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Single-Pulse Shock-Tube Study of the Thermal Decomposition of Ethyl Fluoride and n-Propyl Chloride

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The thermal decomposition kinetics of dilute mixtures of ethyl fluoride and *n*-propyl chloride in argon have been investigated in a single-pulse shock tube in the temperature range ~990–1140 K by the absolute and the comparative rate method. Under the experimental conditions used the decompositions proceed almost exclusively via the concerted elimination of hydrogen halide to yield the corresponding olefins. With the absolute rate method the following rate constants are obtained: for $C_2H_5F \rightarrow C_2H_4 + HF$ (R1), $k_1^{\circ}/s^{-1} = 10^{13.65\pm0.20} \exp[-(59.5 \pm 1.0 \text{ kcal mol}^{-1})/RT]$ and for $n-C_3H_7Cl \rightarrow CH_3CHCH_2 + HCl$ (R2), $k_2^{\circ}/s^{-1} = 10^{13.44\pm0.28} \exp[-(54.8 \pm 1.3 \text{ kcal mol}^{-1})/RT]$. The comparative rate method, using a 0.125% C_2H_5F -0.125% $n-C_3H_7Cl$ -99.75% Ar mixture, yielded a compatible result: log (k_1°/s^{-1}) = (1.101 ± 0.016) log (k_2°/s^{-1}) – (0.960 ± 0.031). The results are discussed and compared with other data in the literature.

Introduction

The thermal decomposition kinetics of simple fluorohydrocarbons have received considerable attention in the recent past. Specifically, the pyrolysis of ethyl fluoride has been studied by a number of investigators using a variety of methods, including conventional static apparatus,¹ flow systems,^{2,3} and a shock tube.⁴ While there is general consensus that the principal mode of decomposition at moderate temperatures is the formation of ethylene, the rate constants for the molecular elimination of hydrogen fluoride are not in such a good agreement. For example, the more recent work of Dastoor and Emovon³ in a flow system yielded rate constants which differ by more than one order of magnitude from earlier similar studies.² The comparative shock tube study as carried out by Cadman et al.,⁴ while yielding a rate constant expression not too different from the earlier static pyrolysis work of Day and Trotman-Dickenson,¹ suffers from an erroneous specification of the gas-dynamic flow/reaction conditions. As has been pointed out by Tsang,⁵ shock-tube data obtained with incorrect specification and setting of reaction conditions have very serious implications, which tend to discredit the usefulness of the single-pulse shock tube as an instrument for quantitative high temperature kinetics studies. Tsang's analysis and criticism were with reference

to the thermal decomposition studies of 1,1-difluoroethane and 1,1,1-trifluoroethane,⁶⁻⁸ however, the same experimental technique has been employed by Cadman et al.⁴ in the case of ethyl fluoride. It was therefore felt desirable to reinvestigate the pyrolysis of C_2H_5F by use of a shock tube which provides an environment free from heterogeneous effects.

Recently we have made a detailed comparison⁹ of the two single-pulse shock-tube techniques which may be referred to as the *comparative* method, as originally developed by Tsang,^{10,11} and the *absolute rate* (isolationsection) method as used in this laboratory for a number of fluorohydrocarbon thermolysis investigations.¹² The advantages and shortcomings of both methods were noted, and it was shown that, with careful examination of the gas-dynamic flow conditions, the two methods, employed simultaneously, led to internally consistent results.

In the present paper we report on the thermal decomposition of ethyl fluoride as studied by both methods. In the case of the comparative study *n*-propyl chloride was used as an internal standard.

Experimental Section

Apparatus. The single-pulse shock tube (brass; 4.9-cm i.d.), ball valve, and gas-handling equipment were generally

the same as outlined in an earlier publication.¹³ The electronic instrumentation and method of data acquisition, storage, and display have been updated, as described recently.⁹ Driver and channel sections were 2.14 and 3.73 m, respectively, and the ball valve was centered 3.36 m from the diaphragm. Incident shock velocities were measured by means of four pressure transducers (Kistler) located on both sides of the ball valve and recorded by means of two electronic counters (Hewlett-Packard, Model 5325A). The transit times of the shock front between the first pair and last pair of transducers provided a measurement of shock deceleration. The last transducer, located 10 cm from the end plate, was also used to monitor the pressure profile behind the incident and reflected shock waves and in the rarefaction region. Aluminum diaphragms of 0.076, 0.15, and 0.20 mm thickness allowed coverage of reflected shock conditions in the pressure range $P_5 \simeq 2.8-10.7$ atm and temperature range $\bar{T}_5 = 989-1137$ K by using helium as driver gas.

Materials. Reaction mixtures were prepared from ethyl fluoride (Peninsular Chemresearch, 99.6% purity), *n*-propyl chloride (Aldrich Chemical Co.), and argon (Matheson, UHP grade). The *n*-propyl chloride was purified by repeated vacuum distillations to a minimum purity of 99.5%. The residual impurities were identified by gas chromatography as 0.20% C₂H₃F and 0.20% C₂H₄ in C₂H₅F, and 0.38% *i*-C₃H₇Cl, 0.05% C₂H₄, and 0.07% CH₃CHCH₂ in *n*-C₃H₇Cl. The results were accordingly corrected for ethylene and propene which are reaction products. Three series of experiments were carried out which were designed for both comparative and absolute rate measurements, the latter also providing a test of any possible chemical interaction between the two reactants in the comparative study.

For the comparative rate measurement a mixture of 0.125% C₂H₅F and 0.125% *n*-C₃H₇Cl in argon was used, while for the absolute measurement the mixture compositions were 0.25% C₂H₅F-99.75% Ar and 0.25% *n*-C₃H₇Cl-99.75% Ar, respectively.

Product Analysis. After initiation of the shock, the pneumatically operated ball valve was closed isolating the reaction mixture in the end section. Samples of the fully mixed gases were then withdrawn and analyzed by flame-ionization gas chromatography (Hewlett-Packard, Model 5840A) with a 2-m Porapak Q column with temperature programming between 50 and 100 °C at a flow rate of ~30 cm³/min. The olefinic reaction products (C₂H₄ and CH₃CHCH₂) were identified and their ratios to the unreacted parent compounds were quantitatively determined by comparison with standard calibration mixtures.

Data Reduction. Incident and reflected shock conditions were calculated from measured incident shock velocity, due account being taken of shock deceleration,⁹ and the temperature dependence of the heat capacity of the mixture, but neglecting the endothermicity of the reaction. These calculations were carried out with the use of a NASA computer program.¹⁴ Temperature-dependent thermodynamic data for C₂H₅F and n-C₃H₇Cl required by this program were taken from the literature.^{15,16}

In the temperature range encompassed in this study $(\sim 990-1140 \text{ K})$ the principal decomposition channels are the dehydrohalogenation reactions leading to the observed product olefins:

$$C_2H_5F \xrightarrow{k_1} CH_2 = CH_2 + HF$$
 (R1)

$$i - C_3 H_7 Cl \xrightarrow{k_2} CH_3 CH = CH_2 + HCl$$
 (R2)

Accordingly, rate constants were evaluated from corre-

sponding first-order rate laws

$$k_1 = (1/t_d) \ln (1 + R_1) \tag{1}$$

$$k_2 = (1/t_d) \ln (1 + R_2) \tag{2}$$

where $R_1 = [C_2H_4]/[C_2H_5F]$ and $R_2 = [C_3H_6]/[n-C_3H_7Cl]$ are the measured product-to-reactant ratios, and t_d is the reaction dwell time evaluated from gas dynamic flow measurements (pressure profile) and shock tube/ball valve geometry.¹⁷

For the absolute rate measurements two corrections were applied to the rate constants, k_i , evaluated from eq 1 or 2. These corrections may be represented in the form

$$k_i^{\ c} = \alpha_i \beta_i k_i \tag{3}$$

where the factor $\beta_i = (1 - \epsilon/t_d)^{-1} \leq 1$ corrects for the finite cooling rate in the rarefaction wave,¹⁷ and α_i takes into account the effect of the boundary layer on the reaction rate, using an approximate treatment.¹⁸ These corrections have opposite effects on the rate constant k_i and partially compensate each other. Thus, multiplication by β_i lowers the rate constant by about 15%, while the factor α_i increases the rate constant by ~7%.

For the comparative rate measurements, rate constants for each individual run were again evaluated from the measured ratios R_i and residence time t_d , using eq 1 and 2, but with the correction factors α_i and β_i omitted. This procedure was adopted here, since it is more in keeping with the original comparative rate method of Tsang¹ which did not consider the effects of finite cooling or boundary layer on the relative rates. Secondly, the evaluation of α_i and β_i requires prior knowledge, or an estimate, of the reflected shock temperature, T_5 , as well as the activation energy for each reaction. While the temperature coefficient for the reference reaction is presumably known, and that for the unknown reaction can sometimes be estimated, evaluation of the reflected shock temperatures from shock velocity measurements would be contrary to the idea of the comparative rate technique and would be tantamount to reducing the data for both reactants by the absolute rate method. However, it may be noted that for dilute mixtures these correction are relatively minor in the first instance, and the comparative rate technique inherently provides compensating effects. It is for this reason that the temperature dependence of the heat capacities of the reaction mixture was also neglected in the comparative rate study.

For a series of comparative experiments the rate constants evaluated as outlined above were plotted in logarithmic form according to the empirical relation

$$\log k_1 = a \log k_2 + b \tag{4}$$

and the slope, a, and intercept, b, were determined. If, now, k_2 is assumed to refer to the standard or reference reaction for which the Arrhenius expression is $k_2 = A_2$ $\exp(-E_2/RT)$, then, the Arrhenius parameters for the unknown reaction are given by

$$\log A_1 = a \log A_2 + b \tag{5}$$

$$E_1 = aE_2 \tag{6}$$

Results and Discussion

The results of the absolute rate measurements for ethyl fluoride and *n*-propyl chloride are listed in Tables I and II, respectively. Figure 1 shows the corresponding Arrhenius plots with the corrected rate constant values (k_i°) .

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TABLE I: C₂H₅F Experimental Results

$T_{5}/$	$P_{\mathfrak{s}}/$					- 0/)
K ^a	torr	$t_{\rm d}/\mu s^c$	β_1	R_1^a	k_1/s^{-1}	k_1^c/s^{-1}
996	5440	1588	0.885	0.00717	4.50	4.20
996	5620	1364	0.832	0.00747	5.46	4.78
998	5670	1447	0.839	0.00807	5.56	4.91
1004	5450	1630	0.881	0.00830	5.07	4.72
1006	5700	1428	0.789	0.00872	6.08	5.03
1010	5690	1429	0.783	0.00926	6.45	5.29
1011	5720	1489	0.819	0.0104	6.95	5.98
1014	5520	1549	0.883	0.0128	8.24	7.68
1021	5550	1679	0.875	0.0145	8.58	7.93
1029	55 9 0	1535	0.853	0.0187	12.0	10.8
1038	5550	1456	0.834	0.0225	15.3	13.4
1038	5390	1616	0.856	0.0279	17.0	15.4
1044	5440	1658	0.858	0.0266	15.9	14.3
1047	8840	1799	0.868	0.0326	17.8	16.3
1050	5550	1518	0.848	0.0347	22.5	20.1
1051	2620	1636	0.872	0.0289	17.4	16.0
1063	5590	1501	0.831	0.0478	31.1	27.2
1069	5560	1542	0.840	0.0530	33.5	29.7
1070	8740	1869	0.861	0.0558	29.1	26.5
1072	5470	1608	0.863	0.0583	35.4	32.3
1077	5530	1544	0.863	0.0724	45.2	41.2
1079	5320	1617	0.836	0.0878	52.1	45.9
1085	2600	1482	0.869	0.0942	60.8	55.8
1089	5500	1566	0.853	0.0961	58.6	52.7
1097	8150	1756	0.835	0.140	74.4	65.4
1105	5450	1608	0.844	0.142	82.5	73.4
1118	5400	1600	0.862	0.198	113	103
1129	8030	1838	0.854	0.381	176	158
1130	5510	1653	0.839	0.269	144	127
1134	5320	1634	0.873	0.355	186	172
1137	2480	1696	0.889	0.352	178	167

^a Calculated reflected shock temperature (see text). Estimated uncertainty ±10 K. ^b Calculated reflected shock pressure (see text), rounded to nearest 10 torr. ^c Calculated reaction dwell time. Estimated uncertainty ±20 μ s. ^d $R_1 = [C_2H_4]/[C_2H_3F]$.



Figure 1. Temperature dependence of the rate constants for hydrogen halide elimination. Data points and solid (least-squares) lines correspond to the absolute rate method. Solid symbols: $k_1(C_2H_5F\rightarrow C_2H_4+HF)$ at total pressures (torr): (**II**) $P_5 = 2480-2620$; (**II**) $P_5 = 5320-5720$; (**II**) $P_5 = 8030-8840$. Open circles: $k_2(n-C_3H_7Cl\rightarrow C_3H_6+HCl)$. Broken lines: Comparative rate data, reduced by absolute method (see text).

The solid lines represent a least-squares analysis of the data yielding the Arrhenius equations:

$$k_1^{\infty}/s^{-1} = 10^{13.65 \pm 0.20} \exp[-(59.5 \pm 1.0)/RT]$$
 (7)

$$k_2^{\infty}/s^{-1} = 10^{13.44 \pm 0.28} \exp[-(54.8 \pm 1.3)/RT]$$
 (8)

where R is in kcal mol⁻¹ and the error limits are standard deviations. Also shown in Figure 1 (broken line) are the least-squares plots of the rate constants evaluated by the absolute method for the 0.125% C₂H₅F-0.125% *n*-

TABLE II: $n-C_3H_7Cl$ Experimental Results^a

-			3-170				
	T_{5}/K	P_{5}/torr	$t_{\rm d}/\mu { m s}$	β2	R_2^{b}	k_2/s^{-1}	k_{2}^{c}/s^{-1}
	989	5530	1569	0.881	0.0437	27.3	25.4
	991	5490	1620	0.869	0.0391	23.7	21.7
	993	5410	1607	0.880	0.0484	29.4	27.4
	997	5530	1630	0.860	0.0431	25.9	23.5
	1001	5530	1620	0.866	0.0502	30.2	27.6
	1001	5390	1631	0.875	0.0594	35.4	32.7
	1002	5520	1611	0.860	0.0523	31.7	28.8
	1006	5480	1663	0.855	0.0540	31.6	28.5
	1009	5440	1662	0.871	0.0685	39.8	36.7
	1012	5420	1664	0.890	0,0842	48.6	45.8
	1013	5420	1643	0.887	0.0806	47.2	44.3
	1015	5450	1665	0.847	0.0667	38.8	34.7
	1022	5480	1685	0.870	0.0938	53.2	48.9
	1024	5410	1648	0.879	0.112	64.6	60.1
	1031	5470	1720	0.892	0.134	72.9	68.9
	1037	5470	1678	0.865	0.128	71.8	65.6
	1043	5450	1661	0.847	0.148	83.0	74.2
	1045	5390	1672	0.876	0.197	107	99.4
	1047	5440	1652	0.855	0.197	109	98.1
	1048	5370	1722	0.883	0.206	109	102
	1051	5360	1644	0.884	0.254	137	129
	1057	5370	1682	0.875	0.265	140	129
	1058	5330	1704	0.892	0.301	155	146
	1071	5340	1747	0.886	0.418	200	188
	1074	5400	1727	0.876	0.381	187	173
	1074	5450	1748	0.891	0.432	205	194
	1076	5310	1747	0.879	0.420	201	187
	1078	5310	1707	0.894	0.554	258	244
	1088	5350	1749	0.898	0.692	301	286
	1093	5450	1751	0.868	0,661	290	266
	1094	5320	1709	0.886	0.805	346	324
				,	-		

^a See footnotes to Table I. ^b $R_2 = [C_3H_6]/[n-C_3H_7Cl]$.



Figure 2. Comparative rate measurements for the decomposition of a mixture of 0.125% C₂H₅F and 0.125% n-C₃H₇Cl in argon.

 $C_3H_7Cl-99.75\%$ Ar mixture, used for the comparative study. These lines agree, within experimental error, with the results for the single reactant mixtures and indicate that in the $C_2H_5F-n-C_3H_7Cl-Ar$ mixture (R1) and (R2) proceed independently from each other under the experimental conditions chosen. This fact satisfies one of the requirements for the comparative rate measurements. Further, it should be noted that the data points for the C_2H_5F/Ar mixture in Figure 1 encompasses three pressure ranges which vary by a factor of more than 3.5 between the lowest (3.3 atm) and highest (11.6 atm) total reflected shock pressures. Since all the data are represented by the same straight line this provides support that (R1) is first order and in the high pressure limit. The same must hold true for the n-C₃H₇Cl-Ar data ($P_5 \sim 7.0-7.3$ atm) since the *n*-propyl chloride molecule possesses more internal degrees of freedom and hence is expected to reach the high pressure limiting rate at lower pressures than ethyl fluoride.

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TABLE III:	Experimen	ital Results,	Compara	tive Study
$t_{\rm d}/\mu s^a$	R_1^{b}	R_2^c	k_1/s^{-1}	k_2/s^{-1}
1599	0.00596	0.0421	3.72	25.9
1606	0.00488	0.0346	3.03	21.2
1550	0.00746	0.0443	4.79	28.0
1621	0.00793	0.0547	4.87	32.9
1609	0.00812	0.0482	5.03	29.3
1642	0.00749	0.0539	4.54	32.0
1611	0.0103	0.0676	6.33	40.6
1564	0.0113	0.0798	7.18	49.1
1682	0.0102	0.0626	6.00	36.1
1614	0.0176	0.104	10.8	61.4
1593	0.0158	0.108	9.81	64.3
1633	0.0199	0.109	12.1	63.6
1618	0.0199	0.123	12.2	71.6
1656	0.0216	0.132	12.9	74.8
1681	0.0267	0.178	15.7	97.8
1598	0.0334	0.226	20.5	127
1638	0.0356	0.187	21.4	105
1699	0.0307	0.187	17.8	101
1659	0.0314	0.196	18.6	108
1721	0.0440	0.273	25.0	141
1642	0.0493	0.292	29.3	156
1683	0.0620	0.386	35.7	194
1706	0.0625	0.392	35.5	194
1706	0.0951	0.564	53.2	262
1745	0.0812	0.512	44.7	237
1687	0.112	0.716	62.9	320
1730	0.111	0.733	60.6	318
1607	0.136	0.889	79.4	396
^{<i>a</i>} See footn	ote c to Ta	ble I. $^{b} R$,	$= [C, H_{4}]$	[C,H,F].

 $^{c}R_{2} = [C_{3}H_{6}]/[n-C_{3}H_{7}Cl].$

The results of the comparative rate study are listed in Table III and a comparative plot of the rate constants according to eq 4 is shown in Figure 2. A least-squares treatment of the data leads to the expression

 $\log (k_1^{\infty}/s^{-1}) = (1.101 \pm 0.016) \log (k_2^{\infty}/s^{-1}) - (0.960 \pm 0.031)$ (9)

If eq 8 is now taken as the "standard" reaction one obtains

$$k_1^{\infty}/s^{-1} = 10^{13.84 \pm 0.56} \exp[(-60.3 \pm 2.3 \text{ kcal mol}^{-1})/RT]$$
(10)

which is within experimental error of the absolute measurement, eq 7. The use of other, independently determined Arrhenius parameters for reference reaction $R2^{9,19,20}$ leads to similar results.

Table IV summarizes the rate constant data for (R1) obtained by various investigators, and an extended Arrhenius plot is shown in Figure 3. With the exception of the data of Dastoor and Emovon³ obtained in a silica flow reactor, our results are in excellent agreement with the extrapolated data of Sianesi and co-workers² and the static pyrolysis study of Day and Trotman-Dickenson.¹

The cause of the deviation in the work of Dastoor and Emovon cannot be ascertained, except that the measured preexponential factor is an order of magnitude lower than



Figure 3. Comparison of Arrhenius expressions for the thermal elimination of HF from C_2H_5F : (\bullet - \bullet) present work, eq 7; (\circ - \circ) ref 4; (\diamond - \diamond) ref 2; (Δ - Δ) ref 1; (\Box - \Box) ref 3.

in the other reported studies, and this lower value is not supported by reasonable entropy of activation calculations.

In the case of the shock tube study of Cadman et al.,⁴ who also employed $n-C_3H_7Cl$ as an internal standard, the apparent agreement is deceptive and, as discussed below, must be largely due to massive cancellation of errors in their adoptation of the comparative rate technique. Thus in constrast to Tsang's method in which the reaction temperature (the chief source of uncertainty in shock-tube work) is eliminated and which has been outlined in the preceding section, Cadman et al.⁴ used, for the stated reason of simplified instrumentation, a plausible alternate method in which the reaction time is eliminated and the reflected shock temperature is calculated from measured incident shock Mach numbers by using the ideal one-dimensional theory.²¹ Accordingly, in this variant of the comparative method the rate constant, k, for the reaction under investigation in any given experiment may be written as

$$k = k_{\rm s} \frac{\ln (C_0/C_{\rm f})}{\ln (C_0/C_{\rm f})_{\rm s}} = A_{\rm s} \exp(-E_{\rm s}/RT) [\ln (C_0/C_{\rm f})_{\rm s}]^{-1} \ln (C_0/C_{\rm f}) (11)$$

where the subscript s refers to the "standard" reaction with known Arrhenius parameters A_s and E_s ; C_0 and C_f are, respectively, initial and final concentrations of the two reactants as determined by gas-chromatographic analysis of the shocked gas mixture, and T is the calculated temperature. From a number of experiments at different reflected shock temperatures an Arrhenius plot for the unknown can be constructed. This procedure, though less effective than Tsang's method, should yield, in principle, reasonable results. It is therefore most surprising that the published percent conversion $[=(1 - C_f/C_0)100]$ and rate constant data of Cadman et al.,⁴ when used to estimate the

TABLE IV: Comparison of Rate Constants for the Thermal Elimination of HF from C_2H_5F

temp range, K	k_{1}/s^{-1}						
	$\log\left(A/\mathrm{s}^{-1}\right)$	$E/(\text{kcal mol}^{-1})$	700 K	1000 K	method ^{<i>a</i>}	ref	
~684-739	13.31 ± 0.41	58.2 ± 1.3	1.38×10^{-5}	3.89	SP	1	
$\sim 1275 - 1659$	13.42 ± 0.30	59.9 ± 1.0	$5.23 imes10^{-6}$	2.13	CST,t	4	
~793-873	12.16 ± 0.04	59.2 ± 2.0	4.75×10^{-7}	0.167	FS	3	
~883-943	14.43	62.6 ± 2	7.68×10^{-6}	5.61	\mathbf{FS}	2	
~996-1137	13.65 ± 0.20	59.5 ± 1.0	1.18×10^{-5}	4.43	SPST	this work	
	13.84 ± 0.56	60.3 ± 2.3	1.03×10^{-5}	4.58	CST.T	this work	

 a SP = static pyrolysis; CST,t = comparative shock-tube study, time eliminated; FS = flow system; SPST = single-pulse shock tube; CST,T = comparative shock-tube study, temperature eliminated.

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reaction time from a reverse calculation

$$t = (1/k) \ln (C_0/C_f)$$
 (12)

yields residence times of a few microseconds or less. Such residence times are about three orders of magnitude lower than those normally expected and experimentally verified in single-pulse shock-tube studies. Cadman and coworkers⁴ ascribed these very much shorter reaction times to either the arrival of the contact surface quenching the reaction or some boundary layer effect. The physical infeasibility of such arguments has been discussed by Tsang.⁵ Thus, in the work of Cadman et al.,^{4,6} the reported shock Mach numbers and hence temperatures are either much too high, or the listed percent decomposition (conversions) are much too low. Since gas-chromatographic analysis of the products and reactants can be carried out with a high degree of accuracy, and incident shock velocities can be measured to within 1-2%, these are unlikely sources of error. Hence it is not possible to trace the cause for the unique shock-tube results of Cadman et al. Allowance for shock deceleration (leading to lower calculated reflected shock temperatures) could not nearly account for this large-scale discrepancy. However, the very low conversion measurements could be due to extremely nonideal flow conditions, resulting from technical problems such as very nonideal diaphragm rupture. This could have led to large-scale mixing of the driver and driven gases and could explain, perhaps, why the bulk of the sampled gases was probably never exposed to the high temperature pulse. With reference to Figure 3 we therefore conclude that the apparent reasonably good agreement of the high temperature data of Cadman and co-workers is fortuitous and is due to cancellation of errors in the data reduction when using eq 11, where the measured ratio $\ln (C_0/C_f)/\ln$ $(C_0/C_f)_s$ for the unknown and standard would be similarly affected by flow nonidealities. This observation raises an interesting point with regard to the sensitivity of the "alternate" comparative rate technique, in general. Finally, in this connection, we note again the advantage of the isolation section (ball valve) technique which allows one to place the "slab" of reactant gases downstream and away from perturbations associated with the region of shock front formation, nonideal diaphragm rupture, and coldfront mixing at the interface. Moreover, it largely avoids the use of an average residence time as in early single-pulse

shock-tube work or as in Tsang's comparative method, by confining (and subsequently isolating) the reaction mixture, following incident and reflected shock passage, to a small length of the shock-tube test section as close to the endplate as desired.¹⁷

In concluding we also note that the experimental activation energies given by eq 7 and 8 are in excellent agreement with those calculated from the reverse, hydrogen halide addition reactions to the corresponding olefins obtained by using the modified semiion pair model.²² For (R1) and (R2) the calculated activation energies were 60.2 and 55.0 kcal mol⁻¹, respectively.²²

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