

Photochemistry of Benzene Isomers. 1. Fulvene and 3,4-Dimethylenecyclobutene

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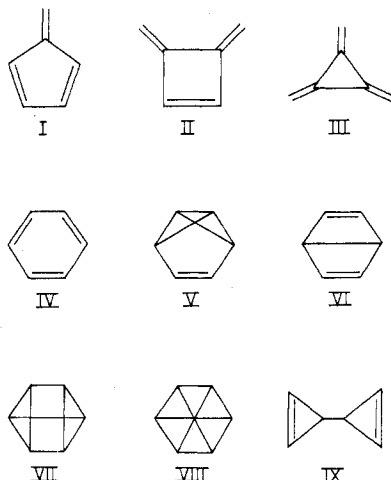
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The photochemical behavior of the benzene isomer fulvene is investigated at various excitation wavelengths. The only observable photoproduct is benzene, produced in high quantum yield below about 275-nm excitation. The quantum yield is dependent upon excitation wavelength indicating the photoisomerization requires vibrational activation. Quenching by various added gases is efficient and suggests that the photochemistry does not involve triplet-state or free-radical mechanisms. Another isomer, 3,4-dimethylenecyclobutene, also shows photochemical behavior upon excitation at 240 and 215 nm to produce a polymeric material.

Introduction

Isomers of the unsubstituted benzene molecule can be classified into two distinct groups.

1. Molecules in which the empirical formula C_6H_6 is retained, and the rules of basic valency are satisfied, but six C-H bonds are *not* present. In theory there are 211 such species most of which are unknown. Of specific interest to us are the three isomers consisting of a single ring structure with exocyclic methylene groups, that is, fulvene (I), 3,4-dimethylenecyclobutene (DMCB, II), and tri-



methylenecyclopropane (III). We will refer to these isomers of benzene as the methylene isomers.

2. Molecules that retain not only the empirical formula C_6H_6 , but also can be written as $(CH)_6$, that is, the valence isomers. Here there are only six possibilities namely benzene (IV) itself, Dewar benzene (V), benzvalene (VI), prismane (VII), Claus benzene (VIII), and bicyclopropenyl (IX).¹ All of these valence isomers lie on the same multidimensional potential surface.

Historically, of course, interest in benzene valence isomers arose in the proposals put forward to explain the structure of benzene itself in the 19th century by Kekulé, Dewar, Claus, Ladenburg, and Hückel.²⁻⁶ Currently, with the exception of Claus benzene and bicyclopropenyl, all the unsubstituted valence isomers have been prepared by independent chemical methods.⁷⁻¹¹ Extensive spectroscopic investigations of these unsubstituted valence isomers have yielded reliable data throughout the electromagnetic spectrum. Similarly, two of the methylene isomers, fulvene and 3,4-dimethylenecyclobutene, are well-characterized spectroscopically.¹³

Benzene itself is a much studied molecule by spectroscopists,¹⁴ but there is one aspect of its spectroscopy that is of special interest. This is the so-called "channel 3" through which vibrationally excited benzene in its first excited single state, $^1B_{2u}$, is deactivated.¹⁵ The onset of this channel has a well-defined threshold some 3000 cm^{-1} above the absorption band origin. At this point the non-radiative decay rate increases rapidly at the expense of both fluorescence and triplet state formation (channels 1 and 2) to such an extent that relaxation from rovibronic levels 3500 cm^{-1} above the origin appears to be exclusively due to channel 3.¹⁶ A number of proposals have been suggested for this behavior based on accepted theories of radiationless decay processes including internal conversion via a sudden coupling to the ground state, extra triplet and/or singlet excited electronic states not yet characterized, photodissociation, and also photoionization.¹⁴ Experimentally, the channel 3 enigma is difficult since the principle measurement possible, i.e., fluorescence, becomes impracticable as the emission yield rapidly drops to nearly zero as the channel 3 gate opens.

If photochemistry is occurring then the increase in photoproduct yield would be expected to correlate with the decrease in fluorescence. However, there is no evidence of H_2 evolution that would indicate photodissociation and, although benzene is by no means inert to photoisomerization, as will be seen shortly, the product yields of the isomers are extremely low.

Despite this we were intrigued by continuing reports that benzene does photoisomerize to fulvene, benzvalence,

(1) Systematic names for the various benzene valence isomers are as follows: Dewar benzene (bicyclo[2.2.0]hexa-2,5-diene); benzvalene (tricyclo[3.1.0.0^{2,6}]hex-3-ene); prismane (tetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane); Claus benzene (tetracyclo[2.2.0.0^{2,5}.0^{3,6}]hexane).

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(4) Claus, A. "Theoretische Betrachtungen un den Anwendung zur Systematik der Organischen Chemie"; Freiburg, 1867.

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Dewar benzene, and even prismane under certain conditions.¹⁷⁻²⁶ In particular, work by Wilzbach, Harkness, and Kaplan, who excited S_1 in 1,3,5-trideuteriobenzene and showed that the 1,2,5-trideuteriobenzene product could be explained via a benzvalence intermediate, indicated that a reversible photoprocess may be the reason for the low product yield of isomers.¹⁷ Kaplan and Wilzbach subsequently concluded that benzvalence was formed not from triplet benzene, but probably from higher vibrational states of the S_1 ($^1B_{2u}$) state of benzene. This finding was subsequently confirmed by Lee, White, and Noyes.²⁴

Thus in summary, we believe that photochemical isomerization of benzene may be at least a partial explanation for the channel 3 problem. Excitation into S_1 produces benzvalene and the quantum yield increases with decreasing wavelength.^{17,25} Excitation into the S_2 ($^1B_{1u}$) and S_3 ($^1E_{1u}$) states seems to give Dewar benzene as well as benzvalene.^{22,23} In all cases fulvene is also formed, but it is questionable as to whether fulvene is a primary photoproduct, or a secondary one derived from benzvalene. The quantum yields of isomer formation are low, but since all of the isomers mentioned have absorption systems beginning above 260 nm, reisomerization to benzene of any isomer formed during benzene photochemistry would seem to be a distinct possibility. Indeed in preliminary reports both fulvene and benzvalene have been shown to photolyze to benzene.^{21,25}

More data are clearly required on the photochemical behavior of the unsubstituted benzene isomers. We report here the photochemistry of fulvene and 3,4-dimethylenecyclobutene and, in the following paper, the photochemistry of Dewar benzene and benzvalene.

Experimental Section

Synthesis and Handling of Fulvene and 3,4-Dimethylenecyclobutene. There is a simple one-step synthesis available involving the thermolysis of hexa-1,5-diyne that can be used to produce both fulvene and 3,4-dimethylenecyclobutene in high yield.²⁷ Purification of the isomers is accomplished by using preparative gas chromatography at ambient temperatures with a 20% squalane on acid washed, 60–80 Chromosorb W column. The liquid isomers are prone to polymerization and react readily with air at room temperature so that special handling precautions must be observed. Under vacuum at 77 K both compounds are docile and we found no evidence of any decomposition or polymerization under these conditions for periods in excess of 6 months. Furthermore, neither isomer presented any difficulty when handled as a vapor. The room temperature vapor pressure of fulvene is 10.6 kPa (79.5 torr), while 3,4-dimethylenecyclobutene has a vapor pressure of 13.3 kPa (100 torr), at 298 K. Samples at saturated vapor pressure showed no decomposition over periods in excess of 24 h.

Photochemical Techniques. The photochemical experiment utilized a standard in-line optical train. The source was a forced-air-cooled 1600-W xenon arc whose output was cooled with distilled water and focussed onto the entrance slit of a 0.5-m monochromator. The bandpass of this monochromator operated in first order was 8 nm. The light was collected by a lens train to a near parallel, circular cross section beam 4.5 cm in diameter prior to entering the photolysis cell containing either the sample or actinometer. Great care was taken in the design of the optical train to ensure reproducible alignment of the front cell window. After passing through the sample or actinometer cell, the radiation was focussed onto an RCA 931 photodiode and the current output measured with a Keithley picoammeter. All lenses and windows throughout the system were grade 1 Supracil quartz selected to have the same transparency from 500 to 200 nm.

Quantum yields were determined from

$$\phi_p = \frac{N_p}{I_0 F t} \quad (1)$$

in the usual fashion where N_p is the number of product molecules formed, I_0 is the incident intensity that is multiplied by the fraction of light absorbed, F , during the exposure time, t .

The fraction of radiation absorbed was determined by measuring the light incident upon the photodiode without the cell in position, with an evacuated cell in position, and finally with the cell filled with fulvene or DMCB in position. After exposure for the required period, usually of the order of 1 h, the cell was removed and the contents analyzed.

The fraction of light absorbed was calculated according to the method given by Hunt and Hill which takes into account the amount of light reflected from an air-window interface using Fresnel's law.²⁸ The actual amount of radiation absorbed in passage through a vapor sample is given by

$$F = \frac{\left(1 - \frac{\Delta_F}{\Delta_E}\right) \left(\frac{\Delta_E}{\Delta_0}\right)^{1/2} (1-f)^2}{\frac{\Delta_E}{\Delta_0} - f \left[1 + \frac{\frac{\Delta_E}{\Delta_0}}{(1-f)^2}\right] \frac{\Delta_F}{\Delta_0}} \quad (2)$$

where the quantities Δ_0 , Δ_E , and Δ_F are the photocurrents for no cell, evacuated cell, and filled cell, respectively, and f is the fraction of light reflected from the air-window interface.

If the sample is a liquid this equation must be modified slightly to incorporate the different refractive index of the liquid.

The incident intensity I_0 was measured with a potassium ferrioxalate actinometer.²⁹ Since most experiments were performed with radiation below 350 nm no problems were encountered by using the equation for F given above as the actinometer absorbs all of the radiation incident within the front window of the cell. We found it necessary to calibrate the ferrioxalate actinometer below 254 nm with a uranyl oxalate actinometer.³⁰ Over the range 254–225 nm the quantum yield of the ferrioxalate actinometer, $\phi_{Fe^{3+}}$,

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remained constant at the 254-nm value of 1.25. Duplicate ferrioxalate actinometers were developed in the standard manner with 1,10-phenanthroline and the absorbance of the Fe(II) phenanthroline complex measured on a Cary 17 spectrophotometer using as a reference identical solutions prepared from unirradiated actinometer solution.

Product Analysis. Product analysis proved a difficult proposition even though in the case of fulvene the only product formed is benzene. The oscillator strength of the benzene ${}^1B_{2u} \rightarrow {}^1A_{1g}$ transition is only $20 \text{ m}^2 \text{ mol}^{-1}$. In addition, the benzene methylene isomers absorb below 260 nm and for the most part have much higher extinction coefficients, thus effectively eliminating absorption spectrophotometry as a usable technique. As other spectroscopic techniques such as NMR and IR although possessing sufficient sensitivity were lacking linearity over the three decades of concentration required we chose to use vapor phase chromatography.

The chromatograph used was a Perkin-Elmer Model F-11 fitted with a flame ionization detector and high precision oven. The column was of the support-coated open tubular type coated with either Apiezon L or squalane.

Samples of fulvene and DMCB were prepared on a grease-free vacuum line. Pressures were measured with an MKS Barocell capacitance manometer fitted with a 10-torr head. Each of the added gases used was checked for absorption below 260 nm but showed negligible absorption in samples below 13.3 kPa.

On completion of each photochemical run, the sample cell contents were transferred on the vacuum line to a sample vial filled with a vacuum-tight subseal. Triply distilled 1,2,4-trimethylpentane ($200 \mu\text{L}$) was carefully degassed and trapped into the vial which was then removed from the line for chromatographic analysis. Samples were kept frozen at 77 K and warmed briefly to room temperature for each injection into the chromatograph. A primary standard of ultrapure benzene (99.999%) was made up gravimetrically and diluted with 1,2,4-trimethylpentane providing a range of benzene reference concentrations from 100 ppm to 1 ppb. Analysis of the amount of benzene in each solution was by measurement of peak areas. All determinations of benzene concentrations were done in quintuplicate and careful checks were made to ensure reproducibility of the standard solutions, the linearity of the chromatograph amplifier, and syringe repeatability.

Errors. Calculation of the errors involved in a photochemical experiment is always difficult. For example, in the calculation of fraction of light absorbed the quantity of importance is $1 - d_F/d_E$ and, as this term becomes smaller the fraction of light absorbed, F , decreases, and the percentage error increases dramatically. Other terms in F also contribute to the error, but not as significantly as the $1 - d_F/d_E$ term. We calculate the minimum error which can be expected from F to be of the order of 2% when $1 - d_F/d_E$ is near unity and as high as 100% when $1 - d_F/d_E$ is near zero. Errors involved in the determination of I_0 from the actinometer should be constant over a wide range and are of the order of 5%, in line with those expected from chemical actinometry. Similarly, the product analysis error estimated by taking repeated measurements of peak areas, dilution factors, and the manufacturers specifications for the microsyringes is of the order of 7.5%.

Results and the Photochemistry of Fulvene

The vapor phase electronic spectrum of fulvene shows four absorption bands between 450 and 167 nm.³¹ The

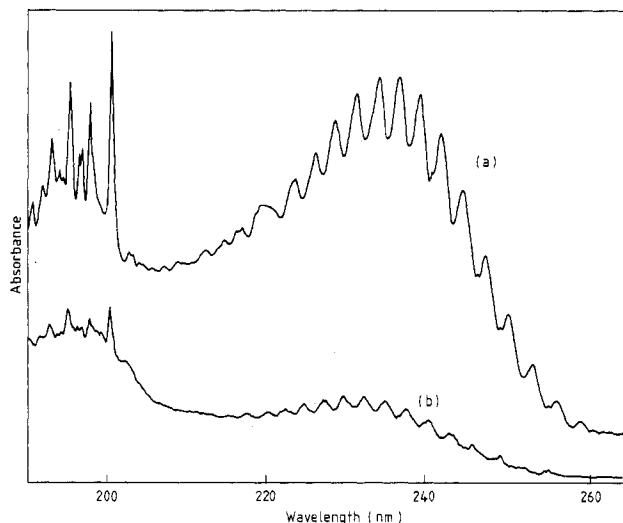


Figure 1. Spectra of fulvene vapor after photolysis. Curve a is the spectrum after irradiation at 500 or 350 nm for a 4-h period. It is identical with the spectrum of an unirradiated sample (ref 31). Curve b is the spectrum after irradiation at 255 nm for 1 h. Curves a and b are displaced for clarity.

TABLE I: Wavelength Dependence of ϕ_{Bz} from Fulvene^a

λ , nm	ϕ_{Bz}	std dev
235	0.407 ^b	0.029
245	0.532 ^b	0.034
254	0.668 ^b	0.059
275	0.189 ^b	0.063
315	0.032 ^c	
335	<0.01 ^c	
400	<0.02 ^c	

^a Determined on 13.3-Pa samples of fulvene photolyzed for 1 h. ^b Mean of five determinations. ^c Mean of three determinations.

lowest energy band is broad ($\lambda_{\text{max}} = 350 \text{ nm}$) and vibronic structure is only observable at the onset of absorption. The intense yellow color of fulvene is attributable to this absorption. The second transition extending from 267 to 205 nm shows two vibrational progressions, a strong one of 20 members and a weaker one of about 6 members, both having a spacing of 495 cm^{-1} . The two higher energy transitions with $\lambda_0 = 202 \text{ nm}$ and $\lambda_0 = 177 \text{ nm}$ are believed to be Ryberg bands.³² The vibronic structure of all the bands is not sharp, indicating the presence of some rapid nonradiative deactivation of the excited states of fulvene.

Figure 1 shows part of the absorption spectrum of fulvene after excitation at 500 or 350 nm for a 4-h interval and at 255 nm for a 1-h interval. From this qualitative measurement it is obvious that the visible band of fulvene represents a transition to a photochemically inert state whereas excitation into the second excited state produced obvious photochemistry as evidenced by the decrease in fulvene absorption and appearance of new peaks at 259.5, 254.7, 247.9, and 242.1 nm corresponding to the strong bands in ${}^1B_{2u}$ band of benzene. This is just discernable in figure 1 and becomes readily observable after irradiation for a 2-h period. We measured the quantum yield of benzene formation as a function of wavelength, pressure, and effects of added gases. The wavelength dependence of the quantum yield for benzene production from fulvene, ϕ_{Bz}^F , at 67 Pa pressure is shown in Table I. The quantum

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TABLE II: Effect of Fulvene Pressure on ϕ_{Bz}^a

press., Pa	ϕ_{Bz}^b	% std dev
13.3	0.668	11.2
67.0	0.417	16.3
133.0	0.342	6.7
267.0	0.239	21.7
467.0	0.144	1.4
667.0	0.122	15.6

^a Determined at 254 nm. Fulvene samples were photolyzed for 1 h. ^b Mean of five determinations.

TABLE III: Effect of Isopentane on ϕ_{Bz}^a

press., Pa	ϕ_{Bz}^b	% std dev
13.3	0.520	2.7
67.0	0.462	9.5
133.0	0.331	9.4
267.0	0.256	2.3
467.0	0.206	18.4
667.0	0.117	17.9
866.0	0.100	21.0
1066	0.097	13.0
1332	0.068	27.9

^a Determined at 254 nm on 40-Pa samples of fulvene photolyzed for 1 h. ^b Mean of five determinations.

yield of benzene from excitation in S_1 at 400, 355, and 315 nm is very low. The visible band of fulvene is inherently diffuse so that deactivation from this state must proceed preferentially via nonradiative routes other than photoisomerization.

At wavelengths shorter than 300 nm the quantum yield of benzene formation begins to rise dramatically. Thus for excitation at 275 nm, slightly below the origin band of the second transition in fulvene, the quantum yield is low but increases at 254 nm to 0.67. Such a variation of a quantum yield with wavelength may indicate a lack of vibrational equilibration within the electronically excited state. The most likely explanation for this behavior is that the photoisomerization requires vibrational activation. The drop in quantum yield at 245 and 235 nm is no doubt due to increasing competition from nonradiative deactivation pathways such as internal conversion and inter-system crossing.

The quantum yield of benzene formation as a function of fulvene pressure is shown in Table II. The yield drops rapidly as the pressure of fulvene is increased, leading to two conclusions. First, below what is normally regarded as isolated molecule conditions, the quantum yield of benzene formation is at its highest value. Thus only one fulvene molecule participates in the formation of each benzene, confirming the reaction as unimolecular. Second, self-induced collisional deactivation is a very efficient process in fulvene, as this pathway is able to effectively compete with other processes deactivating the S_2 state.

Further insight into the mechanism of fulvene photochemistry comes from the effect of added gases on the quantum yield of benzene production. Table III shows the effect of isopentane as a quenching partner and Table IV shows similar results from less exhaustive experiments with CO, NO, and N_2 .

The addition of nitric oxide appears to have no effect on the quantum yield apart from that due to collisional quenching. This suggests that the photochemistry does not involve triplet-state or free-radical mechanisms.³³ Thus the postulated diradical intermediate for the reverse process fulvene or benzvalene formed via photolysis of

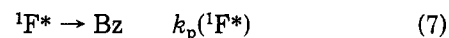
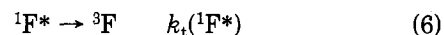
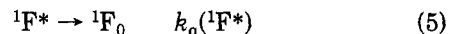
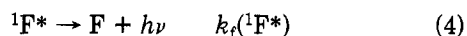
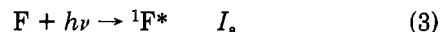
TABLE IV: Effect of Added Gases on ϕ_{Bz}^a

press., Pa	ϕ_{Bz}^b		
	N_2	CO	NO
67.0	0.393	0.417	0.407
267.0	0.366	0.318	0.356
667.0	0.314	0.162	0.294
1332	0.231	0.080	0.141

^a Determined at 254 nm on 40-Pa samples of fulvene photolyzed for 1 h. ^b Mean of three determinations.

benzene and termed "prefulvene" by Bryce-Smith and Longuet-Higgins³⁴ does not seem to be involved in this case and the photochemistry proceeds via the singlet manifold of fulvene.

Kinetic Scheme and Mechanism. We can rationalize the quantum yield experiments at 254 nm in terms of the following mechanism:



where F is a fulvene molecule, Bz is benzene, and M collectively, a quenching species. The "state" reached after excitation, ${}^1F^*$, is expected to be a series of vibronic levels in S_2 , lying approximately 3000 cm^{-1} above the zero-point level of the state. The unimolecular deactivation pathways, (4), (5), and (6), are slow in comparison to (7).

In the absence of added gases, the steady-state approximation give

$$({}^1F^*) = I_a(k_f + k_q + k_t + k_p + k_{ff}(F))^{-1} \quad (10)$$

and since

$$d(Bz)/dt = k_p({}^1F) \quad (11)$$

$$\phi_{Bz}^F = [d(Bz)/dt](1/I_a) \quad (12)$$

we get

$$\phi_{Bz}^F = k_p(k_f + k_q + k_t + k_p + k_{ff}(F))^{-1} \quad (13)$$

The plot of $1/\phi_{Bz}^F$ vs (F) is shown in Figure 2. The slope, equal to k_{ff}/k_p , is $1.15 \times 10^{-2} Pa^{-1}$ and the intercept, $(k_f + k_q + k_t + k_p)/k_p$, is 1.38.

Similarly in the presence of added gas

$$\phi_{Bz}^M = k_p(k_f + k_q + k_t + k_p + k_{ff}(F) + k_{fm}(M))^{-1} \quad (14)$$

so the ratio ϕ_{Bz}^F/ϕ_{Bz}^M for a given fulvene pressure should again be linear with a slope equal to $k_{fm}(k_f + k_q + k_t + k_p + k_{ff}(F))^{-1}$ and an intercept of unity.

The experimental data in Figure 3 give a slope of $4.2 \times 10^{-3} Pa$ and an intercept of 1.07. The lack of absolute values of any of the rate constants makes further inves-

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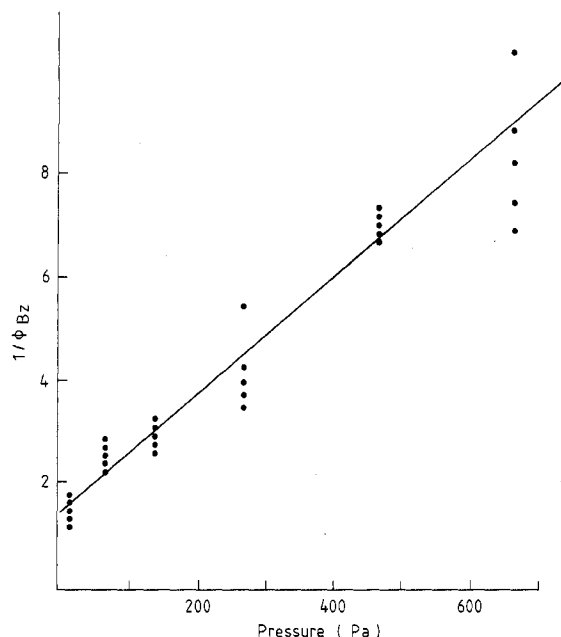


Figure 2. Plot of $1/\phi_{Bz}^F$ vs. fulvene pressure. Five determinations at each pressure are shown.

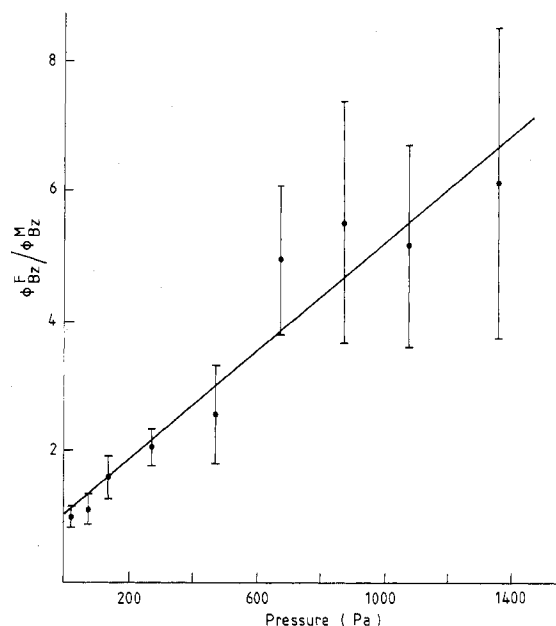


Figure 3. plot of ϕ_{Bz}^F/ϕ_{Bz}^M vs. isopentane pressure. Error limits are determined as outlined in the text.

tigation difficult but if we estimate a zero pressure lifetime based on a product yield of 0.5, i.e.

$$t = 1/2k_p$$

and use the isopentane "quenching" slope to get

$$k_{fm} = 4.2 \times 10^{-3}/T \text{ Pa}^{-1} \text{ s}^{-1}$$

then a nanosecond lifetime gives a value of k_{fm} of around $2 \times 10^{-6} \text{ dm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value indeed shows the quenching efficiency of isopentane as it corresponds to a collision cross section of hundreds of square nanometers. Undoubtedly, the lifetime is somewhat longer than a nanosecond which could reduce the cross section accordingly. The value for k_p from these estimates is about 10^8 s^{-1} .

Results of the Photochemistry of 3,4-Dimethylenecyclobutene

The absorption spectrum of DMCB commences at 294 nm and displays very weak structure that is, in the main, not resolvable.³⁵ The band maximum is at 240 nm. A second much more intense absorption begins at around 227 nm, has a broad shoulder at 212 nm and twin maxima at 206 and 204 nm, and then decreases with no further structure. A third absorption has been reported in the quartz ultraviolet with $\lambda_{\text{max}} = 173 \text{ nm}$.

Excitation into either the 240- or 250-nm bands produced the same result photochemically. In both cases the DMCB decomposed but there was no evidence of benzene or, for that matter, of any volatile products. Examination of the cell windows revealed the formation of a polymeric material that proved difficult to remove. Because of this, estimation of the quantum yield of DMCB disappearance is very qualitative but, with an incident intensity of $10^{14} \text{ quanta s}^{-1}$ at 240 nm, better than 40% of DMCB at 13 Pa was destroyed within 1 h indicating the yield is high.

Since DMCB has never, to our knowledge, been reported as a product of benzene photochemistry we did not pursue its photochemical behavior further.

Conclusions

The investigation of the photochemistry of fulvene can be summarized by the following:

1. Excitation into S_1 does not cause any observable photochemical reaction despite the fact that some rapid deactivation processes are depleting the state as witnessed by the diffuseness of the S_1 - S_0 absorption. Neither fluorescence nor triplet formation are observed indicating an internal conversion mechanism to S_0 as the most probable deactivation pathway.

2. Excitation into S_1 above the zero-point level produces solely benzene in high quantum yield and, due to the efficient self-quenching of the photoisomerization, the zero-pressure yield may be unity. The mechanism clearly requires vibrational activation but does not appear to proceed via triplet states.

3. The quantum yield of benzene decreases as the excitation wavelength is decreased below 250 nm, apparently due to increasing competition from other deactivation pathways.

4. Collision-induced relaxation with the S_2 manifold is rapid and, although absolute values have not been measured, the rate of self-relaxation is at least equal to the rate of deactivation by all other channels at 254 nm and 133 Pa pressure.

The high quantum yield of benzene formation is of importance to the "channel 3" problem in benzene and is discussed in more detail in the following paper dealing with the photochemistry of two of the valence isomers, namely, benzvalene and Dewar benzene.

Finally, photochemistry of 3,4-dimethylenecyclobutene produced no benzene, but rather a polymeric material in apparently high quantum yield.

Acknowledgment. This work was generously supported by the Australian Research Grants Committee. P.J.H. acknowledges receipt of a Commonwealth Postgraduate Award. Many useful discussions with Professor I. G. Ross, G. W. Robinson, and L. F. Phillips are also acknowledged.

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