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Aromatic Substitution in the Gas Phase. On the Mechanism of the Dehalogenation Reactions of Halobenzenes and Dihalobenzenes Promoted by Gaseous Brønsted Acids

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Received August 2, 1976

Abstract: The attack of CH_5^+ and $C_2H_5^+$ ions, obtained in the dilute gas state from the γ radiolysis of methane, on halo- and dihalobenzenes causes extensive dehalogenation via two distinct channels, leading respectively to protodehalogenated and methyldehalogenated products, whose relative rate depends primarily on the nature of the leaving halogen. Kinetic and mass spectrometric evidences suggest that direct attack of the Brønsted acid to the halogen substituent leads to formation of the correspondent arylium cation, via hydrogen halide elimination, at a rate which decreases in the order F $\gg$ Cl $\geq$ Br. The subsequent electrophilic attack of the arylium cations on CH_4, the bulk constituent of the system, yields methylated arenium ions, and eventually the observed methyldehalogenated products. On the other hand, attack of the Brønsted acid to the aromatic ring of halobenzenes promotes protodehalogenation, at a rate increasing in the order F $\ll$ Cl < Br. Direct comparison of the rates of the two dehalogenation processes has been obtained from the study of dihalobenzenes containing different halogens. Furthermore, isolation of a mixture of *m*- and *p*-xylene among the dehalogenation products of *p*-fluorotoluene has provided direct evidence for the isomerization of the *p*-tolyl cation formed from the attack of the gaseous Brønsted acid to the n-type center of the substrate and/or of the xylenium ion formed from the attack of the tolyl ion to methane. The present results, and supporting mass spectrometric evidence, underline the typical ambident behavior of halobenzenes toward charged electrophiles, and allow a unified interpretation of the dehalogenation processes promoted by different Brønsted acids. The gas-phase reactivity of halobenzenes is compared with their behavior in similar processes occurring in solution.

In previous papers[1-4] we reported evidence showing that dehalogenation, a major reaction channel in the gas-phase attack of strong Brønsted acids, such as HeT^+ and D_2T^+, to halobenzenes,[5] occurs via two distinct mechanisms, involving respectively the attack of the electrophile to the halogen substituent (n-type center) and to the aromatic ring (π-type center) of the ambident substrate. In order to obtain a sharper discrimination between the two dehalogenation channels, and to gain further insight into the factors regulating their competition, we have now extended the investigation to a pair of milder electrophiles, the CH_5^+ and $C_2H_5^+$ ions that can be conveniently obtained in the gas phase from the radiolysis of methane, and whose attack to halo- and dihalobenzene has been studied in the dilute gas state.[6]

Experimental Section

Materials. Methane, a research grade product from Matheson Co., with a stated purity of over 99.99 mol %, and oxygen, from SIO Co., with a stated purity of over 99.9 mol %, were used without further purification. Samples of halo- and dihalobenzenes, obtained from Fluka AG, were purified by preparative GLC, until the purity of the recovered fractions, determined by analytical GLC, exceeded 99.99 mol %. A particularly difficult problem was represented by the analysis of *p*-fluorotoluene, necessary to exclude the presence of significant concentrations of the ortho and meta isomers. The resolution of a synthetic mixture of the three isomers required a 30-m Carbowax 20M capillary column, operated at 60 °C. Analysis of the sample revealed the absence of detectable amounts of *o*- and *m*-fluorotoluene.

Procedure. Carefully outgassed 1-L Pyrex bulbs, evacuated to 10^{-5} Torr on a greaseless vacuum line, were filled with a gaseous mixture consisting of CH_4 (760 Torr), O_2 (2 Torr, used as a thermal radical scavenger), and the aromatic substrate (ca. 10 mg, corresponding to 1-2 Torr), and irradiated with the ^{60}Co γ radiation in a 220 Gammacell (Nuclear Canada Ltd.) at the temperature of ca. 34 °C, at a dose rate of 0.4 Mrad h^{-1} to a total dose of 4.8 Mrad, as determined by a Fricke dosimeter. The analysis of the products was carried out using a Model 5700A Hewlett-Packard gas chromatograph, equipped with a FID unit. The following columns were used: 4-m tricresyl phosphate, 4-m diisodecyl phthalate, and 4-m DC 550 silicone oil, all employing acid-washed Chromosorb W as the solid support and N_2 as the carrier gas. The ICR data mentioned in this paper were obtained by bombarding with 15-eV electrons a 10:1 CH_4 (CD_4)-halobenzene

Table I. Dehalogenated Products from the Attack of CH_5^+ and $C_2H_5^+$ Ions to Halobenzenes

Substrate	Products	μmol formed[a]	G value	Absolute yield,[a] %
p-Fluorotoluene	Toluene			
	Xylene[b]	1.64 ± 0.09	0.49	18
Fluorobenzene	Benzene	0.017 ± 0.002	5.1×10^{-3}	0.2
	Toluene	1.42 ± 0.06	0.43	15
Chlorobenzene	Benzene	0.62 ± 0.01	0.19	6.6
	Toluene	0.017 ± 0.004	5.1×10^{-3}	0.2
Bromobenzene	Benzene	0.83 ± 0.20	0.25	8.9
	Toluene	0.045 ± 0.020	1.3×10^{-2}	0.5
o-Difluorobenzene	Fluorobenzene			
	Fluorotoluenes	0.011 ± 0.001	3.3×10^{-3}	0.1
m-Difluorobenzene	Fluorobenzene			
	Fluorotoluenes	0.28 ± 0.03	8.4×10^{-2}	3.0
p-Difluorobenzene	Fluorobenzene			
	Fluorotoluenes	0.11 ± 0.01	3.3×10^{-2}	1.2
o-Chlorofluorobenzene	Chlorobenzene			
	Fluorobenzene	0.36 ± 0.10	0.11	3.9
	Chlorotoluenes			
	Fluorotoluenes	0.006 ± 0.001	1.8×10^{-2}	0.06
m-Chlorofluorobenzene	Chlorobenzene			
	Fluorobenzene	0.14 ± 0.01	4.2×10^{-2}	1.5
	Chlorotoluenes	0.186 ± 0.002	5.6×10^{-2}	2.0
	Fluorotoluenes	0.013 ± 0.001	3.9×10^{-2}	0.1
p-Chlorofluorobenzene	Chlorobenzene			
	Fluorobenzene	0.74 ± 0.10	0.22	7.9
	Chlorotoluenes	0.064 ± 0.002	1.9×10^{-2}	0.7
	Fluorotoluenes	0.011 ± 0.002	3.3×10^{-3}	0.1

[a] See text. [b] The isomeric composition of products corresponds to 90% of *p*-xylene and 10% of *m*-xylene.

mixture in the source region of a modified Syrotron spectrometer (Varian Associates), in the pressure range from 10^{-6} to 10^{-4} Torr.

Results

The yields of the products from the gas-phase attack of CH_5^+ and $C_2H_5^+$ ions on selected halobenzenes and dihalobenzenes in a highly diluted CH_4 solution are listed in Table I.

It should be noted that only dehalogenated products are taken into account, omitting other species not directly relevant to the present study, such as alkylated products from the condensation of $C_2H_5^+$ with halobenzenes. The table gives, in the first place, the micromoles of each product formed from the γ-irradiation of a 1-L sample of CH_4, measured at 25 °C and 760 Torr, containing 60 μmol of the substrate, to a total dose of 4.8 Mrad. The data are the mean values from several separate irradiations, whose reproducibility is expressed by the standard deviations quoted. In addition, the *G* values measured at 4.8 Mrad are listed. Since the halobenzenes are only one of the nucleophiles, either initially contained in the gas or formed from its radiolysis, which compete for the CH_5^+ and $C_2H_5^+$ reagent, the *G* values are expected to be pressure dependent. This is confirmed by a series of irradiations carried out at doses ranging from 2.8 to 7.2 Mrad showing that the absolute *G* values decrease at higher doses, owing to the increased fraction of CH_5^+ and $C_2H_5^+$ consumed by radiolytically formed nucleophiles, whereas the *relative* yields of products are independent of the dose, at least within the range investigated. Competition experiments involving different pairs of halobenzenes indicate that the unreacted fraction of each substrate is fairly constant, suggesting that the overall rate of attack of CH_5^+ and $C_2H_5^+$ is largely independent of the particular halobenzenes concerned, i.e., that the *substrate* selectivity of these electrophiles is quite low. The table summarizes also the *absolute* yields of products, expressed by the ratio of the micromoles of each product to the micromoles of CH_5^+ and $C_2H_5^+$ formed within the system, calculated from the known[7] *G* values of the two ions. Owing to the many sources of uncertainty and errors,[8] the *absolute* yields listed represent extremely crude estimates, and have been included in the table essentially to provide the order of magnitude of the efficiency of dehalogenation processes. The ionic character of these reactions is underlined by the sharp decrease of the yields of dehalogenated products caused by addition of NH_3, an effective interceptor of CH_5^+ and $C_2H_5^+$. Thus, the yield of benzene formed from C_6H_5Br is decreased *by a factor of 5* by addition of 2 mol % of ammonia to methane.

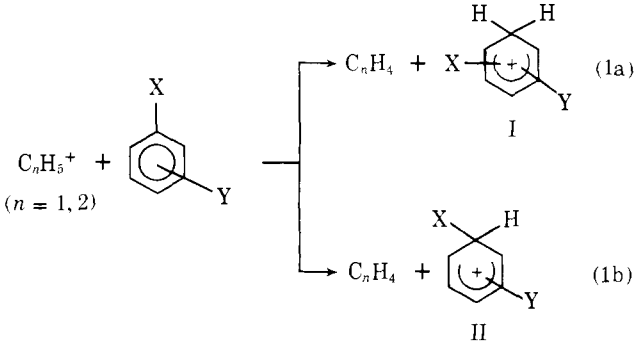
The most relevant feature of the experimental results is the predominant substitution of F with a methyl group, and of Cl and Br with a hydrogen atom. The presence of an electron-releasing substituent like CH_3 in fluorobenzenes appears to *increase* the yield of methyldehalogenated products, which is correspondingly depressed by the presence of an electron-attracting substituent, like a second F atom, as illustrated by a comparison of the reactivity of *p*-fluorotoluene and, respectively, of *p*-difluorobenzene, with that of C_6H_5F. Finally, it is worth mentioning that in the methyldehalogenation of fluorobenzenes the methyl group is found predominantly, but not exclusively, in the ring position formerly occupied by F, as shown by the isomeric composition (10% meta, 90% para isomer) of the xylenes formed from *p*-fluorotoluene.

Discussion

Nature of the Dehalogenation Process and of the Electrophiles. As previously observed in related studies,[1-4] several factors, including the composition of the system, which contains only traces of the aromatic substrate(s) and a large excess of CH_4, the effect of NH_3 on the yields, the trend in the dehalogenation rate[9] ($F \gg Cl \simeq Br$), together with concurrent mass spectrometric evidence, exclude direct radiolysis of halobenzenes as a significant dehalogenation process, and suggest that dehalogenation must be somehow related to the attack to halobenzenes by CH_5^+ and $C_2H_5^+$, the major ionic species formed in the radiolysis of methane,[6d,10] which represents the bulk constituent of the system. The role of these cations as gaseous Brønsted acids has been exhaustively demonstrated by chemical ionization mass spectrometry (CIMS),[11,12] and by independent radiolytic studies.[13] The CH_5^+ ion, $\Delta H_f^\circ = 221$ kcal/mol,[14] reacts essentially as a

strong protonating agent (proton affinity (PA) of CH_4 = 127 kcal/mol), whereas the $C_2H_5^+$ ion, ΔH_f° = 219 kcal/mol,[14] is a milder Brønsted acid (PA of C_2H_4 = 159 kcal/mol) that, in addition to protonation, undergoes condensation with halobenzenes, as shown by the isolation of the correspondent alkylated products.[15]

A. Protodehalogenation. In agreement with the conclusions reached in the study of the HeT^+ reactivity toward halobenzenes,[1] it is suggested that protodehalogenation is initiated by the attack of the CH_5^+ and $C_2H_5^+$ ions formed from the radiolysis of methane, and thermalyzed by many unreactive[10] collisions with CH_4 molecules, to the aromatic ring, i.e. to the π-type center of the ambident substrate:

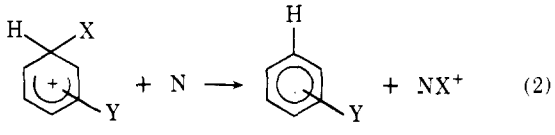


(1a)

(1b)

The *upper limit* for the exothermicity of 1a and 1b can be calculated from the known[16] PA values of halobenzenes, which refer to the formation of the *most stable* protonated isomer. Proton transfer from CH_5^+ to C_6H_5F is characterized by a ΔH° value ≥ -60 kcal/mol, whereas the exothermicity of the proton transfer from $C_2H_5^+$ does not exceed 26 kcal/mol. Very close ΔH° limits, within a range of 1-2 kcal/mol, can be calculated for other substrates, including C_6H_5Cl, C_6H_5Br, and m-$C_6H_4F_2$.

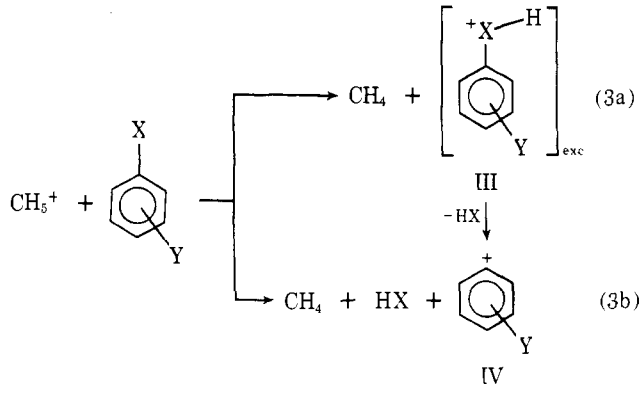
Several reaction pathways are available, which lead from the excited intermediates I and II to the observed dehalogenated products, including halonium ion transfer to any acceptor molecule contained in the gas, or homolytic cleavage of the C-X bond, followed by the charge transfer of the $C_6H_5Y^+\cdot$ cation formed to a suitable species present in the system.[17] It is interesting to note, in connection with reaction 2, that the



(2)

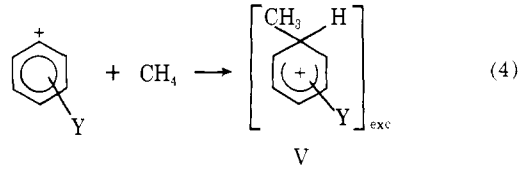
relative extent of protodehalogenation (F ≪ Cl ≃ Br) parallels the relative rate of isomerization of dihalobenzenes following their gas-phase protonation by strong Brønsted acids,[2]

B. Methyldehalogenation. It is suggested that the first step of the process is represented by the CH_5^+ attack to the unshared electrons of the halogen substituent, i.e. to the n-type nucleophilic center of the substrate, leading either directly, by halide ion abstraction (3b), or indirectly (3a) to the formation of a phenylium cation (IV). Whereas the energetics of the process will be discussed in detail in a following section, it should be noted that attack of $C_2H_5^+$ to the substituent cannot lead to formation of the phenylium ion, owing to the endothermic character of the overall reaction sequence. Phenylium ions from reactions 3a and 3b are suggested to attack CH_4, the only nucleophile contained at high concentration within the system, yielding a toluenium ion (V), excited by the considerable exothermicity of the process.[18] Following collisional stabilization in methane at 760 Torr, V can subsequently lose a proton to a base contained in the gaseous system, yielding the observed methyldehalogenated products. Isomerization of either the phenylium ions (IV) or of the toluenium ions (V)

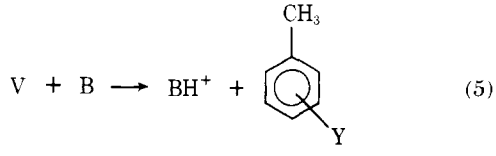


(3a)

(3b)



(4)



(5)

from their exothermic attack to methane[19] is demonstrated by isolation of ca. 10% of the meta isomer in the xylenes formed from the dehalogenation of *p*-fluorotoluene.

Mass Spectrometric Evidence. In their CIMS study,[5] Harrison and Lin identified as major ionic species from the attack of CH_5^+ on fluorobenzene and fluorotoluenes in CH_4 at 0.3-0.5 Torr *all the charged intermediates* postulated in the reaction scheme outlined in the previous sections, with the notable exception of the phenylium ion (IV), i.e., the $(M - X)^+$ cation. This was barely detectable in CH_4/fluorotoluenes systems, and could not be detected at all in the CH_4/C_6H_5F system. On the other hand, protonated halobenzenes, i.e., $(M + H)^+$ ions, corresponding to intermediates I, II, and III, were the most abundant species, demonstrating the efficiency of collisional stabilization even at low CH_4 pressures. Most interestingly, high abundances of the $(M - X + CH_4)^+$ species, correspondent to the toluenium ions (V), were measured in the CH_4/C_6H_5F and $CH_4/C_6H_4FCH_3$ systems. However, formation of toluenium ions was ascribed by Harrison and Lin to a single-step reaction, excluding the intermediacy of the phenylium ions (IV).

$$CH_5^+ + C_6H_4FY \rightarrow CH_3\text{-}C_6H_5Y^+ + HF \qquad (6)$$

(Y = H or CH_3)

Their interpretation is consistent with ICR results,[20] where a correlation between the CH_5^+ parent, and the $C_7H_9^+$ daughter was verified in the CH_4/C_6H_5F system. A similar one-step mechanism was suggested to account for the formation of $(M - X + H_2)^+$ ions from the attack of H_3^+ to fluorobenzene and fluorotoluenes.[5] The results, relevant to this discussion, of a subsequent ICR study on the reactions of H_3^+ (D_3^+) and CH_5^+ (CD_5^+) with a variety of halobenzenes and dihalobenzenes,[21] in the pressure range from 10^{-6} to 10^{-4} Torr, can be summarized as follows.

(1) The protonated substrate, $(M + H)^+$, correspondent to the intermediates I, II, and III is the major *secondary* ion from the attack of CH_5^+ to halobenzenes.

(2) Phenylium ions, $(M - X)^+$, are also abundant *secondary* ions. Double resonance experiments in the CH_4/C_6H_5F system show that the correlation between CH_5^+ and $C_6H_5^+$

has an exothermic, or thermoneutral, character. This observation, that provides crucial support to the two-step mechanism outlined in eq 3 and 4, does not conflict with recent appearance potential measurements, that assign to the phenylium ion a $\Delta H_f°$ value from 274 to 276 kcal/mol.[22] Calculations based on these figures indicate that the overall process has a thermoneutral, or slightly exothermic, character, with a $\Delta H°$ value ranging from 0 to −2 kcal/mol. On the other hand, similar

$$CH_5^+ + C_6H_5F \rightarrow C_6H_5^+ + HF + CH_4 \qquad (3)$$

calculations underline the slightly endothermic character of process 3 for chlorobenzene and bromobenzene, in agreement with the very low yields of methyldehalogenation products from these substrates measured in the present work.

(3) Methyldehalogenated arenium ions, $(M - X + CH_4)^+$, corresponding to V, are abundant *tertiary* ions. Double resonance experiments, while confirming that CH_5^+ is a precursor of $(M - X + CH_4)^+$, reveal, in addition, a strong parent-daughter correlation between the phenylium ions, $(M - X)^+$, and the $(M - X + CH_4)^+$ ions, indicating a large cross-section for reaction 4. Consequently, it appears that earlier ICR evidence[20] can be readily reconciled with the two-step mechanism outlined in eq 3 and 4, where CH_5^+ retains indeed its role as a precursor of the arenium ions $(M - X + CH_4)^+$, even if through the intermediacy of the phenylium ions (IV), as clarified by the subsequent ICR work.[21] The absence of an appreciable abundance of phenylium ions in the CIMS of fluorobenzenes and fluorotoluenes in CH_4 is not surprising, in the light of the latest ICR results. In fact, considering the relatively high pressure of CH_4, and the large cross-section of reaction 4, the steady-state concentration of phenylium ions is probably very low, falling below the detection limit of the CIMS instrument.

As a whole, the ICR evidence strongly supports the reaction scheme suggested in the previous sections, in particular the two-step mechanism for the formation of methyldehalogenated arenium ions (V).[23] Finally, the CH_5^+ attack to the n electrons of halobenzenes, particularly significant in the case of fluorobenzenes, postulated as the first step of methyldehalogenation, finds interesting analogies with the ICR results of Ridge and Beauchamp,[24] who demonstrated the formation, and the chemical consequences, of strong hydrogen bonding between gaseous Brønsted acids and several *fluorinated* molecules.

Conclusions

Gas-phase protonation of halobenzenes by CH_5^+ and $C_2H_5^+$ ions in dilute methane solution promotes dehalogenation via two different channels. Attack to the ring by both CH_5^+ and $C_2H_5^+$ leads to protodehalogenation, whose rate increases in the order $F \ll Cl \simeq Br$ (channel A), while attack to the halogen substituent leads to formation of the correspondent phenylium cation, following the loss of a hydrogen halide molecule (channel B). The subsequent attack of the phenylium cations to CH_4 yields the observed methyldehalogenated products, via the intermediate formation of the correspondent toluenium ions. The second channel is significant for fluorinated substrates, its rate increasing in the order $F \gg Cl \simeq Br$. The presence of an electron-releasing substituent in the fluorobenzene molecule enhances the rate of channel B, which is depressed by the presence of an electron-withdrawing substituent, as shown by comparison of the *p*-fluorotoluene and *p*-difluorobenzene reactivity.

The choice of CH_4 as the reaction environment has allowed a sharp discrimination between the two competing reaction channels, and a unified interpretation of the gas-phase reactivity of halobenzenes toward strong Brønsted acids. Thus, the tritiodehalogenation process promoted by the highly exothermic attack of HeT^+ cations to halobenzenes,[1] whose rate increases in the order $Br > Cl \gg F$, corresponds to dehalogenation channel A. Those experiments, however, carried out in a large excess of the gaseous aromatic substrate, failed to demonstrate channel B, since any phenylium ions that could be formed had no chance of yielding *tritiated* products, the only ones that could be detected. On the other hand, the study of the gas-phase reaction of D_3^+ (D_2T^+) ions with halobenzenes[2] suggested a reaction sequence corresponding to channel B, the only diversity being represented by the different nucleophile (D_2 vs. CH_4) attacked by the phenylium ions formed in the first step of the sequence, i.e., the protonation of the n electrons of fluorine. In fact, the relative rate of this process increases in a parallel way in both the CH_4 and the D_2 systems, passing from Br and Cl to F. Nevertheless, the composition of the D_2/halobenzenes systems, containing a large excess of D_2, prevented discrimination between reaction channels A and B based exclusively on the analysis of the neutral dehalogenated products, *that were the same* from the protodehalogenation mechanism (channel A) and from the attack of phenylium ions to D_2 (channel B). It is tempting to rationalize the variation of the relative efficiency of the two competing dehalogenation processes with the nature of the leaving halogen on purely energetic grounds, since only for fluorinated substrates reaction 3, the source of phenylium ions, has a slightly exothermic, or at least thermoneutral, character, in contrast with the slightly endothermic character of the correspondent reactions involving chlorobenzene and bromobenzene. However, taking into account, inter alia, the small energy differences involved, and the uncertainty as to the $\Delta H_f°$ value of the phenylium ion, it seems safer to suggest, in agreement with the conclusions of our previous studies, that the increased rate of the protonation at the n center of the ambident substrate, which is observed along the $Br \simeq Cl \ll F$ series, is related to the increased polarization of the C–halogen bond. Another, partially equivalent, interpretation, based on the ICR evidence of Ridge and Beauchamp,[24] could involve the formation of a gas-phase hydrogen bond between CH_5^+ and the F substituent, such as $C_6H_5F—HCH_4^+$, that could be regarded as a long-range precursor of the phenylfluoronium ion formed from process 3a, kinetically favoring attack to the n center of the halobenzenes. No such gas-phase hydrogen bonding is known for chlorinated or brominated substrates, and their stability should be, in any case, substantially lower. The interpretation based on the polarity order of C–halogen bonds finds close analogies in solution chemistry, where the *arylating* ability of halobenzenes in Friedel–Crafts reactions is known to increase in the order $C_6H_5Br \leq C_6H_5Cl \ll C_6H_5F$, a trend traced to the increased polarization of the C–halogen bond,[25,26] and to the incipient cationic nature of the phenyl group in fluorobenzenes, which appears the solution-chemistry counterpart of the actual formation of a free phenylium cation observed in the gas phase. The same behavior has been observed in the aluminum halides catalyzed halogen-exchange reactions of halobenzenes, which involve fission of the C–halogen bond, and whose rate increases with the polarity of the C–halogen bond.[26]

Acknowledgment. M.S. wishes to thank J. M. S. Henis and M. D. Sefcik for extending their hospitality in allowing the use of the ICR mass spectrometer at Monsanto Co. Laboratories, St. Louis, Mo., and P. P. Gaspar for his hospitality at Washington University, St. Louis, Mo. The financial support of Monsanto Co., Washington University, and the U.S. Energy Research and Development Administration (ERDA) to one of the authors (M.S.) is gratefully acknowledged. The authors are grateful to P. P. Gaspar for useful discussion and suggestions.

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Isotope Effects in Hydrogen Atom Transfers. 9.[1] Neighboring Group Participation

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Abstract: The tritium isotope effects in hydrogen abstraction by bromine atoms from $HC(Me)_2CH_2X$ have been measured in the photobromination reaction by a technique which measures the specific activity of the HBr product. At 1 °C and with the reverse reaction suppressed or irrelevant the values for k_H/k_T are 3.9, 8.2, and 11.6 for X = CH_3, Cl, and Br, respectively. An isotope effect of 3.5 for X = H was also measured, but the contribution of the reverse reaction was not established. The relatively large isotope effect for X = Br is interpreted in terms of a weakening of the CH bond by neighboring bromine participation. The smaller effect of chlorine may correspond to a minor participation, but the unfavorable inductive effect of the chlorine is also a factor. The case of X = Br is the microscopic reverse of the addition of HBr to 2-methylpropene, and the results are compared with isotope effects in the addition to HBr to olefins. The measurement of isotope effect is, within some described limitations, a convenient and general method for detecting neighboring group participation in hydrogen atom abstractions.

Hydrogen atom transfer isotope effects have been proposed as a means of determining bond energies to hydrogen, for example, D_{CH}.[3,4] This is based on the observation that in the reaction

$$A\cdot + HC \rightarrow AH + \cdot C \qquad (1)$$

the isotope effect appears to be maximum in the case of $D_{AH} = D_{HC}$, i.e., for $\Delta H^\circ = 0$. The correlation with ΔH is imperfect,[5,6] but still appears to be useful with a single A· as long as steric effects are constant and there is no major variable contribution of polar structures to the transition state. In this paper we address the problem of whether or not D_{CH} is sensitive to various β substituents. This problem is equivalent to asking whether there is any special stabilization of the radical $R_2\dot{C}CR'_2X$ by interaction between the X group and the singly occupied orbital of the radical. For the case X = Br, considerable evidence for interaction has been collected based on regiospecificity[7] (favoring substitutions on the carbon adjacent to that bearing the bromine), on a favored trans stereochemistry,[7a,8] on enhanced rates,[9] and on some rearrangements accompanying the chlorination of alkyl bromides.[10] The isotope effects in the addition of hydrogen bromide[11] to olefins were considered anomalous unless there was considerable radical stabilization by β-bromine, but the arguments were based on radicals all containing the β-bromine. Without controls lacking the bromine, the arguments lacked strength. The interaction of radicals with β atoms of various sorts, including bromine, has been studied by ESR; interaction is observed, but the consequent stabilization is obscure.[12] Thus the evidence for participation is very stong, although not yet universally accepted.