photolyses. The low quantum yield for the formation of this product ($<10^{-6}$) indicates that the rate of recombination is slow compared with that of competing processes; for example

$$CF_3 + I_2 \longrightarrow CF_3I + I \qquad (3)$$

Verification that CF_3I is dissociating is provided by the experiment with NO added. The rate constant[16] for the reaction $CF_3 + NO \rightarrow CF_3NO$ is about one-tenth of k_3; hence the amount of CF_3NO formed sets a lower limit on the extent of photodissociation.

The contrasting reactivity of hot CF_3 and CH_3 radicals can be explained by differences in the distribution of vibrational and translational energy in the two photodissociation processes.[17] It has been proposed that photodissociation at 2537 Å involves excitation of the alkyl iodide to an unstable (n,σ^*) state in which the H–C–H or F–C–F angle is less than tetrahedral,[18] followed by C–I bond rupture, probably during the first vibration in the excited state. Since the methyl radical is planar,[19] the configuration with an interbond angle of less than 120° would correspond to an excited level of the deformation mode, with about 10 kcal/mole of vibrational energy for a tetrahedral angle.[20] On the other hand, CF_3 has an interbond angle of 111°,[21] and one would not expect the deformation vibration to be excited during dissociation. A difference in the partition of translational and internal energy could then influence the rate of abstraction, either because of more effective transfer of vibrational energy to the reaction coordinate representing hydrogen atom abstraction or because the relatively low efficiency of vibrational relaxation compared with translational relaxation permits a hot CH_3 radical to retain its excess energy longer than the CF_3 radical does.

The original suggestion[11,12] that vibrational energy was involved in hot reactions was based on the observation that He, Ne, Ar, and CO_2 had the same deactivation efficiency, contrary to predictions made for the transfer of translational energy. However, Doepker and Ausloos[13] point out that this result would also be predicted if the average kinetic energy of hot radicals is barely above the threshold energy for reaction 1. Their measurements of Φ_{CH_4} in this reaction indicate that several hydrocarbons are of nearly equal efficiency in collisional deactivation, but do not provide absolute values of the deactivation rate.

Simons and coworkers[17,22-24] have shown that photodissociation of certain polyhalomethanes leads to radicals containing enough vibrational energy to undergo unimolecular decomposition as an alternative path to hydrogen abstraction. In these cases, at least part of the vibrational energy probably results from extension of a carbon–halogen bond (other than the one being ruptured) in the excited state of the molecule.[17] Such an effect would be greatest when the two carbon–halogen bonds have similar dissociation energies and would be minimized in CF_3I.

We have also carried out photolyses of CF_3I at 1849 Å and find that reaction with hydrogen takes place with a quantum yield of about 0.1. This is an upper limit, since we have evidence of a contribution from a surface reaction. In addition to the much larger amount of total energy available (65 kcal/mole instead of 36), dissociation takes place from a higher excited state[18] in which the distribution of energy may differ from that in the state excited by 2537-Å radiation.

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The Vacuum Ultraviolet Photolysis of Liquid Benzene. Photoisomerization of Benzene to Dewar Benzene[1]

Sir:

Among the more intriguing aspects of the known photochemistry of benzene are the pronounced differences between liquid-phase and vapor-phase photolyses. For example, when benzene is photolyzed[2] in hydrocarbon solvent at 2537 Å, the primary product, formed in isolable quantities, is benzvalene (I).[3] Benzene vapor, however, is virtually inert to 2537-Å radiation,[4] at least with respect to formation of well-defined photoproducts other than benzene itself. The dideuteriobenzenes undergo intramolecular photoisomerizations[5] apparently analogous to those reported for the 2537-Å photolyses of substituted benzenes.[6] The recovered photolysate, however, contains only benzene within the limits of detection by flame ionization gas chromatography.[5a] Upon prolonged irradiation of benzene vapor at 2537 Å (Vycor 7910 filter) biphenyl is formed in addition to uncharacterized polymer.[5a] The photolysis of neat liquid benzene at 2537 Å has been reported to yield fulvene (II) as the major photoproduct,[7] but it has been suggested that fulvene is in fact a secondary product arising from benzvalene.[8] The direct photoconversion of benzene to Dewar benzene (III)[9] has not yet been reported. However, the photolysis of hexafluorobenzene,[10] tri-*t*-butylbenzenes,[11] and 1,2,4,5-tetra-*t*-butylbenzene[12] does give the corresponding Dewar form in each case.

In view of these results, we have undertaken a study of the vacuum ultraviolet photolysis of liquid benzene

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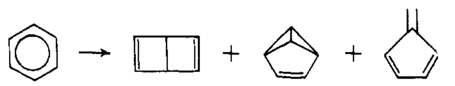
as a complement to our investigation of the vacuum ultraviolet photolysis of benzene vapor.[13] We should like now to present the results of this study.

Neat liquid benzene was irradiated with the emission from a microwave-powered oxygen discharge (bands extending from ~2000 to ~1650 Å).[14] The resulting product mixture, in contrast to the complex photolysate of the vapor-phase reaction,[13,15] was remarkably simple, with only three volatile products being observed. These have been identified as Dewar benzene (III), benzvalene (I), and fulvene (II).



III I II

Fulvene,[16] Dewar benzene,[17] and benzvalene[2] were prepared independently by known methods, and their chromatographic properties were compared with those of the photoproducts. Molecular weights were obtained for the photoproducts by mass spectral parent ion analysis using a gas chromatograph–mass spectrometer[18] combination in which part of the effluent from the gas chromatograph passed directly into the mass spectrometer. In each case, the parent ion corresponded to mol wt 78. These results are summarized in Table I. In addition, the product ultimately identified as Dewar benzene was isolated, along with a small amount of benzene, by preparative gas chromatography. When heated in pyridine, the photoproduct reverted to benzene.[19] Biphenyl was also formed in small amounts, and irradiation for more than 40 min (~4 × 10^{18} quanta) produced noticeable polymer on the lamp window. No fragmentation products were observed. An attempt was made to detect prismane[20] using highly basic gas chromatography columns,[11a] but no evidence for this compound was found.

Table I. Chromatographic Properties of Photoproducts and Known Compounds

Compd	Retention time relative to benzene		
	UCON (40°)	Squalane (30°)	DDP–TEA (25°)[b]
Dewar benzene	0.45	0.63	
Photoproduct **1**	0.45	0.61	0.45[c]
Fulvene	0.90	0.77	*d*
Photoproduct **2**	0.89	0.77	*d*
Benzvalene	*a*	*a*	0.80
Photoproduct **3**	*a*	*a*	0.80

[a] Benzvalene does not elute from these columns. [b] Didecyl phthalate–triethanolamine. To our knowledge, this is the only chromatographic system which does not decompose benzvalene.[2] [c] Has not been determined for authentic Dewar benzene. [d] Fulvene is decomposed on this column.

The relative concentrations of the photoproducts were found to be about 1:2:5 (Dewar benzene:fulvene: benzvalene), but it is possible that some of the fulvene arises from the acid-catalyzed rearrangement of benzvalene.[21] This ratio corresponds to quantum yields (oxygen actinometry[22]) of $\Phi = 0.006$ (Dewar benzene), 0.012 (fulvene), and 0.03 (benzvalene). The low quantum yield for this reaction suggests that radiationless transitions to the ground electronic state may be important in this system, since neither fluorescence nor phosphorescence is significant when neat liquid benzene is irradiated in the vacuum ultraviolet.[23]

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[18] The mass spectrometer used in this study was purchased with funds supplied by the National Science Foundation.

[19] Dewar benzene is known to isomerize to benzene under these conditions.[17]

[20] Tetracyclo[2.2.$0^{2,6}$.$0^{4,5}$]hexane.

[21] The fulvene:benzvalene ratio appears to be a strong function of the acidity of the lamp surface. A base-washed surface results in a predominance of fulvene, while a base-*coated* surface gives the results reported above. The Dewar benzene is apparently not affected by these changes.

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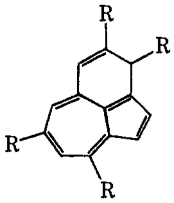
An 8H-Azuleno[1,8-*bc*]thiophene Derivative

Sir:

Hafner and Schaum[1] have recently reported that a cyclization reaction which should have yielded the tetramethyl derivative of an azulenocyclohexadiene (**1a**) gave instead 3,4,7,9-tetramethyl-2H-benz[*cd*]-azulene (**2a**). Boekelheide and Smith[2] prepared the parent system **2b** and, noting the relative ease of formation of the anion, raised the question of tautomerism and the position of the "extra" hydrogen in the molecule. They established the structure as **2b** in contrast to other tautomers such as **1b** on the basis of the similarity of its ultraviolet spectrum (λ_{max} 427 mμ) to that of heptafulvene. Tautomer **1b**, which is an azulene, should have its principal maximum at a wavelength longer than 500 mμ.



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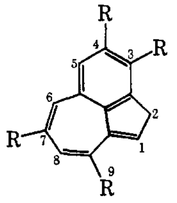

2

a, R = CH_3; **b**, R = H

These data clearly show that the benzoheptafulvene system **2** is more stable than the azulenocyclohexadiene tautomer **1**. Delocalization energies (Table I) calculated by us using simple HMO and ω-variation, self-consistent-field methods[3] suggest a relative order of stabilities consistent with the experimental observations.

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