Table I. Yields (%) of Hot Fluorine Replacement Reactions[a]

	Reactant molecule					
Reaction type	CH_4	CH_3F	CH_2F_2	CHF_3	CF_4	CH_3Cl
Replacement for F or Cl		4.7 (CH_3F)	2.6 (CH_2F_2)	1.4 (CHF_3)	2.8 (CF_4)	7.9 (CH_3F)
Replacement for H	15.8 (CH_3F)	3.4 (CH_2F_2)	0.9 (CHF_3)	1.3 (CF_4)		<0.5 (CH_2ClF)
Replacement for 2F			2.8 (CH_2FI)	3.3 (CHF_2I)	2.5 (CF_3I)	
Replacement for H and F or Cl		2.1 (CH_2FI)	2.9 (CHF_2I)	1.0 (CF_3I)		7.3 (CH_2FI)
Replacement for 2H	4.6 (CH_2FI)	0.4 (CHF_2I)	0.8 (CF_3I)			<0.5 ($CHClFI$)
Other reactions	<0.5	<0.5	<0.5	<0.5	<0.5	
Total hot yield, %	20.4	10.6	10.0	7.0	5.3	15.2–16.2
Calcd area available for reaction	1.00	0.73	0.50	0.26	0.05	0.73
Calcd hot yield, %	(20.4)	14.9	10.0	5.3	1.0	14.9

[a] Per cent of total F^{18} incorporated in product shown in parentheses.

While these processes are analogous to those of the better understood hot hydrogen, yield data and kinetic analyses indicate significant differences in mechanism.[2,3] We communicate here results of a survey of hot fluorine atom reactions sufficiently complete to establish systematic trends. The accompanying paper reports on parallel work with hot chlorine. On the basis of these data, we attempt to define the mechanistic factors controlling the reactions of fast halogen atoms.

Hot F^{18} was produced in the Bremsstrahlung beam of the 40-Mev Yale electron accelerator by the $F^{19}(\gamma,n)F^{18}$ nuclear reaction. Samples at 1 atm and 25° contained the reagent mixed with small quantities of ethylene and iodine to scavenge thermalized atoms[2] and help suppress radiation effects. In the cases of CH_4 and CH_3Cl, CF_4 was added as a source of fluorine.[3] Details of irradiation procedures and the radiogas chromatographic analysis have already been reported.[2,3]

Data on F^{18} reactions in the absence of moderator are shown in Table I. Two apparently opposing trends emerge. (1) The total hot yield decreases as the number of halogen substituents on the reagent increases. (2) When halogen atoms are present, they are replaced in preference to hydrogen. These striking trends, observed here for the first time, appear to dominate hot halogen reactions.

In attempting to find a model, we assume what is now well established for hot hydrogen reactions with saturated hydrocarbons: that reaction is direct, occurring on a time scale comparable with a bond vibration.[1c,4] It is then reasonable that replacement reactions can occur only when the hot halogen atom strikes the central carbon atom or one of the bonds uniting it with its ligands. This implies no such reactions occur when a bound halogen is struck on the side away from the carbon atom. Such an impact may result in abstraction, although even this may not be very likely, because of the weakness of the halogen–halogen bond formed.

The basic model suggests that two factors will be important in determining the reaction: steric[2] and translational inertial (the latter being discussed in the following paper). The importance of the steric factor is measured by the fraction of collisions in which the hot halogen atom strikes a bound halogen without also interacting with the central carbon. To a first approximation this corresponds to the solid angle over which the incident hot atom collides with a bound halogen. It is assumed that the hydrogen provides no hindrance to reactive approach. This is plausible, not so much because the hydrogen atoms are small, but because their vibrational relaxation times are short or comparable to the time of the collision. Thus they can adiabatically adjust to the incoming halogen atom—in other words, get out of the way.

The total probability of reaction with any given molecule can now be predicted very simply. The experimentally determined probability of reaction with the sterically unhindered methane molecule is multiplied by the estimate of the fractional solid angle of the molecule in question that is available for reaction. These calculated values are included in Table I. Comparison with the total experimental yields shows that the steric factor serves well in correlating and predicting trends of total reactivity.[5]

Acknowledgment. The authors wish to thank the staff of the Yale University linear electron accelerator for their help. This work was supported by the U. S. Atomic Energy Commission under Contract SAR/AT(30-1)1957.

Effects of Nuclear Transformations," Vol. I, International Atomic Energy Agency, Vienna, 1965, p 149.

(3) J. F. J. Todd, N. Colebourne, and R. Wolfgang, *J. Phys. Chem.*, **71**, 2875 (1967).

(4) M. A. El-Sayed, P. J. Estrup, and R. Wolfgang, *ibid.*, **62**, 1356 (1958).

(5) Even if the steric effect were the sole factor controlling total probability of reaction on collision, there would not be exact agreement between the calculated and experimental trends. There are two reasons for this. (1) The calculation of steric hindrance is only approximate, as it considers only "head-on" collisions (events of zero impact parameter with respect to the carbon atom) and assumes normal Lennard-Jones cross sections. (2) The total yield depends not only on the average probability of reaction per collision, but on the number of collisions. The latter quantity will vary with the moderating properties of the medium (as measured by the collisional energy loss parameter α).[6] This will change somewhat between different reagent molecules. Such an effect could be eliminated by comparing not yields but rather "reactivity integrals" which are obtained by extrapolation to infinite dilution with an inert moderator and are therefore independent of the moderating properties of the reagent. We have determined a few of these reactivity integrals, and they correlate well with the calculated steric effect.

(6) R. Wolfgang, *J. Chem. Phys.*, **39**, 2983 (1963).

L. Spicer, J. F. J. Todd, Richard Wolfgang
Department of Chemistry, Yale University
New Haven, Connecticut

Received November 22, 1967

Systematics and Mechanism of Hot Halogen Reactions. Product Distribution

Sir:

Reactions of hot chlorine atoms produced by Bremsstrahlung *via* the $Ar^{40}(\gamma,p)Cl^{39}$ process have been

Table I. Yields (%) of Hot Chlorine Replacement Reactions[a]

Reaction type	Reactant molecule: CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4	C_2H_5Cl	CH_3F
Replacement for Cl or F		2.4 (CH_3Cl)	1.7 (CH_2Cl_2)	0.6 ($CHCl_3$)	0.6 (CCl_4)	2.0 (C_2H_5Cl)	3.5 (CH_3Cl)
Replacement for H	6.4 (CH_3Cl)	1.2 (CH_2Cl_2)	<0.5 ($CHCl_3$)	<0.2 (CCl_4)		<0.2 ($C_2H_4Cl_2$)	<0.5 (CH_2ClF)
Replacement for CH_3						0.8 (CH_2Cl_2)	
Replacement for CH_2Cl						1.3 (CH_3Cl)	
Replacement for 2Cl			1.2 (CH_2ClI)	<0.2 ($CHCl_2I$)	. . .[b]		
Replacement for H and Cl or F		1.4 (CH_2ClI)	<0.5 ($CHCl_2I$)	. . .[b]			2.0 (CH_2ClI)
Replacement for 2H	1.3 (CH_2ClI)	<0.5 ($CHCl_2I$)	. . .[b]				<0.5 ($CHClFI$)
Replacement for C and Cl						1.8 (CH_2ClI)	
Other reactions	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Total hot yield, %	7.7	5.0–5.5	2.9–3.9	0.6–1.0	0.6	5.9–6.1	5.5–6.5
Calcd area available for reaction	1.00	0.70	0.39	0.22	0.0		0.73
Calcd hot yield, %	(7.7)	5.4	3.0	1.7	0		5.6

[a] Performed at 60% moderation with argon. Per cent of total Cl^{39} incorporated in product shown in parentheses. [b] Cannot be detected because of long elution time and interference from scavenger. Yield probably small.

studied. As small amounts of ethylene and iodine were found to be effective scavengers in these systems also, procedures followed were substantially similar to those for hot fluorine[1,2] (described in the preceding communication[1]), except that argon was present in all samples. Data shown in Table I represent absolute yields based on monitor samples of argon and scavenger. Because of the presence of argon which acts as a moderator, yields are systematically lower than they would be in unmoderated systems.

As in the case of hot fluorine, the total yield of replacement reaction decreases with halogen substitution in the reagent molecule, a trend correlating well with estimated steric hindrance. Yet when reaction does occur, it is the halogen that is replaced in preference to hydrogen. This apparent contradiction becomes reasonable upon consideration of the appropriate inertial factor. There are two such factors. The first requires that a reaction, to be efficient, must not require rotational–vibrational relaxation motions which are slow compared with the time of collision. This has been well established in the case of recoil tritium. In the reaction of T with C_2H_5Cl, for instance, the yield ratio $CH_3T/CH_2TCl \approx 6$, presumably because the CH_3 group can more readily relax to accept the T atom in the time of collision ($\sim 10^{-14}$ sec) than can the CH_2Cl.[3] This factor appears to be much less important in halogen than in tritium systems. For example, a replacement reaction of Cl^{39} at the C–C bond of C_2H_5Cl (Table I) shows only a moderate preference for combination with the lighter fragment to give CH_3Cl^{39} (1.3%) over combination with the heavier group yielding CH_2ClCl^{39} (0.8%). This result is reasonable since relaxation times of carbon–halogen bonds are comparable to the slower characteristic collision times (10^{-13} sec) for the hot halogen atoms.

Distinct from this "rotational–vibrational inertial factor" is a "translational inertial factor." This postulates that, in the center-of-mass coordinates of the collision, the inertia associated with the translational motion of a heavy ligand causes it to be preferentially detached. This factor, invoked here for the first time, appears important in hot halogen reactions. It does not seem significant in recoil tritium systems, since the mass of hot hydrogen is so small that the center-of-mass velocity of its collision partner is usually low. The effect is schematically illustrated in Figure 1 for a collision between Cl^{39} and CH_3Cl. The hot Cl^{39} and the CH_3Cl approach each other at high relative velocity until, as assumed by the steric model, replacement collision takes place at the carbon atom. In case I, this reverses the direction of the CH_3 group while the ligand chlorine atom tends to continue moving in its original direction. The resulting stretching of the C–Cl bond excites or weakens it by the order of a few electron volts. Any such weakening of the C–H bond will be much smaller.[4] Consequently, it becomes reasonable that it is the Cl atom that is preferentially replaced. Case II illustrates the situation for a reaction involving Walden inversion in which the original C–Cl bond is weakened by compression. As has been indicated by the work of Wai and Rowland, this mechanism appears to be much less important.[5,6]

To the extent that double displacement occurs by a

---

(1) L. Spicer, J. F. J. Todd, and R. Wolfgang, *J. Am. Chem. Soc.*, **90**, 0000 (1968).

(2) (a) N. Colebourne, J. F. J. Todd, and R. Wolfgang, "Chemical Effects of Nuclear Transformations," Vol. I, International Atomic Energy Agency, Vienna, 1965, p 149; (b) J. F. T. Todd, N. Colbourne, and R. Wolfgang, *J. Phys. Chem.*, **71**, 2875 (1967).

(3) R. Odum and R. Wolfgang, *J. Am. Chem. Soc.*, **85**, 1050 (1963).

(4) If a 10-eV Cl^{39} atom initially shares its momentum exclusively with the CH_3 group of CH_3Cl^{35}, the resultant internal energy of the CH_3–Cl^{35} bond will be 2.8 eV. (On the other hand, even given the much more implausible situation of the Cl^{39} sharing momentum with the CH_2Cl^{35} group, the resultant internal energy of the carbon–hydrogen bond would be less than 0.1 eV.)

(5) C. M. Wai, C. T. Ting, and F. S. Rowland, *J. Am. Chem. Soc.*, **86**, 2525 (1964).

(6) C. M. Wai and F. S. Rowland, *J. Phys. Chem.*, **71**, 2753 (1967).

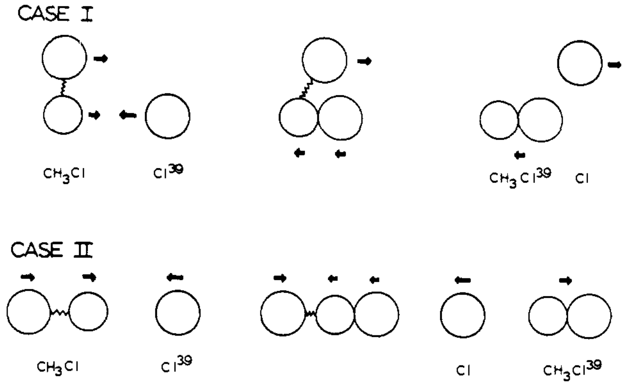


Figure 1. Schematic representation in the center of mass system of extreme cases involving the translational inertial effect on the reaction between Cl^{39} and CH_3Cl. Case I: Approach of Cl^{39} normal to CH_3–Cl bond axis and collision at CH_3 group tend to stretch and thereby to vibrationally excite and weaken the existing C–Cl bond. Case II: Coaxial approach tends to excite existing C–Cl bond by compression. In both cases, rupture of this bond is thereby facilitated.

one-step mechanism,[7] the translational inertial factor predicts preferential replacement of two halogens or a halogen and a hydrogen. The interesting result that displacement of two hydrogen atoms is rare in molecules which also contain halogen is consistent with this expectation.

In summary, it appears that steric and translational-inertial factors can correlate the main features of hot halogen reactions in the gas phase. The fact that in the liquid phase yields are much higher and do not appear to follow the trends observed here is presumably a result of caging effects, known to be important for halogen atoms.[10]

Acknowledgment. The authors wish to thank the staff of the Yale University linear electron accelerator for their help. This work was supported by the U. S. Atomic Energy Commission under Contrast SAR/AT(30-1)1957.

---

(7) We do not here discuss the extent to which "double-displacement" products are formed in a single step or by decomposition of an internally excited product of a single replacement reaction. To the extent to which the latter mechanism holds, the product yields measured deviate from the actual primary product yields.[8,9] However, even if all double-displacement products resulted from secondary decomposition, the trend in appropriately corrected single-displacement results would still indicate a strong preference for halogen replacement.

(8) Y. Tang, E. K. C. Lee, and F. S. Rowland, *J. Am. Chem. Soc.*, 86, 1280 (1964)

(9) Y. N. Tang and F. S. Rowland, *J. Phys. Chem.*, 72, 707 (1968).

(10) M. Milman, *Radiochim. Acta*, 2, 180 (1964).

L. Spicer, Richard Wolfgang
Department of Chemistry, Yale University
New Haven, Connecticut

Received November 22, 1967

Macrobicyclic Amines. I. *out–in* Isomerism of 1,(*k* + 2)-Diazabicyclo[*k.l.m*]alkanes

Sir:

Macrobicyclic diamines with bridgehead nitrogen atoms potentially can exist as conformations in which the lone pairs are both outside and inside the cavity defined by the hydrocarbon bridges. To test this idea, a series of 1,(*k* + 2)-diazabicyclo[*k.l.m*]alkanes was synthesized with $k, l, m > 6$.

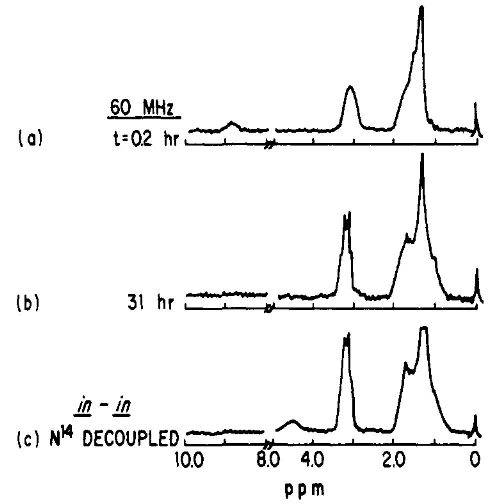


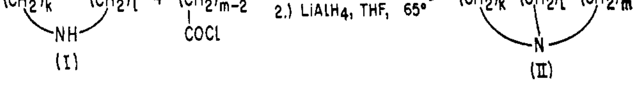
Figure 1. (a, b) Time dependence of the 60-MHz pmr spectrum of 1,10-diazabicyclo[8.8.8]hexacosane bishydrochloride in 50% TFA at 25°. (c) The ^{14}N decoupled spectrum of the i^+i^+ isomer.

1,(*k* + 2)-Diazacycloalkanes (I) were prepared by the procedure of Stetter[1] and converted by an extension of the same method to the crystalline 1,(*k* + 2)-diazabicyclo[*k.l.m*]alkanes (II) (Table I),[2] which have low solubility in water and alcohol but are soluble in nonpolar solvents. The symmetrical amines II ($k = l = m$) have simple infrared spectra whose absorptions are much sharper when the chains contain an even number of methylenes.

Table I. Properties of 1,(*k* + 2)-Diazabicyclo[*k.l.m*]alkanes (II)

II, [*k.l.m*]	Yield, %[a]	Mp, °C	δ, ppm[b] o^+o^+	o^+i^+	i^+i^+	K_e[b]
7.7.7	20	35	9.2		4.4	0.85
8.8.8	75	120	9.0		4.6	>100
9.9.9	50	32	8.8		4.8	0.41
10.10.10	75	114	8.7	8.5[c]	4.8	3.3
6.6.8	40	45	9.2		4.3	24
6.8.10	60	<0	8.9		4.7	0.70
8.8.10	70	55	8.9		4.5	1.5
$[(C_2H_5)_3N]$			8.2			

[a] Over-all yield based on amines I, which in turn were prepared in 50–70% yields.[1] [b] Chemical shifts of N*H*+ and equilibrium constants of the ammonium ions in 50% TFA determined with the 220-MHz pmr spectrometer at 23°; $K_e = [i^+i^+]/[o^+o^+]$. [c] This absorption is presumably due to the *out* proton of the o^+i^+ isomer.



The 100-MHz pmr spectrum of [8.8.8]-II has resonances at 2.20 (12 H) and 1.36 ppm (36 H) in $CFCl_3$ at 25°. Below −95° the α-CH_2 resonance is split into two broad lines (~3:2) separated by 45 Hz. This observation suggests that a conformational change, possibly nitrogen inversion, occurs with an activation energy of 7.7 kcal/mole and $k = 1.4 \times 10^7$ sec^{-1} at 25°.

---

(1) H. Stetter and J. Marx, *Ann.*, 607, 59 (1957).

(2) New compounds have appropriate elemental analyses, molecular weights, and spectral constants.