COMMUNICATIONS TO THE EDITOR

Comparison of Energy Partitioning from Three-Centered Processes. Bimolecular Transfer and Unimolecular Elimination Reactions

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Sir: Infrared chemiluminescence from gas phase chemical reactions allows direct measurement of the energy partitioning patterns.[1-4] We wish to report on infrared chemiluminescence from HF and HCl which are products from two types of three centered reactions: (1) hydrogen abstraction by fluorine atoms from methane, ethane, neopentane, and dichloromethane; (2) unimolecular elimination from vibrationally excited halomethanes. The abstraction reactions and their thermochemistry[5,6] are given below (the small activation energy for abstraction is neglected).

$$\mathrm{F + CH_4 \longrightarrow HF^{\dagger}{}_{V,J} + CH_3} \qquad (\Delta H^\circ{}_0 = -33\ \mathrm{kcal\ mol^{-1}}) \tag{1}$$

$$\mathrm{F + C_2H_6 \longrightarrow HF^{\dagger}{}_{V,J} + C_2H_5} \qquad (\Delta H^\circ{}_0 = -38\ \mathrm{kcal\ mol^{-1}}) \tag{2}$$

$$\mathrm{F + (CH_3)_4C \longrightarrow HF^{\dagger}{}_{V,J} + CH_2C(CH_3)_3} \qquad (\Delta H^\circ{}_0 = -37\ \mathrm{kcal\ mol^{-1}}) \tag{3}$$

$$\mathrm{F + CH_2Cl_2 \longrightarrow HF^{\dagger}{}_{V,J} + CHCl_2} \qquad (\Delta H^\circ{}_0 = -42\ \mathrm{kcal\ mol^{-1}}) \tag{4}$$

Vibrationally excited $\mathrm{CHFCl_2^*}$ was produced in the F plus $\mathrm{CH_2Cl_2}$ system *via* secondary combination of $\mathrm{CHCl_2}$ with fluorine atoms. At the pressures of our experiments, all of the chemically activated molecules eliminate HCl or HF; the former is the predominant reaction.[7]

$$\mathrm{CHCl_2 + F \longrightarrow CHFCl_2^*} \qquad (\Delta H^\circ{}_0 = -103\ \mathrm{kcal\ mol^{-1}}) \tag{5}$$

$$\mathrm{CHFCl_2^* \longrightarrow CFCl + HCl^{\dagger}{}_{V,J}} \qquad (\Delta H^\circ{}_0 = 51\ \mathrm{kcal\ mol^{-1}}) \tag{6}$$

It also was possible to observe HF and HCl emission from two entirely different three-centered unimolecular elimination reactions by utilizing the interaction of hydrogen atoms with $\mathrm{CCl_3Br}$ and $\mathrm{CF_3I}$.

$$\mathrm{CX_3Y + H \longrightarrow CX_3 + HY} \tag{7}$$

$$\mathrm{CX_3\ (X = Cl,\ F) + H \longrightarrow CHX_3^*} \qquad (\Delta H^\circ{}_0 = -90,\ -100\ \mathrm{kcal\ mol^{-1}}) \tag{8}$$

$$\mathrm{CHX_3^*\ (X = Cl,\ F) \longrightarrow CX_2 + HX^{\dagger}{}_{V,J}} \qquad (\Delta H^\circ{}_0 = 61,\ 59\ \mathrm{kcal\ mol^{-1}}) \tag{9}$$

The energy available for partitioning is the difference between the C–H or C–F bond energies and the energy change for the elimination reaction. The latter are not known well[8] but the estimates given above should be reliable to within ±5 kcal mol^{-1}. Since the thresholds[8b] for the reverse reactions ($\mathrm{CX_2 + HX \rightarrow CHX_3}$) are probably less than 5 kcal mol^{-1}, virtually all of the energy arises from (8) or from (5) and not from release of potential energy by elimination of HX.

The reactions were studied in two vessels. One vessel was a 4.25-in. i.d. stainless steel flow reactor which was pumped by a liquid nitrogen trap, a 4-in. diffusion pump, and a mechanical pump. Observations were made through an NaCl window placed 3 cm downstream from the reagent and atom mixing zone. The second vessel, which had walls cooled to liquid $\mathrm{N_2}$ temperature, had a diameter of 6 in. and was pumped with a liquid nitrogen trap, a 6-in. diffusion pump, and a mechanical pump. The vessel was fitted with internal mirrors for more efficient collection of light. Hydrogen atoms were generated by a Wood's tube discharge and fluorine atoms were formed by passing $\mathrm{CF_4}$ or $\mathrm{SF_6}$ through a microwave discharge. Results from both F-atom sources were the same, which provide evidence against the possibility of complicating reactions from other products from the discharge. Because of the weak intensity from the unimolecular elimination reactions, the population ratio for the $v = 2$ and $v = 3$ levels was obtained by scanning the overtone region with a wide

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(5) B. deB. Darwent, "Bond Dissociation Energies in Simple Molecules," U. S. Department of Commerce National Bureau of Standards, Washington, D. C., NSRDS-NBS 31, 1970.

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(7) H. W. Chang; unpublished RRKM calculations give 10^{-11} sec as a typical lifetime of the chemically activated halomethanes produced by reactions 5 and 7.

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Table I: Vibrational Distributions of HX Products

			Relative population of HF and HCl						
			$v = 1$		$v = 2$		$v = 3$		
Reaction	Vessel	Pressure, μ	Exptl[a]	Cor[b]	Exptl[a]	Cor[b]	Exptl[a]	Cor[b]	$\%E_V$[c]
$CH_4 + F$	1	1	0.29	0.18	0.64	0.74	0.07	0.08	64
	2	3.8	0.33	0.27	0.55	0.57	0.12	0.16	
$C_2H_6 + F$	1	0.5	0.19	0.12	0.45	0.42	0.37	0.47	68
$C(CH_3)_4 + F$	1	0.5	0.24	0.17	0.55	0.58	0.21	0.25	62
$CH_2Cl_2 + F$	1	0.5	0.30	0.26	0.32	0.26	0.38	0.48	>58
$CH_2Cl_2 + F$[d]	2	5.0	0.65		0.23		0.12		
$CHFCl_2$*	2	40.0	0.92		0.08				
CHF_3*	2	5.0	0.84		0.10		0.06		>6
$CHCl_3$	2	5.0	0.80		0.10		0.10		>5

[a] Vessel 1 and 2 denote the 6-in. cooled-wall and the 4-in. flow reactors, respectively. Experiments were done at the pressures indicated in the third column. The rotational distributions in vessel 2 were characterized by a single rotational temperature of ~350°K. The rotational distributions from vessel 1 could not be fitted to a single Boltzmann temperature, which is evidence that most of the vibrational relaxation has been arrested. [b] The steady-state populations were corrected for radiative cascade using integrated absorption data [G. A. Kuipers, *J. Mol. Spectrosc.*, **2**, 75 (1955)] which give an emission lifetime of 5 msec for $HF_{v=1}$. The observation time for our experiments was taken as ~0.5 msec. [c] The per cent of energy released to HF or HCl as vibrational energy; the population for $v = 0$ was obtained from extrapolation of the measured populations in $v' = 1$, 2, and 3. For the abstraction reactions the population in $v = 0$ was taken as zero. [d] Included so the degree of relaxation of the last two entries can be estimated by comparison with the $F + CH_2Cl$ experiments. We suspect that H_2–CF_3I or H_2–CCl_3Br mixtures (1:8) are less efficient at vibrational deactivation than CF_4–CH_2Cl_2 mixtures due to the large dipole moment of CH_2Cl_2.

slit. However, the intensity from the abstraction reactions was sufficient to resolve the rotational lines in the fundamental spectra. The area of each rotational line was converted into a relative population using the detector response and the transition probability for that rotational line.[9,10] The relative vibrational populations were obtained by summing the rotational populations.

The relative steady-state vibrational populations are shown in Table I. The distribution obtained from CH_4 is very close to that obtained by Parker and Pimentel[11] in their laser work. Jonathan, Meiliar-Smith, and Slater[12] have investigated reaction 1 in a fast-flow apparatus and found N_1:N_2:N_3 = 0.21:0.64:0.15. All three studies are in reasonably close agreement, and we conclude that most of the vibrational relaxation was arrested in our cold wall experiments with CH_4. The vibrational relaxation for ethane and neopentane also must have been arrested, perhaps even to a greater degree than for methane, because (i) the rotational distributions are non-Boltzmann, (ii) the pressure was considerably lower for the condensable reagents and SF_6 as the F-atoms source, (iii) moderate variation in pressure in the cold-wall vessel did not significantly affect the relative populations, and only small differences in relative populations were found for experiments in the two vessels. Unfortunately, CH_2Cl_2 seems to be more efficient at removing energy from $HF^\dagger$ because variation of pressure in the cold-wall vessel caused a change in population, as did changing from one vessel to another. Nevertheless, formation rates into the highest vibrational levels of HF are favored by (4) although our data provide only lower limits for the formation of $v = 2$ and 3.[13] In general, the abstraction of hydrogen from a carbon atom seems to favor the highest accessible levels of HF and the shift toward $v = 3$ for reactions 2, 3, and 4 reflects the increase in the available energy.

The unimolecular eliminations result from secondary reactions and they only could be observed in the 4-in. flow vessel. Relaxation of the initial $HCl_V{}^\dagger$ distribution from the $CHFCl_2$ elimination reaction undoubtedly is very serious; however, relaxation should be less for the HCX_3* cases, which were studied at lower pressure. The degree of relaxation can be estimated by comparison (see footnote d) with the distributions from $F + CH_2Cl_2$ at the two pressures listed in Table I. We feel that the trend of strongly declining populations for the higher vibrational levels is a true feature of the energy partitioning for the unimolecular three-centered elimination reactions.

The most definitive and interesting result is that replacing H atoms by methyl groups did not alter the energy partitioning for $F + H$–CR_3 type reactions. We also have found the same result for $F + CF_3CH_3$, $Si(CH_3)_4$, and c-C_6H_{12}. Evidently the release of potential energy occurs in such a way that little energy is made accessible to the internal degrees of freedom of

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(9) H. S. Heaps and G. Herzberg, *Z. Phys.*, **133**, 48 (1952).

(10) R. Herman and R. F. Wallis, *J. Chem. Phys.*, **23**, 637 (1955).

(11) (a) J. H. Parker and G. C. Pimentel, *ibid.*, **51**, 91 (1969), reported N_2/N_1 = 2.7 ± 0.6; (b) more recent work by W. H. Green and M. C. Lin, private communication, gives a similar but somewhat improved ratio.

(12) N. Jonathan, C. M. Melliar-Smith, and D. H. Slater, *Mol. Phys.*, **20**, 93 (1971).

(13) M. C. Lin and W. H. Green, *J. Chem. Phys.*, **53**, 3383 (1970).

the CR$_3$ radical. A similar result was deduced from earlier studies[4] of H + SCl$_2$ and S$_2$Cl$_2$. This result from covalent reactions seems to be slightly different from molecular beam results[14] for K + RI reactions. Our data also demonstrate that any effect of a substituent, *e.g.*, R = H, Cl, CH$_3$, and CF$_3$, upon the pattern of energy release for H-atom abstraction from carbon by fluorine atoms is small.

Our measurements are the second example of infrared chemiluminescence from products of unimolecular reactions[15] proceeding on ground electronic surfaces. Although having more energy and fewer degrees of freedom, the elimination reactions partition less energy to HX than the abstraction reactions, even if some allowance is made for relaxation in the unimolecular reaction experiments. In fact, the HX† distribution from three-centered elimination is similar to a statistical distribution. According to statistical theories of unimolecular reactions, any energy in the molecule *above the threshold* is randomly distributed[16] among the internal degrees of freedom of the chemically activated CHX$_3$* molecule and, consequently, should be distributed statistically to the degrees of freedom of the products. Since reactions 6, 8, and 9 have quite small activation energies for the reverse reactions, *i.e.*, the release of potential energy is small, the pattern for the energy release is expected to be nearly statistical, and these data provide a qualitative confirmation for randomization of the internal energy above the threshold of the molecule in a unimolecular reaction.[16]

We also have measured the energy partitioned to HF† and HCl† by the unimolecular *four-centered* elimination reactions of chemically activated haloethanes.[17a] Our results agree with Clough, Polanyi, and Taguchi[15a] who found the HX vibrational energy to be somewhat larger than the statistical amount,[17b] although the fraction of the energy released to HF† is relatively small compared with the F + HCR$_3$ reactions of Table I.

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[14] G. H. Kwei, J. A. Norris, and D. R. Herschbach, *J. Phys. Chem.*, **52,** 1317 (1970).

[15] (a) P. N. Clough, J. C. Polanyi, and R. T. Taguchi, *Can. J. Chem.*, **48,** 2919 (1970); (b) M. J. Berry and G. C. Pimentel, *J. Chem. Phys.*, **49,** 5190 (1968); (c) M. J. Berry and G. C. Pimentel, *ibid.*, **53,** 3453 (1970). This interesting paper describes the HCl vibrational populations resulting from flash photolysis of dichloroethylene. Both three- and four-centered processes were found; however, it was not established whether these reactions occur from electronically excited or from ground states. Nevertheless, the HCl† populations declined with increasing *v*.

[16] Y. N. Lin and B. S. Rabinovitch, *J. Phys. Chem.*, **74,** 1769 (1970).

[17] (a) D. W. Setser, American Chemical Society and Chemical Institute of Canada Joint Conference, Toronto, Canada, May 1970; (b) the energy available for partitioning by the CH$_3$CF$_3$ unimolecular reaction consists of both *excess energy above the threshold for reaction* and *potential energy* released after crossing the barrier in about equal amounts.

Kinetic Energy Isotope Effects of Bromine Reactions Activated by Radiative Neutron Capture in Gaseous CH$_3$F and CD$_3$F[1]

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Sir: Although there have been many studies[2-4] relating to isotope effects (differences in organic yields) of (n,γ)-activated bromine reactions in condensed state hydrocarbons, aromatics, and alkyl halides, no study reports, for a single gaseous system, organic yields for (n,γ)-activated ^{80}Br, ^{80}Br^m, and ^{82}Br^m + ^{82}Br reactions. For condensed-state systems employing high-purity reagents and correcting for ^{82}Br^m(I.T.) ^{82}Br reactions,[5,6] no bromine isotope effects were generally found.

Unlike the reactions of (n,γ)-activated ^{128}I with CH$_4$,[7] reactions of (n,γ)-activated ^{80}Br with CH$_4$[8] occur principally as a result of the recoil kinetic energy acquired by the ^{80}Br in the (n,γ)-activation process. While other activation processes such as the (γ,n) and (n,p) processes impart to the atom a very high kinetic energy (>10^5 eV), the (n,γ) activation process results in a distribution of energies ranging from some very low value (near zero) to a maximum of ~10^2 eV.[9] If the three activation processes ^{79}Br(n,γ)^{80}Br, ^{79}Br(n,γ)^{80}Br^m, and ^{81}Br(n,γ)^{82}Br^m + ^{82}Br impart to the respective atoms different kinetic energy spectra,[10] and if the pop-

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[2] For references to the earlier literature see J. E. Willard, *Annu. Rev. Nucl. Sci.*, **3,** 193 (1953); *Annu. Rev. Phys. Chem.*, **6,** 141 (1955); *Nucleonics*, **19** (10), 61 (1961); *Chem. Eff. Nucl. Transform. Proc. Symp., 1961*, **1,** 215 (1961); *Chem. Eff. Nucl. Transform 1964*, **1,** 221 (1965).

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[7] E. P. Rack and A. A. Gordus, *J. Chem. Phys.*, **34,** 1855 (1961).

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[9] In ref 8, it is seen that ^{80}Br can have maximum of about 357 eV.

[10] Since the complete neutron capture γ-ray cascade spectrum is not known for bromine isotopes, it is not possible to calculate the distribution of bromine recoil energies. Because of partial cancellation of γ-recoil momenta in cascade γ-emission, bromine atoms will be formed with a distribution of energies.