by applying the van der Waals sphere model for atoms to the available quantum mechanical information on the structural changes, are found to be much smaller in magnitude than the observed activation and reaction volumes. The present work discloses that the most important factor controlling the large gap between $\Delta V^{\ddagger}$ (ΔV) and $\Delta V_W^{\ddagger}$ (ΔV_W) is the size dependence of the packing coefficient η. $\Delta V^{\ddagger}$ and ΔV predicted for the prototype 1,3-dipolar cycloaddition on the basis of V_W and η are in reasonable agreement with those observed for the 1,3-dipolar cycloaddition reactions of complicated molecules. Thus, no serious problems have been brought about in the present volumetric study even if we have calculated $\Delta V^{\ddagger}$ values by neglecting the pressure dependence of the transmission coefficient in the transition-state theory (see eq 1).

Registry No. BPN, 5492-70-6; DMM, 624-48-6; DMF, 624-49-7; MA, 96-33-3; HCNO, 51060-05-0; HCCH, 74-86-2; $H_2C{=}CHCH{=}CH_2$, 106-99-0; $H_2C{=}CH_2$, 74-85-1.

Reactions with Aromatic Compounds of Recoiling Bromine Atoms Formed from the $^{76,77}Kr \rightarrow {}^{76,77}Br$ Transformations. Liquid-Phase Reactions[1a]

Stephen M. Moerlein,[1b,c] Michael J. Welch,*[1b] and Alfred P. Wolf[1d]

Contribution from the Division of Radiation Sciences, The Edward Mallinckrodt Institute of Radiology, Washington University School of Medicine, St. Louis, Missouri 63110, and the Department of Chemistry, Brookhaven National Laboratory, Upton, Long Island, New York 11973. *Received November 8, 1982*

Abstract: Bromine atoms produced via the $^{76}Kr(EC)^{76}Br$ and $^{77}Kr(\beta^+/EC)^{77}Br$ transformations were reacted with simple benzenoid compounds in the liquid phase. For both ^{76}Kr and ^{77}Kr, bromodeprotonation resulted in a reactivity constant $\rho^+ \simeq -0.6$, with higher yields for ^{76}Br. Whereas bromodeprotonation was hypothesized to occur via formation of a product-determining σ-complex by radical bromine species, ipso substitution was described in terms of a two-step addition–elimination mechanism in which bond breakage is product determining. While radical bromine species are probably involved in substituent displacements from monosubstituted arenes, polysubstituted aromatic compounds activated to nucleophilic attack were shown to involve an additional nucleophilic reaction pathway.

The use of solution chemistry to study the mechanisms of aromatic substitution is complicated by the occurrence of several side processes, such as disproportionation of the substrate,[2-4] halogen exchange with the catalyst,[5,6] internal halogen transfer[3,5,7] catalyzed arylation, or polymerization by the Scholl reaction,[8] solvation effects,[9,10] and ion pairing.[11-13] These problems not only make elucidation of substitution mechanisms difficult, but may also constrain mechanistic information to a particular set of reactions or experimental conditions.

A useful technique that avoids these problems is the study of nucleogenic decay in organic substrates.[14] Electrophilic, homolytic, and nucleophilic processes may be studied in an environment consisting solely of the aromatic substrate and carrier-free quantities of the parent nuclide. Because of the efficiency of radioanalytical techniques, only picomolar concentrations of parent isotope are required, which makes double-substitution pathways improbable and minimizes radiolytic degradation of the substrate compounds. Finally, due to the variety of charge states and kinetic energies imparted to the daughter atom of different decay systems, different reaction pathways can be studied that may shed light on the general problem of aromatic hydrogen substitution mechanisms.

In addition to the commonly studied aromatic hydrogen substitution reactions, mechanisms of ipso attack and aromatic substituent displacement are of interest because the particular reaction pathways that are followed are a function of several parameters, such as the nature of the attacking species, the mobility of the displaced atom or group, the nature of the acceptor for the displaced group, substituent-induced activation or deactivation of the respective aromatic nucleus, and solvation effects on the reactant or product species. This plethora of chemical variables allows for electrophilic,[15,16] free-radical,[17,18] as well as

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nucleophilic[19,20] reaction mechanisms to be involved in aromatic group displacement. The application of nucleogenic atoms as reactive species is therefore useful in the study of these types of substitution reactions. The large variety of decay systems allows for the production of recoiling species with different degrees of translational energy, electronic excitation, and charge states.[14] In principle, one should be able to select an appropriate parent–daughter decay system that generates energetic cations, radicals, and anions so that elucidation of electrophilic, free-radical, and nucleophilic reaction pathways is possible. Because the nucleogenesis results in a nascent reactive species free of catalytic agents, reaction mechanisms are expectd to be of a simpler nature than those usually reported in the literature.

This investigation concerns the aromatic reactivity of nucleogenic ^{76}Br and ^{77}Br, which are generated by the decay systems

$$^{76}\mathrm{Kr} \xrightarrow{\mathrm{EC}} {}^{76}\mathrm{Br}$$

and

$$^{77}\mathrm{Kr} \xrightarrow{\beta^{+}/\mathrm{EC}} {}^{77}\mathrm{Br}$$

As described previously,[21] the two bromine isotopes are produced with different charges and kinetic energies, which is expected to result in differences in their reactivity in aromatic substitution pathways. Calculations indicate that ^{76}Br is initially formed with a high positive charge spectrum (average ca. +5), while ^{77}Br is initially formed as approximately 50% negatively charged, 10% neutral, and 40% positively charged (average ca. +5).[21] In addition to the differences in charge states between the two bromine isotopes, their initial states of kinetic excitation are different, allowing possible discrimination of the chemical parameters of the substrate on the formation of aromatic substitution products. The recoil energies are 7.5 eV for ^{76}Br, 67.5 eV for electron-capture decay formation of ^{77}Br, and 9.1–37.8 eV for ^{77}Br formed following positron decay.[22]

Experimental Section

The methods used for the production and purification of ^{76}Kr and ^{77}Kr have been previously described.[21] For work done at the Brookhaven National Laboratory, the selenium target material was irradiated with 54-MeV ^{3}He (10 μA, 5 μA h) at the BNL 60-in. isochronous cyclotron, while experiments done with the Washington University 52-in. cyclotron employed a 25-MeV ^{3}He beam. Purified, carrier-free ^{76}Kr and ^{77}Kr were Toepler pumped into reaction vessels to which aromatic components were added. The vessels were completely filled with liquid substrates, so that gas-phase reactions were minimized or eliminated. Thick-walled glass vessels of approximately 0.5-mL volume fitted with TFE needle valves were used.

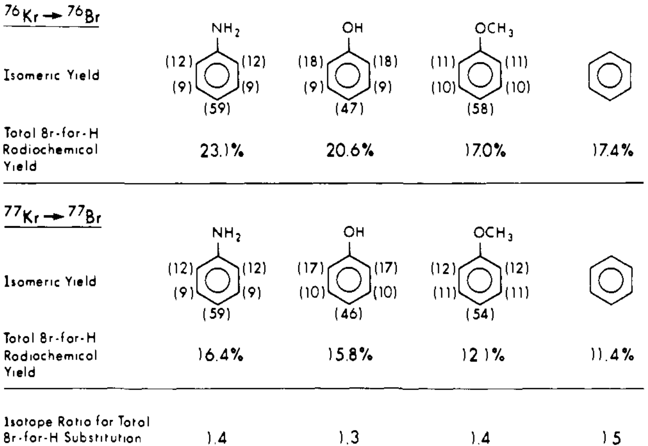

Figure 1. ^{76,77}Kr → ^{76,77}Br hydrogen substitution yields for arenes activated toward electrophilic attack (liquid phase, 25 °C).

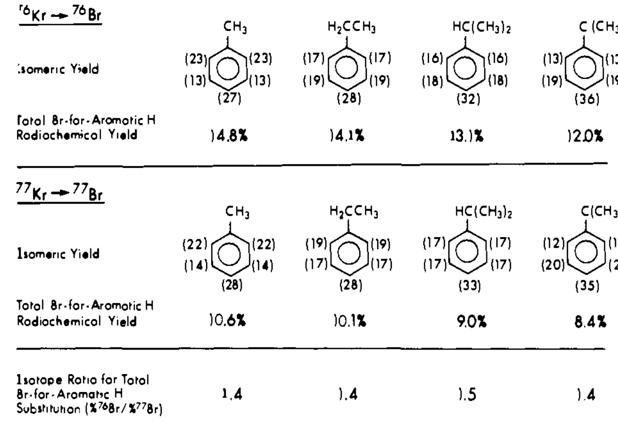

Figure 2. ^{76,77}Kr → ^{76,77}Br hydrogen substitution yields for alkyl arenes (liquid phase, 25 °C).

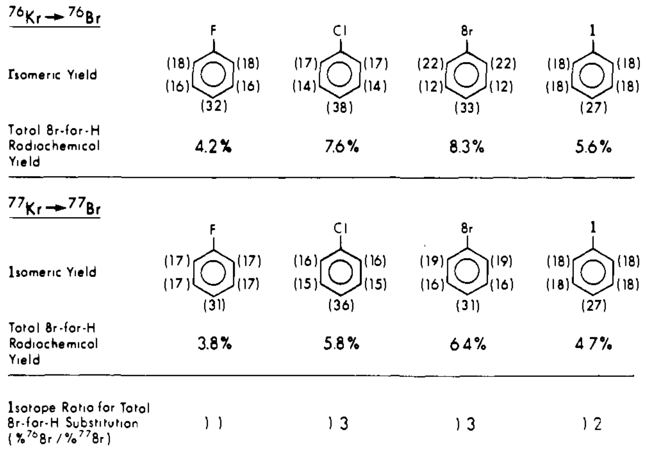

Figure 3. ^{76,77}Kr → ^{76,77}Br hydrogen substitution yields for halogenated arenes (liquid phase, 25 °C).

Liquid-phase samples were simply allowed to stand at room temperature during the decay period. The only exception was phenol, which was heated in an oil bath at 52 ± 2 °C for the duration of the experiment to maintain a liquid environment. After approximately 24 h (vessel in the dark at 25 °C), essentially all of the ^{77}Kr had decayed to ^{77}Br and ^{76}Br, and the series ^{76}Kr → ^{76}Br → ^{76}Se reached a maximum. At this time, the contents were removed with a syringe and quickly injected onto high-presure liquid chromatographic columns. Separations were carried

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Table I. Aromatic Substitution Yields and π-Complex Stabilities for Isomers of Xylene

	o-xylene	*m*-xylene	*p*-xylene
yield, % ^{76}Br	13.9 ± 1.5	10.8 ± 1.2	10.3 ± 1.0
yield, % ^{77}Br	10.0 ± 0.9	7.2 ± 0.7	6.9 ± 0.7
π-complex stability with Br_2 (C_6H_6 = 1)[a]	2.2	2.1	2.2

[a] Reference 23.

out with a stationary phase consisting of three C_{18} reverse-phase columns (Partisil-10 ODS Magnum 9, Whatman, Clifton, New Jersey) connected in series. Mobile phases consisted of various combinations of methanol, acetonitrile, water, and tetrahydrofuran.[22] Retention times were determined for aromatic products with commercially available authentic compounds and on-line UV detection of mass peaks (Schoeffel UV Detector Model 770). Alkyl bromide products were determined in a similar manner with on-line RI detection (Perkin-Elmer). All bromo products were able to be separated in a single pass, with the exception of those formed from toluene and anisole. For these substrates, bromo isomers could be separated by recycle HPLC (three–four cycles on-line before fraction collection).

The eluent was collected in fractions and counted off-line in an automated NaI(Tl) well scintillation counter. These counts gave the radioactive peaks corresponding to each brominated product and represented the sum of ^{76}Br and ^{77}Br products. The peak fractions were counted in a fixed geometry by Ge(Li) γ-ray spectrometery (Princeton Gamma Tech Model RG-110) and multichannel analysis (Canberra Model 8100). The ratio of the activity of ^{77}Br to the activity of ^{76}Br for each component was thereby determined following correction for photopeak intensity and Ge(Li) crystal efficiency. From this ratio and the total [NaI(Tl)] peak counts, the absolute yields of ^{76}Br and ^{77}Br for each product were calculated. By summing all of the ^{76}Br and ^{77}Br product activities, the yield of each component could then be expressed as the percent ^{76}Br of total ^{76}Br activity and the percent ^{77}Br of total ^{77}Br activity.

Results

The results for ^{76}Br and ^{77}Br bromodeprotonation of various benzenoid systems in the liquid phase at 25 °C are shown in Figures 1–4. Each value reported represents the average of two–three experiments. The isomeric (positional) yields are shown in parenthesis at each respective location on the ring. These numbers give the percentage of total Br-for-aromatic H substitution yield for each position (normalized to 100%). Below each aromatic substrate is shown the total substitution yield for each decay process with the respective compound in terms of percentage of total radioactivity. The error in the total substitution yields was less than 3% ^{76}Br (^{77}Br) for all substrates. Also shown in each figure is the yield ratio (percent ^{76}Br/percent ^{77}Br) of total Br-for-aromatic H substitution in each substrate. Figure 1 gives the results for benzenoid systems activated toward electrophilic attack, while Figure 2 shows the data for a series of alkyl arenes. Figures 3 and 4 present the results for halogenated aromatics and benzenoid systems deactivated toward electrophilic substitution, respectively. The substitution yields for the isomers of xylene are shown in Table I, while Table II gives the brominated products from protonated and deuterated benzene and toluene as substrates.

Tables III–V show the results of ipso substitution by the ^{76,77}Kr → ^{76,77}Br decy processes in three categories of aromatic substrates.

Table II. ^{76,77}Kr → ^{76,77}Br Bromination of Protonated and Deuterated Substrates in the Liquid Phase at 25 °C

	radiochemical yield of brominated products					
	bromobenzene		α-bromotoluene		Σ *o,m,p*-bromotoluene	
substrate	% ^{76}Br	% ^{77}Br	% ^{76}Br	% ^{77}Br	% ^{76}Br	% ^{77}Br
benzene	17.4 ± 1.3	11.4 ± 0.8				
benzene-d_5	18.2 ± 1.1	12.1 ± 0.08				
toluene	1.3 ± 0.4	1.4 ± 0.3	5.4 ± 1.2	4.7 ± 0.6	14.8 ± 1.4	10.6 ± 0.9
toluene-d_8	1.4 ± 0.6	1.4 ± 0.4	5.6 ± 0.4	4.8 ± 1.1	13.7 ± 1.1	11.2 ± 1.2

Table III. Ipso Substitution and Side-Chain Reaction Products for ^{76,77}Kr → ^{76,77}Br Decay in Alkyl Arenes (Liquid Phase, 25 °C)

				bromination yield		
substrate	brominated product	bond energy, eV[a]	ΔH°, eV[b]	% ^{76}Br	% ^{77}Br	% ^{76}Br/ % ^{77}Br
		Aromatic (Ipso) Substitution				
C_6H_5–CH_3	C_6H_5Br	4.33	0.94	1.4 ± 0.3	1.3 ± 0.3	1.1
C_6H_5–C_2H_5	C_6H_5Br	4.19	0.78	1.3 ± 0.2	1.1 ± 0.3	1.2
C_6H_5-*i*-C_3H_7	C_6H_5Br	4.12	0.72	1.3 ± 0.3	1.0 ± 0.3	1.3
C_6H_5-*t*-C_4H_9	C_6H_5Br	3.94	0.46	1.1 ± 0.2	0.8 ± 0.3	1.4
		Alkyl Substitution				
C_6H_5–CH_3	C_6H_5–CH_2Br	3.70[b]	1.24	5.4 ± 1.3	4.1 ± 1.0	1.3
C_6H_5–C_2H_5	C_6H_5–CH_2Br	3.12	0.61	4.8 ± 1.1	3.7 ± 0.7	1.3
C_6H_5–C_2H_5	C_6H_5–$CHBrCH_3$	3.60[b]	1.16[c]	2.3 ± 1.0	1.6 ± 0.9	1.4
C_6H_5–C_2H_5	C_6H_5–CH_2CH_2Br		1.30[c]	5.0 ± 1.9	3.1 ± 1.4	1.6
C_6H_5-*i*-C_3H_7	C_6H_5–$CHBrCH_3$	3.08	0.56[c]	4.8 ± 0.9	4.0 ± 1.9	1.2
C_6H_5-*i*-C_3H_7	C_6H_5–$CBr(CH_3)_2$		1.12[c]	0.9 ± 0.4	0.6 ± 0.4	1.5
C_6H_5-*i*-C_3H_7	C_6H_5–$CH(CH_3)CH_2Br$		1.30[c]	4.4 ± 1.2	4.3 ± 1.2	1.0
C_6H_5-*t*-C_4H_9	C_6H_5–$C(CH_3)_2Br$		0.16[c]	4.9 ± 1.4	3.5 ± 0.9	1.4
C_6H_5-*t*-C_4H_9	C_6H_5–$C(CH_3)_2CH_2Br$		1.30[c]	3.0 ± 1.4	2.6 ± 1.0	1.2
		Alkyl Abstraction				
C_6H_5-CH_3	CH_3Br	4.33	1.00	0.5 ± 0.2	0.4 ± 0.2	1.2
C_6H_5–C_2H_5	CH_3Br	3.12	0.03	1.4 ± 0.9	1.4 ± 0.7	1.0
C_6H_5–C_2H_5	C_2H_5Br	4.19	0.91	0.6 ± 0.3	0.5 ± 0.2	1.1
C_6H_5-*i*-C_3H_7	CH_3Br	3.08	0.08	2.8 ± 1.0	2.2 ± 1.0	1.3
C_6H_5-*i*-C_3H_7	*i*-C_3H_7Br	4.12	0.82[c]	0.9 ± 0.3[d]	0.6 ± 0.3[d]	1.5
C_6H_5-*t*-C_4H_9	CH_3Br			4.9 ± 1.0	3.2 ± 1.1	1.5
C_6H_5-*t*-C_4H_9	*t*-C_4H_9Br	3.94	0.78[c]	1.3 ± 0.6[e]	1.2 ± 0.2[e]	1.1

[a] Energy of bond broken in substrate. Calculated from enthalpies of formation given in ref 24 and 25, unless otherwise noted. [b] ΔH° of reaction, calculated from enthalpies of formation given in ref 24, 25, and 26, unless otherwise noted. [c] Some product formation enthalpies estimated by the additivity methods of ref 27, in addition to the data given in ref 24, 25, and 26. [d] May include isomeric three-carbon compounds. [e] May include isomeric four-carbon compounds.

Table IV. Ipso Substitution Products from ^{76,77}Kr → ^{76,77}Br Decay in Group-Substituted Arenes (Liquid Phase, 25 °C)

substrate	bond energy, eV[a]	electro-negativity[b]	bond moment, μ (θ)[c]	pK_a[d]	bromination yield % ^{76}Br	 % ^{77}Br	 % ^{76}Br/% ^{77}Br
C_6H_5-NO_2	3.56[e]	3.0	4.19 D (180°)	3.3	2.0 ± 0.6	2.2 ± 0.9	0.9
C_6H_5-OH	4.25	3.5	1.40 D (90°)	15.7	0.9 ± 0.4	0.8 ± 0.3	1.1
C_6H_5-CH_3	4.34	2.5	1.35 D (0°)	40	1.4 ± 0.3	1.3 ± 0.3	1.1
C_6H_5-NH_2	4.51	3.0	1.48 D (48.5°)	36	0.9 ± 0.2	0.6 ± 0.3	1.5
C_6H_5-CF_3	4.73[f]	2.5	2.86 D (180°)	28[g]	1.6 ± 0.5	1.5 ± 0.4	1.1
C_6H_5-OCH_3	4.73	3.5	1.35 D (72°)	16	1.2 ± 0.1	1.1 ± 0.3	1.1
C_6H_5-CN	5.49[f]	2.5	4.39 D (180°)	9.1	0.4 ± 0.2	0.3 ± 0.2	1.3

[a] Energy of bond broken in substrate, ref 25, unless otherwise noted. [b] Electronegativity of group atom bonded to aromatic ring, ref 28. [c] Reference 29. For 0° ⩽ θ ⩽ 90°, ring carbon is negative end of dipole. For 90° ⩽ θ ⩽ 180°, ring carbon is positive end of dipole. [d] pK_a of conjugate acid of displaced group, ref 30, unless otherwise noted. [e] Calculated from enthalpies of formation given in ref 25 and 31. [f] Calculated from enthalpies of formation given in ref 24 and 25. [g] Reference 32.

Table V. Ipso Substitution Products from ^{76,77}Kr → ^{76,77}Br Decay in Haloarenes (Liquid Phase, 25 °C)

substrate	bond energy, eV[a]	electro-negativity[b]	bond moment, μ (θ)[c]	pK_a[d]	bromination yield % ^{76}Br	 % ^{77}Br	 % ^{76}Br/% ^{77}Br
C_6H_5-F	5.42	4.0	1.61 D (180°)	3.2	2.2 ± 0.3	2.2 ± 0.3	1.0
C_6H_5-Cl	4.12	3.0	1.76 D (180°)	−7	16.2 ± 1.7	9.2 ± 1.0	1.8
C_6H_5-Br	3.47	2.8	1.64 D (180°)	−9	32.1 ± 3.4	15.8 ± 1.7	2.0
C_6H_5I	2.78	2.5	1.71 D (180°)	−10	25.5 ± 2.6	11.6 ± 1.2	2.2

[a] Energy of bond broken in substrate, ref 25. [b] Electronegativity of displaced halogen, ref 28. [c] Reference 29. For 0° ⩽ θ ⩽ 90°, ipso carbon is negative end of dipole. For 90° ⩽ θ ⩽ 180°, ipso carbon is positive end of dipole. [d] pK_a of conjugate acid of displaced halogen, ref 30.

Table VI. Aromatic Substitution Yields for ^{76,77}Kr → ^{76,77}Br Decay in Simple Benzenoid Compounds and Their Aromatic Fluorinated Analogues (Liquid Phase, 25 °C)

compound (substrate)	total aromatic substitution yield % ^{76}Br	 % ^{77}Br	 % ^{76}Br/% ^{77}Br	fluorinated analogue (substrate)	total aromatic substitution yield % ^{76}Br	 ^{77}Br	 % ^{76}Br/% ^{77}Br
C_6H_6	17.4 ± 1.8	11.4 ± 1.2	1.5	C_6F_6	19.3 ± 3.4	16.2 ± 4.0	0.7
C_6H_5F	6.4 ± 0.7	6.0 ± 0.6	1.1	C_6F_5H	9.4 ± 2.7	11.6 ± 1.9	0.8
C_6H_5-CH_3	16.2 ± 1.7	11.9 ± 1.2	1.4	C_6F_5-CF_3	25.4 ± 4.2	33.1 ± 4.8	0.8
C_6H_5-CF_3	7.6 ± 0.8	7.0 ± 0.7	1.1	C_6F_5-CH_3	7.5 ± 1.9	8.3 ± 2.3	0.8

Each table presents the substitution yield in terms of percent ^{76}Br, percent ^{77}Br, and the relative yield ratio percent ^{76}Br/percent ^{77}Br. The latter value allows for easier comparison of the various reaction systems. Each table also shows the reported literature values for relevant product-determining variables, such as bond energies, electronegativities, and acidity constants of displaced groups. The displacement yields of aromatic fluorine and those of aromatic hydrogen are compared in Table VI. Changes in fluorine substitution caused by substituent-induced alteration in the benzenoid system are shown in Table VII.

Para-substituted fluoro derivatives were used as substrates, and the yields of the corresponding *p*-bromo derivatives are tabulated as percent ^{76}Br, percent ^{77}Br and the ratio percent ^{76}Br/percent ^{77}Br.

Discussion

Reactive Species in Hydrogen Displacement. The relatively higher ^{76}Br substitution yields and the large positive-charge spectrum of the reactive bromine atoms generated from decay of ^{76}Kr suggests that the bromodeprotonation mechanism may involve an electron-deficient intermediate. To test this hypothesis, a linear free energy correlation between the aromatic substitution yields of Figures 1–4 and the Brown–Okamoto σ^+ substituent constant[33] was investigated. The σ^+ constant expresses ΔG effects of enhanced mesomeric interactions in which the reaction center is directly conjugated with the substituent.[34,35] Because all of the substituents except the alkyl groups contain lone p electrons that are able to take part in through conjugation, the σ^+ relationship is a more appropriate correlation than the original Hammett σ calculation.[36] In addition, the alkyl groups may be involved in hyperconjugation, so σ^+ is also applicable to these substituents.[33,34] A Brown–Okamoto correlation for the ^{76}Kr → ^{76}Br bromo deprotonation of aromatic compounds in the liquid

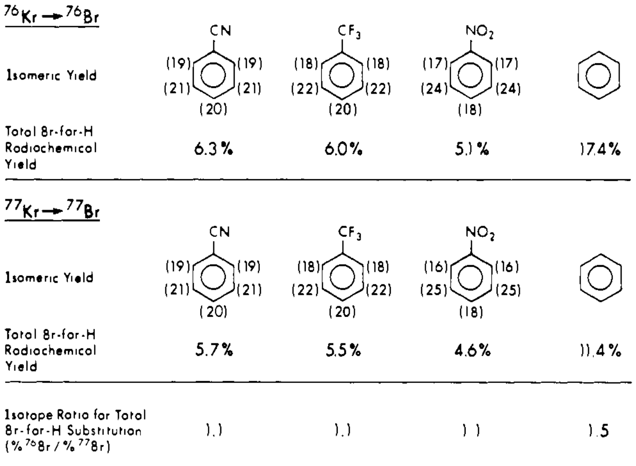

Figure 4. ^{76,77}Kr → ^{76,77}Br hydrogen substitution yields for arenes deactivated toward electrophilic attack (liquid phase, 25 °C).

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Table VII. Bromodefluorination Yields for $^{76,77}Kr \rightarrow {}^{76,77}Br$ Decay in 1,4-Substituted Fluorobenzene Derivatives (Liquid Phase, 25 °C)

		radiochemical yield		
substrate	brominated product	% ^{76}Br	% ^{77}Br	% ^{76}Br/% ^{77}Br
p-F–C_6H_4-NO_2	*p*-Br–C_6H_4-NO_2	2.8 ± 0.4	4.4 ± 0.8	0.6
p-F–C_6H_4-$COCH_3$	*p*-Br–C_6H_4–$COCH_3$	2.2 ± 0.5	3.0 ± 0.9	0.7
p-F–C_6H_4–CF_3	*p*-Br–C_6H_4–CF_3	2.2 ± 0.3	2.8 ± 0.4	0.8
p-F-C_6H_4Br	*p*-Br–C_6H_4–Br	2.0 ± 0.2	2.1 ± 0.3	1.0
p-F–C_6H_4–I	*p*-Br–C_6H_4–I	2.0 ± 0.3	2.2 ± 0.2	0.9
p-F–C_6H_4–F	*p*-Br–C_6H_4F	2.0 ± 0.4	2.0 ± 0.2	1.0
F–C_6H_5	Br–C_6H_5	2.2 ± 0.6	2.2 ± 0.3	1.0
p-F–C_6H_4–CH_3	*p*-Br–C_6H_4–CH_3	3.3 ± 0.5	2.3 ± 0.4	1.4
p-F–C_6H_4–OCH_3	*p*-Br–C_6H_4–OCH_3	3.2 ± 0.4	2.8 ± 0.3	1.1
p-F–C_6H_4–OH	*p*-Br–C_6H_4-OH	3.9 ± 0.6	3.3 ± 0.5	1.2
p-F–C_6H_4–NH_2	*p*-Br–C_6H_4–NH_2	7.5 ± 1.8	4.1 ± 0.6	1.8
o,p-F-C_6H_3-$(NO_2)_2$	*o*,(*p*)-Br–C_6H_3–$(NO_2)_2$	4.0 ± 1.6	8.0 ± 2.3	0.5
C_6F_6	Br–C_6F_5	3.2 ± 0.5	4.4 ± 0.7	0.7

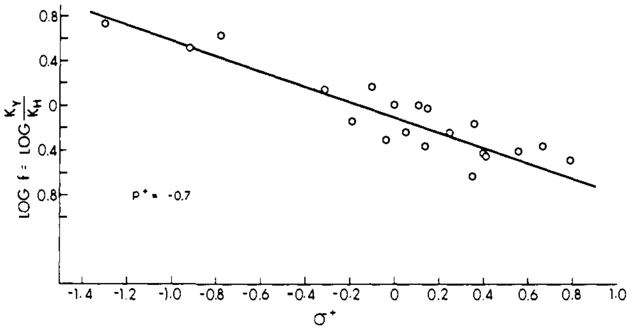

Figure 5. Brown–Okamoto linear free energy correlation for $^{76}Kr \rightarrow {}^{76}Br$ bromodeprotonation of benzene derivatives (liquid phase, 25 °C). K_Y is the ^{76}Br radiochemical yield (per position) for meta and para bromination of the substituted benzene derivatives shown in Figures 1–4. K_H is the ^{76}Br radiochemical yield (per position) for bromodeprotonation of benzene.

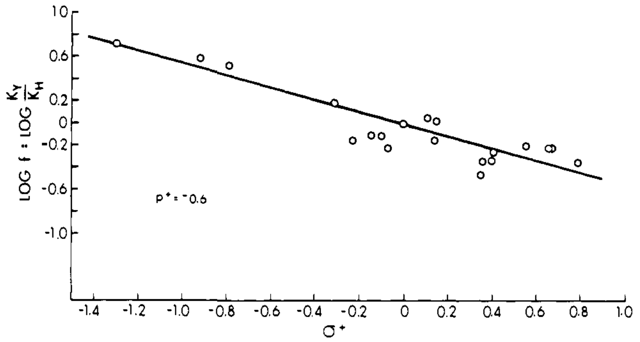

Figure 6. Brown–Okamoto linear free energy correlation for $^{77}Kr \rightarrow {}^{77}Br$ bromodeprotonation of benzene derivatives (liquid phase, 25 °C). K_Y is the ^{77}Br radiochemical yield (per position) for meta and para bromination of the substituted benzene derivatives shown in Figures 1–4. K_H is the radiochemical yield (per position) for bromodeprotonation of benzene.

Table VIII. Competitive Reaction Pathways of Bromine Species with Benzene

species	reaction	mechanism	ΔH, eV^a
Br^+	electron transfer	$Br^+ + C_6H_6 = Br\cdot + C_6H_6^+$	−2.56
	hydrogen abstraction	$Br^+ + C_6H_6 = HBr + C_6H_5^+$	−0.51
	hydrogen substitution	$Br^+ + C_6H_6 = C_6H_5Br + H^+$	3.18
$Br\cdot$	electron transfer	$Br + C_6H_6 = Br^- + C_6H_6^+$	6.36
	hydrogen abstraction	$Br + C_6H_6 = HBr + C_6H_5\cdot$	0.98
	hydrogen substitution	$Br + C_6H_6 = C_6H_5Br + H\cdot$	1.42
Br^-	electron transfer	$Br^- + C_6H_6 = Br + C_6H_6^-$	4.08
	hydrogen abstraction	$Br^- + C_6H_6 = HBr + C_6H_5^-$	2.32
	hydrogen substitution	$Br^- + C_6H_6 = C_6H_5Br + H^-$	4.21

[a] Calculated from data given in ref 26.

phase at 25 °C is shown in Figure 5. Although free energy relationships are usually applied to the partial rate factors in bromodeprotonation reactions, in this case we have applied the isomeric yields to the correlation on the basis of the reasonable assumption that they are proportional to the relative rate factors. The ordinate represents the ratio of the bromodeprotonation yield for the respective hydrogen atom substituted in a substrate compound relative to the bromodeprotonation yield for a single hydrogen atom in benzene. The reaction constant was determined by regression analysis to be $\rho^+ = -0.7$, with a coefficient of correlation $r = 0.89$ and a standard error of the estimate $s_e = 0.17$. Similarly, the ρ^+ calculation for the $^{77}Kr \rightarrow {}^{77}Br$ decay process is shown in Figure 6 and gave $\rho^+ = -0.6$ ($r = 0.88$, $s_e = 0.15$). The essentially identical reaction constants for the $^{76}Kr \rightarrow {}^{76}Br$ and the $^{77}Kr \rightarrow {}^{77}Br$ decay processes strongly suggests that hydrogen substitution occurs by the same mechanism for both isotopes. Since the magnitude of ρ^+ reflects the degree of positive charge delocalization in the aromatic nucleus of the transition state, the low ρ^+ value and low inter-intramolecular selectivity for these systems indicates that the reactive bromine species is a radical. While these $^{76,77}Kr \rightarrow {}^{76,77}Br$ reaction constant results contrast with typical electrophilic bromination constants of $\rho^+ = -12.1$ (Br_2, HOAc–H_2O, 25 °C)[37] and $\rho^+ = -6.2$ (HOBr, $HClO_4$, 50% dioxane, 25 °C),[38] they show a close resemblance to the reaction constants for free-radical photobromination ($\rho^+ = -1.1$)[39] or NBS bromination ($\rho^+ = -1.38$)[40] of substituted toluenes. The results of this work also agree with the ρ^+ value of −0.45 previously reported for reactions of nucleogenic bromine species with aromatic compounds.[41,42] The slight difference in reactivity constants in this case may be due to differences in analytical techniques used in separating the reaction products (GC vs. HPLC).

The explanation for the reactivity of Br· and the absence of reaction products involving Br^{n+} lies in the relative ease of charge transfer and aromatic substitution. For simplicity, we can consider ion–molecule reactions as occurring in two steps:

$$Br^{n+} + Ar \rightarrow [Br\text{–}Ar]^{n+} \rightarrow \text{products}$$

The first step is formation of a bimolecular complex, which is a function of ion–molecule collision cross sections. The second step ivolves collapse of the complex into products, which may also include charge-transfer products.

From calculated cross sections it was shown that the tendency for ion–molecule impact and complex formation is exceeded by the ability for Br^{n+} to undergo charge transfer and neutralization

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Table IX. Aromatic Substitution Yields and π-Complex Stability Parameters for Various Alkyl Arenes

	toluene	ethylbenzene	isopropylbenzene	*tert*-butylbenzene
yield, % ^{76}Br	14.8 ± 1.4	14.1 ± 1.4	13.1 ± 1.2	12.0 ± 1.0
yield, % ^{77}Br	10.6 ± 0.9	10.1 ± 1.0	9.0 ± 0.8	8.4 ± 0.8
+I effect of alkyl substituent (H = 1)[a]	10	13	13	20
dipole moment[b]	0.37 D	0.39 D	0.43 D	0.45 D
π-complex stability with HCl (C_6H_6 = 1)[c]	1.47	1.76	1.96	2.14

[a] References 48 and 49. [b] Reference 50. [c] Reference 51.

with the aromatic substrate.[22] In addition to this greater barrier to complex formation, there is also an angular momentum barrier to decomposition of the bimolecular complex, which must be surmounted in product formation.[43] Although the various output pathways from the intermediate may be detailed by the phase-space theory,[44] for our purposes it is sufficient to note that the energy available for barrier penetration is inversely related to the enthalpy of reaction. That is, as more energy is required for completion of the reaction, less energy is available for crossing the angular momentum barrier. Table VIII shows how the relative enthalpy changes for electron transfer, hydrogen abstraction, and hydrogen substitution vary widely for bromonium (Br^+), bromine (Br·), and bromide (Br^-) reactants. Multiply charged bromine species were ignored without loss of generality because any brominated products that form would be unstable to Coulomb explosion/charge neutralization processes.[45] As shown in Table VIII, the charge-transfer reaction of bromonium is highly exothermic, while the competitive substitution pathway is endothermic. Thus, charge-exchange neutralization of Br^+ is expected to occur to a much greater extent than bromodeprotonation. It is therefore not surprising that a greater ρ^+ value corrseponding to highly electrophilic Br^+ substitution was not found. By contrast, the reaction pathways of bromine atoms are all endothermic, but further reduction of bromine to bromide is more endothermic than hydrogen abstraction or substitution reactions. Thus, Br^{n+} is generally expected to undergo sequential charge-transfer neutralization until the Br· species is formed, where the oxidation state is thermodynamically "trapped" for other reaction pathways. Although not all of this Br· will react in deprotonation reaction pathways, the kinetic/excitation energy of the nucleogenic ^{76,77}Br may assist in overcoming the energetic barriers to reaction, thereby allowing completion of reaction by a certain fraction of the bromine species. The relatively high ^{76}Br substitution yield is presumably due to a greater percentage of $^{76}Br^{n+}$ ions produced that eventually pass through the reactive Br· channel. The reactions of bromide are also shown in Table VIII, where hydronium abstraction is least energetically hindered.

Mechanism of Aromatic Hydrogen Substitution. From the above discussion it is seen that charge transfer and neutralization predominates over other reactions by Br^{n+} and that it is the Br· species that actually enters into hydrogen substitution reactions. On the basis of the negative sign of the ρ^+ constant, it can be surmised that the electron affinity of the reactive bromine atom allows an electrophilic mechanism to be followed even though the bromine is uncharged. The classical reaction profile for electrophilic bromodeprotonation is shown by the dotted line of Figure 7, in which Olah π-complexes and the Wheland π-complex play roles as intermediates. Whereas the aromaticity of the π-complex is undisturbed because the bromine atom binds to the entire π-electron cloud,[46,47] the σ-complex involves severe distortion of the benzenoid nucleus as the bromine binds to a ring carbon in a cyclohexadienyl structure.[33] The σ-complex is represented as a dipolar structure in Figure 7, since the aromatic polarization is expected to be less for the case of radical attack than for substitution by bromine bearing a formal charge. As one proceeds along the reaction coordinate, an initial bromine–aromatic π-complex forms, which degenerates to a σ-complex, which then proceeds to expel the substituted hydrogen via a second hydrogen–aromatic π-complex.

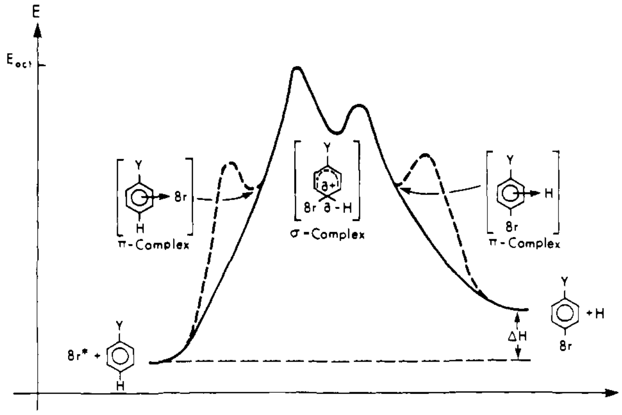

Figure 7. Energy–reaction coordinate profile for classical aromatic electrophilic substitution by bromine, where Y can be any substituent group. Broken line is pathway including π-complex intermediates. Solid line is for best explanation of our experimental results.

Formation of an initial bromine–aromatic π-complex was not found to be product determining, if it occurs at all. Table IX shows that the total aromatic H substitution by the $^{76,77}Kr \rightarrow {}^{76,77}Br$ decay processes decreases as the number of carbon atoms in the alkyl substituent increases. This rank order is opposite that expected for π-complexation, since as the π-electron density is enhanced, the π-complex stability should also increase. On the basis of the +I inductive effect of the alkyl groups, the aromatic electron density should increase with the number of alkyl carbons.[48,49] The order of dipole moments[50] also corresponds with measured stabilities of isolated HCl–arene π-complexes.[51] The discrepancy between these ^{76,77}Br results and π-complex stability parameters is not merely a result of steric hindrance because size factors should only affect the positional selectivity of the substitution products. That is, while the para and meta yields may be enhanced at the expense of the ortho yield, the *total* aromatic substitution yield should remain a function of the total ring electron density. The fact that $^{76,77}Kr \rightarrow {}^{76,77}Br$ bromodeprotonation follows the so-called Baker–Nathan order[52] for activation of electrophilic substitution ($CH_3 > C_2H_5 > i\text{-}C_3H_7 > t\text{-}C_4H_9$) suggests that hyperconjugative effects are important[53] and that the π-complex is not an important intermediate.

Corroborating this evidence are the results of aromatic bromodeprotonation of isomeric xylenes in Table I. While the π-electron density and π-complex stability should not vary for the different xylene systems,[54] the substitution yields were found to

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follow the order ortho > meta > para. The first hypothetical π-complex is thus of negligible product-determining importance.

Similarly, the lack of a primary isotope effect in the aromatic substitution yields of benzene-d_6 or toluene-d_8 shows that the effect of the second (hydrogen–aromatic) π-complex can be ignored (Table II). These results also suggest that bond breakage of the C–H bond in the σ-complex is not decisive in determining the product spectrum. Whether this results from a one-step reaction involving a kinetically excited species in which the C–H bond strength is relatively low or is due to a two-step mechanism in which the transition state resembles the reactants more than the products according to the Hammond postulates[55a] is difficult to ascertain at this point.[55b] In either case, it is the *formation* of a σ-complex that is yield determining, and $^{76,77}Kr \rightarrow {}^{76,77}Br$ bromodeprotonation is represented by the solid line in Figure 7.

Reactions with Alkyl Substituents. Table III shows the many reaction products formed by $^{76,77}Kr \rightarrow {}^{76,77}Br$ decay in alkyl arene substrates. Although alkyl side-arm substitution and alkyl group hydrogen abstraction do not fall under the topic of ipso attack per se, we will discuss how complicated substituents offer multiple reaction pathways, some of which may interfere or compete with the ipso displacement of the group. Because all of the $^{76}Br/^{77}Br$ yield ratios in Table III fall within the range 1.3 ± 0.3, the same type of reaction bromo species may be involved in ipso substitution and alkyl group abstraction. This value also has a close resemblance to that for aromatic H substitution, where it was argued that the reactive species were ^{76}Br and ^{77}Br radicals. There seems to be a rough correlation between the bromination reaction enthalpy and the product yield, although statistical and steric corrections must also be made. For example, the yield of *n*-bromoalkyl products is often higher than the yield of *sec*-bromo- or *tert*-bromoalkyl arenes, in spite of the fact that the latter C–H bond energies, and the respective reaction enthalpies, are lower. This may be due to increased steric hindrance to the interior bonding sites or because there are a greater number of terminal C–H bonds which may be attacked. Similarly, the yield of methyl abstractions from the alkyl group increases at a faster rate than expected from the respective decrease in bond energy. This has the effect of a preferential increase in methyl bromide formation relative to alkyl group abstraction as branching in the substituent increases, which is opposite to what is expected from inductive considerations.

As in the competitive reactions within the alkyl groups, there also exist competitive effects between the alkyl substituent and the aromatic system, i.e., in group abstraction and ipso substitution. That is, while alkyl hydrogen displacement and methyl abstraction increase relative to substituent abstraction when branching increases, the yield of substituent abstraction also increases relative to ipso substitution. Ipso displacement yields decrease as the substituent is enlarged ($CH_3 > C_2H_5 > i\text{-}C_3H_7 > t\text{-}C_4H_9$) whereas group H abstraction follows the opposite order for the reasons discussed above. Steric hindrance probably increases for both product paths as branching increases, but the increasing inductive +I effect of the substituent gives rise to increased competition by the alkyl group for the bromine reactant relative to the aromatic benzenoid system.[55c]

Reactions with Small Group Substituents. By simplifying the substituents to the small groups shown in Table IV, many of the extraneous side reactions with the substituent have been eliminated. Because ipso substitutions involve (at some point) a σ-complex in which the attacking bromine and the displaced group are bonded to the same (ipso) ring carbon atom, it is interesting to consider whether the electronic characteristics of the leaving group have an effect on the substitution yield. Electron-donating substituents are expected to increase ipso attack by electrophiles, while electron-withdrawing substituents are anticipated to undergo enhanced substitution by nucleophiles. This corresponds to the definition of acidity in the Lewis sense,[56] so that higher nucleophilic substitution yields should be found for groups with lower acidity constants, while electrophilic ipso substitution should be assisted by basic groups.

The differences in yields for the arenes of Table IV are too low to justify any hypotheses about the electronic effects of these substituents. In addition, the small differences in physical characteristics of these groups prevent discussion of the variable aspects of kinetic energy transfer from the energetic bromo species to the displaced group (and into bond rupture). We have defined a "bond-breaking efficiency" (BBE) term that compares the fraction of energy upon collision by a bromine atom transferred from the displaced group to its sp^2 carbon bond energy. For uniformity, this value was normalized to the BBE for bromine collision with aromatic hydrogen. The results of this calculation[22] show that the energy transfer to the different bonds of the arenes of Table IV lies in the range BBE = 9.2 ± 2.4, so that there is very little variation in energy deposition into the substrate.

Reactions with Halogen Substituents. With halogen substituents, the energy transfer is much greater per collision. The BBE for bromine collision with F, Cl, Br, and I is within the previous BBE of 9.2 ± 2.4, 16.6, 22.9, and 26.9, respectively.[22] This difference in BBE creates greater probability for reactions to occur, which gives enhanced yields as well as magnified differences in the substrate yields.

Aside from the greater yields and simpler reaction pathways available using halogen substituents, the haloarenes are also interesting substrates because of the systematic variation in halogen electronic and bonding character. Bond energies and halogen electronegativities both follow the order F > Cl > Br > I (see Table V) so that the yields are expected to increase in the order F < Cl < Br < I due to bond energy effects and decrease in the same order due to electronegativity effects. Also, the –I inductive effects should decrease electron density at the ipso carbon in the order F > Cl > Br > I, while the +M mesomeric characteristics of the halogens should increase electron density at the ipso ring location in the identical order.[57]

As Table V indicates, the ^{76}Br and ^{77}Br yields increase when going from F to I. Similar to the data in Tables III and IV, these results correspond with decreasing bond strengths of the displaced substituent, with the exception of the relatively low yield for the bromodeiodination process. This discrepancy will be discussed later in this section. The yields can also be correlated to a decrease in the halogen electronegativity, suggesting that as the halogen substituent increases in atomic number, the ease of electrophilic ipso attack is enhanced. This is also supported by the increasing percent ^{76}Br/percent ^{77}Br yield ratio as lower period halogens are used. One is also tempted to hypothesize that +M mesomeric effects predominate over –I inductive effects because of the rank order of ipso substitution yields, but this effect is clouded by the variable bond dipole moments shown in Table V. If the mesomeric effect were a dominating electronic characteristic, the bond moments would follow a more uniform change with the different halogens. Apparently, the contribution of inductive (–I)[57] as well as atom–atom polarization (the I_π effect)[58,59] is significant compared to the mesomeric (+M)[57] factors.

To explain the decrease in yield when going from bromobenzene to iodobenzene, physical impact parameters may be involved. For energy transferred to the halogen substituent by energetic ^{76}Br or ^{77}Br, only $12/(12 + 127) = 8.6\%$ of the energy will be distributed from the target iodine atom to the ipso carbon atom. This contrasts with the $12/(12 + 80) = 13.0\%$ transferred from a target bromine atom to the ipso carbon. This represents a greater than 50% increase in bond-breaking force delivered in the case of C–Br relative to the C–I situation and presents itself as a primary yield-determining factor. The relative carbon–halogen mass is

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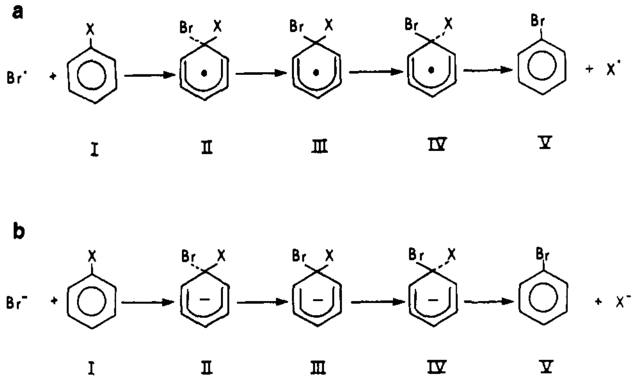

Figure 8. Two-step addition-elimination mechanism for (a) free radical and (b) nucleophilic ipso attack and group displacement. I, initial reactants; II, transition state 1; III, intermediate complex; IV, transition state 2; V, final products.

less important for fluorine and chlorine since the lower van der Waals radii of these halogens results in less steric hindrance to direct bromine-ipso carbon atom collisions. Even so, the relationship between ipso substitution yields in Table V and the BBE values seems closer than with the corresponding electronic and acidity factors listed in Table VI. We therefore suggest that the differences in ipso substitution yield values is primarily due to the variation in impact parameters in relationship to the bond strength.

Mechanism of Substituent Displacement. In the above section concerning aromatic hydrogen substitution, we have argued that charge-exchange neutralization of Br^{n+} cations occurs at a faster rate than aromatic substitution. We therefore limit our discussion of substitution mechanisms to substituent replacement by bromine radicals or bromide ions. It is fortuitous that bromine radicals react with electrophilic character, for this adds a measure of distinction from the bromide nucleophile and a difference in the reaction constraints for these two species.

Whereas experimental dissection of Br-for-aromatic H substitution mechanisms was possible by studying differences in yields for substrates that differed isotopically or isomerically, this technique is not an option for the study of ipso substitution. However, the formation of a geminally disubstituted intermediate during ipso displacement reactions is widely accepted for both bimolecular free radical (S_H2)[17,18] and bimolecular nucleophilic (S_N2)[19,20,60] mechanisms. While there is no direct evidence that this intermediate is involved in hot reactions, this model will be applied in this work to test the correlation between $^{76,77}Kr \rightarrow {}^{76,77}Br$ bromination of arenes and thermal substitution reactions. The hypothetical geminally substituted carbon atom involves sp^3 hybridization of the ipso carbon with subsequent loss of benzenoid aromaticity.[19] The major difference between the intermediate complexes formed in the two mechanisms is that for free radical substitution a cyclohexadienyl radical results, while for nucleophilic attack a benzenide anion (Meisenheimer adduct[61]) is formed. Ipso substitution is therefore presumed to occur via a two-step addition-elimination process,[19,62] shown in Figure 8a for radicals and in Figure 8b for anionic nucleophiles. In both figures, I and V represent the initial and final states, respectively, III represents the intermediate complex, and II and IV are the first and second transition states, respectively.

Although extended Hückel or CNDO-type calculations for these bromination intermediates have not been reported, the relative energies of the isomeric σ-complex intermediates that are formed by the attack of electrophilic, radical, and nucleophilic CH_3, H, or Cl on chlorobenzene and toluene have been calculated by the MINDO/3 method.[63] According to these calculations, the relative stabilities of the ipso intermediates increased as the reaction changed from electrophilic to free radical to nucleophilic attack.

Table X. Estimated Energies of Mechanistic Intermediates for the Nucleophilic Ipso Substitution Process

$Br^- + C_6H_5\text{-}X \rightarrow C_6H_5\text{-}Br + X^-$

X	energy, eV[a]			
	II[b]	III[c]	IV[d]	V[e]
NO_2	3.20	3.04	3.33	1.84
OH	3.08	2.98	3.54	2.19
CH_3	2.92	2.68	3.98	3.33
NH_2	3.06	2.90	4.07	3.38
CF_3	2.83	2.59	3.80	2.94
OCH_3	3.06	2.90	4.45	3.95
CN	2.75	2.48	3.41	2.04
F	2.92	2.85	4.00	1.91
Cl	2.82	2.63	2.91	0.60
Br	2.80	2.59	2.81	0.00
I	2.78	2.50	2.64	−0.44
H	2.69	2.41	5.46	4.21

[a] Normalized to the energy of initial state I in Figure 8b. Energies were calculated according to the methods of ref 62 by using data in the sources footnoted in Tables III-V. These values are subject to 10% relative error. [b] Transition state 1. [c] Intermediate complex. [d] Transition state 2. [e] Final products. Energy of final products (V) equals the enthalpy change for the reaction.

The ortho, meta, para, and ipso intermediates formed by the attack of free radicals showed the smallest range of energy differences, but ipso attack was predicted to be most probable when the attacking group has a lower electronegativity than the leaving group.

Assuming that the ipso substitution mechanism involves formation of intermediate Meisenheimer complex III, the potential energy reaction coordinate profiles can be calculated for nucleophilic ipso attack using the procedures of Miller and coworkers.[62,64,65] Although this method was developed for nucleophilic substitution, it can also be applied to radical mechanisms because of similar bonding requirements.[19] Basically, the procedure involves calculating the energy differences between the intermediate complex III and the initial state I as well as the final state by using the appropriate electron affinites and bond dissociation energies. These calculations reflect the changes from alkyl bond character to conjugated aromatic bond character and in the loss of the charge distribution found in intermediate III. For reasons previously presented,[65] it was assumed that solvation was unimportant in its differential effects on the potential energy and was therefore neglected in the calculations to give a constant term in the results. These energy differences were then used to find the energy levels for transition-state structures II and IV, respectively, by applying a semiempirical function relating the fraction of bond dissociation energy to the exothermicity of the energy change from III to I or from III to V.[62] These energy levels for the transition states (relative to the intermediate complex III) were then corrected for the α-effect,[62] since the electronegativity of the remaining group (X or Br) enhanced nucleophilic bond formation and lowers the transition-state energy. All energies were then normalized for structure I at zero base-line energy. The estimated energies of the intermediates of the nucleophilic reaction sequence shown in Figure 8b are presented in Table X for group-substituted arenes as well as for halobenzene substrates. The corresponding estimates for the intermediates of free radical ipso substitution (Figure 8a) are shown in Table XI.

Concerning the group-substituted arenes, our data suggests that free-radical ipso substitution is energetically favored over nucleophilic ipso displacement for all compounds except benzonitrile. This suggests that the percent ^{76}Br/percent ^{77}Br yield ratios of Tables III-V are greater than unity because of a greater number of nucleogenic ^{76}Br atoms that are produced in a charge state that is able to be charge-exchange neutralized to the reactive Br·

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Table XI. Estimated Energies of Mechanistic Intermediates for the Radical Ipso Substitution Process

$Br\cdot + C_6H_5\text{–}X \rightarrow C_6H_5\text{–}Br + X\cdot$

X	energy, eV[a]			
	II[b]	III[c]	IV[d]	V[e]
NO_2	1.04	0.58	0.95	−0.05
OH	0.95	0.52	2.18	1.30
CH_3	0.86	0.22	1.52	0.87
NH_2	0.92	0.43	1.68	1.04
CF_3	0.80	0.13	2.07	1.26
OCH_3	0.87	0.43	1.38	0.78
CN	0.44	0.02	4.80	2.18
F	0.79	0.39	3.10	1.95
Cl	0.75	0.17	1.27	0.65
Br	0.73	0.13	0.73	0.00
I	0.74	0.04	0.40	−0.69
H	0.69	0.04	2.22	1.42

[a] Normalized to the energy of initial state I in Figure 8a. Energies were calculated according to the methods of ref 62 by using data in the sources footnoted in Tables III–V. These values are subject to 10% relative error. [b] Transition state 1. [c] Intermediate complex. [d] Transition state 2. [e] Final products. Energy of final products (V) equals the enthalpy change for the reaction.

species. Using the thermodynamic arguments as above, we can hypothesize that the Br· is "trapped" for reaction at the neutral charge state, and hence the yields for benzonitrile are independently lower than for the other substrates since for this arene nucleophilic substitution is favored. Although ipso substitution and aromatic hydrogen substitution probably both involve radical species, in the latter case σ-complex formation was found to be product determining. This differs from ipso substitution, because the calculations in Tables X and XI indicate that it is transition state 2 (structure IV in Figures 8a and 8b) that is most energy demanding. Thus, ease of bond breaking is of primary importance in ipso substitution, which explains the correlations between the bond energy of the displaced group and the ipso substitution yield. It also shows why the electronegativity and acidity constant of the displaced group has little effect on the ipso substitution yield. An exception to these generalities is nitrobenzene, where the relative importance of transition state 1 and the negative net enthalpy change for the bromination reaction are reflected in the high ipso yields for this substrate (see Table IV).

The calculated results for halogen-substituted benzenoid systems show a trend of decreasing importance of transition state 2 (IV) and increasing importance of transition state 1 (II) in going from iodine to fluorine. As with the group-substituted arenes, the energetics of radical ipso substitution make it a more facile process than nucleophilic bromodehalogenation.

Comparison of Fluorine and Hydrogen Substitution. Fluorine is the most interesting halogen to investigate because of the similar ΔH values for the nucleophilic and free-radical bromodefluorination processes (1.91 and 1.95 eV, respectively). This thermodynamic equivalence means that both types of mechanisms are possible in the ipso substitution of this halogen.[66,67] Fluorine is a key element in the understanding of nucleophilic aromatic substitution mechanism because its mobility can vary up to 3 orders of magnitude with different type of nucleophiles. With reactive nucleophiles such as alkoxides or amines, the halogen mobility follows the order F $\gg$ Cl > Br > I, whereas with less reactive nucleophiles such as thiocyanate or iodide, the displacement order is I > Br > Cl $\gg$ F.[68,69] This dependence of halogen mobility on the nature of the attacking nucleophile is related to the potential energy–reaction coordinate profile of the substitution reaction. For reactive nucleophiles the formation of the intermediate is the rate-determining step, while for less reactive nucleophiles, bond breakage in the intermediate is rate determining. The electronegativity of the displaced group is therefore the primary factor that determines its mobility for substitution by a reactive nucleophile, while additional factors such as the bond strength, electron affinity, and heat of solvation are important parameters that affect halogen mobility when a poor nucleophile is the attacking group. The ease of displacement of fluorine by a nucleophile can therefore give information on the nucleophilicity of the attacking species.

Fluorine is also interesting as an aryl substituent because of the similarities and differences between the physical characteristics of the fluorine atom and of the hydrogen atom.[22] Most importantly, the steric values for hydrogen and fluorine are approximately the same, so that C_6F_6 retains the C_{2v} symmetry of benzene and the aromatic planarity is not destroyed as in the other perhalobenzene compounds.[70] Notable differences between fluorine and hydrogen are in the mass and electron affinity of these elements.[71a] The greater mass of the fluorine atom results in a greater fraction of energy transferred upon collision by energetic bromine atoms, which may lead to alterations in the degree of fluorine displacement. In addition, the larger electron affinity of fluorine results in a dipole moment within the C–F bond which causes a depletion of electron density on the carbon ipso to the fluorine, resulting in a greater ease of nucleophilic attack. Bromodefluorination is therefore equally possible by a nucleophilic as a free-radical mechanism, whereas only free-radical bromodeprotonation is probable. The enthalpy changes for these processes are 1.94, 1.99, and 1.42 eV, respectively, while the ΔH for nucleophilic bromodeprotonation by Br· is 4.21 eV.

As can be seen in Table VI, the percent ^{76}Br/percent ^{77}Br yield ratio exceeds unity for the benzene derivatives, while it is less than unity for the perfluorobenzene derivatives. The products from benzene are probably due to bromine radical reactions, but the low yield ratio for the fluorinated analogs suggests that they are undergoing nucleophilic substitution reactions. This is also shown by the alteration in yields caused by different substituents on the C_6H_6 and C_6F_6 molecules. Whereas electron-donating methyl increases the yield of bromodeprotonation, it decreases the yield of bromodefluorination. This contrasts with the effects of electron-withdrawing trifluoromethane, which increases bromodefluorination and decreases bromodeprotonation. These effects on the yield, which are caused by electronic depletion or enhancement of the aromatic π-electronic cloud, are explicable only if bromodefluorination is occurring via a nucleophilic mechanism in which electron-withdrawing substituents are able to aid the displacement reaction by removing shielding electrons from the ipso carbon atoms.

Nucleophilic Ipso Substitution. Due to the charge state of the species formed from the decay of both ^{76}Kr and ^{77}Kr,[21] both ^{76}Br and ^{77}Br have the potential of undergoing nucleophilic ipso substitution reactions. No such substitution was observed with the monosubstituted arenes because there is no stabilization of the charge donated by the anionic nucleophile in structures II-IV in Figure 8 (electron-rich carbanions are much less stable than electron-poor carbonium ions[19]). The nucleophilic components of the decay processes were emphasized by using disubstituted benzenoid compounds containing an electron-withdrawing group para to the ipso site. Para substitution was most advantageous because it minimized steric hindrance while achieving mesomeric and inductive activation to nucleophilic attack.

The magnitude of intermediate stabilization for fluorophenyl derivatives has been estimated according to ref 62 and is tabulated in Table XII. Only electron-withdrawing substituents were used, because the destabilizing influence of electron donation on nu-

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Table XII. Estimated Energies of Mechanistic Intermediates for the Nucleophilic Bromodefluorination Process

$Br^- + p\text{-}G\text{-}C_6H_4\text{-}F \rightarrow p\text{-}G\text{-}C_6H_4\text{-}Br + F^-$

G	energy, eV[a] II[b]	III[c]	IV[c]	V[d]
2,4-NO_2	0.92	0.55	2.99	1.91
NO_2	1.22	0.94	2.96	1.91
$COCH_3$	2.98	2.55	3.32	1.91
CF_3	2.43	2.35	3.21	1.91
Br	0.79	0.39	3.17	1.91
I	0.97	0.64	3.02	1.91
F	0.76	0.35	3.30	1.91
H	2.92	2.85	4.00	1.91

[a] Normalized to the energy of initial state I in Figure 8b. Energies were calculated according to the methods of ref 62 by using data in the sources footnoted in Tables III–V. These values are subject to 10% relative error. [b] Transition state 1. [c] Intermediate complex. [d] Transition state 2. [e] Final products. Energy of final products (V) equals the enthalpy change for the reaction.

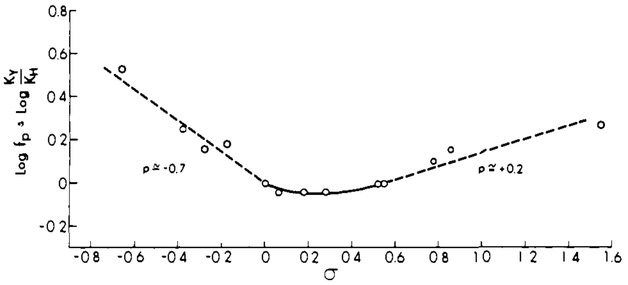

Figure 9. Hammett free-energy correlation for $^{76}Kr \rightarrow {}^{76}Br$ bromodefluorination of para-substituted fluorobenzene derivatives. K_Y is the ^{76}Br radiochemical yield for bromodefluorination of the para-substituted fluorobenzene derivatives shown in Table VII. K_H is the ^{76}Br radiochemical yield for bromodefluorination of fluorobenzene.

cleophilic substitution is of little importance to this discussion.[71b] A calculation for 2,4-dinitrofluorobenzene was also made to show the large decrease in reaction barriers induced by *two* additional electron-withdrawing substituents.

Table XII shows that substitution of a second electron-withdrawing group para to the substitution site lowers the energy requirements from the monosubstituted substrates shown in Table X. This effect is most dramatic on transition state 1, i.e. benzenide complex formation. Unfortunately, the effect on transition state 2 is not as dramatic, as there is little than can be done by using mesomeric or inductive forces to decrease the bond strength of the displaced substituent. However, the energy of transition-state two is lowered below that for free-radical ipso substitution (see Table XII), albeit by a nominal magnitude. Moreover, the energy decrease for the product-determining nucleophilic transition state 2 is occurring in benzenoid systems that are *deactivated* to electrophilically characterized bromine radicals. We therefore expect the nucleophilic reaction pathway to predominate over free-radical ipso substitution in these substrates.

Experimentally, plots were made of the $^{76,77}Kr \rightarrow {}^{76,77}Br$ bromodefluorination yields of the disubstituted arenes in Table VII against the Hammett substituent constant σ,[72] as shown in Figures 9 and 10. Both figures illustrate biphasic linear free energy relationships, with increased yields for both electrophilically and nucleophilically activated benzenoid systems. The enhancement of ipso substitution yields at negative substituent constant values (electron-donating substituents) is greater for the $^{76}Kr \rightarrow {}^{76}Br$ decay process ($\rho \sim -0.6$) than for the $^{76}Kr \rightarrow {}^{76}Br$ decay process ($\rho \sim -0.4$). This may result from the fact that the former decay process produces a larger fraction of the nascent bromine in a positive charge state,[21] and hence more of the ^{76}Br is able to be sequestered by the radical ipso substitution pathway. By contradistinction, the Hammett plot at positive substituent constants (electron-withdrawing substituents) shows a sharper increase for $^{77}Kr \rightarrow {}^{77}Br$ bromodefluorination ($\rho \sim +0.7$) than for fluorine displacement by the $^{76}Kr \rightarrow {}^{76}Br$ decay process ($\rho \sim +0.2$). This increased nucleophilic character for ^{77}Br can be attributed to the fact that ^{77}Kr decays 84% via β^+ decay, resulting in approximately 60% of the nascent bromine initially in the charge state 1−,[21] and hence available for nucleophilic ipso substitution reactions. This contrasts with ^{76}Kr, which decays solely via electron capture to give initially only nonnegative charge states to the generated ^{76}Br species.[21] Only ca. 10% of the ^{76}Br is charged 2+ or less, so that a lower percentage is reduced past the reactive Br· channel and undergoes nucleophilic ipso substitution. This empirical support for the theoretical charge states of nucleogenic ^{76}Br and ^{77}Br[21] as well as the hypothesized two-step ipso substitution mechanism[62] is quite gratifying in view of the several opposing variables involved.

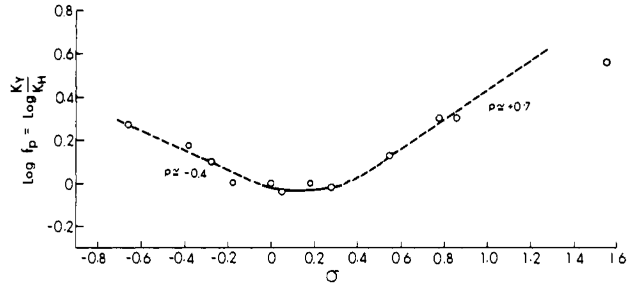

Figure 10. Hammett free-energy correlation for $^{77}Kr \rightarrow {}^{77}Br$ bromodefluorination of para-substituted fluorobenzene derivatives. K_Y is the ^{77}Br radiochemical yield for bromodefluorination of the para-substituted fluorobenzene derivatives shown in Table VII. K_H is the ^{77}Br radiochemical yield for bromodefluorination of fluorobenzene.

Summary and Conclusions

Previously[21,41,73] studies of the reactivity of nucleogenic bromine species from the $^{76}Kr \rightarrow {}^{76}Br$ and the $^{77}Kr \rightarrow {}^{77}Br$ decay systems have been extended to include aromatic hydrogen substitution reactions in condensed phases. For both ^{76}Kr and ^{77}Kr decay, the reactive species was found to be the Br· radical cation formed from charge-transfer neutralization of Br^{n+} cations. The greater yield of ^{76}Br relative to ^{77}Br is attributed to a larger fraction of the former isotope being generated as a radical or in a positive charge state and thereby able to be reduced to the reactive Br· oxidation state. The aromatic substitution reactions are correlated by a Brown–Okamoto calculation, with $\rho^+ \simeq -0.6$ for both decay processes. The product-determining step in the reaction mechanism is hypothesized to be formation of a σ-complex.

The group substitution reactions of $^{76}Kr \rightarrow {}^{76}Br$ and $^{77}Kr \rightarrow {}^{77}Br$ decay in a series of alkyl-, halogen-, and simple group-substituted arenes in the liquid phase were also investigated. The mechanisms of ipso substitution is clouded by complicating factors as the displaced group increases in size. In particular, as alkyl substituents become more branched, competitive reaction pathways such as methyl abstraction, alkyl hydrogen displacement, and alkyl substituent abstraction increase rapidly to make ipso substitution products relatively unimportant. For simple non-alkyl groups, multiple modes of energy deposition among the different atoms of each group also increase reaction mechanism uncertainties. For these reasons, the study of ipso substitution mechanisms is probably most straightforward when limited to single-atom substituents.

The halogens were investigated because of their simplicity as well as because of their opposing rank orders of bond strength, electronegativity, and polarizability. The rank order for $^{76,77}Kr \rightarrow {}^{76,77}Br$ bromodehalogenation was found to be F < Cl < Br > I, which is opposite the sequence for halogen electronegativity. The relative decrease in the bromodeiodination yield was attributed to less energy being distributed across the C–I bond of iodobenzene relative to the C–Br bond of bromobenzene. This sequence for ipso halogen displacement suggests that bond energy of the

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substituent is the primary yield-determing factor.

Semiempirical calculations were used to estimate the intermediates in $^{76,77}Kr \rightarrow {}^{76,77}Br$ ipso substitution based on a two-step addition–elimination mechanism.[62] These calculations indicate that the second transition state involving bond breakage of the displaced substituent is the highest energy step, explaining the close relationship between the ipso substitution yield and bond energy. These calculations also indicate that free-radical displacement is much more favorable than nucleophilic substitution, showing agreement with the results of $^{76,77}Kr \rightarrow {}^{76,77}Br$ aromatic bromodeprotonation. Apparently, as in the latter case, reduction of reactive bromonium cations occurs until the nucleogenic species is charge-exchange neutralized to bromine radicals. Since electron-captive decay ^{76}Kr produces relatively more Br^{n+} charged species than β^+-decay ^{77}Kr, the ipso yield of ^{76}Br exceeds that of ^{77}Br.

Nucleophilic ipso substitution does not occur in monosubstituted benzene derivatives because the donated electron density from anionic bromdie leads to high-energy reaction intermediates. By adding substituents with electronegativity exceeding that of carbon, π-electron shielding of the ipso carbon atom nucleus is reduced, and stabilization of intermediate Meisenheimer adducts is achieved. Semiempirical calculations verified that the energy of all substitution intermediates can be decreased in this manner, and experimental verification was found by a biphasic linear free energy Hammett plot of nucleogenic aromatic bromodefluorination. For $^{76}Kr \rightarrow {}^{76}Br$, electron-donating substituents greatly increased the yield of radical ipso displacement of fluorine ($\rho \sim -0.7$), while electron-donating substituents also activated nucleophilic bromodefluorination ($\rho \sim +0.2$). By contrast, $^{77}Kr \rightarrow {}^{77}Br$ bromodefluorination showed a slower rate of enhancement of substitution yields with electron-donating substituents ($\rho \sim -0.4$), but a larger response to nucleophilic activation by electron-donating substituents ($\rho \sim +0.7$). These results are explanable on the basis of the charge spectra of the two bromine species resulting from the decay process of their krypton parents. ^{76}Kr decays via electron capture, generating primarily cationic species that are reduced to reactive bromine radicals, while ^{77}Kr decays chiefly by β^+ decay to generate a large fraction of nucleogenic ^{77}Br as reactive bromide anions.[21] This effect of substituent control over $^{76,77}Kr \rightarrow {}^{76,77}Br$ aromatic bromodefluorination gives credence to the two-step ipso addition–elimination mechanism and suggests that even greater yield effects are possible for larger halo substituents, where Meisenheimer complex formation rather than decomposition is the primary energy-demanding step.

Registry No. ^{76}Kr, 28522-17-0; ^{77}Kr, 14983-72-3; ^{76}Br, 15765-38-5; ^{77}Br, 15765-39-6; D, 7782-39-0; C_6H_6, 71-43-2; $C_6H_5CH_3$, 108-88-3; $C_6H_5C_2H_5$, 100-41-4; C_6H_5-*i*-C_3H_7, 98-82-8; C_6H_5-*t*-C_4H_9, 98-06-6; $C_6H_5NO_2$, 98-95-3; C_6H_5OH, 108-95-2; C_6H_5NH0, 62-53-3; $C_6H_5CF_3$, 98-08-8; $C_6H_5OCH_3$, 100-66-3; C_6H_5CN, 100-47-0; C_6H_5F, 462-06-6; C_6H_5Cl, 108-90-7; C_6H_5Br, 108-86-1; C_6H_5I, 591-50-4; *p*-$FC_6H_4NO_2$, 350-46-9; *p*-$FC_6H_4COCH_3$, 403-42-9; *p*-$FC_6H_4CF_3$, 402-44-8; *p*-FC_6H_4Br, 460-00-4; *p*-FC_6H_4I, 352-34-1; *p*-FC_6H_4F, 540-36-3; *p*-$FC_6H_4CH_3$, 352-32-9; *p*-$FC_6H_4OCH_3$, 459-60-9; *p*-FC_6H_4OH, 371-41-5; *p*-$FC_6H_4NH_0$, 371-40-4; *o*,*p*-$FC_6H_3(NO_2)_2$, 70-34-8; C_6F_6, 392-56-3; H, 1333-74-0.

Reaction Selectivity of Translationally and Electronically Excited Carbon-11 Atoms with Ethylene[1]

Richard A. Ferrieri,*[1a] Alfred P. Wolf,[1a] and Yi-Noo Tang[1b]

Contribution from the Departments of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, and Texas A&M University, College Station, Texas 77843. *Received November 22, 1982*

Abstract: Measurement of the ^{11}C distribution in allene-^{11}C provided a means to distinguish the extent to which recoil carbon-11 atoms underwent C—H and C═C insertion pathways into ethylene. Combined moderator and scavenger studies also provided a means to alter the translational energy and electron spin distributions of the carbon-11 atoms. Results from these studies indicated that at the upper end of the energy range where carbon atoms become chemically reactive, C═C insertion occurred preferentially over C—H insertion for both $C(^3P)$ and $C(^1D)$ atoms. At the low end of the energy range, $C(^3P)$ carbon atoms reacted preferentially via C—H insertion. On the other hand, $C(^1D)$ atoms were not reactive toward C—H insertion, at least in the formation of allene-^{11}C.

The present model of carbon atom chemistry has evolved largely through two decades of effort where elaborate techniques to generate and to study the atom–molecule chemistry include nuclear recoil,[2-5] thermal evaporation,[6] thermal decomposition,[7] and photolytic decomposition[8] methods. The quadravalent carbon atom was predicted to undergo a set of characteristic reactions in order to reduce its electron deficiency. According to the present model, carbon atom reactions with hydrocarbons were categorized as (i) insertion into C–H bonds,[9,10] (ii) addition to carbon–carbon double bonds,[11-13] and (iii) abstraction of hydrogen from hydrocarbons.[14-20]

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[1] Dedicated to William von Eggers Doering on his 65th birthday. (a) Department of Chemistry, Brookhaven National Laboratory, Upton, NY. (b) Department of Chemistry, Texas A&M University, College Station, TX.

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