Activation Energies for the Elimination of Hydrogen Fluoride from Alkyl Fluorides obtained by the Activated Molecule and Competitive Shock-tube Techniques

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Summary Critical energies for the elimination of hydrogen fluoride from a series of alkyl fluorides have been determined by the activated molecule technique by application of RRKM treatment and confirmed by determination of Arrhenius parameters in competitive shock-tube experiments; the reactivities of alkyl fluorides fit the pattern established for chlorides, bromides, and iodides.

KNOWLEDGE of the Arrhenius parameters for the elimination of hydrogen fluoride from alkyl fluorides is of interest because of the very complete information available on chlorides, bromides, and iodides. The normal method of kinetic study in static systems is not generally applicable with fluorides because heterogeneous reactions interfere. Nevertheless it has proved possible to study the following reactions in this way.

C_2H_5F	$= C_2H_4 + HF$	$\log A = 13\cdot31$	$E = 58\cdot2$[1]
$CH_2Cl\cdot CH_2F$	$= CHCl{:}CH_2 + HF$	$12\cdot95$	$60\cdot0$
	$= CH_2{:}CHF + HCl$	$13\cdot59$	$62\cdot3$

rate constants in (sec^{-1}) and activation energies in kcal mole^{-1}.

We have used two methods to obtain series of activation energies. The activated molecule technique depends upon the synthesis of molecules of high energy content by exothermic reactions and the interpretation of their rates of elimination in terms of the Rice–Ramsperger–Kassel–Marcus treatment of unimolecular reactions. Thus activated ethyl fluoride[2] can be formed in three ways with the energy contents shown:

	$\log k_e$ (sec^{-1})	kcal mole^{-1}
Abstraction:		
$C_2H_5 + F_2 = C_2H_5F^* + F$	$6\cdot8$	66
Combination:		
$CH_3 + CH_2F = C_2H_5F^{**}$	$9\cdot0$	90
Insertion:		
$CH_2 + CH_3F = C_2H_5F^{***}$	$10\cdot2$	105

The rates of decomposition of these molecules at room temperature are measured on the assumption that deactivation occurs with a rate constant given by $k_d = 10^7$ torr^{-1} sec^{-1}. Small but significant changes in these energy contents can be made by alteration of the temperature of the experiment. Application of RRKM theory showed good agreement when the Arrhenius parameters from the static experiments were employed.

Competitive experiments have been carried out in a shock tube similar to that used by Tsang.[3] Each compound was compared with one of known Arrhenius parameters. On the assumption that elimination of hydrogen bromide from ethyl bromide is given by[3]

$$\log k = 13\cdot19 - 53{,}700/2\cdot3\boldsymbol{R}T.$$

It was found that between 1136 and 1510°K, the rate of elimination of hydrogen chloride from isopropyl chloride is given by:

$$\log k = 13\cdot56 \pm 0\cdot45 - (50{,}800 \pm 1400)\ 2\cdot3\boldsymbol{R}T$$

which is in excellent agreement with[4,5]

$$\log k = 13\cdot40 - 50{,}500/2\cdot3\boldsymbol{R}T$$
$$\log k = 13\cdot64 - 51{,}100/1\cdot3\boldsymbol{R}T$$

which are among the most recent studies in the literature. Two reactions were used as standards for comparison of the fluorides.

Ethyl chloride	$\log A = 13\cdot43$	$E = 56{,}600$[6]
n-Propyl chloride	$13\cdot48$	$55{,}040$[7,8]

The mixtures of alkyl halides and alkenes left after passage of the shock were analysed by gas chromatography. By this means the values shown in Table 1 were obtained; the probable errors in each case lie between 1 and 2 kcal mole^{-1}. Internal consistency was established by the comparison of one fluoride with another.

TABLE 1

The elimination of hydrogen fluoride from alkyl fluorides

Alkyl fluoride	Activated molecule Abs.	Comb.	Ins:	ϵ_0	Shock tube $\log A$ (sec^{-1})	E
C_2H_5F	66	90	107	57	$13\cdot42$	$59\cdot9$
					$13\cdot31$[a]	$58\cdot2$[a]
$C_3H_7{}^nF$ ..	—	88	108	58	$13\cdot26$	$58\cdot3$
$C_4H_9{}^nF$ ..	—	—	—	—	$13\cdot28$	$56\cdot8$
$C_4H_9{}^iF$	—	—	—	—	$13\cdot31$	$58\cdot6$
$C_3H_7{}^iF$ ..	—	—	110	54	$13\cdot36$	$53\cdot9$
$C_4H_9{}^tF$	—	87	110	48	$13\cdot42$	$51\cdot5$
$CH_3\cdot CHF_2$ ..	70	91	—	59	$13\cdot74$	$66\cdot6$
$CH_3\cdot CF_3$ ..	75	92	—	65	$13\cdot47$	$71\cdot1$
$CH_2Cl\cdot CH_2F$ ..	67	—	—	62	$12\cdot95$	$60\cdot0$
					$12\cdot95$[a]	$60\cdot0$[a]

[a] Values obtained in static systems.

There is fair correspondence between the activation energies found with the shock tube and the critical energies (ϵ_0) found from the activated molecule experiments. Measurements were made for molecules formed by abstraction, combination, or insertion for those systems for which energy contents are given. For these molecules ϵ_0 should be about 2 or 3 kcal mole^{-1} below the activation energies. Differences in the two sets of results could be caused by the

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TABLE 2

Activation energies for the decomposition of alkyl halides (kcal mole^{-1})

Alkyl group	C_2H_5	$C_3H_7^i$	$C_4H_9^t$
Fluoride	59 9	53 9	51 5
Chloride[9]	56 6	50 8	44·6
Bromide[9]	53·7	47 8	41 2
Iodide[9]	50 8	45 0	37 6

use of incorrect thermochemical data for the fluoride none of which are well established, some are estimates based on assumptions that cannot yet be tested

The activation energies obtained with the shock tube are in line with those found for other alkyl halides as shown in Table 2

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