

to the difference in conditions employed. A possible explanation is that the addition of methyl radical to the aromatic ring is reversible but in our system the presence of lead tetraacetate intercepts the radical intermediate very rapidly by electron transfer and hence decreases the over-all reversibility of addition. This could also explain the high percentage of the *o*-xylene isomer produced in our system, 64%, compared with the reported value of 56% using acetyl peroxide.⁷

From the intercept of Figure 2 the ratio k_3/k_4 was found to be 0.27; *i.e.*, the $\cdot\text{CH}_2\text{COOH}$ radical, unlike the more reactive methyl radical, adds to toluene faster than it abstracts the benzylic hydrogen atom. The difference in behavior between this radical and methyl radical can be attributed to the electrophilicity of the $\cdot\text{CH}_2\text{COOH}$ radical and/or its greater stability, as indicated by its ready formation in competition with the resonance stabilized benzyl radical. The more stable radical would be expected to favor the reaction of lower activation energy, which in this case is addition to the ring.⁸

The average ratio k_1/k_2 obtained from the slopes of Figures 1 and 2 was found to be 3.9 ± 0.5 ; *i.e.*, the $\cdot\text{CH}_3$ radical abstracts an α -hydrogen atom from toluene four times as fast as it does from acetic acid.⁹ The observed reactivity of acetic acid toward hydrogen abstraction by methyl radical, which is relatively insensitive to polar effects,¹⁰ suggests the existence of considerable resonance stabilization for the $\cdot\text{CH}_2\text{COOH}$ radical.

Our proposed mechanism serves to explain the conflicting observations in the literature and allows one to predict the conditions required to optimize the yield of any desired product, thereby increasing the synthetic utility of lead tetraacetate.

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Differences in the Reactivities of Trifluoromethyl and Methyl Radicals Produced by Photodissociation¹

Sir:

Laser emission from the $^2\text{P}_{1/2} \rightarrow ^2\text{P}_{3/2}$ iodine atom transition has been observed in the photodissociation of several alkyl iodides.^{2,3} The optical gain coefficient in a laser depends inversely on the Doppler width of the emitted line, and this in turn is related to the molecular dynamics of the photodissociation process.⁴ In this communication we report preliminary results of the photolysis of trifluoroiodomethane in the presence of

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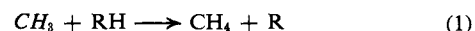
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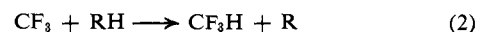
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hydrogen-containing substrates. The contrast in the behavior of these systems with the analogous methyl iodide systems is relevant to the question of energy distribution in photodissociation.

The near-ultraviolet absorption spectrum of CF_3I ⁵ is very similar to that of CH_3I ,⁶ as is the estimated C-I bond dissociation energy (54 kcal/mole).⁷ In both cases, the iodine atom from dissociation is excited to the $^2\text{P}_{1/2}$ state, 22 kcal/mole above the ground state. With 2537-Å radiation, this leaves 36 kcal/mole to be distributed among the radical and the iodine atom. If the energy is entirely translational, this division is determined by the conservation of momentum and energy; the CF_3 radical is produced with 23 kcal/mole of excess energy, whereas the CH_3 radical would have 32 kcal/mole. Methyl radicals produced in this way are capable of undergoing hydrogen abstraction reactions of the type⁸⁻¹³



where RH is methyl iodide or an added hydrogenic compound. Activation energies for such reactions are typically several kilocalories per mole. For analogous reactions of the CF_3 radical



the activation energy is 10-11 kcal/mole when RH is H_2 ¹⁴ or CH_4 .¹⁵ The similarity in the energetics of the $\text{CF}_3\text{I-RH}$ and $\text{CH}_3\text{I-RH}$ systems would lead one to expect a quantum yield for fluoroform in reaction 2 comparable to that for methane in reaction 1. The latter value is 3×10^{-8} for the photolysis of methyl iodide at 2537 Å and 1.5×10^{-4} for the photolysis of CD_3I at 3130 Å (13 kcal/mole of excess energy).

The data of Table I show that this is not the case. In

Table I. Photolysis of CF_3I by 2537-Å Radiation at Room Temperature

Reactant concn ^a		Product concn ^b		$\Phi_{\text{CF}_3\text{H}}$
CF_3I	Other	CF_3H	Other	
1.22	6.23 (H_2)	0.22		3×10^{-5}
0.19	0.82 (CH_4)	≤ 0.005		$\leq 5 \times 10^{-6}$
0.15	0.27 (CH_3I)	< 0.001	14.4 (CH_4) 0.12 (C_2H_6)	$< 5 \times 10^{-6}$
0.28	0.23 (NO)		220 (CF_3NO)	

^a In units of 10^{-3} M. ^b In units of 10^{-6} M.

particular, the experiment with a mixture of CH_3I and CF_3I shows that $\Phi_{\text{CF}_3\text{H}}/\Phi_{\text{CH}_4} \leq 3 \times 10^{-4}$. No C_2F_6 was detected in the reaction products from any of these

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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



Verification that CF_3I is dissociating is provided by the experiment with NO added. The rate constant¹⁶ for the reaction $\text{CF}_3 + \text{NO} \rightarrow \text{CF}_3\text{NO}$ 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 Ausloos¹³ 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_3} 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-halo-

gen 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 state¹⁸ 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 Benzene¹

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 photolyzed² 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 diduteriobenzenes undergo intramolecular photoisomerizations⁵ 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*-butylbenzene¹² 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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