expected value of 12.6×10^{10} dpm/mole, which is one-half of the specific activity of c-C_3H_5T if no other isotopic fractionation is permitted except for the stoichiometry of reaction 7a. Therefore, there is a slight degree of isotopic fractionation when reactions 6 plus 7a and reactions 10 plus 11a are compared, but the observed difference may well be within the over-all accuracy of the experiment.

A measurable tritium isotope effect observed for the secondary decomposition reaction 12b in which the vibrationally excited c-$C_3H_5T^{**}$ decomposes to C_3H_5T is clearly outside of the experimental error and is significant. This unimolecular isomerization kinetic isotope effect is about 10% in the direct photolysis at 2537 Å (see Table I), favoring the isomerization of c-$C_3H_6^{**}$ by a 10% greater rate constant than of c-$C_3H_5T^{**}$. Exactly the same kinetic isotope effect has been observed in the thermal unimolecular isomerization of c-C_3H_6 and c-C_3H_5T at 500° and 200 mm[29] and in the unimolecular isomerization of the vibrationally excited cyclopropanes produced by the addition of CH_2 and CHT to C_2H_4 at room temperature.[30] Therefore, the present data are in excellent agreement with the data obtained previously from the system of vibrationally excited cyclopropanes.

The tritium isotope effect observed in the benzene photosensitization of CB and CBT (see Table I) is very much like that in the direct photolysis, within the over-all accuracy of the experiment, although the specific activities in the former are slightly greater than those in the latter. As in the case of the benzene photosensitization of cyclopentanone-2-t,[8] no large additional isotope effect seems necessary to explain the data for the benzene photosensitization of cyclobutanone-2-t. The low degree of tritium isotope effect observed in the benzene photosensitization is an interesting contrast to the large deuterium isotope effect observed in the $Hg(^3P_1)$ photosensitization of alkanes.[31]

G. Concluding Remarks. Cyclobutanone,[7] cyclopentanone,[8] and cyclohexanone[32] intercept the excited singlet benzene with about equal quenching cross sections ($K_S^{-1} = 3.0$ mm of ketone), while monoolefins do not quench the excited singlet benzene.[26] This observation might be indicative of the simple electronic energy-transfer process operating between the excited singlet benzene and ketones rather than the formation of a long-lived complex between them. This may also be the case for the triplet-energy-transfer processes. In any case, the benzene photosensitization method provides a rich source of information on the vibronic excitation-transfer process.

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(30) (a) C. McKnight, E. K. C. Lee, and F. S. Rowland, *J. Am. Chem. Soc.*, **89**, 469 (1967); (b) F. S. Rowland, C. McKnight, and E. K. C. Lee, paper presented at the International Conference on Photochemistry, Munich, Germany, Sept 6–9, 1967.

(31) (a) Y. Rousseau and H. E. Gunning, *Can. J. Chem.*, **41**, 465 (1963); (b) Y. Rousseau, G. N. C. Woodall, and H. E. Gunning, *J. Chem. Phys.*, **37**, 2722 (1962); (c) S. Penzes, O. P. Strausz, and H. E. Gunning, *ibid.*, **45**, 2322 (1966).
(32) R. G. Shortridge, Jr., unpublished work in our laboratory.

The Reactions of Energetic Chlorine Atoms with Methyl Chloride in the Gas Phase[1]

Chien M. Wai and F. S. Rowland

Contribution from the Department of Chemistry, University of California, Irvine, California 92664. Received December 18, 1967

Abstract: The reactions of energetic chlorine atoms with methyl chloride in the gas phase have been studied in detail, using the technique of nuclear recoil. Both substitution products, Cl for Cl and Cl for H, were observed in yields of 3.1 and 0.7%, respectively, for well-scavenged gaseous samples. The substitution reactions were confirmed as hot, and not thermal, processes by diminishing their yield with helium and neon as inert moderators. Quantitative evaluation of the kinetic theory parameters shows that the α values (moderator efficiencies) of CH_3-Cl/Ne/He are in the ratio 3.0/1.0/0.41. The high value for CH_3Cl indicates substantial energy loss in highly inelastic collisions; the "billiard-ball" ratio for Ne/He would be 1.0/0.26. The chemical reactions have been studied using both $Cl^{37}(n,\gamma)Cl^{38}$ and $Ar^{40}(\gamma,p)Cl^{39}$ as the nuclear reaction source, with results in excellent agreement with each other. The absolute yields of the $Cl^{37}(n,\gamma)Cl^{38}$ reaction have been internally monitored with the $Ar^{40}(n,\gamma)Ar^{41}$ reaction. All of the observed reactions can be consistently interpreted as chemical reactions of neutral ground-state chlorine atoms with excess kinetic energy.

E nergetic atoms from nuclear recoil provide abundant additional information about the kinetic behavior of atomic species, especially in reactions with covalent molecules, as has already been shown in detail for atomic hydrogen and carbon, and as is now being shown for atomic fluorine.[2–4] The chemistry of energetic

Table I. Nuclear Characteristics of Cl^{34m}, Cl^{38}, and Cl^{39} and of Reactions Used in Their Formation

Nuclear characteristic	Isotope		
	Cl^{34m}	Cl^{38}	Cl^{39}
$t_{1/2}$	32.4 min	37.3 min	56 min
Decay mode	β^+ to stable S^{34}	β^- to stable Ar^{38}	β^- to Ar^{39} ($t_{1/2}$ = 265 years)
Energy of decay	69% direct to S^{34} (67% by 2.41 or 1.24 MeV β^+ plus γ's; 2% EC^c or weak β^+) 31% IT^c to 1.6 sec Cl^{34}, followed by 4.40 MeV	53% 4.81 MeV β^- 16% 2.77 MeV β^- + γ 31% 1.11 MeV β^- + γ's	7% 3.45 meV β^- 8% 2.18 MeV β^- + γ 85% 1.91 MeV β^- + γ's
Nuclear reaction for production	$Cl^{35}(\gamma,n)Cl^{34m}$	$Cl^{37}(n,\gamma)Cl^{38}$	$Ar^{40}(\gamma,p)Cl^{39}$
Energetics of nuclear reaction	12.7 MeV endoergic	6.1 MeV exoergic	12.5 MeV endoergic
Recoil energy	0.19 ± 0.05 MeV^a	527 eV^b	0.27 ± 0.07 MeV^a

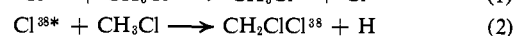^{a} Spread by momentum of γ radiation; calculated for the maximum cross section of the giant resonances: $Cl^{35}(\gamma,n)$, 19 MeV; $Ar^{40}(\gamma,p)$, 23 MeV. ^{b} Assuming one 6.1-MeV γ ray; less if multiple γ emission. ^{c} EC, electron capture; IT, isomeric transition.

chlorine atoms has not been studied as intensively as these other recoil species, and the majority of such investigations have been carried out in condensed-phase systems, especially with alkyl halides.[5-8] The condensed-phase behavior in these systems, as measured by the formation of Cl-labeled organic molecules, is dominated by the recombination of atoms and radicals in a "cage" of surrounding molecules, and direct substitution processes of lower yield are almost completely obscured by the high yield of these cage reactions.[5,6,9] Consequently, while a reasonable amount of information is available about the gaseous reactions of thermal chlorine atoms,[10] very little material has been published about the direct reactions of atomic chlorine in gaseous systems.[11,12]

Our present experiments have involved the detailed study of recoil chlorine atom reactions with methyl chloride. The utility of studies such as this is strongly dependent upon the correct identification of the charge and excitation state of the atomic chlorine, i.e., neutral or charged, kinetic or electronic excitation, etc., at the time of reaction. The use of nuclear recoil sources of energetic atoms carries the additional difficulties implicit in undiscovered short-lived nuclear isomers, Auger transitions following internal conversion from such states, etc., such as those intimately involved in the chemistry of recoil bromine atoms.[5] Since an energetic Cl atom requires $\sim 10^{-10}$ sec to decelerate in 1 atm of CH_3Cl, only nuclear isomeric states that are delayed for $\geq 10^{-10}$ sec are likely to cause serious complications in gas-phase experiments.

Earlier experiments with various alkyl chlorides had shown that products corresponding to the replacement by Cl* of Cl or H, as in (1) and (2),[13] should be antici-

pated,[11] and these labeled species are indeed found in all of the present experiments. However, more recent investigations have disclosed the somewhat unexpected

$$Cl^{38}* + CH_3Cl \longrightarrow CH_3Cl^{38} + Cl \qquad (1)$$
$$Cl^{38}* + CH_3Cl \longrightarrow CH_2ClCl^{38} + H \qquad (2)$$

difficulties involved in obtaining a satisfactory experimental system for scavenging thermal atomic halogens,[9,14] and the nonthermal nature of the reactions leading to these products needed to be definitely established.

Thermal Cl atoms abstract H atoms very efficiently from a wide variety of C–H bonds,[10] and the formation of HCl^{38} is therefore a likely fate for thermal Cl^{38} in almost any hydrogenous system. Consequently, the energetic abstraction of an H atom by Cl^{38}, also leading to HCl^{38}, will be very difficult to isolate from the thermal process, and total hot yields must remain uncertain until techniques are devised to distinguish hot and thermal HCl^{38} from one another.

Nuclear Properties of Chlorine Isotopes Useful in Hot Atom Chemistry. Three isotopes of chlorine have half-lives long enough to permit reasonably normal radio gas chromatographic procedures, and yet short enough to permit the attainment of satisfactory counting rates without prohibitive radiation damage to the system.[15] A summary of the most pertinent nuclear properties of the three usable isotopes of chlorine is given in Table I, together with characteristics of the nuclear reactions used for their production in these experiments.[16] The nuclear reaction $Cl^{35}(n,2n)Cl^{34m}$ would also provide recoil chlorine atoms with energies in the range of 2 $\times$ 10^5 eV. The capture γ radiation spectrum is not well known for Cl^{37}, but most probably includes a number of γ rays with varying angular correlation. The 527-eV recoil energy listed for Cl^{38} is therefore only a maximum energy, and the median energy is probably in the 200–300-eV range.

An excited nuclear isomer, Cl^{38m} ($t_{1/2}$ = 0.74 sec), is also known, decaying entirely by 0.66-MeV γ emission

(2) R. Wolfgang, Progr. Reaction Kinetics, 3, 97 (1965).
(3) F. Schmidt-Bleek and F. S. Rowland, Angew. Chem. Intern. Ed. Engl., 3, 669 (1964).
(4) R. Wolfgang, Ann. Rev. Phys. Chem., 16, 15 (1965).
(5) J. E. Willard, "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, 1965, p 221.
(6) F. S. Rowland, C. M. Wai, C. T. Ting, and G. Miller, ref 5, p 333.
(7) J. M. Miller, J. W. Gryder, and R. W. Dodson, J. Chem. Phys., 18, 579 (1950).
(8) J. M. Miller and R. W. Dodson, ibid., 18, 865 (1950).
(9) C. M. Wai and F. S. Rowland, J. Phys. Chem., 71, 2752 (1967).
(10) G. C. Fettis and J. H. Knox, Progr. Reaction Kinetics, 2, 1 (1964).
(11) J. E. Quinlan, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1958.
(12) J. C. W. Chien and J. E. Willard, J. Am. Chem. Soc., 75, 6160 (1953).
(13) The asterisk is used in reactions 1 and 2, and throughout this

paper, to symbolize an energetic, nonthermal species. These reactions have been written with Cl^{38} as the radioactive isotope, although both Cl^{34m} and Cl^{39} could equally well have been chosen as the isotope for illustrative purposes.

(14) N. Colebourne, J. F. J. Todd, and R. Wolfgang, ref 5, p 149.
(15) Too much radiation damage ordinarily results from the long irradiation times required for long-lived Cl^{36}.
(16) C. M. Wai, Ph.D. Thesis, University of California, Irvine, 1967. Copies of this thesis can be obtained through University Microfilms, Ann Arbor, Mich.

Table II. Absolute Yields of CH_3Cl^{38} and CH_2ClCl^{38} in Methyl Chloride vs. Internal Monitor Ar^{41} [a]

Products	Obsd activity, counts	Abs time, min $(t = t_r + t_s)$	Corr factor to $t = t_0$	Corr activity, counts	(A_{Cl}/A_{Ar})	Y, %
Ar^{41}	$184,500 \pm 500$	36.6	1/0.791	$233,300 \pm 600$		
CH_3Cl^{38}	$267,400 \pm 500$	40.7	1/0.469	$570,100 \pm 1100$	2.45 ± 0.01	4.65 ± 0.02
CH_2ClCl^{38}	$40,300 \pm 220$	72.4	1/0.261	$154,400 \pm 800$	0.66 ± 0.01	1.25 ± 0.01

[a] Sample gas pressure (cm): Ar, 1; O_2, 2; CH_3Cl, 70. Sample irradiation: 3 min at 10^{12} n/(cm² sec). t_0 = absolute zero time, the time that neutron irradiation is completed. t_s = time between the completion of neutron irradiation and the sample injection. t_r = retention time of the observed activity peak from radio gas chromatogram. t = absolute time, which is the time period between t_0 and the time of the observed radioactivity peak.

to Cl^{38}, internally converted in only 5×10^{-4} of these decays. The recoil energy resulting from the emission of a 0.66-MeV γ ray is 61 eV, while the cross section for the formation of Cl^{38m} in the (n,γ) process is estimated to be only 1% as large as that of Cl^{38}. The existence of Cl^{38m} introduces a negligible effect on the use of Cl^{38} as a reaction source for energetic Cl atoms: first, its yield from the (n,γ) reaction is small; and second, those atoms of Cl^{38} originating in the decay of Cl^{38m} are produced, just as are those from the (n,γ) reaction directly, with a recoil energy well above both bond energies and the chemical reaction energy range. In the absence of internal conversion of the γ radiation, the reactions of pure 60-eV and pure 500-eV Cl atoms might very well prove to give identical product distributions; the inclusion of a small percentage of 61-eV atoms in among those from the (n,γ) reaction is certainly not distinguishable.

Irradiations to form Cl^{38} have been carried out in the thermal neutron flux of a TRIGA nuclear reactor, usually for a period of 3 min at a flux of approximately 10^{12} n/(cm² sec). The production of Cl^{34m} and Cl^{39} has been carried out in the bremsstrahlung beam from the General Atomics electron accelerator, with a maximum electron energy of 45 MeV. [16]

Absolute Yield Measurements. Our experiments with the bremsstrahlung beam from the electron accelerator are subject to enough variables out of our direct control that we do not feel that any of these measurements warrants more than a qualitative estimate of its absolute yield. Therefore, all of the Cl^{39} and Cl^{34m} results are reported solely on an internal basis relative to one arbitrarily chosen product, CH_3Cl.

We have used the $Ar^{40}(n,\gamma)Ar^{41}$ reaction as an internal monitor reaction for Cl^{38} because of its advantages: (a) convenient half-life and neutron cross section for comparison with $Cl^{37}(n,\gamma)Cl^{38}$; (b) single chemical product, monatomic Ar^{41}, in 100% yield, and easily measurable in the usual radio gas chromatographic procedure; and (c) negligible effect of argon on the hot-atom chemical processes of moderation and reaction when present in 1-5% concentration. The largest errors in this measurement arise from lack of accurate control over the concentration of Ar in the sample; the ratio of the thermal neutron cross sections of Cl^{37} and Ar^{40} is insensitive to the exact fast-thermal ratio in the neutron beam. [17] The relative rates of decay, corrected to the end of the irradiation, have been used in eq 3 for the calculation of the fractional yield, P_i, of each Cl^{38}-containing compound, as in Table II. [18]

The equation as given applies only for sample irradiations short compared to either of the half-lives involved, a condition amply fulfilled in each of our experiments.

$$P_i \text{ (in per cent)} = 131\left(\frac{X_{Ar}}{X_{CH_3Cl}}\right)\left(\frac{A^i_{Cl}}{A_{Ar}}\right) \qquad (3)$$

In a mixture of 1 cm of Ar and 70 cm of CH_3Cl, the observed radioactivities in the Ar^{41}, CH_3Cl^{38}, and CH_2ClCl^{38} peaks are all in a convenient range of counting rates (see Figure 1).

Sample Preparation and Irradiation. The preparation of samples followed the routine procedures used in this laboratory for gas-phase hot-atom chemistry experiments and frequently described in the literature. [2-4] Methyl chloride was used directly as obtained from Matheson Co., since it showed no impurity greater than 0.01% by gas chromatography. Oxygen, neon, and helium gases were also used directly from lecture bottles. cis- and trans-1,2-dichloroethylene were purified, primarily from each other, by gas chromatographic separation and trapping prior to use. As indicated in Figure 1, severe macroscopic radiation damage was not observed ($\sim 0.1\%$), and perturbation of the hot-atom product distribution by secondary radiation is not an important factor for the products measured in this work.

Radio Gas Chromatography. The radio gas chromatographic procedures were routine [19,20] and have been described in detail in the Ph.D. thesis of Wai. [16] Inorganic species such as HCl^{38} or $ClCl^{38}$ formed in these systems were not measured. Stationary-counting assay has shown that essentially all of the radioactivity is present in the form of volatile chemical species readily transferable by standard vacuum-line techniques.

Scavenger Procedures. An essential requirement for the study of the reactions of hot Cl atoms is that the products must be separable experimentally from identical or similar products formed by chemical reactions involving thermalized atoms or radicals. The choice of a suitable scavenger for the removal of thermalized radicals (or, more precisely, for their diversion into other products, usually not measured) is not difficult, for O_2, I_2, olefins, NO, etc. all have good success in this role. The removal of thermal Cl atoms is

(17) D. J. Hughes and R. B. Schwartz, "Neutron Cross Sections," BNL 325, 2nd ed, 1958, and Supplement No. 1, 1960, U. S. Government Printing Office, Washington, D. C.

(18) X_{CH_3Cl} and X_{Ar} are the respective mole fractions of the components in the mixtures. P_i and A^i_{Cl} refer to the yield of the ith Cl-labeled product and its observed radioactivity, respectively. Thermal neutron cross sections: Ar^{40}, 0.53 barn; Cl^{37}, 0.56 barn. Half-lives: Ar^{40}, 1.83 hr; Cl^{38}, 37.3 min; Natural isotopic abundance: Ar^{40}, 99.6%; Cl^{37}, 24.5%.

(19) J. K. Lee, E. K. C. Lee, B. Musgrave, Y.-N. Tang, J. W. Root, and F. S. Rowland, Anal. Chem., 34, 741 (1962).

(20) F. Schmidt-Bleek and F. S. Rowland, ibid., 36, 1696 (1964).

Table III. Radioactive Products of Recoil Cl^{38} Reaction in Gaseous CH_3Cl

Gas pressure (cm) of CH_3Cl	60	60	58	60	54	50
Added molecule	None	$3N_2$	$0.6O_2$	$3O_2$	$6O_2$	$10O_2$
Product yield (CH_3Cl = 100)						
CH_3Cl^{38}	100	100	100	100	100	100
CH_2ClCl^{38}	33 ± 1	34 ± 1	28 ± 1	26 ± 1	20 ± 1	17 ± 1
$CH_3CH_2Cl^{38}$	4	4	...	...	...	...
$CH_3CHClCl^{38}$	4	2	...	...	...	...
$CH_2ClCH_2Cl^{38}$	25 ± 1	27 ± 1	...	...	...	...
Specific activity of CH_3Cl^a	6600	6300	5700	5100	5500	5200

^{a} Specific activity of parent in counts/arbitrary mass unit; the estimated reproducibility is ±5%.

Table IV. Products of Recoil Cl^{38} Reactions in Mixtures of CH_3Cl and $CHCl=CHCl$

Pressure, cm^a	60	55	56	52	57	55
1,2-DCE^b	0	1 cis	3.9 cis	4 trans	6 cis	10 cis
Product yields^c (% of total Cl^{38} produced)						
CH_3Cl^{38}	4.65 ± 0.02	3.26 ± 0.02	2.93 ± 0.02	2.91 ± 0.02	2.74 ± 0.03	2.53 ± 0.03
CH_2ClCl^{38}	1.25 ± 0.01	0.70 ± 0.01	0.57 ± 0.01	0.61 ± 0.01	0.50 ± 0.01	0.45 ± 0.01
trans-DCE–Cl^{38}	...	1.08 ± 0.01	1.75 ± 0.01	2.00 ± 0.01	2.10 ± 0.01	2.60 ± 0.01
cis-DCE–Cl^{38}	...	2.15 ± 0.02	3.31 ± 0.02	3.68 ± 0.02	4.05 ± 0.02	5.30 ± 0.03
Activity ratios						
CH_2Cl_2/CH_3Cl	0.27 ± 0.01	0.22 ± 0.01	0.20 ± 0.01	0.21 ± 0.01	0.18 ± 0.01	0.18 ± 0.01
trans-DCE/cis-DCE	...	0.50 ± 0.01	0.53 ± 0.01	0.55 ± 0.01	0.52 ± 0.01	0.49 ± 0.01

^{a} Including 2 cm of O_2 in each sample. ^{b} cis- or trans-1,2-DCE, as indicated. ^{c} Absolute yield relative to Ar^{41} as internal monitor. The quoted statistical error includes only the random error of counting, and not systematic errors in cross sections, half-lines, etc.

more difficult, and we have earlier reported that O_2, C_2H_4, and C_2H_4–O_2 mixtures all failed to suppress some alkyl halide products involving thermal, bimolecular reactions in the 2,3-dichlorobutane system.[9] In those experiments, the combination of 1,3-butadiene plus O_2 provided an efficient scavenging action. In many of our experiments here, we have resorted to the similar pair of cis-$CHCl=CHCl$ plus O_2—both 1,3-butadiene and cis-$CHCl=CHCl$ have lower activation energies than C_2H_4 toward reaction with radicals.

The thermal neutron irradiation of CH_3Cl gas alone leads to five simple organic radioactive products, whose yields are listed in Table III relative to the yield of labeled methyl chloride as 100. The addition of a small amount of N_2 has no effect on these yields. However, when a small amount of O_2 is introduced into the system, all two-carbon-atom products are removed, and only the substitution products, CH_3Cl^{38} and CH_2-$ClCl^{38}$, were found. (Oxygenated species would not have emerged from the gas chromatographic columns during the period of analysis.) This sensitivity to O_2 obviously indicates that the two-carbon-atom products were not formed in hot reactions, but involved at least one thermal combination step. Moreover, the specific activity of CH_3Cl decreased, indicating that the choice of CH_3Cl = 100 is actually a shifting base, and therefore that a fraction of both CH_3Cl^{38} and CH_2ClCl^{38} was formed in the O_2-free system by scavengeable processes.

As the amount of O_2 in the system is increased further, the specific activity of CH_3Cl does not decrease very much further, although the ratio of $CH_2ClCl^{38}/$ CH_3Cl^{38} does continue to fall.

Reactions of Cl^{38} with CH_3Cl When Scavenged with 1,2-Dichloroethylene. An efficient alternate scavenger for thermal Cl atoms and labeled radicals is a substituted olefin, such as $CHCl=CHCl$. Reactions were carried

out in mixtures of CH_3Cl and 1,2-dichloroethylene (1,2-DCE), using the formation of Ar^{41} as a neutron flux monitor. The absolute yields of labeled products from these reactions are given in Table IV. The *total* organic yield increases with the addition of a small
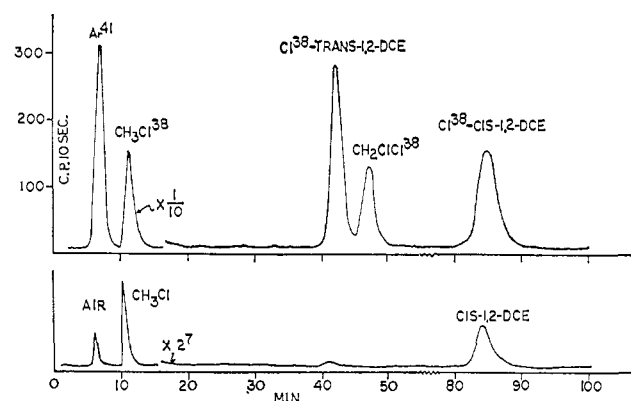

Figure 1. Radio gas chromatogram of neutron-irradiated mixture of gaseous CH_3Cl (with O_2 and cis-1,2-dichloroethylene as scavenger, and Ar as internal monitor): upper trace, radioactivity of Ar^{41}- and Cl^{38}-labeled products; lower trace, thermal conductivity response of components after irradiation.

amount of 1,2-DCE into CH_3Cl, showing that the primary source of the radioactive Cl atoms reacting with $CHCl=CHCl$ is *not* from among atoms which would otherwise have undergone hot substitution reactions, but presumably from thermal or low-energy Cl atoms. The observation is similar to that of Hamill, Williams, and Schwarz, who found that atomic bromine exchanges with 1,2-dibromoethylene by an addition–elimination mechanism.[21] The similarity in re-

(21) W. H. Hamill, R. R. Williams, Jr., and H. A. Schwarz, *J. Am. Chem. Soc.*, **72**, 2831 (1950).

Table V. Comparison of Energetic Cl-Atom Reactions in CH_3Cl Initiated by Nuclear Reactions $Cl^{37}(n,\gamma)Cl^{38}$ and $Ar^{40}(\gamma,p)Cl^{39}$

Cl isotope	Cl^{39}			Cl^{38}		
Activation process	$Ar^{40}(\gamma,p)Cl^{39}$			$Cl^{37}(n,\gamma)Cl^{38}$		
Gas pressure, cm						
CH_3Cl	50	34	29	60	48	20
Ar	12	24	20	5	12	42(Ne)[a]
O_2	3.0	2.9	1.0	3.0	3.0	1.0
cis-1,2-DCE	...	...	0.8	...	...	0.6
Products[b]						
CH_3Cl	100	100	100	100	100	100
CH_2Cl_2	27 ± 2	28 ± 1	30 ± 2	27 ± 1	30 ± 2	28 ± 1
trans-1,2-DCE	...	...	78 ± 4	...	...	85 ± 3
cis-1,2-DCE	...	...	150 ± 10	...	...	168 ± 8

[a] To avoid large yield of Ar^{41}. [b] All labeled products are expressed in yields relative to CH_3Cl activity = 100.

sults for cis- and trans-1,2-DCE in Table IV is evidence for an excited $CHClCl^{38}$–$CHCl\cdot$ radical as the primary intermediate in the formation of the labeled 1,2-dichloroethylene isomers.

The O_2-scavenged yield of CH_3Cl^{38} dropped by about 30% with the addition of 1 cm of 1,2-DCE, an additional decrease comparable to the initial drop in specific activity with the addition of O_2. An additional factor of 10 in concentration of 1,2-DCE only decreased the CH_3Cl^{38} yield by an additional 15%. The latter reduction in yield probably represents direct competition between $CHCl\!\!=\!\!CHCl$ and CH_3Cl for *hot* atoms, for the olefinic concentration is no longer really at a "scavenger" level but is an appreciable component in the system. The remaining CH_3Cl^{38}, unaffected by a small amount of 1,2-DCE or of O_2, must be the product of direct hot substitution reaction. The residual yield of CH_2ClCl^{38} must also arise from hot processes; the decrease in yield of CH_2ClCl^{38} with the addition of increasing amounts of 1,2-DCE parallels the observations made with O_2 scavenger in Table III. We assume that the yields observed in the presence of O_2 and 1–5 cm of 1,2-DCE represent the true substitution yields and would therefore be the yields of the primary substitution reactions if none of the products underwent subsequent secondary decomposition or isomerization.

If the chemical reactions under study are those of neutral chlorine atoms with excess kinetic energy, as postulated, identical experimental results should be observed for chlorine atoms of equivalent energy, regardless of source.[22] Differences in initial energy become less important if the energy is well above the chemical reaction range, since the characteristics at the time of reaction are then dependent upon the energy loss processes in the nonbond-forming collisions intervening between formation and chemical reaction, and will quickly lose any residual "memory" of the initial energy.

Atoms produced in the 10^5-eV range can be expected to be in charge and excitation equilibrium with the surroundings by the time they are slowed to $\sim$100 eV; atoms formed at 500 eV might be very near equilibrium, with exact knowledge dependent upon various scattering and charge exchange cross sections, as yet unmeasured, between 500 eV and the chemical reaction range.[2] The equilibrium distribution of such atoms among the various charge and excitation states is also unknown through this energy range for Cl atoms.

The ground electronic state of Cl is $3p^5$-$^2P^0{}_{3/2}$, and its first excited state, $3p^5$-$^2P^0{}_{1/2}$, has an energy only 0.11 eV above ground.[23] We consider these to be indistinguishable for our present hot-atom experiments and imply either one when we describe a chlorine atom as being in its neutral ground state. The next electronic state, $4s\,^4P_{5/2}$, occurs at 8.9 eV.[23] In the absence of any contrary experimental information, either spectroscopic or chemical-kinetic, and in analogy with the comparable circumstance in tritium systems,[2–4] we assume that a negligible fraction of such electronically excited atoms is present for an equilibrium chlorine atom beam in methyl chloride at 50 eV or below.

A comparison of experimental results from Cl^{37}(n,γ)-Cl^{38} and $Ar^{40}(\gamma,p)Cl^{39}$ in reactions with CH_3Cl + cis-$CHCl\!\!=\!\!CHCl$ is given in Table V. The observed relative yields are quantitatively identical within the limits of experimental error. No comparisons of the absolute yields can be made for our results. However, the absolute yields from Cl^{39} reaction with CH_3Cl are also in the several per cent range, as reported by Spicer and Wolfgang,[24] and are consistent with our Cl^{38} absolute yields within the respective errors in absolute calibrations. The close similarity of the results shown in Table V makes reasonable the assumption that the reacting chlorine species are essentially identical; a similar identity of results was found for the stereochemical observations of Cl^{38} and Cl^{39} reactions with dl- and meso-2,3-dichlorobutane.[9] The close similarity in observed reactions for these two chlorine isotopes in two different systems, involving molecules bracketing the ionization potential of atomic chlorine, provides strong support to our assignment of the reacting chlorine species as the neutral ground state with excess kinetic energy. The moderator experiments discussed below are also indicative of the reactions of hot, neutral atoms.

Some comparable experimental observations with Cl^{34m} reactions are reported in Table VI. The short half-life (especially when compared to the transit time between San Diego and Irvine) and lower yield of Cl^{34m} make these experiments much less satisfactory than those with the othe two chlorine isotopes. Qualitatively, the labeled products are again the same, but the ratios are not in quantitative agreement. Under our experimental conditions, approximately equal amounts of C^{11} and Cl^{34m} activity were observed, and rigorous

(22) Excluding the small kinetic isotope effect from the variation in mass of the chlorine isotopes. Even in thermal reactions, chlorine isotope effects are generally less than 10% in magnitude, and the effect should be diminished in hot reactions.

(23) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular No. 467, U. S. Government Printing Office, Washington, D. C., 1949.

(24) L. Spicer and R. Wolfgang, reported at the 4th Informal Conference on Hot Atom Chemistry, Kyoto, Japan, Oct 1967.

Table VI. Chemical Reactions of Energetic Cl^{34m} with CH_3Cl $[Cl^{35}(\gamma,n)Cl^{34m}]$

Gas pressure, cm					
CH_3Cl	58	63	57	60	62
O_2	1	2.9	5.9	9	2
cis-1,2-DCE	...	...	...	...	2
Products[a] (Cl^{34m} labeled)[b]					
CH_3Cl	100	100	100	100	100
CH_2Cl_2	49 ± 1	41 ± 1	30 ± 2	27 ± 4	28 ± 2
trans-1,2-DCE	...	...	...	...	53 ± 3
cis-1,2-DCE	...	...	...	...	97 ± 5
Others	...	...	...	...	2 ± 1

[a] All product yields relative to parent CH_3Cl^{34m} = 100. [b] C^{11} in CO was observed in most runs in yields about equal to the total Cl^{34m} activities observed.

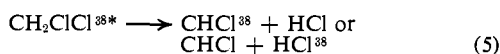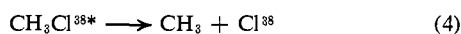**Table VII.** Pressure Dependence of Recoil Cl^{38} Reactions with Methyl Chloride[a]

Pressure, cm	2.5	6	12	24	35	66
Product yield, %[b]						
CH_3Cl^{38}	2.97 ± 0.04	2.78 ± 0.03	2.77 ± 0.03	2.94 ± 0.03	2.98 ± 0.02	3.10 ± 0.02
CH_2ClCl^{38}	0.64 ± 0.02	0.62 ± 0.02	0.62 ± 0.02	0.59 ± 0.02	0.61 ± 0.01	0.60 ± 0.01
trans-DCE-Cl^{38}	4.75 ± 0.05	4.02 ± 0.04	2.94 ± 0.03	2.32 ± 0.02	1.69 ± 0.01	1.30 ± 0.01
cis-DCE-Cl^{38}	10.20 ± 0.15	8.90 ± 0.10	5.90 ± 0.06	4.34 ± 0.04	3.28 ± 0.02	2.54 ± 0.02
Ratio $CH_2ClCl^{38}/CH_3Cl^{38}$	0.22 ± 0.01	0.22 ± 0.01	0.22 ± 0.01	0.20 ± 0.01	0.20 ± 0.01	0.19 ± 0.01
Ratio trans-Cl^{38}/cis-Cl^{38}	0.47 ± 0.01	0.45 ± 0.01	0.50 ± 0.01	0.54 ± 0.01	0.52 ± 0.01	0.51 ± 0.01

[a] Mole ratios of gas mixture $Ar:O_2:cis$-DCE:CH_3Cl = 1:2:2:70 for all samples. [b] Absolute yield relative to Ar^{41} as internal monitor. Statistical errors do not include systematic error in cross section, half-life, etc., but are based on random error of counting only.

separation of the contributions of the two activities was not possible with our apparatus. Additional experiments with Cl^{34m} are desirable to clarify the comparison.

Pressure Dependence of Product Yields. The substitution of an energetic recoil atom into a molecule has been shown to be accompanied by high excitation energy of the products in both recoil tritium and recoil fluorine atom systems.[2-4,25-30] In these cases, the molecules are excited enough to undergo secondary isomerization or decomposition, as detected by a pressure-dependent competition between collisional stabilization and secondary reaction. The main products of interest in this study, CH_3Cl and CH_2Cl_2, have been shown to undergo the secondary decompositions corresponding to (4) and (5), respectively, when formed by recoil tritium substitution reactions.[27-29] In the recoil

$$CH_3Cl^{38*} \longrightarrow CH_3 + Cl^{38} \qquad (4)$$

$$CH_2ClCl^{38*} \longrightarrow CHCl^{38} + HCl \text{ or } CHCl + HCl^{38} \qquad (5)$$

tritium systems, the pressure dependence of these products was established from the ratios of secondary products to stabilized molecules: in Br_2, CH_2TBr vs. CH_2-TCl; in C_2H_4, c-C_3H_4TCl vs. $CHTCl_2$. Neither of these procedures works well with the Cl^{38}-CH_3Cl system—the former because the CH_3 radical of (4) carries no radioactive label and is therefore undetectable, and the latter because the reaction of Cl^{38*} with C_2H_4 alone leads to the formation of c-$C_3H_5Cl^{38}$, presumably through the formation of $CHCl^{38}$ by an initial Cl^{38} reaction with ethylene.[31]

(25) J. K. Lee, B. Musgrave, and F. S. Rowland, Can. J. Chem., 38, 1756 (1960).

(26) E. K. C. Lee and F. S. Rowland, J. Am. Chem. Soc., 85, 897 (1963).

(27) Y.-N. Tang, E. K. C. Lee, and F. S. Rowland, ibid., 86, 1280 (1964).

(28) Y.-N. Tang and F. S. Rowland, ibid., 87, 1625 (1965).

(29) Y.-N. Tang and F. S. Rowland, ibid., 90, 570, 574 (1968).

(30) Y.-N. Tang and F. S. Rowland, J. Phys. Chem., 71, 4576 (1967).

(31) Y.-N. Tang and F. S. Rowland, unpublished experimental results.

Studies of pressure dependence in the Cl^{38}-CH_3Cl systems have thus been confined to (a) measurement of the specific activity of CH_3Cl^{38} from CH_3Cl, and (b) absolute measurements vs. $Ar^{40}(n,\gamma)Ar^{41}$. The range of recoil Cl^{38} is very short and even a few centimeters of CH_3Cl is quite enough to stop 99+ % of the recoil chlorine atoms in the gas phase.[16] Since the formation of Cl^{38} is linearly dependent upon the amount of Cl^{37} present in the system, one would expect the specific activity, i.e., CH_3Cl^{38}/CH_3Cl, to remain constant barring pressure-dependent decomposition effects. Such measurements of specific activity have actually been constant within ±10%, the limits of error imposed by the irreproducibility of positioning of a series of samples in our nuclear reactor experiments.

A series of absolute measurements vs. the yield of Ar^{41} is shown in Table VII. These measurements provide no evidence for a pressure dependence of the yield of CH_3Cl^{38} or CH_2ClCl^{38}, while clearly showing the pressure-dependent decomposition of the excited radical $CHClCl^{38}$-$CHCl\cdot*$ to form the labeled cis and trans isomers of dichloroethylene. We do not infer from the results of Table VII that the molecules of CH_3Cl^{38} and CH_2ClCl^{38} are formed with insufficient internal excitation energy to cause secondary decomposition; we, in fact, believe the opposite to be true and think that extensive decomposition probably occurs for products, by analogy with the experimental observations on F^{18} and Cl^{39} reactions with cyclanes.[30,31] We draw only the experimental conclusion that pressure dependence is sufficiently slight that measurements made at pressures differing by a factor of 10 or so can be reasonably compared to one another without introducing serious errors from variations in the fraction undergoing secondary reaction.

Moderator Experiments. Energetic reactions initiated through the extra kinetic energy of a recoil atom should have the property that these characteristic reactions gradually disappear with progressive dilution of the reaction system with inert moderators whose only

Table VIII. Moderator Effects for Recoil Cl³⁸ Reactions in Gaseous CH_3Cl + cis-1,2-DCE

Mole fraction[a] of CH_3Cl	Yields, %				
	P_{CH_3C}	$P_{CH_2Cl_2}$	P_{obsd}	$P_{trans\text{-}1,2\text{-}DCE}$	$P_{cis\text{-}1,2\text{-}DCE}$
	A. Neon Results				
1.0	3.09 ± 0.03	0.71 ± 0.02	3.80 ± 0.05	1.19 ± 0.03	2.46 ± 0.04
0.690	2.92 ± 0.03	0.71 ± 0.02	3.63 ± 0.05	1.25 ± 0.02	2.44 ± 0.03
0.330	2.18 ± 0.04	0.62 ± 0.02	2.80 ± 0.06	1.94 ± 0.04	3.76 ± 0.07
0.185	1.45 ± 0.02	0.50 ± 0.02	1.95 ± 0.04	2.26 ± 0.04	4.85 ± 0.08
0.122	1.26 ± 0.02	0.40 ± 0.01	1.66 ± 0.03	2.46 ± 0.04	5.10 ± 0.07
0.105	0.99 ± 0.02	0.37 ± 0.01	1.36 ± 0.03	2.11 ± 0.04	4.40 ± 0.07
0.073	0.83 ± 0.03	0.34 ± 0.03	1.17 ± 0.05	1.74 ± 0.04	3.60 ± 0.07
0.052	0.59 ± 0.05	0.22 ± 0.05	0.81 ± 0.10	1.66 ± 0.07	3.10 ± 0.09
	B. He Moderator Results				
0.346	2.83 ± 0.04	0.70 ± 0.02	3.53 ± 0.06	1.90 ± 0.05	3.63 ± 0.07
0.121	1.92 ± 0.03	0.57 ± 0.02	2.49 ± 0.05	2.92 ± 0.07	5.90 ± 0.09
0.099	1.82 ± 0.03	0.56 ± 0.02	2.83 ± 0.05	2.70 ± 0.07	5.50 ± 0.09
0.052	1.12 ± 0.06	0.39 ± 0.04	1.51 ± 0.10	2.07 ± 0.06	3.90 ± 0.08

[a] The ratio of CH_3Cl to cis-CHCl=CHCl was 76:1 in all samples; 1 cm of O_2 in all samples.

intended function in the system is collisional removal of translational energy from the recoil atom. We have carried out moderator experiments with both helium and neon, utilizing the Ar⁴¹-monitored CH_3Cl system to obtain absolute activity measurements. Moderator experiments could also be carried out with Ar, Kr, or Xe, albeit with greater experimental complication.

The experimental yields from Cl³⁸ reactions with moderated CH_3Cl are given in Table VIII and Figure 2 vs. the mole fractions of the helium and neon moderators. Both yields approach zero as the mole fraction of moderator approaches unity. These results are con-
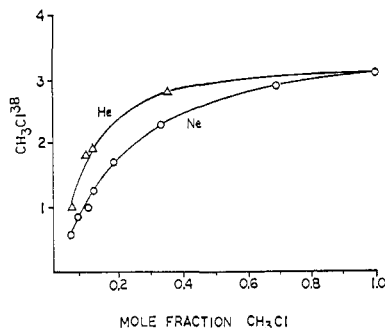

Figure 2. Effect of helium and neon moderators on yield of CH_3Cl^{38} from reaction of energetic Cl³⁸ with gaseous CH_3Cl moderators: △, He; ○, Ne (yields in per cent total activity).

sistent with the postulated moderator action of removal of excess kinetic energy. A corollary conclusion is that the reduction and eventual suppression of the yields of both CH_3Cl^{38} and CH_2ClCl^{38} with increasing moderator concentration is consistent with their identification as products of the reactions of high kinetic energy chlorine atoms.

Since the ionization potentials of He (24.58 eV) and Ne (20.56 eV) are higher than that of Cl (13.01 eV), the transition from lower ionization potential (CH_3Cl, 11.46 eV) to higher could conceivably involve the transition from neutral or partially or entirely ionic chlorine atom reactions. Qualitatively, one would expect that helium, with the higher IP, should be more effective than neon in altering these reactions if the effect were a change to the ionic state; experimentally, neon is the

more effective in suppressing the hot reactions, as expected for the relative masses of Ne and He in moderating the kinetic energy of Cl atoms.

Kinetic Theory Parameters. The yields of hot reactions can be expressed through the kinetic theory of hot reactions, in which the hot yield of the ith product, P_i, is written in terms of the fraction of collisions with its parent molecule, f_i, the probability of reaction at that energy, $P_i(E)$, and the number density of collisions at that energy, $n(E)$, as in eq 6. While this equation

$$P_i = \int_{E_1}^{E_2} f_i P_i(E) n(E) \, dE \qquad (6)$$

was actually first written by Miller and Dodson to describe the reactions of energetic Cl³⁸ atoms (in the liquid phase),[8] the quantitative evaluation of the appropriate parameters for such an equation relies upon the procedures developed by Wolfgang, et al., and applied by them to tritium and fluorine atom reactions;[2-4] these have not been previously applied to Cl-atom reactions. The graphical evaluation involves as kinetic parameters the reactivity integral, $I = \Sigma_i \int_{E_i}^{E_i'} p_i(E)$ d ln E, and the average logarithmic energy loss, α, for both the parent molecule and the moderator molecule, as given in eq 7. An equivalent formulation of this

$$\frac{-1}{\ln(1-P)} = \frac{\alpha_{reactant}}{I} + \frac{\alpha_{moderator}}{I}\left(\frac{1-f}{f}\right) \qquad (7)$$

equation involves the substitution of mole fractions, X, and collision cross sections, S, for $(1 - f)/f$ in order to permit direct plotting of functions of the experimental quantities.[32] If the total hot reaction yield is small, then the left-hand term can be satisfactorily approximated as $1/P$. Further, if the total hot yield is small, the relative yields of products will not change appreciably with moderation, and a satisfactory plot can be made with only a partial summation of the yields, as in eq 8, in

$$\frac{1}{P_{obsd}} = \frac{k(\alpha_{react})}{I} + \frac{k(\alpha_{mod})}{I}\left(\frac{S_{mod}}{S_{react}}\right)\left(\frac{1-X}{X}\right) \qquad (8)$$

which $P_{obsd} = P_{total}/k$, with the value of $k > 1$. A plot of $1/P_{obsd}$ vs. $(1 - X)/X$ is shown in Figure 3. Straight lines are obtained for the results in both He

(32) J. W. Root and F. S. Rowland, *J. Chem. Phys.*, **46**, 4299 (1967).

and Ne moderators, with the following parameters: (He) slope 2.0 ± 0.1, intercept, 25.0 ± 0.5; (Ne) slope, 5.2 ± 0.2; intercept, 25.0 ± 0.5. Ratios of collision cross sections for atomic chlorine with the various species have been obtained from reasonable assumptions concerning the collision radii of the individual species.[33] Combination of these collision cross-section ratios with the intercept/slope values from Figure 3 provides estimates of the relative values of α, the average logarithmic energy loss per collision, as summarized in Table IX. The energy losses in collisions with methyl chloride are much greater than with either of the noble gases, indicating substantial inelasticity in the collisions with the polyatomic molecule, just as previously observed for tritium atom collisions with hydrocarbons vs. inert gases or D_2.[2,4,32] The ratio of 0.41 ± 0.03 for the two inert gases does not correspond precisely to the ratio of 0.26 expected for isotropic, hard-sphere scattering ("billiard-ball"), indicating the inadequacy of the assumption of this simple model even for the calculation of energy loss ratios for atom–atom collisions.

Figure 3. Kinetic theory plot for yields of CH_3Cl^{38} plus CH_3ClCl^{38} in helium and neon moderated reactions of Cl^{38} with gaseous methyl chloride: ●, He; ○, Ne.

Table IX. Relative Values of α, Average Logarithmic Energy Loss per Collision, for Cl-Atom Collisions

Experimental source		
From He moderator data	$\alpha_{CH_3Cl}/\alpha_{He}$	7.40 ± 0.41
From Ne moderator data	$\alpha_{CH_3Cl}/\alpha_{Ne}$	3.03 ± 0.13
From He vs. Ne	α_{He}/α_{Ne}	0.41 ± 0.03

The graphical analysis of Figure 3 has been carried out on the basis of the sum of the yields of CH_3Cl^{38} and CH_2ClCl^{38}. Examination of the data in Table VIII on individual product yields shows, however, that the ratio of these two products changes substantially between highly moderated systems and unmoderated ones. Such a ratio change is outside the limits permitted by the assumptions of the graphical analysis of eq 8, based as it was on the presumption of nearly constant ratios for all hot products. However, this ratio is also sensitive to the amount and nature of scavengers present (Tables III and IV), and further experiments with a variety of scavengers in moderated systems are required to understand the causes of the ratio variations. The ratio of products is apparently more sensitive toward such minor changes than is the total yield, and no serious error is implied for the analysis based on the sum of product yields.

Among other reasons, the change in the ratio of $CH_2ClCl^{38}/CH_3Cl^{38}$ could be attributed to (a) high total probability of energetic reaction in unmoderated systems, with the additional hot yield attributed to unmeasured products such as HCl^{38}, or (b) nonconstant values of α in different energy ranges. A very high total yield of hot products (>50%) would require a very large yield of HCl^{38}, and should also lead to appreciable curvature in Figure 3, and does not appear to be consistent with the experimental evidence. Variations in α with energy may certainly occur, but experiments of this type will have to be conducted with greatly increased precision in order to test such a hypothesis.

(33) S_{He}/S_{CH_3Cl} = 0.59; S_{Ne}/S_{CH_3Cl} = 0.63. Assumed collision radii, based on Lennard-Jones potentials fitted to viscosity data: He, 2.58 Å; Ne, 2.78 Å; CH_3Cl, 4.38 Å; Cl (=Ar), 3.42 Å. See K. A. Kobe and R. E. Lynn, Jr., Chem. Rev., 52, 117 (1953).
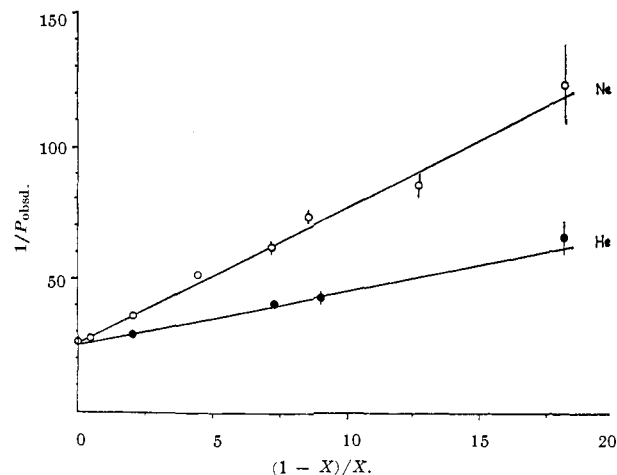
Factors Affecting the Yields of Energetic Substitution Reactions.

One important conclusion from the quantitative data is that the hot substitution reactions with CH_3Cl in the gas phase account for only a few per cent of the total available hot Cl atoms. This conclusion is parallel to the observations on fluorine atom reactions, while the yields from both halogens are very much lower than the yields found for recoil tritium reactions with simple hydrocarbons and halocarbons.[2-4] Although the precise factors responsible for these differences cannot be easily isolated from experiments with a single target molecule, the velocity of the energetic atom of a given energy is substantially lower and its linear momentum is higher for either halogen atom than for a tritium atom. If the ease with which a recoil atom can change direction in response to a newly available chemical potential in a different direction is important in facilitating the formation of a new bond, then the heavier mass of the halogen atom may very well hinder such bond formation and result in substantially lower yields than in the corresponding tritium system.

Chlorine-atom reactions with alkyl halides show a very substantial phase effect: an increase in organic yield in condensed phases of a factor of 5 or 10.[5,6,9] The liquid-phase yield is quite similar in distribution of products to that observed for direct, gas-phase substitution, but with higher yields.[16] Such an observation can be satisfactorily explained if the gas-phase collisions lead to many "near-misses" for stable bond formation: in the gas phase, the chlorine atom escapes completely; in the liquid phase, the recoil chlorine is held in the vicinity of the nascent radical, and the two rapidly combine with one another in the cage. The observation of partial racemization of optically active radicals in the liquid phase in the reactions of Cl^{38} with 2,3-dichlorobutane indicates that the Cl atom and the radical actually do separate in the liquid-phase cage reaction prior to their bond-forming combination.[6]

The experimental data indicate that it is much easier for energetic Cl to replace the single Cl in CH_3Cl than it is to replace any one of the three H atoms. These numbers presumably need correction for the partial decomposition of the excited products, as in (4) and (5), but such correction is unlikely to alter the qualita-

tive conclusion that Cl is much easier (*i.e.*, factor of ~10 per bond) to replace than H in CH_3Cl. The bond strength of the C–H bond (97.4 kcal/mole) is considerably larger than that of C–Cl (83.5 kcal/mole) in CH_3Cl,[34] and the substitution of Cl for H is certainly endothermic by nearly 15 kcal/mole. However, since the threshold energies for both substitution reactions are probably 35–50 kcal/mole, it is not clear that a more endothermic reaction is necessarily unfavored in its yield. Further experiments with other parent molecules are certainly needed for assessment of the various factors controlling the quantitative yields of hot Cl substitution reactions.[16,24]

These experiments with energetic Cl atom reactions with CH_3Cl, have, however, established or confirmed several important characteristics of such substitution reactions: (a) the nuclear reactions $Cl^{37}(n,\gamma)Cl^{38}$ and

(34) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. 1, Princeton University Press, Princeton, N. J., p 24.

$Ar^{40}(\gamma,p)Cl^{39}$ produce chlorine atoms whose chemical behavior with CH_3Cl can be very plausibly described as the chemical reactions of neutral, ground-state atoms with excess kinetic energy; (b) Cl atoms react with methyl chloride in high kinetic energy reactions to form CH_3Cl and CH_2Cl_2 by substitution for Cl and H, respectively (the hot yields of these substitution products account for only a small per cent of the total energetic chlorine produced when the reactions are carried out in the gas phase, about 3.1% as CH_3Cl and 0.7% as CH_2Cl_2); (c) the hot yields of both substitution products can be substantially reduced by moderating the kinetic energy in collisions with inert helium or neon (the moderating efficiency of CH_3Cl for Cl is about three times greater than that of neon, consistent with a large fraction of highly inelastic collisions for the polyatomic molecule; neon, whose mass is closer to that of Cl, is 2.5 times more efficient as a kinetic energy moderator than helium).

Reactions of Methyl Radicals with Aromatic Hydrocarbons. Effect of Conformation and Carbon–Hydrogen Orientation upon the Rate, the Activation Energy, and the *A* Factor

A. E. Eachus, J. A. Meyer, J. Pearson, and M. Szwarc

Contribution from the Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210. Received January 26, 1968
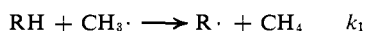
Abstract: Competition between $RH + CH_3 \cdot \rightarrow R \cdot + CH_4$ (k_1) and $C_6H_5CH_3 + CH_3 \cdot \rightarrow C_6H_5CH_2 \cdot + CH_4$ (k_T) was investigated in the liquid phase over a temperature range 0–95°. Methyl radicals were produced by the photolysis of azomethane, and tritiated toluene, $C_6H_5CH_2T$, was used to distinguish between the products of the reaction of RH and toluene. The following compounds were studied: *o-*, *m-*, and *p-*xylenes, mesitylene, ethylbenzene, 1,2-diphenylethane, indan, tetralin, cumene, *p-t*-butylcumene, cyclohexylbenzene, diphenylmethane, and triphenylmethane. The results show that the reactivity is governed primarily by the nature of the carbon–hydrogen bond: tertiary > secondary > primary. Within each series the ratio A_1/A_T (per active H atom) remains essentially constant if the effect of conformation is taken into account. Changes in reactivity are caused by changes in the respective activation energies, again corrected for the effect of conformation which introduces an additional term, Δ, in the observed activation energy. It was found that the abstraction of a tritium atom requires 2.7 kcal/mole higher activation energy than the abstraction of hydrogen.

Tetralin and indan are unusually reactive toward radicals.[1,2] It seems that the process
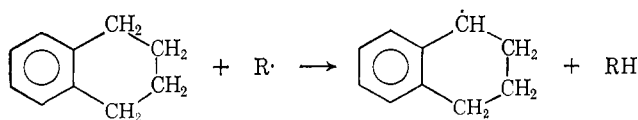
is much faster than other analogous reactions involving a secondary hydrogen atom located on a carbon α to the benzene ring. These observations were confirmed by our past study of the H abstraction[3]

$$RH + CH_3 \cdot \longrightarrow R \cdot + CH_4 \qquad k_1$$

where RH = toluene, the xylenes, mesitylene, ethylbenzene, cumene, indan, and tetralin. Those results provided the ratios k_1/k_T, where k_T refers to the reaction

$$PhCH_3 + CH_3 \cdot \longrightarrow PhCH_2 \cdot + CH_4 \qquad k_T$$

The experiments were performed in the liquid phase at one temperature only (65°) and led us to the following conclusions. Tetralin has a "normal" reactivity; *i.e.*, the ratio k_1(tetralin)/k_T(per active hydrogen atom) has a value similar to that found in the aliphatic series when a secondary hydrogen is compared with a primary one. However, ethylbenzene and cumene are less reactive than anticipated, since the most probable conformation of these molecules is unfavorable for the H abstraction. We expected, therefore, that the "abnormally" low relative reactivity of ethylbenzene and cumene should be reflected in the relatively high activa-

(1) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).
(2) A. L. Williams, A. E. Oberright, and J. W. Brooks, *ibid.*, **78**, 1190 (1956).
(3) J. A. Meyer, V. Stannett, and M. Szwarc, *ibid.*, **83**, 25 (1961).