3CCD
2599	...	0.142	0.130	0.107	$D(C\equiv C)_2D$
2597	...	0.145	...	...	$D(C\equiv C)_2D$
2594	0.019	0.166	0.168	...	$D(C\equiv C)_2D$
2592	...	0.162	0.167	0.183	$D(C\equiv C)_2D$
2380	0.233	...	...	...	Group A
2136	0.036	0.021	0.298	0.506	CO
1867	0.154	...	...	...	Group A
1861	0.207	...	...	...	Group A
1800	0.100	...	...	...	Group A
1683	0.170	0.070	0.100	0.078	
1625	0.525	0.149	...	...	Group A
1618[b]	1.195	0.153	...	...	Group A
1550	0.405	...	...	...	Group A
1475	0.218	...	...	...	Group A
1470	0.309	0.205	0.127	0.058	Group A
1465	0.379	...	...	...	Group A
1459	0.574	...	...	...	Group A
1452[b]	0.771	0.132	0.058	...	Group A
1445	0.095	0.368	0.263	...	
1435	0.105	0.021	...	...	Group A
1404	0.145	...	...	...	Group A
1394	0.283	...	...	...	Group A
1389[b]	0.275	...	...	...	Group A
1340	0.147	...	...	...	Group A
1324	0.475	...	...	...	Group A
1320	0.295	...	...	...	Group A
1215	...	0.134	0.081	0.038	Group B
1210	0.059	0.170	0.123	0.070	Group B[e]
1184	0.210	...	...	0.011	Group A
1178	0.224	...	...	0.019	Group A
1162	0.404	...	...	...	Group A
1066	0.089	0.348	0.255	0.133	C_2D_4
1056	0.097	...	...	...	Group A
984	0.064	...	...	...	
972	0.313	...	...	...	Group A
970	0.340	...	...	...	Group A
966	0.116	...	...	...	Group A
951	0.084	...	...	...	
944	0.238	...	...	...	Group A
938	0.115	...	...	...	CD_3CCD
930	0.157	...	...	...	Group A
922	0.080	...	...	...	
848	0.239	...	...	...	Group A
829	0.118	0.326	0.019	...	Group B
822	0.961	...	...	...	Group A
815	c	0.442	0.211	...	Group A
800	0.308	...	...	...	Group A
797	0.200	...	...	...	Group A
794	0.588	...	...	...	Group A
791	0.289	0.179	0.129	...	Benzyne-d_4
780	0.189	0.036	...	...	Group A
773	0.079	0.653	0.554	0.276	Group B

(continued)

TABLE 3. (continued)

Band (cm^{-1})	Absorbance				Assignment[f]
	Ar/C_6D_6 250:1	500:1	1000:1	2000:1	
753	...	0.063	0.163	0.014	Group B
732	0.066	0.261	0.166	0.077	Group B
727	...	0.258	0.192	0.094	C_2D_4
715	...	0.197	0.130	0.063	Group B
713	0.122	0.154	0.113	0.060	Group B
656	0.157	0.228	0.121	0.085	Group B
654	...	0.118	...	...	
652	0.174	0.070	...	...	
611	0.609	0.329	0.087	...	Group A
600	0.100	...	...	...	Group A
578	0.229	...	...	...	Benzyne-d_4
529	0.444	0.071	0.035	...	Group A
518	1.317	0.036	...	...	C_6D_5·
493	c	0.173	0.100	...	CD_3CCD
489	c	0.905	0.647	...	CD_3CCD
487	c	1.068	0.820	0.408	CD_3CCD
474	...	0.100	0.025	...	Benzyne-d_4
458	...	0.106	0.110	0.109	Group B
411	0.154	0.107	...	...	

[a]Samples were irradiated during deposition.
[b]Present in blank experiments.
[c]Overlap with parent band.
[d]Group A, bands associated with C_6D_6 isomers (see text).
[e]Group B, bands associated with C_6D_6 fragments (see text).
[f]See text for references used in making assignments.

the gas phase, liquid and solid state photochemistry of benzene at a variety of wavelengths and provide guidance as to possible products. In general, isomerization and fragmentation channels are likely; isomers include fulvene, benzvalene, prismane and Dewar benzene. Comparison with literature spectra [20–23] for these isomeric species leads to the conclusion that all are formed, although the relative yield varied with the isomer and the experimental conditions. This comparison with the literature leads to the assignments made to these four species in Tables 1 and/or 2. Fragmentation may occur as well, and again previous studies provide assistance in identifying possible fragment products. Literature spectra [24–32] are known for many of the stable (non-radical) species and thus assignment of a number of bands to the following species is made in Tables 1 and/or 2: benzyne (C_6H_4), propyne ($CH_3C\equiv CH$), 1,3-butadiyne ($HC\equiv C-C\equiv CH$), hexatriyne (triacetylene, $HC\equiv C-C\equiv C-C\equiv CH$), ethyne ($HC\equiv CH$), ethyne dimer (($HC\equiv CH)_2$) and ethene ($H_2C=CH_2$). A weak band was present at 708 cm^{-1} in many of the C_6H_6 experiments, particularly at higher concentration. This band position coincides very well with

TABLE 4. Product bands following excimer laser irradiation of $Ar/C_6H_6/Cl_2$ samples in argon matrices and behavior after mercury arc lamp irradiation[a]

Band (cm^{-1})	Absorbance				Assignment[e]
	$Ar/C_6H_6/Cl_2$ 250:1:1	Arc lamp[b]	250:1:2	Arc lamp	
3324	0.141	n/c	...	n/c	CH_3CCh
3319	0.282	n/c	0.153	n/c	CH_3CCH
3314	...	n/c	0.076	n/c	CH_3CCH
3304	...	n/c	0.022	n/c	C_2H_2
2866	...	n/c	0.062	n/c	HCl monomer
2837	...	n/c	0.022	n/c	HCl monomer
2818	...	n/c	0.035	n/c	HCl monomer
2795	...	n/c	...	0.168	HCl polymer
2787	0.490	n/c	0.256	0.168	HCl polymer
2777	0.519	n/c	0.260	0.183	HCl polymer
2766	0.261	n/c	0.145	n/c	HCl polymer
2740	0.301	n/c	0.173	n/c	HCl polymer
2340	0.470	n/c	0.605	n/c	CO_2
2137	0.307	n/c	0.399	n/c	CO
2120	0.226	n/c	0.242	n/c	CH_3CCH
1889	0.105	n/c	0.167	n/c	Biphenyl
1887	0.081	n/c	0.138	n/c	Biphenyl
1599	0.242	n/c	0.363	n/c	
1593	0.463	n/c	0.400	n/c	
1584	0.751	n/c	0.449	n/c	Biphenyl
1579	0.211	n/c	0.316	n/c	o-, m-$C_6Cl_2H_4$
1467	0.111	n/c	0.291	n/c	m-$C_6Cl_2H_4$
1459	0.628	n/c	1.105	n/c	o-$C_6Cl_2H_4$
1453	...	n/c	0.316	n/c	
1446	0.855	n/c	0.675	n/c	C_6H_5Cl
1443	...	n/c	...	0.437	C_6H_5Cl/biphenyl
1437	0.338	n/c	0.571	n/c	o-$C_6Cl_2H_4$
1424	0.105	n/c	0.176	0.253	m-$C_6Cl_2H_4$
1422	0.063	n/c	0.194	0.247	m-$C_6Cl_2H_4$
1392[c]	0.496	n/c	0.434	n/c	p-$C_6Cl_2H_4$/biphenyl
1349[c]	...	n/c	0.295	n/c	
1135	0.100	n/c	0.174	n/c	o-$C_6Cl_2H_4$
1128	0.253	n/c	0.456	n/c	o-$C_6Cl_2H_4$
1124	0.399	n/c	0.371	n/c	
1117	0.164	n/c	0.119	n/c	
1107	0.111	n/c	0.213	n/c	p-$C_6Cl_2H_4$
1090	2.142	n/c	3.030	n/c	p-$C_6Cl_2H_4$/biphenyl
1073	0.116	0.095	0.176	0.116	
1068	0.405	n/c	0.178	0.189	C_6H_5Cl
1048	0.141	0.116	0.073	0.014	
1039[c]	1.053	n/c	0.900	0.884	o-$C_6Cl_2H_4$/biphenyl
1023	0.954	n/c	0.576	n/c	C_6H_5Cl
1014	1.184	n/c	1.658	n/c	p-$C_6Cl_2H_4$/biphenyl
1006	0.131	n/c	0.218	n/c	
1002	0.166	n/c	0.061	n/c	C_6H_5Cl
901	0.116	n/c	0.066	n/c	C_6H_5Cl
888	0.028	n/c	0.064	n/c	
861	0.039	n/c	0.100	n/c	
848	...	0.178	...	0.106	C_6H_6
844	0.338	n/c	0.221	0.113	Benzyne
841	0.175	0.130	0.137	n/c	Benzyne
829	0.201	n/c	...	n/c	C_6H_5Cl
820	1.011	n/c	2.234	n/c	p-$C_6Cl_2H_4$
804	0.046	n/c	0.122	n/c	
788	0.060	n/c	0.090	n/c	m-$C_6Cl_2H_4$
752	0.921	n/c	0.995	n/c	o-$C_6Cl_2H_4$

(*continued*)

TABLE 4. *(continued)*

Band (cm^{-1})	Absorbance				Assignment[e]
	Ar/C$_6$H$_6$/Cl$_2$ 250:1:1	Arc lamp[b]	250:1:2	Arc lamp	
740	7.163	n/c	1.415	n/c	C$_6$H$_5$Cl/biphenyl
734	0.767	0.695	0.433	0.172	Benzyne
722	0.079	n/c	0.500	0.267	
718	...	n/c	0.316	0.479	
716	0.063	n/c	0.400	0.479	
711	0.041	n/c	0.232	0.363	C$_6$H$_5$·
704[c]	1.438	n/c	0.824	n/c	C$_6$H$_5$Cl
685[c]	d	n/c	0.984	1.000	C$_6$H$_5$Cl/biphenyl
678[c]	d	n/c	0.737	n/c	Biphenyl
675	d	n/c	0.805	0.616	
661	0.227	n/c	0.429	n/c	o-C$_6$Cl$_2$H$_4$/biphenyl
653	0.124	n/c	0.111	n/c	
640	0.105	n/c	0.051	n/c	CH$_3$CCH
625	0.231	n/c	0.134	n/c	CH$_3$CCH
615	0.126	n/c	0.079	n/c	CH$_3$CCH
610	0.083	n/c	0.048	n/c	Biphenyl
550	1.095	n/c	1.743	n/c	p-C$_6$Cl$_2$H$_4$
546	0.791	n/c	1.369	n/c	Biphenyl
542	0.202	n/c	0.356	n/c	Biphenyl
538	0.740	0.321	0.247	0.095	
486	0.419	n/c	0.942	n/c	p-C$_6$Cl$_2$H$_4$/biphenyl
473	...	0.374	0.104	0.300	C$_6$H$_5$Cl
469	0.694	0.773	0.285	0.374	C$_6$H$_5$Cl/benzyne
460	0.361	0.266	0.138	0.035	
417	0.286	0.258	0.121	0.068	
411	0.136	0.094	0.095	n/c	C$_6$H$_5$Cl

[a]All samples were excimer laser irradiated during deposition.
[b]Band intensity following H$_2$O-filtered Hg arc irradiation, where n/c indicates no change in intensity.
[c]Some parent absorption noted at this position in blank experiments, but growth at these positions indicates underlying product band.
[d]Overlap with fundamental.
[e]See text for references used in making assignments.

the most intense absorption [33] of the phenyl radical C$_6$H$_5$·. This species is a potential photo-product in this system, and while product identification is difficult on the basis of one band, such an assignment is certainly plausible. As can be seen in these two tables, nearly all the product bands are accounted for and assigned; only one weak band remains in Table 2. It is also noteworthy that all bands (except the weak 708 cm^{-1} absorption) are assigned to closed-shell species, so that although radicals are formed first in collision-free molecular beam studies, recombination and further reactions dominate during matrix deposition.

Tables 1 and 2 represent C$_6$H$_6$ irradiation experiments under quite similar conditions, except for sample concentration. Table 1 describes an experiment conducted with Ar/C$_6$H$_6$ = 250, while Table 2 describes experiments with Ar/C$_6$H$_6$ = 1000 and 2000. It is important to note that the relative

yield of isomerization products to fragmentation products was a sensitive function of sample concentration. As the intensities listed in Tables 1 and 2 show, isomerization products dominated in more concentrated experiments, while fragmentation was relatively more important in more dilute experiments. While possible explanations for this observation will be discussed below, the fact that it occurred is needed to help in the assignment of the products in the C$_6$D$_6$ experiments.

In a manner similar to the C$_6$H$_6$ experiments, product bands in the C$_6$D$_6$ irradiation experiments could readily be sorted into two groups based on concentration dependence. Group A had decreasing intensities with decreasing sample concentration, while group B showed increasing intensity with decreasing sample concentration. In the C$_6$H$_6$ experiments, group A bands were assigned to the four isomerization products, while group B bands were identified as fragmentation products. A sim-

TABLE 5. Product bands following excimer laser irradiation of $Ar/C_6D_6/Cl_2$ samples in argon matrices[a]

Band (cm⁻¹)	Absorbance					Assignment[d]
	$Ar/C_6D_6/Cl_2$ 250:1:0.25	250:1:0.50	250:1:1	250:1:2	500:1:1	
2594	0.182	0.427	0.100	0.537	0.310	CD_3CCD/D $(C\equiv C)_2D$
2338	0.126	...	...	0.153	0.168	C_2D_4
2135	0.126	0.020	0.019	0.068	0.105	CO
2014	...	0.389	...	0.595	0.177	Polymer DCl
2004	...	0.274	...	0.319	0.131	Polymer DCl
1995	...	0.288	...	0.351	0.156	Polymer DCl
1989	...	0.393	0.354	0.515	0.206	
1971	...	0.258	...	0.361	0.127	
1568	...	0.126	0.273	0.182	0.057	$C_{12}D_{10}$
1563	...	0.149	0.328	0.268	0.085	$C_{12}D_{10}$
1558	...	0.126	0.389	0.213	...	
1546	...	0.210	0.609	0.402	0.122	$o\text{-}C_6Cl_2D_4$
1367	0.061	0.552	0.389	1.568	0.312	$p\text{-}C_6Cl_2D_4$
1361	0.096	0.114	0.137	0.422	0.044	$o\text{-}C_6Cl_2D_4$
1348	0.170	0.473	1.519	1.113	0.220	$C_{12}D_{10}$
1315	...	0.048	0.175	0.213	0.020	$o\text{-}C_6Cl_2D_4$
1131	0.095	...	...	...	...	
1111	0.166	0.076	0.102	0.037	0.035	
1041	0.045	0.350	0.860	0.701	0.147	CD_3CCD
1033	0.053	...	0.603	...	...	
1028	0.058	0.266	...	1.013	0.116	$o\text{-}C_6Cl_2D_4$
1020	...	0.126	...	0.302	0.075	$p\text{-}C_6Cl_2D_4$
1014	0.097	0.294	0.330	1.290	0.168	$p\text{-}C_6Cl_2D_4$
1005	...	0.028	...	0.116	0.023	
992	...	0.119	0.081	0.225	0.057	D $(C\equiv C)_2D$
959	...	...	0.138	0.046	...	C_6D_5Cl
888	0.063	0.080	0.030	0.096	0.038	
867[b]	0.316	0.126	0.432	0.095	0.068	
749	0.084	0.103	0.200	0.268	0.047	C_6D_5Cl
747	0.095	0.092	0.200	0.284	0.041	C_6D_5Cl
722	0.252	0.223	0.097	1.107	0.221	C_2D_4
710	...	...	0.184	...	...	
694[b]	...	0.274	0.163	0.626	0.121	$p\text{-}C_6Cl_2D_4$
671	0.042	0.277	0.795	0.554	0.101	$C_6D_5Cl/C_{12}D_{10}$
587	0.023	0.031	0.145	0.171	0.016	$o\text{-}C_6Cl_2D_4$
569	0.051	0.313	0.108	0.529	0.095	$o\text{-}C_6Cl_2D_4$
545	0.154	0.558	1.587	0.794	0.230	$C_2D_2/C_{12}D_{10}$
533	0.221	0.368	0.297	0.838	0.131	$p\text{-}C_6Cl_2D_4$
525	...	0.059	...	0.152	...	
513[b]	0.568	0.416	0.753	0.368	0.211	
508	[c]	0.368	[c]	0.376	[c]	
493	1.347	0.442	[c]	0.326	0.239	CD_3CCD
488	1.240	0.679	[c]	0.453	0.411	CD_3CCD/D $(C\equiv C))_2D$
486	sh	0.837	[c]	0.589	0.584	
476	0.102	0.089	...	0.133	...	D $(C\equiv C)_2D$
465	0.082	0.115	0.251	0.165	...	Benzyne-d_4
462	...	0.245	0.221	0.294	0.165	$C_{12}D_{10}$
457	0.070	0.537	0.113	0.832	0.249	$C_{12}D_{10}$
417	...	0.192	...	0.529	0.071	$C_{12}D_{10}$
413	0.408	0.242	0.589	0.447	0.112	$C_{12}D_{10}$
401	0.053	0.051	0.046	0.050	0.039	$C_{12}D_{10}$

[a]All samples were irradiated during deposition.
[b]Some intensity was noted at this position in blank experiments, but growth in experiments employing laser irradiation indicates underlying product band.
[c]Overlap with parent band.
[d]See text for references used in making assignments.
sh, Shoulder.

ilar assignment of the two groups for the C_6D_6 products is reasonable, although the IR spectra of many of the possible products have not been reported. Specifically, no IR spectra are known for the four isomerization products, so specific assignments cannot be made. However, IR spectra are known for several of the possible fragmentation products [26–28, 31, 34]. As noted in Table 3, a number of the bands in group B match well-known absorptions of $CD_3C\equiv CD$, $DC\equiv C-C\equiv CD$, C_6D_4 and $D_2C=CD_2$ and are so assigned. These assignments provide confirmation that group B bands are due to fragmentation products and further support the suggestion that group A bands are due to isomerization products. However, without independent synthesis and spectral assignment for each isomer, assignment of group A bands to individual isomeric species cannot be made at this time. One band, at 518 cm^{-1}, agrees very well with the most intense absorption [33] of the fully deuterated phenyl radical $C_6D_5^{\cdot}$ and is so assigned.

While doping Ar/C_6H_6 samples with CCl_4 led to no new product species, irradiation of $Ar/C_6H_6/Cl_2$ samples led to many new IR absorptions. Most of these did *not* match those observed in the undoped experiments: no isomerization products were observed and only a few weak bands due to fragmentation products. Specifically, propyne and benzyne were definitely observed as fragments and a weak band at 3304 cm^{-1} may be assigned to monomeric ethyne. However, many of the bands can be assigned to known, stable species. HCl has been trapped in matrices on many occasions and the monomer and several aggregate species identified [35]. As noted in Table 4, HCl was certainly a product in these experiments. Additional products may be assigned by comparison with the literature, including chlorobenzene (C_6H_5Cl) [36], ortho- and para-dichlorobenzene [37], a small amount of meta-dichlorobenzene [37] and biphenyl [38].

Additional bands were observed in these $Ar/C_6H_6/Cl_2$ experiments that decreased or were destroyed by Hg arc irradiation. In previous matrix studies [39] this photosensitivity has been due either to the presence of an extremely unstable intermediate species or to the presence of a cation. (Hg arc irradiation of electron traps has been shown to release electrons which may then neutralize trapped cations, destroying the cation spectrum.) The latter situation has been much the more common occurrence. As noted in Table 4, three of the bands that were reduced but not completely destroyed may be assigned to benzyne.

A number of photosensitive bands remain, at 417, 460, 538, 675, 1048 and 1073 cm^{-1}. Many candidates might be envisioned; the most likely include the $C_6H_6^+$ radical cation, the 1-chloro-cyclohexadienyl radical and a σ complex, $C_6H_6Cl^+$. The first alternative, $C_6H_6^+$, has been seen in low temperature experiments and might be anticipated here. However, it is hard to understand why this species would form when Cl_2 was used as the electron trap and not CCl_4. Thus, although a candidate, $C_6H_6^+$ seems less likely than other options. Jacox [40] has investigated the reaction of F atoms with C_6H_6 and reported trapping of the 1-fluorocyclohexadienyl radical. This species should have many vibrations quite similar to the 1-chlorocyclohexadienyl radical, yet the photosensitive bands here did not match at all well absorptions attributed to 1-fluorocyclohexadienyl. Thus this candidate is not particularly likely. Walters et al. [41] have postulated the formation of a σ complex, $C_6H_6Cl^+$, in the gas phase as an intermediate in the photo-ionization of van der Waals complexes. While the IR spectrum of this cation is not readily predicted, the fact that primarily ortho- and para-dichlorobenzene were observed in these experiments with only small amounts of meta-dichlorobenzene provides support for the σ complex. It is well known [42] that electron-donating substituents control the orientation of a second substituent. In particular, a chlorine substituent is ortho–para directing, in agreement with the observation here of primarily ortho- and para-dichlorobenzene. Nonetheless, this evidence is insufficient to definitively assign some or all of these bands to the σ complex, although it appears to be a likely candidate. Indeed, intensity ratios suggest that there may be more than one photosensitive product, but band overlap prevents a firm conclusion on this point.

The excimer laser irradiation of samples of $Ar/C_6D_6/Cl_2$ did not yield as many new product bands as had the $Ar/C_6H_6/Cl_2$ experiments. As can be seen in Table 5, several fragmentation products were observed, including C_6D_4, $DC\equiv C-C\equiv CD$, $CD_3C\equiv CD$ and $D_2C=CD_2$. In addition, new product bands were seen that can be assigned by comparison with the literature to DCl, DCl aggregates [35], C_6D_5Cl [43], ortho- and para-dichlorobenzene-d_4 [37] and biphenyl-d_{10} [38]. These are entirely consistent with the products observed in the C_6H_6/Cl_2 experiments. A few bands remain unassigned in Table 5; these may be due to isomers of C_6D_6, but cannot readily be assigned as such, since spectra of the deuterated isomers are not available.

4.2. Mechanism of product formation

One-electron excitation from the highest filled molecular orbital ($1e_{1g}$) to the lowest empty molecular orbital ($1e_{2u}$) of benzene leads to six different electronic states: $^{1,3}B_{2u}$, $^{1,3}B_{1u}$ and $^{1,3}E_{1u}$. The three singlet states have been located experimentally near 4.96, 5.95 and 7.07 eV (corresponding to excitation wavelengths of 250, 208 and 175 nm respectively) [44]. 193 nm excimer laser excitation populates the $^{1}B_{1u}$ or S_2 state of benzene. Previous studies have measured the lifetime of S_2 to be 20 ps and found [45] the relaxation rate of S_2 to lower electronic states to be 25 times faster than the transition rate between S_2 and ionization to $C_6H_6^+$. This too argues against formation of $C_6H_6^+$, particularly when the matrix environment is expected to enhance relaxation rates. Nakashima and Yoshihara [4, 5] have proposed a "hot molecule" mechanism for the formation of fulvene from benzene after 193 nm laser excitation. In this mechanism, molecules initially excited to S_2 undergo very rapid internal conversion to high vibrational states of S_0, from which fulvene is formed.

An unusual finding of the current study is that the product distribution is a distinct function of sample concentration, with a sample concentration $Ar/C_6H_6 = 250$ leading primarily to fulvene and isomerization products and a sample concentration $Ar/C_6H_6 = 2000$ leading primarily to fragmentation. In that sense the high concentration experiments behave similarly to the earlier studies of neat liquid benzene [3] and the low concentration experiments mimic the gas phase results [1, 2]. This is surprising in the sense that these are very low temperature, dilute systems and the change occurs over a relatively small concentration range. The competition between isomerization and fragmentation may rest with the rate at which energy can be removed from the excited species. At a lower rate of energy loss the molecule stays in more highly excited states longer and may undergo fragmentation and separation of the product fragments. At a higher rate of energy loss the molecule relaxes rapidly and undergoes isomerization. Argon, of course, is present in great excess but must be very inefficient in the relaxation process. However, increasing the concentration of C_6H_6 increases the number of collisions between $C_6H_6^*$ and ground state C_6H_6. These collisions must be very effective in relaxing the excited molecule below the threshold for fragmentation, so that isomerization competes effectively. It is also interesting to note that although benzvalene and fulvene are both present in reduced amount in the low concentration experiments,

Dewar benzene is totally absent. This is in agreement with the matrix isolation study of van der Zwet *et al.* [7], where a concentration $Ar/C_6H_6 = 10\,000$ was employed. It is not clear why this would be the case, but it suggests that a second benzene molecule may be required for the formation of Dewar benzene.

The mechanism of formation of the products in the Cl_2-doped experiments is of interest as well. A 193 nm photon has sufficient energy to dissociate a Cl_2 molecule into two Cl atoms, with considerable excess energy. The newly formed Cl atom may either undergo addition to the ring, forming the chlorohexadienyl radical, or abstract a hydrogen to form HCl and a phenyl radical. Jacox [40] observed precisely this first reaction when F atoms reacted with C_6H_6 during matrix deposition. As noted above, definitive assignment of product bands to C_6H_6Cl could not be made, but this avenue cannot be ruled out. H atom abstraction would form HCl, which was seen in high yield, and the phenyl radical. While only weak evidence was obtained for the phenyl radical in these experiments, the yield of biphenyl was large and its production probably comes from the radical recombination of two phenyls. Thus hydrogen atom abstraction by a photogenerated Cl atom can account for the significant yield of biphenyl.

Chlorine atom reactions cannot as readily account for the formation of the mono- and dichlorobenzene products, although the addition of a second Cl atom to a phenyl radical would lead to C_6H_5Cl. An alternative mechanism involves initial formation of a weak complex between Cl_2 and C_6H_6 during the deposition process. These complexes have been suggested for years to be intermediates in the electrophilic substitution reactions of benzene [46]. Direct spectroscopic evidence for complexes of molecular halogens with benzene and other π electron donors has been obtained in a number of instances [46–50]. Absorption of a 193 nm photon by this complex may lead to monochlorobenzene directly or through formation of a σ complex as proposed by Walters *et al.* [41]. Formation of dichlorobenzene probably arises from the photolytically induced reaction of C_6H_5Cl with a second Cl_2 molecule, again with the possible intermediacy of a molecular complex. While a sequence of steps all involving Cl atoms and leading to dichlorobenzene could be envisioned, this would require a minimum of four two-body steps. In comparison, reactions involving Cl_2 and a molecular complex with C_6H_6 could lead to dichlorobenzene in as few as two bimolecular steps. Since matrix deposition and freezing occur

very rapidly, a mechanism with as few steps as possible is generally the more likely pathway. Nonetheless, formation of biphenyl very probably occurs via Cl atom reactions as discussed above. In either case it is not surprising that an increase in the Cl_2/C_6H_6 ratio led to an increase in $C_6H_4Cl_2$ relative to C_6H_5Cl.

Acknowledgment

References

1 J.E. Wilson and W.A. Noyes, Jr., *J. Am. Chem. Soc.*, *63* (1941) 3025.
2 L. Kaplan and K.E. Wilzbach, *J. Am. Chem. Soc.*, *89* (1967) 1030.
3 H.R. Ward and J.S. Wishnok, *J. Am. Chem. Soc.*, *90* (1968) 1085.
4 N. Nakashima and K. Yoshihara, *Stud. Org. Chem. (Amsterdam)*, *31* (1987) 523–528.
5 N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, *79* (1983) 2727.
6 A. Yokoyama, X. Zhao, E.J. Hintsu, R.E. Continetti and Y.T. Lee, *J. Chem. Phys.*, *92* (1990) 4222.
7 G.P. van der Zwet, M.S. de Groot, F. Baas and J.M. Greenberg, *NATO ASI Ser. C*, *191* (1987) 183–195.
8 D.E. Johnstone and J.R. Sodeau, *J. Phys. Chem.*, *95* (1991) 165.
9 T. Shida and W.H. Hamill, *J. Chem. Phys.*, *44* (1966) 2375.
10 J.H. Miller, L. Andrews, P.A. Lund and P.N. Schatz, *J. Chem. Phys.*, *73* (1980) 4932.
11 J.H. Miller and L. Andrews, *Chem. Phys. Lett.*, *72* (1980) 90.
12 N.P. Machara and B.S. Ault, *J. Chem. Phys.*, *88* (1988) 2845.
13 N.P. Machara and B.S. Ault, *J. Phys. Chem.*, *93* (1989) 1908.
14 B.S. Ault, *J. Am. Chem. Soc.*, *100* (1978) 2426.
15 N.P. Machara and B.S. Ault, *J. Phys. Chem.*, *92* (1988) 6241.
16 L. Fredin and B. Nelander, *Mol. Phys.*, *4* (1974) 885.
17 L. Andrews, G.L. Johnson and R.S. Davis, *J. Phys. Chem.*, *89* (1985) 1706.
18 M. Spoliti, S. Nunziante Cesaro and V. Grosso, *Spectrochim. Acta A*, *32* (1976) 145.
19 K.G. Brown and W.B. Person, *Spectrochim. Acta A, 34* (1978) 117.
20 R.D. Brown, P.J. Domaille and J.E. Kent, *Aust. J. Chem.*, *23* (1970) 1707.
21 P.J. Domaille, J.E. Kent and M.F. O'Dwyer, *Aust. J. Chem.*, *27* (1974) 2463.
22 W.T. Griffith, J.E. Kent and M.F. O'Dwyer, *Aust. J. Chem.*, *28* (1975) 1397.
23 T.J. Katz and N. Acton, *J. Am. Chem. Soc.*, *95* (1973) 2738.
24 O.L. Chapman, C.C. Chang, J. Kole, N.R. Rosenquist and H. Tomioka, *J. Am. Chem. Soc.*, *97* (1957) 6586.
25 O.L. Chapman, K. Mattes, C.L. McIntosh, J. Pacansky, G.V. Calder and G. Orr, *J. Am. Chem. Soc.*, *95* (1973) 6134.
26 I.R. Dunkin and J.G. MacDonald, *J. Chem. Soc., Chem. Commun.* (1979) 772.
27 J.G. Radziszewski, B. Andes Hess, Jr. and R. Zahranik, *J. Am. Chem. Soc.*, *114* (1992) 52.
28 N.L. Owen, C.H. Smith and G.A. Williams, *J. Mol. Struct.*, *161* (1987) 33.
29 B. Jarnov, D.H. Christensen, O.F. Nielsen, E. Augdahl, E. Kloster-Jensen and A. Rogstad, *Spectrochim. Acta A, 30* (1974) 1255.
30 D.J. Hucknall and J.V. Shepherd, *Spectrosc. Lett.*, *7* (1974) 381.
31 M.E. Jacox and D.E. Milligan, *Chem. Phys.*, *4* (1974) 45.
32 A.J. Barnes and J.D.R. Howells, *J. Chem. Soc., Faraday Trans. 2*, *69* (1973) 532.
33 M.E. Jacox, *J. Phys. Chem.*, *86* (1982) 670.
34 G. Herzberg, *Molecular Spectra and Molecular Structure II: Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, New York, 1945, p. 326, Table 92.
35 L.F. Keyser and G.W. Robinson, *J. Chem. Phys.*, *44* (1966) 3225.
36 D.H. Whiffen, *J. Chem. Soc.*, *6* (1956) 1350.
37 J.R. Scherer and J.C. Evans, *Spectrochim. Acta*, *19* (1963) 19.
38 J.R. Katon and E.R. Lippincott, *Spectrochim. Acta*, *11* (1959) 627.
39 L. Andrews, *Ann. Rev. Phys. Chem.*, *30* (1979) 79.
40 M.E. Jacox, *J. Phys. Chem.*, *86* (1982) 670.
41 E.A. Walters, J.R. Grover, M.G. White and E.T. Hui, *J. Phys. Chem.*, *91* (1987) 2758.
42 J.D. Roberts and M.J. Caserio, *Basic Principles of Organic Chemistry*, Benjamin, Menlo Park, CA, 2nd edn., 1977, p. 1063.
43 H.J.K. Koser, *Spectrochim. Acta A*, *40* (1984) 117.
44 G. Nordheim, H. Sponer and E. Teller, *J. Chem. Phys.*, *8* (1940) 455.
45 J.P. Reilly and K.L. Kompa, *J. Chem. Phys.*, *73* (1980) 5468.
46 R.S. Mulliken, *J. Am. Chem. Soc.*, *72* (1950) 600.
47 R.S. Mulliken, *J. Chem. Phys.*, *23* (1955) 397.
48 J. Collin and L. D'Or, *J. Chem. Phys.*, *23* (1955) 397.
49 L. Fredin and B. Nelander, *J. Am. Chem. Soc.*, *96* (1974) 1672.
50 H. Bai and B.S. Ault, *J. Phys. Chem.*, *94* (1990) 199.