PHOTOCHEMISTRY OF PHENYLCYCLOPROPANE[a]

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Summary

The 213.9 nm gas phase photolysis of phenylcyclopropane yields *cis*-1-phenylpropene, *trans*-1-phenylpropene and 3-phenylpropene as the principal products. The formation of these products is efficiently quenched by either neopentane or tetramethylsilane. Xenon is an inefficient quencher. The total product quantum yield as pressure tends to zero is found to be 0.25 ± 0.05. Since fluorescence is not observed, 75% of the absorbed photons are unaccounted for. The results of this study are discussed in terms of photochemical and photophysical mechanisms for aromatic hydrocarbons.

1. Introduction

Photophysical and photochemical studies of aromatic hydrocarbons under "isolated molecule" conditions have resulted in an intriguing question. A general finding for many aromatic hydrocarbons is an abrupt decrease in the fluorescence quantum yield at a certain energy in excess of the $S_0 \rightarrow S_1$ 0–0 band [1 - 8]. For benzene the cut-off in fluorescence occurs at about 3300 cm^{-1} in excess of the 0–0 band, and fluorescence is not observed after excitation of higher vibrational levels in S_1 or of any levels in S_2 or S_3 [1 - 3]. Behavior similar to that found for benzene has also been observed in benzene derivatives [8] and polycyclic aromatics [4 - 6]. Since the radiative rate is relatively constant, the abrupt decrease in the fluorescence quantum yield results from a sudden rise in the non-radiative rate. For benzene the non-radiative pathway causing the abrupt increase in the non-radiative rate has been referred to as "channel 3" [1, 2]. Whether the non-radiative path

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that predominates over fluorescence is the same for all aromatic hydrocarbons is an interesting and open question.

It has been suggested that the abrupt increase in the non-radiative rates of benzene [9, 10] and other aromatic hydrocarbon molecules [4, 11] is due to $S_1 \to S_0$ internal conversion. From theoretical calculations it is argued that internal conversion has a much greater excess energy dependence than does intersystem crossing, and beyond a certain threshold energy internal conversion predominates over $S_1 \to T$ intersystem crossing [11]. In a recent photophysical study of naphthalene, direct evidence has been found for the formation of S_0 from highly excited S_1 [12]. However, the process is not direct $S_1 \to S_0$ internal conversion, but is a double intersystem crossing process or a triplet assisted internal conversion, *i.e.* $S_1 \to T \to S_0$.

In the work reported here we have studied the photochemistry of phenylcyclopropane in the far ultraviolet using a zinc resonance lamp, with effective radiation at 213.9, 206.1 and 202.5 nm, and with approximately 75% of the photons emitted at 213.9 nm. The π, π^* transition in this region is allowed and is to the second excited singlet state S_2. Phenylcyclopropane does not fluoresce when excited into S_2 [6]. Decomposition of ground state phenylcyclopropane (S_0) yields 3-phenylpropene, *cis*-1-phenylpropene and *trans*-1-phenylpropene as the principal products [13]. 3-Phenylpropene, *trans*-1-phenylpropene and *cis*-1-phenylpropene constitute 84% of the decomposition products where more than 90% of the starting materials is recovered as volatile products. The total yield of volatile compounds is less than 100% because of polymerization. Therefore, if S_0 is formed by the radiationless decay of S_2 (*i.e.* either $S_2 \to S_1 \to S_0$ or $S_2 \to S_1 \to T_1 \to S_0$) [4 - 6], a total quantum yield of near unity is expected for formation of the above three phenylpropenes.

The photochemistry of phenylcyclopropane has been studied previously at 253.7 nm [14]. *cis*-1-Phenylpropene, *trans*-1-phenylpropene and 3-phenylpropene, all isomers of phenylcyclopropane were found to be the principal products. Styrene was formed in very small amounts. Neither indane or 2-phenylpropene, also isomers of phenylcyclopropane, were observed as products. The total product quantum yield at 31 °C was found to be 0.64 as pressure tended to zero. The fluorescence quantum yield is 0.33 which gives an energy balance at 253.7 nm. A fluorescence quantum yield of 0.23 is reported for cyclopropylbenzene at 253.7 nm [14]. This is based upon a fluorescence quantum yield of 0.22 for 1 Torr of benzene. The benzene fluorescence quantum yield under these conditions is 0.32 instead of 0.22 [15].

2. Experimental method

2.1. Materials

Phenylcyclopropane, 98% pure, was purchased from Chemical Samples Co. and was purified by gas liquid phase chromatography. The chromato-

graphic column used is described later. By comparison with samples purchased from Pfaltz and Bauer, Inc., the impurities in the cyclopropylbenzene were found to be 3-phenylpropene, 2-phenylpropene and *cis*- and *trans*-1-phenylpropene. Neopentane and tetramethylsilane, both 99% pure, were purchased from Matheson Gas Products and Merck, Sharp and Dohme, respectively, and were used as quenching gases. Xenon (99.995% pure) was purchased from Cryogenic Gas Supply and was also used as a quenching gas. Nitrous oxide (98% pure, Matheson Gas Products) and propylene (99% pure, Air Products and Chemicals, Inc.) were used in the actinometry experiments.

2.2. Apparatus

The experimental apparatus consisted of two high vacuum systems, a photolysis system, and a gas chromatograph. Each of these is described below.

One of the high vacuum systems was used for loading the photolysis cells. It consisted of a vacuum pump, an air-cooled single stage oil diffusion pump, a liquid nitrogen cold trap and two vacuum gauges. One of the gauges, a Veeco combination discharge and thermocouple gauge, was used to measure the background pressure of the system (about 1×10^{-5} Torr). The second gauge, an MKS Tru-Torr vacuum gauge which measures absolute pressure from 0.00 to 8.00 Torr, was used for measuring pressures inside the photolysis cells . The part of the vacuum system used for loading the photolysis cells was isolated from the rest of the system by Teflon stopcocks to avoid any absorption into stopcock grease.

The second high vacuum system was used for the actinometry experiments. Its construction is standard and consists of a two-stage mercury diffusion pump, a McCleod gauge, a mercury manometer and a Toepler pump with gas burette. The mercury manometer was incorporated into a greaseless loading volume. The Toepler pump and gas burette were used to determine yields of non-condensable gases at 77 K.

The experiments were performed in three different cylindrical quartz vessels with flat Suprasil end windows. The volumes and lengths of these three cells are: 61 cm^3 and 4.7 cm; 180 cm^3 and 9.0 cm; 815 cm^3 and 30.1 cm. Each of these cells had a small cold finger for introducing the gases.

The total spectrum of a 25 W Phillips zinc lamp was passed through the photolysis cells. The spectral lines absorbed by phenylcyclopropane were at 279.5, 276.5, 270.5, 260.5, 213.9, 206.1 and 202.5 nm. However, the effective radiation was at 213.9, 206.1 and 202.5 nm since these lines are the most intense and the phenylcyclopropane extinction coefficients are about 50 times larger between 200 and 230 nm than above 230 nm. The 206.1 and 202.5 lines were about 6 times less intense than the 213.9 nm line. The extinction coefficients are 6684, 5474 and 5083 $l \, mol^{-1} \, cm^{-1}$ at 213.9, 206.1 and 202.5 nm respectively. Since about 75% of the photons are absorbed at 213.9 nm, this wavelength will be used to denote the radiation in the following sections of this paper.

The intensities of the 213.9, 206.1 and 202.5 nm lines were measured during the course of an experiment using a Jarrell-Ash $\frac{1}{4}$ m monochromator

and a Hamamatsu R 446 photomultiplier tube. The power supply used with the photomultiplier tube was an Oriel model no. 7020 (0 - 2000 V). The output current from the photomultiplier tube was measured with a Keithley 610 B electrometer.

The change in lamp intensity during the course of an experiment was always less than 1% for the photolyses of 30 min and shorter times. However, for the photolyses lasting up to 4 h the change in intensity was sometimes as large as 8%. The same lamp was used for all of the experiments and the flux at 213.9 nm for the new lamp was about 4.4×10^{15} photons s^{-1}. This flux slowly decreased as the lamp aged. At the conclusion of the experiments the flux was 1.2×10^{14} photons s^{-1}.

A Hewlett-Packard 5700 A gas chromatograph with thermal conductivity detector was used to purify the cyclopropylbenzene and to measure the photochemical product yields. A heated injection system was built to inject quantitatively the total contents of a cell after photolysis into the gas chromatograph. Two different columns were used to separate the products from the reactant phenylcyclopropane. The products styrene, 3-phenyl-propene and *trans*-1-phenylpropene were measured on a column of $\frac{3}{16}$ in o.d. and 10 ft long packed with 20% didecylphthalate on 80/100 Chromosorb W (acid washed). This column did not separate 2-phenylpropene and *cis*-1-phenylpropene. A column of $\frac{3}{16}$ in o.d. and 12 ft long packed with 5% SE-30 on 80/100 Chromosorb W (acid washed) was used to accomplish this separation. The gas chromatograph was calibrated by injecting known amounts of the products into the gas chromatograph and correlating the sample size with recorder response (peak height $\times$ retention time).

2.3. Actinometry

The calibration of the photolysis system was done using N_2O as an actinometer. Between 184.9 and 213.9 nm the photodissociation mechanism for N_2O is thought to be [16]

$$N_2O \quad + h\nu \rightarrow N_2 + O(^1D)$$
$$O(^1D) + N_2O \rightarrow N_2 + O_2 \tag{1}$$
$$O(^1D) + N_2O \rightarrow 2NO$$

The quantum yield for N_2 formation is 1.41 ± 0.03 at both 184.9 and 213.9 nm [17]. If sufficient propylene is added to scavenge the $O(^1D)$ atoms, nitrogen is the only non-condensable gas formed at 77 K and its quantum yield Φ_{N_2} is 1.00 [16]. A propylene to N_2O ratio of 2 at an N_2O pressure of 300 Torr was found to give $\Phi_{N_2} = 1.00$ [16] and these conditions were used in our actinometry experiments.

The actinometry experiments were performed in the 180 cm^3 cell. The experimental procedure involved loading 600 Torr of propylene and 300 Torr of N_2O into the cell, photolyzing this mixture and using a Toepler pump and gas burette to measure the amount of N_2 formed. Nitrous oxide only absorbs at the 213.9, 206.1 and 202.5 nm lines of the zinc resonance lamp.

The measured extinction coefficients are 1.09, 4.49 and 7.47 l mol^{-1} cm^{-1} at 213.9, 206.1 and 202.5 nm, respectively.

As a check on the calibration of the photolysis system using N_2O- propylene mixtures, three photolysis experiments were performed using pure N_2O. Here, the non-condensable gases are N_2 and O_2 with a total quantum yield of 1.82 ± 0.06 assuming NO does not react with O_2 [16, 17]. A reaction between NO and O_2 would make the total quantum yield less than 1.82, but greater than 1.41. For the three pure N_2O photolyses we measured quantum yields of 1.63, 1.66 and 1.66 which indicated that we had satisfactorily calibrated the photolysis system.

2.4. Procedure

The experiments were performed in sets of 3 - 4 photolyses. Each set was preceded and followed by an actinometry. The photolyses were performed at room temperature and the photolytic conversion of phenylcyclopropane was kept below 5%. All experiments were performed at room temperature (about 23 °C).

3. Results

3.1. Experimental measurements

Product quantum yields were measured in the following three pressure regimes: 0.01 - 0.1 Torr, 0.1 - 1.0 Torr and at pressures greater than 1.0 Torr. Styrene (sty), 3-phenylpropene (3-pp), trans-1-phenylpropene (t-pp), cis-1-phenylpropene (c-pp) and 2-phenylpropene (2-pp) were formed as products. Indane was looked for in the analysis but not observed. For the unresolved cis-1-phenylpropene and 2-phenylpropene, the abbreviation c+2-pp will be used.

The most accurate quantum yield measurements could be made in the 0.1 - 1.00 Torr regime, and these pressures were investigated first. The results are given in Table 1. Both the actinometry and the photochemistry experiments were performed in the 180 cm^3 cell. The trans-1-phenylpropene peak eluted on the tail of the phenylcyclopropane peak, which made the measurement of the trans-1-phenylpropene peak height difficult. Quantum yields are only reported for trans-1-phenylpropene when its peak height could be accurately measured. The quantum yields given in Table 1 show that 3-phenylpropene, cis-1-phenylpropene and trans-1-phenylpropene are the principal products. Styrene and 2-phenylpropene are formed in much smaller amounts.

Although the product quantum yields appear to be nearly constant between 0.1 and 1.0 Torr, the total product quantum yield is only about 0.25. Since a total product quantum yield of near unity is expected at the low pressure limit if the vibrationally excited ground state is being formed, quantum yield measurements were extended into the 0.01 - 0.1 Torr regime. The results are presented in Table 2. These experiments were performed in

TABLE 1

Product quantum yields between 0.1 and 1.0 Torr

Pressure (Torr)[a]	Photolysis time (min)	Φ_{sty}	$\Phi_{3\text{-pp}}$	$\Phi_{c+2\text{-pp}}$	$\Phi_{t\text{-pp}}$
cis-1-Phenylpropene and 2-phenylpropene unresolved					
1.00	30	0.014	0.087	0.049	0.038
1.00	10	0.006	0.089	0.070	–
1.00	10	0.005	0.092	0.065	–
1.00	10	0.005	0.073	0.047	–
0.79	30	0.015	0.10	0.054	0.051
0.49	30	0.014	0.11	0.059	0.056
0.37	30	0.014	0.10	0.044	0.048
0.33	15	0.010	0.11	0.055	0.055
0.20	30	0.020	0.12	0.055	0.048
cis-1-Phenylpropene and 2-phenylpropene resolved		$\Phi_{2\text{-pp}}/\Phi_{c\text{-pp}}$			
0.51	60	0.14			
0.48	45	0.15			
0.50	30	0.14			

[a]Pressure of phenylcyclopropane.

the 815 cm^3 cell and the lowest pressure at which we could still make quantum yield measurements was about 0.01 Torr. It was extremely difficult to make quantitative measurements of the $c+2$-pp quantum yields at pressures less than 0.1 Torr, since the $c+2$-pp peak height is very small and the calibration of the gas chromatograph is somewhat uncertain for small peak heights. Therefore, quantum yields are not reported for $c+2$-pp. However, the quantum yields did agree to within 50% of those listed in Table 1. The results presented in Tables 1 and 2 show that the product quantum yields become constant at about 1.0 Torr and lower pressures. The limiting value found for $\Phi_{3\text{-pp}}$ is 0.11 ± 0.01. Combining the results in Tables 1 and 2 gives a limiting low pressure total product quantum yield of 0.25 ± 0.05.

TABLE 2

Product quantum yields between 0.01 and 0.1 Torr

Pressure (Torr)[a]	Photolysis time (min)	Φ_{sty}	$\Phi_{3\text{-pp}}$
0.080	15	0.020	0.11
0.062	20	0.020	0.11
0.034	20	0.024	0.11
0.021	45	0.023	0.10
0.012	15	0.023	0.10

[a]Pressure of phenylcyclopropane.

Xenon, neopentane and tetramethylsilane were used to quench product formation. Phenylcyclopropane could not be used as a quencher since its vapor pressure is about 1.0 Torr at 298 K. The results of these quenching experiments are given in Table 3. For most of the experiments the t-pp peak was too small to be measured. The effect of adding neopentane and tetramethylsilane is to reduce significantly the 3-pp and c+2-pp. The decrease in the styrene quantum yields is much less pronounced. In comparison with neopentane and tetramethylsilane, xenon is an ineffective quencher. Stern–Volmer plots for 3-pp and c+2-pp are given in Figs. 1 and 2. With the exception of the plot for c+2-pp with xenon added as a quencher, all the Stern–Volmer plots appear to be linear. The appearance of non-linearity in the c+2-pp plot with xenon quencher is probably due to experimental scatter. The least squares slopes and intercepts of the Stern–Volmer plots are given in Table 4. Three experiments were performed at 10 Torr neopentane in which the 2-phenylpropene and cis-1-phenylpropene quantum yields were resolved. The result is $\Phi_{2\text{-pp}}/\Phi_{c\text{-pp}} = 0.15 \pm 0.01$. This number is essentially

TABLE 3

Product quantum yields with added quencher[a]

Pressure (Torr)		Photolysis time (min)	Φ_{sty}	$\Phi_{3\text{-pp}}$ [c]	$\Phi_{c+2\text{-pp}}$	$\Phi_{t\text{-pp}}$
PCP[b]	Quencher					
Quencher = Xe						
0.24	10.0	60.0	0.012	0.081	0.054	–
0.24	23.0	60.0	0.016	0.073	0.047	–
0.24	50.0	60.0	0.021	0.064	0.044	–
0.23	100.0	60.0	0.022	0.051	0.045	–
Quencher = neopentane						
0.37	5.0	30.0	0.015	0.085	0.061	–
0.34	9.0	30.0	0.018	0.063	0.053	–
0.33	25.0	30.0	0.015	0.034	0.039	–
0.35	49.0	240.0	0.007	(0.019)	0.025	–
0.35	52.0	30.0	0.015	0.019	–	–
0.36	100.0	30.0	0.015	0.010	–	–
0.35	100.0	180.0	–	(0.010)	0.016	–
Quencher = tetramethylsilane						
0.54	1.3	30.0	–	0.086	0.058	0.022
0.51	2.6	30.0	–	0.079	0.060	0.029
0.55	5.3	30.0	0.018	0.061	0.045	–
0.55	10.5	30.0	0.016	0.044	–	–
0.55	22.0	30.0	0.015	0.022	–	–
0.35	26.0	60.0	–	(0.021)	0.025	–
0.54	44.0	30.0	–	0.014	–	–
0.36	51.0	240.0	0.011	(0.012)	0.016	–

[a]Actinometry was performed by assuming $\Phi_{3\text{-pp}} = 0.10$ for pure phenylcyclopropane photolysis between 0.2 and 0.6 Torr.
[b]PCP = phenylcyclopropane.
[c]The 3-pp quantum yields in parentheses were determined from the Stern–Volmer plot (Fig. 1). The remaining quantum yields for this experiment were derived from that for 3-pp.
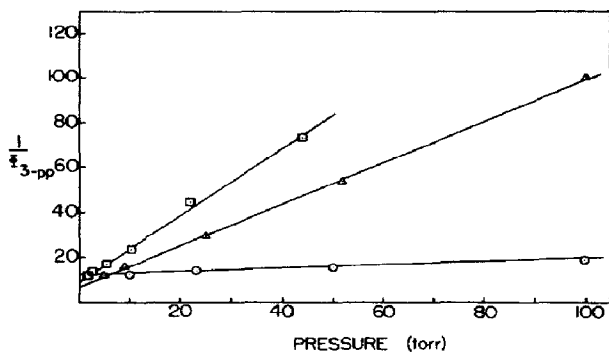
Fig. 1. Stern—Volmer plots for 3-phenylpropene formation. Quencher: □, tetramethyl-silane; △, neopentane; ○, xenon.
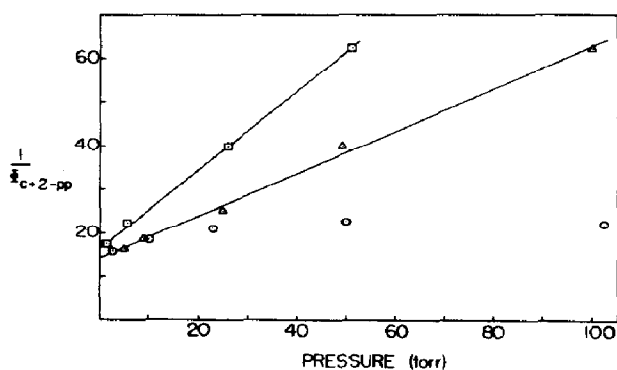

Fig. 2. Stern—Volmer plots for *cis*-1-phenylpropene + 2-phenylpropene formation. The quenchers are the same as in Fig. 1.

the same as that found at 0.5 Torr (Table 1) and shows that the relative 2-phenylpropene and *cis*-1-phenylpropene quantum yields are not pressure dependent.

TABLE 4

Slopes and intercepts of Stern—Volmer plots[a]

Quencher	Intercept	Slope
3-Phenylpropene		
Xenon	11.7 ± 0.3	0.079 ± 0.004
Neopentane	6.5 ± 2.2	0.94 ± 0.03
Tetramethylsilane	9.0 ± 2.7	1.50 ± 0.08
cis-*1-Phenylpropene* + *2-phenylpropene*		
Neopentane	14.3 ± 2.2	0.48 ± 0.03
Tetramethylsilane	15.9 ± 1.9	0.92 ± 0.06

[a]Errors are for a 90% confidence interval.

4. Discussion

The most important finding in this study is an absence of an energy balance. No fluorescence is observed for the wavelengths used in this study and the low pressure total photochemical quantum yield is 0.25 ± 0.05. This result is analagous to previous photochemical studies of aromatic hydrocarbons [7]. The photochemical quantum yields are essentially constant between 0.01 and 1.0 Torr and there is no evidence from this work that they would increase at lower pressures. The correct products are observed for S_0 decomposition, but their total quantum yield at low pressure is only 0.24. Therefore, it seems clear that the predominant radiationless path(s) at 213.9 nm do not form the vibrationally excited ground state of phenylcyclopropane unless there is slow intramolecular vibrational energy redistribution within S_0. Formation of S_0 by the radiationless decay of S_2 will yield vibrationally excited ground state molecules with preferential excitation of the benzene ring. Thus, for isomerization to occur vibrational energy must flow from the benzene to the cyclopropyl ring. There is some evidence for slow intramolecular vibrational energy transfer in highly vibrationally excited aromatic hydrocarbons [4, 18].

Many of our results at 213.9 nm are similar to those found at 253.7 nm [14]. The major difference between the two wavelengths is that an energy balance is found at 253.7 nm. At both wavelengths styrene formation is not quenched by pressure in contrast to phenylpropene formation. This indicates that styrene is formed by a short lived species while the phenylpropenes, which can be quenched, are formed by a much longer lived species. The principal products at both 213.9 nm and 253.7 nm are 3-phenylpropene, cis-1-phenylpropene and trans-1-phenylpropene. These are also the initial products formed by the pyrolytic decomposition of phenylcyclopropane [13], which presumably occurs on the ground electronic state. The product 2-phenylpropene would be formed from the ground electronic state by
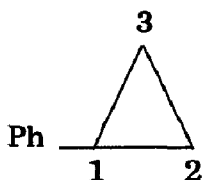
C_2—C_3 bond rupture. The absence of 2-phenylpropene is expected in the pyrolysis studies, since the most substituted bond is the weakest, i.e. C_1—C_2 or C_1—C_3 [13]. In the 253.7 nm photolysis of phenylcyclopropane no 2-phenylpropene was observed [14]. At 213.9 nm 2-phenylpropene is formed, but in very small yields. A comparison between the 213.9 nm and 253.7 nm results is given in Table 5.

The total product quantum yield at 213.9 nm is about 3 times smaller than at 253.7 nm. However, the half quenching pressures, proportional to the inverse of the Stern—Volmer slopes, are about 40 times larger at 213.9 nm,

TABLE 5

Comparison of phenylcyclopropane photochemistry at 213.9 nm and 253.7 nm[a]

	Product quantum yields (p = 0)		Stern–Volmer slopes (Torr^{-1})[b]	
	213.9 nm[c]	253.7 nm[d]	213.9 nm[c]	253.7 nm[d]
Styrene	0.018	–		
3-Phenylpropene	0.11	0.26	0.94	31.5
cis-1-Phenylpropene	0.053	0.19	0.48	21.7
trans-1-Phenylpropene	0.054	0.20		
2-Phenylpropene	0.008	0.00		
	0.24	0.65		

[a]The 213.9 nm photolyses were performed at about 23 °C and the 253.7 nm photolyses were performed at 31 °C.
[b]The quencher at 213.9 nm was neopentane and that at 253.7 nm was phenylcyclopropane.
[c]The actual photolyses were performed with a mixture of 202.5, 206.1 and 213.9 nm lines. More than 75% of the photons were at 213.9 nm.
[d]Results taken from ref. 13.

which means that the precursor(s) for the phenylpropenes is shorter lived at 213.9 nm than at 253.7 nm. At both 213.9 and 253.7 nm the ratio of cis-1-phenylpropene to trans-1-phenylpropene at p = 0 is nearly unity. With respect to the other phenylpropenes, 3-phenylpropene is a more important product at 213.9 than at 253.7 nm.

Excitation at 213.9 nm initially forms the S_2 state of phenylcyclopropane. Previous experiments have shown that for aromatic hydrocarbons the fluorescence spectrum generally corresponds to $S_1 \rightarrow S_0$ emission regardless of the singlet state initially prepared [4 - 6]. This result implies rapid $S_2 \rightarrow S_1$ internal conversion. Birks [19] has estimated the rate of $S_2 \rightarrow S_1$ internal conversion to be 4×10^{10} s^{-1} in benzene and 1.2×10^{12} s^{-1} in naphthalene. Therefore, the non-radiative paths which must be considered at 213.9 nm are those from S_1. The $S_1 \rightarrow S_0$ 0–0 transition is 36 381 cm^{-1} [20] and the S_1 state prepared by 213.9 nm photolysis contains 9890 cm^{-1} (28.3 kcal mol^{-1}) excess vibrational energy. For excitation at 253.7 nm the S_1 state is prepared directly and contains 2556 cm^{-1} (7.3 kcal mol^{-1}) excess vibrational energy.

At both 213.9 and 253.7 nm the rate of cis-1-phenyl propene formation is greater than that for 3-phenylpropene formation, while 3-phenylpropene has a larger low pressure quantum yield (see Table 5). This result suggests that cis-1-phenylpropene and 3-phenylpropene may be formed by different radiationless pathways. However, the same effect may arise if there are pressure dependent reversible unimolecular reactions between the phenylpropenes, and this possibility cannot be discounted. Such effects have been seen in the unimolecular isomerization of methylcyclopropane [21].

One of the limitations of a study of this type is that it does not provide conclusive evidence for a photochemical mechanism. Important questions left unanswered are: what are the radiationless pathways for phenylpropene formation; why does the low pressure phenylpropene quantum yield decrease with increase in excitation energy; and what are the radiationless paths for the excited molecules unaccounted for at 213.9 nm. Our results do provide some insights into these questions and they are discussed below.

That xenon is an ineffective quencher of phenylpropene formation indicates that the phenylpropenes are not formed by S_1 decomposition. Xenon increases spin—orbit coupling via the external heavy atom effect and would effectively relax S_1 via collision induced intersystem crossing. See for example ref. 19, p. 208, and ref. 22. This leaves decomposition from the ground electronic state and/or the triplet manifold as possible paths for phenylpropene formation. The ground electronic state can be formed either by direct $S_1 \rightarrow S_0$ internal conversion or by two intersystem crossing steps, $S_1 \rightarrow T \rightarrow S_0$. In each case the overall process is $S_1 \rightarrow S_0$ internal conversion, for which the rate constant is denoted k_{ic}. Assuming the phenylpropenes are formed by ground state decomposition, the quantum yield for product i is then

$$\Phi_i = \frac{k_{ic}}{k_r + k_{nr}} \quad \frac{k_i}{k_d + w} \tag{2}$$

where k_i is the unimolecular rate constant for i decomposition and w is the collision frequency for S_0 deactivation. The total unimolecular decomposition rate $k_d = \Sigma k_i$. If $1/\Phi_i$ is plotted against pressure, the inverse of the slope multiplied by $(k_r + k_{nr})/k_{ic}$ gives the half quenching pressure $P_{1/2}$. At 253.7 nm with phenylcyclopropane as a deactivator $P_{1/2} = 0.050$ Torr for 3-phenylpropene formation and 0.073 Torr for cis-1-phenylpropene formation. For the experiments at 213.9 nm with neopentane as a deactivator $P_{1/2} = 1.06$ and 2.08 Torr for 3-phenylpropene and cis-1-phenylpropene, respectively. These half quenching pressures agree to within a factor of 10 with those predicted by RRKM calculations where the activation energies and critical configuration structures were estimated by comparison with other cyclopropane isomerizations [23]. Better agreement may result if the Arrhenius parameters for phenylcyclopropane isomerization were known so that more accurate estimates of the activation energies and critical configurations could be made. The inefficiency of xenon in quenching product formation in comparison to neopentane and tetramethylsilane is in agreement with previous studies of intermolecular energy transfer for ground electronic state molecules [24]. Similarly, helium was found to be an inefficient quencher at 253.7 nm in comparison with phenylcyclopropane [14]. Thus, the photochemical results are consistent with but do not prove phenylpropene formation by S_0 decomposition.

The phenylpropenes could also be formed by decomposition from the triplet manifold as well as from the ground state. Becker et al. [25] have found evidence for a low energy triplet state with considerable radical

character in the cyclopropyl ring. The C_1-C_2 bond is severely stretched and the $C_1-C_3-C_2$ bond angle is large (100 - 140°). This triplet state should have a weakened C_1-C_2 bond and a lower isomerization barrier[†] than that in S_0. Decomposition should proceed via C_1-C_2 rupture which gives 3-phenylpropene and cis- and trans-1-phenylpropene as products, and is in agreement with the experiment. If this is the decomposition path, the effect of added gases would be to deactivate the excited triplets vibrationally and/ or to induce $T \rightarrow S_0$ intersystem crossing collisionally with a concomitant removal of internal energy from the excited phenylcyclopropane molecules. The relative inefficiency of xenon and helium in quenching product formation is then due to inefficient vibrational deactivation of the triplet molecules or to inefficient removal of vibrational energy during and after collision induced $T \rightarrow S_0$ intersystem crossing.

The most plausible radiationless path from S_1 to yield the phenyl-propenes is $S_1 \rightarrow T$ intersystem crossing. As discussed above, the phenyl-propenes could then be formed by either dissociation from the triplet mani-fold or dissociation from S_0 following $T \rightarrow S_0$ intersystem crossing. Rather strong arguments have been presented indicating that intersystem crossing is the predominant radiationless path for benzene and related compounds with small excess energies in S_1 [8, 9, 11]. As the excess energy in S_1 is raised, it is thought that intersystem crossing becomes less important [1, 7, 8, 11]. This is what is found here. The $p = 0$ quantum yield for phenylpropene formation decreases from 0.65 to 0.24 in going from 253.7 to 213.9 nm.

Finally, we remark that there is one extremely important question left totally unanswered: what radiationless paths are followed by the 75% of excited phenylcyclopropane molecules not accounted for at 213.9 nm. This is a difficult question to answer either theoretically or experimentally. As has been suggested for benzene, photochemical isomerization of the benzene ring may be an important radiationless path for phenylcyclopropane [7, 27]. No attempt was made to look for isomers of the benzene ring in this study of phenylcyclopropane photochemistry at 213.9 nm.

References

1 C. S. Parmenter, *Adv. Chem. Phys.*, *22* (1972) 365.
2 J. H. Callomon, J. E. Parkin and R. Lopez-Delgado, *Chem. Phys. Lett.*, *13* (1972) 125.
3 G. S. Beddard, G. R. Fleming, O. L. J. Gijzeman and G. Porter, *Chem. Phys. Lett.*, *18* (1973) 481.
4 J. C. Hsieh, C.-S. Huang and E. C. Lim, *J. Chem. Phys.*, *60* (1974) 4345.
5 C.-S. Huang, J. C. Hsieh and E. C. Lim, *Chem. Phys. Lett.*, *28* (1974) 130.
6 C.-S. Huang, *Ph.D. Thesis*, Wayne State University, Detroit, Mich., 1975 (University Microfilms, Ann Arbor, Michigan).
7 W. A. Noyes, Jr., and K. E. Al-Ani, *Chem. Rev.*, *74* (1971) 29.
8 M. Jacon, C. Lardeux, R. Lopez-Delgado and A. Tramer, *Chem. Phys.*, *24* (1977) 145.
9 M. G. Prais, D. F. Heller and K. F. Freed, *Chem. Phys.*, *6* (1974) 331.

[†]The isomerization barrier in substituted cyclopropanes is about 60 kcal mol^{-1} [26].

10 M. Jacon, *Chem. Phys. Lett.*, *47* (1977) 466.
11 S. F. Fischer, A. L. Stanford and E. C. Lim, *J. Chem. Phys.*, *61* (1974) 582.
12 H. Schröder, H. J. Neusser and E. W. Schlag, *Chem. Phys. Lett.*, *54* (1978) 4.
13 J. T. Wood, J. S. Arney, D. Cortes and J. A. Berson, *J. Am. Chem. Soc.*, *100* (1978) 3855.
14 J. K. Foote, *Ph.D. Thesis*, University of California, Riverside, Calif., 1966 (University Microfilms, Ann Arbor, Michigan).
15 S. A. Lee, J. M. White and W. A. Noyes, Jr., *J. Chem. Phys.*, *65* (1976) 2805.
16 R. I. Greenberg and J. Heicklen, *Int. J. Chem. Kinet.*, *2* (1970) 185.
17 R. Simonaitis, R. I. Greenberg and J. Heicklen, *Int. J. Chem. Kinet.*, *4* (1972) 497.
18 P. J. Nagy and W. L. Hase, *Chem. Phys. Lett.*, *54* (1978) 73.
19 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, New York, 1970, p. 187.
20 W. W. Robertson, J. F. Music and F. A. Matsen, *J. Am. Chem. Soc.*, *72* (1950) 5260.
21 E. Jakubowski, H. S. Sandhu and O. P. Strausz, *J. Am. Chem. Soc.*, *93* (1971) 2610.
22 F. A. Carroll and F. H. Quina, *J. Am. Chem. Soc.*, *98* (1976) 1.
   D. Phillips, *J. Photochem.*, *1* (1972/73) 97.
23 Dan W. Thomas, *M.S. Thesis*, Wayne State University, Detroit, Mich., 1977.
24 D. C. Tardy and B. S. Rabinovitch, *Chem. Rev.*, *77* (1977) 369.
25 R. S. Becker, L. Edwards, R. Bost, M. Elam and G. Griffin, *J. Am. Chem. Soc.*, *94* (1972) 6584.
26 P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions*, Wiley, New York, 1972, p. 185.
27 J. E. Kent and P. J. Harman, Photophysics and photochemistry of benzene isomers, *32nd Symp. on Molecular Spectroscopy, Ohio State University Columbus, Ohio, 1977*.