Deuterium Isotope Effect in Halogen Atom Reactions with Methane and Perdeuteriomethane at Energies above Thermal Thresholds

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Abstract: The origin of the isotope effect in the reaction of recoil chlorine atoms with methane and perdeuteriomethane was determined by diluting the systems with inert moderator to establish a unique steady-state collision distribution. The ratio of product yields from the hydrogenated system to those from the deuterated system as a function of moderator suggests that the isotope effect is primarily reactive in nature. The average probability of forming CH_3Cl upon collision compared with CD_3Cl is about 1.8 and that of forming CH_2Cl compared with CD_2Cl is about 1.6 in their respective systems.

The area of high energy kinetics has received increased attention recently as a result of the clear experimental demonstration that (1) a limited number of discrete reaction channels are responsible for the chemistry of atom–molecule systems even in collisions at high relative translational energies; (2) these reaction channels often produce products not normally available at thermal energies; (3) the average probability of reaction upon collision at high energies may be orders of magnitude greater than in thermal kinetics; and (4) primary products formed in hot reactions often contain extremely large amounts of internal energy and thus subsequently decompose rapidly *via* unimolecular kinetics. Many of the overall characteristics of hot reactions have been recently reviewed.[2]

Deuterium isotope effects in hot atom reactions are known to be quite pronounced.[3-5] Such effects in recoil systems may originate from either moderating or reactive characteristics of the reaction mixture. Moderating isotope effects arise from the translational cooling down process accompanying these experiments. The total probability of reaction in the nuclear recoil case is determined by the integrated product of the probability of reaction upon collision and the number of collisions which occur over the range of influence of the excitation function. Since the distribution function for the number of collisions in any energy range is determined by the nature of the colliding species, collision partners containing different isotopes may have distinct moderating effects on the distribution function. Reactive isotope effects in systems utilizing a single hot-atom isotope on the other hand are either a result of differences in the excitation function and thus are manifested in the probability of reaction upon collision or are a result of differences in the probability of unimolecular decomposition of excited primary products.[6]

Most of the reported data on the origin and magnitude of reactive isotope effects in hot systems come from hot tritium reactions.[3-5] These effects are classified as either primary reactive or secondary reactive depending upon whether the isotopic substituent is located at the site of the hot reaction or in another part of the molecule. The nuclear recoil data indicate a primary reactive effect of about 30% in replacement reactions and a primary abstraction effect of about 65% in abstraction reactions both favoring hydrogen sites over deuterium sites.[3] Secondary effects of about 45% favoring hydrogen over deuterium have also been reported for the reaction of nuclear recoil tritium with trifluoromethane to give difluoromethane.[3]

Deuterium isotope effects in hot halogen atom reactions are less well characterized. Unlike tritium, the halogen atom is significantly more massive and larger than either hydrogen or deuterium, and as a result somewhat different dynamical factors will contribute to reactive trajectories in halogen atom systems than in the recoil tritium systems. An early investigation of the reaction of ^{80}Br with methane and perdeuteriomethane, however, demonstrated that such isotope effects may be as large as 100%.[8] Unfortunately in this experiment, it was not possible to distinguish between the reactive and moderating contributions to the observed yields.

More recently, a theoretical trajectory study of the reactions of ^{18}F with HD has both demonstrated that the excitation function for HF formation is quite different from that for DF formation and that unusual dynamical factors may account for part of the reactive isotope effect.[9] In particular two mechanisms appear to be operative with spectator stripping dominating at lower energy and the "abandoned atom" path dominating at higher energies.

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(1) Camille and Henry Dreyfus Teacher-Scholar Grant Awardee, 1971–1976.

(2) (a) L. D. Spicer and B. S. Rabinovitch, *Annu. Rev. Phys. Chem.*, 21, 349 (1970); (b) F. S. Rowland, "Molecular Beams and Reaction Kinetics," Academic Press, New York, N. Y., 1970, p 108

(3) T. Smail and F. S. Rowland, *J. Phys. Chem.*, **74**, 456, 1859 (1970); E. K. C. Lee, G. Miller, and F. S. Rowland, *J. Amer. Chem. Soc.*, **87**, 190 (1965); D. Seewald, M. Gersh, and R. Wolfgang, *J. Chem. Phys.*, **45**, 3870 (1966).

(4) C. C. Chou and F. S. Rowland, *J. Phys. Chem.*, **75**, 1283 (1971); *J. Chem. Phys.*, **46**, 812 (1967).

(5) R. J. Cross, Jr., and R. Wolfgang, *ibid.*, **35**, 2002 (1961).

(6) A further type of isotope effect, the source isotope effect, may result from a change in the isotope of the hot atom used. In practice such a change has not been achieved without also substantially altering the translational and electronic energy spectra of the hot atom as in nuclear recoil experiments.[7]

(7) R. W. Helton, M. Yoong, and E. P. Rack, *J. Phys. Chem.*, **75**, 2072 (1971).

(8) L. D. Spicer and A. A. Gordus, "Chemical Effects of Nuclear Transformations," Vol. 1, IAEA, Vienna, 1965, p 185.

(9) J. T. Muckerman, *J. Chem. Phys.*, **57**, 3388 (1972).

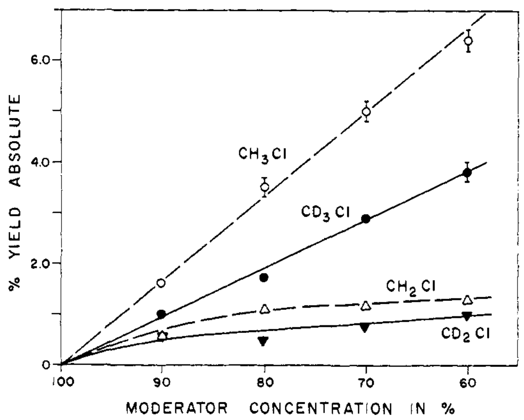

Figure 1. Product yield dependence on moderator concentration in the reactions of hot chlorine atoms with CH_4 and CD_4.

Experimentally the deuterium isotope effect for low energy ^{18}F reactions with methane and hydrogen to give HF and DF has been measured in highly moderated systems.[10] The results indicate reaction with H is favored over reaction with D by about 60 to 80%. This is in general agreement with trajectory calculations for thermal ^{18}F reactions with hydrogen and deuterium gases.[11]

While the observed deuterium isotope effects appear to be substantial in nuclear recoil hot halogen reactions as well as in thermal systems, little is known with respect to the source of such effects. It is the purpose of this study to demonstrate the origin of the isotope effect in the replacement reaction of hot chlorine atoms with methane and perdeuteriomethane to serve as a model for isotope effects in other hot halogen reactions.

Experimental Section

Chemicals used in this study without further purification were the following: methane and ethylene, Phillip's research grade; perdeuteriomethane, Merck, Sharp, and Dohme of Canada; carbon tetrachloride, Mallinckrodt Analytical Reagent; argon, Matheson 99.998% minimum purity; and iodine, Mallinckrodt USP resublimed crystals. Hot chlorine-38 was produced in the $^{37}Cl(n,\gamma)^{38}Cl$ nuclear reaction. Both the californium-252 irradiation source with an average flux of 5×10^8 neutron/(cm^2 sec) and the AGN-201 nuclear reactor with a flux of about 5×10^9 neutron/(cm^2 sec) in the nuclear engineering department at the University of Utah were used as sources of thermal neutrons. Two to three hour irradiations were carried out in 70-ml cylindrical Pyrex ampoules. Radiation damage was measured to be below 0.01 eV per molecule as determined by an acetylene to benzene chemical dosimeter. High-vacuum techniques were used in filling and handling samples to ensure purity. All samples contained 8 cm of carbon tetrachloride which acted both as a source of chlorine atoms and a moderator.[12] Samples also contained 4% ethylene plus iodine at its ambient temperature vapor pressure to act as a scavenger. Radio-gas chromatography incorporating thin window flow proportional counters was used for sample analysis often with carriers to eliminate loss of small amounts of carrier free products.[13] Internal monitoring of ^{41}Ar activity was the basis for absolute yield determinations. Chromatography columns used in this study were (1) 3-m General Electric SF-96 30% Silicone Oil on firebrick, and (2) 3-m 40% hexamethylphosphoramide on firebrick.

Results and Discussion

In order to distinguish between moderating and reactive isotope effects it is necessary to establish a nearly uniform distribution function for high energy collisions in both isotopic systems. This is most easily accomplished by highly diluting the reaction mixture with an inert moderator which essentially determines the steady state collision number over the reactive energy range.[14] Product yields for the reaction of hot chlorine atoms with perdeuteriomethane have been determined in systems containing 60, 70, 80, and 90% argon plus carbon tetrachloride moderator.[12] The results are listed in Table I along with the yields for the reaction of recoil chlorine with methane previously reported.[15,16]

The only primary products of hot reaction observed were methyl chloride and chloromethyl radical (CH_2Cl) measured experimentally as chloroiodomethane-(CH_2ClI) after being scavenged by iodine. The absolute product yields were determined at 1 atm total pressure using internal monitoring with $^{40}Ar(n,\gamma)^{41}Ar$ nuclear reaction and checked using the ethylene plus iodine scavenger. Graphical representation of both systems is presented in Figure 1. It is obvious from both Table I and Figure 1 that the yield of individual products is considerably smaller in the deuterated methane than in the hydrogenated methane. This result is qualitatively similar to that observed in bromine–methane reactions without inert moderation.[8]

Table I. Absolute Yields of Primary Products from the Reaction of Chlorine Atoms with CH_4 and CD_4 as a Function of Moderator Concentration

% moderation	Product yields, %			
	CH_4 reactant		CD_4 reactant	
	CH_3Cl	CH_2Cl	CD_3Cl	CD_2Cl
90	1.6 ± 0.3	0.6 ± 0.1	1.0 ± 0.2	0.6 ± 0.2
80	3.5 ± 0.2	1.1 ± 0.1	1.8 ± 0.3	0.5 ± 0.2
70	5.0 ± 0.6	1.2 ± 0.1	2.8 ± 0.4	0.7 ± 0.2
60	6.4 ± 0.6	1.3 ± 0.2	3.8 ± 0.4	1.0 ± 0.2

In Table II are listed the ratios of individual products as well as the ratio of the total hot yield as a function of moderator concentration. If a moderating isotope effect were dominant, the ratios would approach unity as moderator concentration increases since the collision distribution function approaches the same value in each system at each energy. As can be seen no such trend is obvious suggesting that the observed isotope effect is of a reactive nature. This conclusion is also

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[10] R. L. Williams and F. S. Rowland, *J. Phys. Chem.*, **75**, 2709 (1971).

[11] J. T. Muckerman, *J. Chem. Phys.*, **56**, 2997 (1972); **54**, 1155 (1971).

[12] Carbon tetrachloride has been shown to be very unreactive in hot chlorine atom systems and thus serves mainly as an energy transfer agent or moderator: L. Spicer and R. Wolfgang, *J. Amer. Chem. Soc.*, **90**, 2426 (1968).

[13] R. Wolfgang and C. MacKay, *Nucleonics*, **16**, 69 (1958).

[14] An alternate analytic method of separating moderating effects from reactive effects in nuclear recoil reactions utilizes the kinetic theory of Estrup and Wolfgang (see ref 20). While this theory has been applied successfully to a number of systems, the precision of the results for chlorine reactions with methane does not warrant its use here as a significant improvement over the straightforward method proposed.[15] The kinetic theory is especially difficult to apply with confidence when data covering the whole range of moderation from 10 to 98% are not available as is the case here.

[15] L. Spicer and R. Wolfgang, *J. Chem. Phys.*, **50**, 3466 (1969).

[16] The yields reported for methane were determined for recoil ^{39}Cl reactions from the $^{40}Ar(\gamma,p)^{39}Cl$ nuclear reaction. We have reproduced the results of selected data points using our ^{38}Cl source with CH_4, and we have also found our results in the CD_4 system to be virtually identical with preliminary results for ^{39}Cl plus CD_4. The fact that ^{39}Cl and ^{38}Cl recoil reactions give the same yields is consistent with the work of Wai and Rowland.[17]

[17] C. M. Wai and F. S. Rowland, *J. Amer. Chem. Soc.*, **90**, 3638 (1968).

Table II. Ratios of Absolute Yields of Primary Products from the Reactions of Chlorine Atoms with CH_4 and CD_4 as a Function of Moderator Concentration

% moderation	Yield ratios		
	CH_3Cl/CD_3Cl	CH_2Cl/CD_2Cl	$P_{T(CH_4)}/P_{T(CD_4)}$
90	1.6 ± 0.4	1.0 ± 0.4	1.4 ± 0.3
80	1.9 ± 0.3	2.2 ± 0.9	2.0 ± 0.4
70	1.8 ± 0.3	1.7 ± 0.5	1.8 ± 0.3
60	1.7 ± 0.2	1.3 ± 0.3	1.6 ± 0.2
Average	1.8	1.6	1.7

suggested by data in the binary fluorine reaction systems of CF_4–CH_4 and CF_4–CD_4.[18]

The above data do not directly distinguish between different types of reactive isotope effects. It is, however, possible to present plausible arguments which minimize the effect attributable to unimolecular decomposition. In the hot chlorine atom–methane reaction no pressure dependence among products consistent with unimolecular decomposition was observed over the pressure range of 0.13 to 10 atm.[15] This suggests that any excited molecules which decompose must have at least ~4 eV of internal energy.[19] It might be noted that the path for decomposition of excited product molecules would probably be by elimination of chlorine. This means that the hydrogen or deuterium atoms are not involved directly in the rate determining step and thus contribute only to the energy redistribution.

Because a yield of stable products is observed experimentally at low pressures, reaction paths leading to products containing little internal excitation must be available. The probability of forming these products can be represented by the following equation in the moderated systems studied

$$P_i = \int_{E_1}^{E_2} f_r p_{ir}(E) n(E)\,dE$$

where the probability of reaction to give product i upon collision with reactant r is $p_{ir}(E)$; E_1 and E_2 are the lower and upper energy bounds for the excitation function; f_r is the fraction of hot collisions with reactant r and $n(E)$ is the distribution function for all collisions.[20] At any one moderator concentration both the collision fraction and the steady state collision distribution as demonstrated above are about equal for both isotopic methane species. Thus if $p_{ir}(E)$ is replaced by $\langle p_{ir}\rangle_{av}$, an average probability of reaction upon collision, relative values for this quantity can be found for CH_4 and CD_4 by measuring the ratio of yields provided the $\langle p_{ir}\rangle$ functions are chosen to extend over the same energy range in both cases.

$$P_{i(CH_4)}/P_{i(CD_4)} = \langle p_{i(CH_4)}\rangle_{av}/\langle p_{i(CD_4)}\rangle_{av}$$

From Table II it can be seen that the average probability of forming CH_3Cl from CH_4 plus hot chlorine atoms upon collision is about 1.8 times the average probability of forming CD_3Cl from CD_4 plus hot chlorine atoms upon collision. Likewise $\langle p_{CH_2Cl}\rangle_{av}/\langle p_{CD_2Cl}\rangle_{av} \approx 1.6$. These isotope effects are of the same general magnitude as those observed previously for nuclear recoil tritium reactions.[3] No obvious classical model accounts for such large deuterium isotope effects in hot halogen systems.

Using methane and perdeuteriomethane as reactants, it is impossible to distinguish between primary and secondary isotope effects. If, however, a comparison with recoil tritium reactions can be made, one might expect reasonable contributions from both sources.[3] This implies that sites adjacent to the local point of replacement are participating in the reaction. Such a model has been examined in general for tritium reactions[4] and is supported by the general results of recent trajectory calculations for tritium plus methane.[21] Such a mechanism does not imply a long-lived complex is being formed but merely that substituents located near the reaction site often have a range of influence which includes both the incoming hot atom and the leaving atom or group. This influence tends to affect the dynamics of the reactive collision in unusual ways such as those demonstrated for the simpler ^{18}F plus HD reaction where at high energies the initial collision occurs with the atom which is later released while reaction takes place with the other "abandoned atom" in the hydrogen molecule. Unfortunately the chlorine methane reaction system is much more complex from a calculational point of view and thus no detailed reaction mechanism has been shown to quantitatively account for the observed isotope effect.

Summary

The origin of the deuterium isotope effect in the hot reaction of chlorine atoms and methane was found to be a reactive isotope effect. The ratios of the average probabilities of reaction upon collision to form methyl chloride and methylchloro radical in CH_4 and CD_4 were found to be 1.8 and 1.6, respectively. It is suggested that similar isotope effects in other halogen–methane systems are of the same origin.

Acknowledgment. The author would like to acknowledge many very stimulating discussions with the late Professor Richard Wolfgang relative to this work. Help with irradiations by the Nuclear Engineering Department at the University of Utah was appreciated. Generous support by the U. S. Atomic Energy Commission under Contract AT(11-1)-2190 is gratefully acknowledged.

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(18) L. Spicer and A. Siuda, *Radiochim. Acta*, in press.

(19) A very high energy contribution to the excitation function, if it exists, would imply an additional mechanism for reaction. The isotope effect for such a path leading to highly excited product molecules (5–10 eV internal energy) cannot be explored in the pressure range of 0.1–10 atm due to the fact that complete decomposition occurs without giving products which can be observed directly or uniquely. The fact, however, that there is *no* decomposition of observed products over the 0.1 to 10 atm pressure range while a sizable fraction of product survives at the lower pressures suggests that the mutual overlap and interaction of these excitation functions for the two mechanisms would be minimal.

(20) P. J. Estrup and R. Wolfgang, *J. Amer. Chem. Soc.*, **82**, 2665 (1960); R. Wolfgang, *J. Chem. Phys.*, **39**, 2983 (1963).

(21) D. Bunker and M. Pattengill, *ibid.*, **53**, 3041 (1970).