

# Single-Pulse Shock-Tube Studies on the Decomposition of 1,2-Dibromoperfluoroethane and Allyl Bromide

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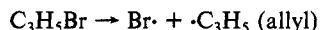
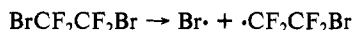
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1,2-Dibromoperfluoroethane and allyl bromide have been decomposed in comparative rate single-pulse shock-tube experiments. Cyclopentane is used as a radical trap and as a source of the ethylene which serves as a direct measure of the number of radicals generated in the system. Under our reaction conditions both decomposition processes  $\text{BrCF}_2\text{CF}_2\text{Br} \rightarrow \text{Br}\cdot + \text{C}_2\text{F}_4\text{Br}\cdot$  (1) and  $\text{allyl Br} \rightarrow \text{allyl}\cdot + \text{Br}\cdot$  (2) are in the beginning of the falloff region,  $k/k_\infty \gtrsim 0.7$ . RRKM calculations yield the following high-pressure rate expressions:  $k_1 = 10^{15.2} \exp(-32480/T) \text{ s}^{-1}$  and  $k_2 = 10^{15.0} \exp(-27540/T) \text{ s}^{-1}$ . This leads to a bond dissociation energy for  $(\text{BrCF}_2\text{CF}_2\text{Br}) = 278 \text{ kJ}$  and  $\Delta H_f(\text{allyl}, 298) = 173.6 \text{ kJ/mol}$ . In combination with the thermodynamics, the recombination rate of allyl and bromine atom is found to be  $10^{14} \text{ cm}^3/(\text{mol s})$  or collisional. The validity of such a general assumption is examined for the methyl bromide, allyl iodide, ethyl iodide, benzyl bromide, and benzyl chloride systems and appear to be in remarkable accord with experiments.

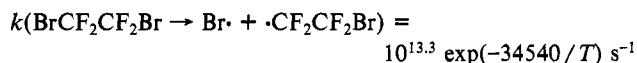
## Introduction

This paper is concerned with the reactions



It represents a continuation of our comparative rate single-pulse shock-tube studies on the thermal stability of intermediate-sized organic compounds.<sup>1</sup> In earlier studies attention was focussed on hydrocarbon systems,<sup>1</sup> where bond cleavage results in the formation of polyatomic fragments. The present investigation involves ejection of an atom. Within the framework of a loose transition state<sup>2</sup> a lowering of the  $A$  factor for unimolecular decomposition should occur. The exact magnitude of this decrease is unclear. Indeed, the quality of the data (unimolecular rate parameters) is highly uncertain.<sup>3</sup> Halogen substitution into a hydrocarbon framework usually results in the opening up of a molecular hydrogen halide elimination channel for decomposition. This is not possible for the dibromoperfluoroethane system. In the case of allyl bromide the four-center elimination process may be minimized by the weakness of the C-Br bond and the greater strength of the  $\beta$  C-H bond.

Skinner has described single-pulse shock-tube studies<sup>4,5</sup> on the thermal stability of 1,2-dibromoperfluoroethane. He estimated the rate expression for initial bond cleavage to be

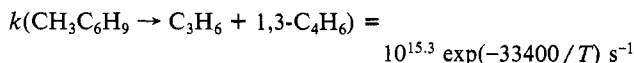


The activation energy for this process is directly relatable to the bond energy if the reverse combination process has no temperature dependence. The activation energy chosen by Skinner is in accord with the bond dissociation energies (BDE) for related systems:  $\text{BDE}(\text{C}_2\text{F}_5\text{-Br}) = 287.4 \text{ kJ/mol}$ <sup>6</sup> and  $\text{BDE}(\text{CH}_3\text{CF}_2\text{-Br}) = 287 \text{ kJ/mol}$ .<sup>7</sup> Allyl bromide decomposition had been studied by Szwarc and co-workers<sup>8</sup> in toluene carrier experiments and Maccoll<sup>9</sup> in a static system. The rate expression of  $10^{12.7} \exp$

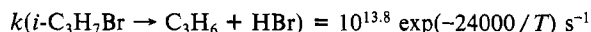
$(-23920/T) \text{ s}^{-1}$  and  $10^{12.3} \exp(-22910/T) \text{ s}^{-1}$  respectively are clearly unacceptable in terms of modern concepts regarding unimolecular decompositions. Benson and O'Neal<sup>3</sup> have recommended the rate expression  $k(\text{C}_3\text{H}_5\text{Br} \rightarrow \text{C}_3\text{H}_5\cdot + \text{Br}\cdot) = 10^{14.3} \exp(-28400/T) \text{ s}^{-1}$ . It should be noted that this implies that the chain length in the earlier studies are of the order of 10 to 100.

## Experimental Section

The experimental setup and procedures have been discussed in detail in earlier papers.<sup>10</sup> The internal standards used in the present studies are the decyclization of 4-methylcyclohexene



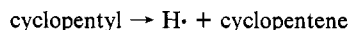
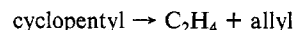
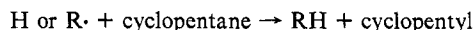
and the dehydrobromination of isopropyl bromide<sup>11,12</sup>



Gas chromatography with flame ionization detection was used for analysis.

The dibromoperfluoroethane sample is from PCR<sup>39</sup> while the other test gases are from Chemical Samples. Except for vigorous degassing all the substances are used without purification. Gas chromatographic analysis failed to reveal significant impurities. The argon is from Matheson and is of Ultrapure grade.

Cyclopentane is used as radical scavenger in these studies. In comparison to the toluene that has hitherto been used it has the added advantage that when attacked by reactive radicals or atoms it decomposes via the reactions



Thus in the presence of a large excess of cyclopentane every reactive radical formed results in the creation of one ethylene molecule. Inherent in this procedure is the assumption that all Br radicals are sufficiently reactive and that allyl radicals are unreactive. From the review by Kerr<sup>13</sup> it is readily attested that the lifetime of Br radicals under the present conditions is of the order of a few microseconds. Furthermore, since under present conditions methyl radical lifetimes are of the order of milliseconds<sup>12</sup> one can expect cyclopentane to be resistant to H-atom abstraction by allyl. This is because the C-H bond in propylene is 60 kJ less

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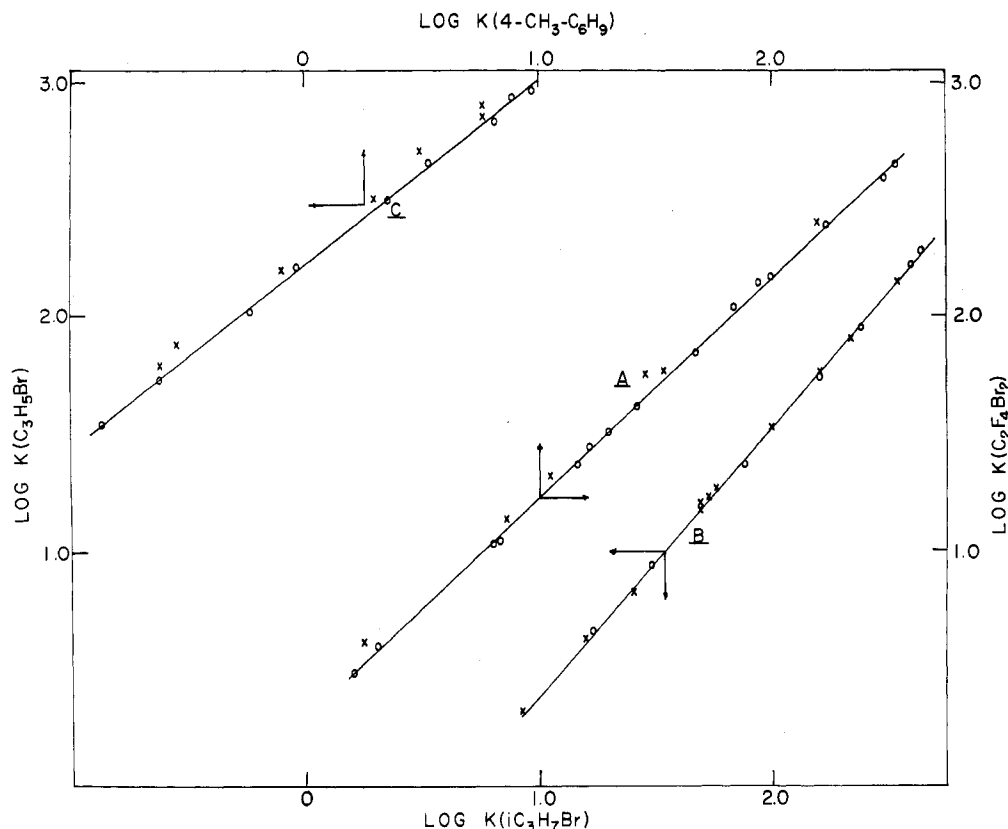
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(11) D. Gutman, W. Braun, and W. Tsang, *J. Chem. Phys.*, **67**, 4295 (1977).

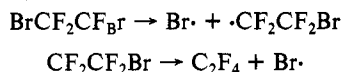
(12) W. Tsang, *Int. J. Chem. Kinet.*, **5**, 651 (1973).

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**Figure 1.** (A) Comparative rate study on the unimolecular decomposition of 1,2-dibromoperfluoroethane with 4-methylcyclohexene decomposition as the internal standard: 0.01%  $\text{BrC}_2\text{F}_4\text{Br}$ , 0.01%  $\text{CH}_3\text{C}_6\text{H}_9$ , and 1% cyclopentane in argon and 0.0025%  $\text{BrC}_2\text{F}_4\text{Br}$ , 0.0025%  $\text{CH}_3\text{C}_6\text{H}_9$ , and 1% cyclopentane in argon; O, experiments at  $\sim 1.7$  atm; X, experiments at  $\sim 5$  atm. The line is drawn through lower pressure results. (B) Comparative rate study on the unimolecular decomposition of allyl bromide with isopropyl bromide as the internal standard: 0.002% isopropyl bromide and 0.001% allyl bromide in 1% cyclopentane and argon; O, experiments at 1.9 atm; X, experiments at  $\sim 5$  atm. (C) Comparative rate study on the unimolecular decomposition of allyl bromide with 4-methylcyclohexene as the internal standard: 0.0005% allylbromide, 0.02% 4-methylcyclohexene, and 1% cyclopentane and argon and 0.000125% allyl bromide, 0.005% 4-methylcyclohexene, and 0.25% cyclopentane in argon; O, experiments at 1.9 atm; X, results at  $\sim 5$  atm. The line is drawn through lower pressure results.

than that for methane and the reaction is endothermic. Decomposition of allyl can be directly determined through measurements of allene formed. The 1,2-dibromoperfluoroethane studies offer an opportunity to check these premises, since the mode of decomposition must be



The activation energy of the latter process is of the order of 80 kJ, leading to  $\cdot\text{CF}_2\text{CF}_2\text{Br}$  lifetimes in the submicrosecond range. The direct evidence for the postulated process is a 2:1 ethylene:  $\text{C}_2\text{F}_4$  ratio in the reaction products.

## Results

The products from the decomposition of 200 ppm of 1,2-dibromoperfluoroethane in 1% cyclopentane and argon are summarized in Table I. The principal products are ethylene and perfluoroethylene. A considerable amount of propylene is present, particularly at the higher conversions. Allene is a minor product. On the basis of the postulated mechanism, quantities of hydrogen bromide, 1,5-hexadiene, and cyclopentene must also be formed. We have not attempted to analyze for these compounds. The absence of quantitative data on these reaction products will not effect our conclusions. The most significant observation from the results of Table I is the 2:1 ethylene:perfluoroethylene ratio at the lower conversions. Since each allene formed yields a hydrogen atom and leads ultimately to ethylene formation, it can be seen that subtraction of allene from the ethylene concentration will extend the range where the 2:1 ratio is maintained. Nevertheless at the highest conversions there remains a 10–15% discrepancy. We suspect that this is largely due to the reactions  $\text{C}_3\text{H}_5\cdot + \text{HBr} \rightarrow \text{C}_3\text{H}_6 + \text{Br}$  and the subsequent attack of Br on cyclopentane.

It will be noted that the rate expression for the process,<sup>13</sup>  $\text{CH}_3 + \text{HBr} \rightarrow \text{CH}_4 + \text{Br}$ , is  $k = 10^{12.6} \exp(-800/T) \text{ cm}^3/(\text{mol s})$ . For allyl radicals the reaction is still thermoneutral. From the data in Table I and assuming the  $A$  factor to be similar to that for  $\text{CH}_3$ , one finds the activation energy for allyl radical abstraction of the order 25 kJ. With such a small activation energy there is also the possibility of reactions after the heating period. This will result in propylene formation. The bromine atom that is formed may have a chance to abstract a H atom from cyclopentane. But cyclopentyl radicals clearly cannot decompose at the lower temperatures, since its activation energy for decomposition is of order of 130 kJ. The above would appear to give a satisfactory rationale for the product distribution. It sets an upper level below which one could expect production of 2 mol of ethylene for every mole of  $\text{C}_2\text{F}_4$  formed. We will use this information to determine rate parameters for the bond breaking reaction in allyl bromide decomposition.

The results of comparative rate studies for the decomposition of 1,2-dibromoperfluoroethane into a bromine atom and the corresponding radical with 4-methylcyclohexene decomposition as the internal standard are summarized in Figure 1. Although the effect is small there is in fact a systematic difference between experiments carried out at 1.7- and 5.0-atm (argon) pressure. The relative rate relationships are at 1.7 atm

$$\begin{aligned}\log k(\text{BrC}_2\text{F}_4\text{Br} \rightarrow \text{Br} + \text{C}_2\text{F}_4\text{Br}) &= (0.938 \pm 0.005) \times \\ \log k(\text{CH}_3\text{C}_6\text{H}_9 \rightarrow 1,3\text{-C}_4\text{H}_6 + \text{C}_3\text{H}_6) &+ (0.288 \pm 0.008)\end{aligned}$$

and at 5 atm

$$\begin{aligned}\log k(\text{BrC}_2\text{F}_4\text{Br} \rightarrow \text{Br} + \text{C}_2\text{F}_4\text{Br}) &= (0.954 \pm 0.011) \times \\ \log k(\text{CH}_3\text{C}_6\text{H}_9 \rightarrow 1,3\text{-C}_4\text{H}_6 + \text{C}_3\text{H}_6) &+ (0.308 \pm 0.01)\end{aligned}$$

The temperature range covered was 967–1136 K. With these

TABLE I: Product Distribution from 1,2-Dibromoperfluoroethane Decomposition in Cyclopentane<sup>a</sup>

100C <sub>2</sub> F <sub>4</sub> / BrC <sub>2</sub> F <sub>4</sub> Br	100C <sub>2</sub> H <sub>4</sub> / 2BrC <sub>2</sub> F <sub>4</sub> Br	100C <sub>3</sub> H <sub>6</sub> / 2BrC <sub>2</sub> F <sub>4</sub> Br	100C <sub>3</sub> H <sub>4</sub> / 2BrC <sub>2</sub> F <sub>4</sub> Br	T, <sup>b</sup> K	t(heating), μs	ρ, <sup>c</sup> torr, NTP
9.57	10.1			1082	800	416
0.66	0.66	0.053	~0.005	988	800	376
23.57	29.20	10.1	2.50	1120	800	424
7.0	7.19	1.39	0.25	1060	800	408
0.204	0.202	0.001		954	800	372
1.14	1.13			1002	900	1162
15.0	17.5	7.6	0.6	1094	900	1260
5.57	5.84	1.63	0.1	1051	900	1212
0.81	0.81	0.06		980	900	1138

<sup>a</sup> 0.02% C<sub>2</sub>F<sub>4</sub>Br in 1% cyclopentane. <sup>b</sup> Temperature calculated by assuming rate parameters for C<sub>2</sub>F<sub>2</sub>Br<sub>2</sub> decomposition as given in text. <sup>c</sup> Density calculated from temperatures and gas dynamic property of system.

results it would appear that the 1,2-dibromoperfluoroethane decomposition rate is  $10 \pm 6\%$  faster at the higher pressure. This is equivalent to a pressure deviation from the unimolecular limit of  $p^{0.09 \pm 0.05}$ . The rate relationship given above leads to the rate expressions at 1.7 atm

$$k(\text{BrC}_2\text{F}_4\text{Br} \rightarrow \text{Br} \cdot + \text{C}_2\text{F}_4\text{Br}) = 10^{14.7} \exp(-31400/T) \text{ s}^{-1}$$

and at 5 atm

$$k(\text{BrC}_2\text{F}_4\text{Br} \rightarrow \text{Br} \cdot + \text{C}_2\text{F}_4\text{Br}) = 10^{15.0} \exp(-31910/T) \text{ s}^{-1}$$

For the subsequent study on allyl bromide decomposition it is also of interest to compare rate constants determined by using ethylene as a measure of 1,2-dibromoperfluoroethane decomposition. We have accordingly used ethylene formed as a mark of the extent of reaction and calculated rate constants on the basis of two ethylene molecule formed for each 1,2-dibromoperfluoroethane molecule decomposed. The rate constant relation comparing rate constants determined by the two methods is

$$\log k(\text{C}_2\text{H}_4) = (0.996 \pm 0.009) \log k(\text{C}_2\text{F}_4) + (0.02 \pm 0.02)$$

and clearly demonstrates that for temperatures below 1100 K ethylene yield from cyclopentane decomposition is an effective quantitative marker for the presence of reactive radicals.

Allyl bromide decomposition was studied over the temperature range 830–1000 K, with allyl bromide concentrations of 0.000125–0.001%, at pressure of 1.9 to 4.7 atm. (argon), and in the presence of 0.25–1% cyclopentane and appropriate internal standards. Under these conditions, no allene can be found and ethylene is overwhelmingly the main light hydrocarbon reaction product except for traces of propylene. This is fully consonant with earlier discussion of the reaction mechanism in such systems. The absence of allene also provides a conclusive demonstration that dehydrobromination does not occur. Comparative rate results with isopropyl bromide as an internal standard are summarized in Figure 1. The experiments at the lower pressure follow the rate relation

$$\log k(\text{C}_3\text{H}_5\text{Br} \rightarrow \text{C}_3\text{H}_5 \cdot + \text{Br}) = (1.144 \pm 0.09) \times \log k(i\text{-C}_3\text{H}_7\text{Br} \rightarrow \text{C}_3\text{H}_6 + \text{HBr}) - (0.76326 \pm 0.02)$$

where at the higher pressure the relationship is

$$\log k(\text{C}_3\text{H}_5\text{Br} \rightarrow \text{C}_3\text{H}_5 \cdot + \text{Br}) = (1.137 \pm 0.07) \times \log k(i\text{-C}_3\text{H}_7\text{Br} \rightarrow \text{C}_3\text{H}_6 + \text{HBr}) - (0.786 \pm 0.01)$$

There is thus very little pressure effect (within experimental error), the actual departure from unimolecular behavior being of the order of  $p^{0.02 \pm 0.06}$ . This in turn leads to the rate expression

$$k(\text{C}_3\text{H}_5\text{Br} \rightarrow \text{C}_3\text{H}_5 \cdot + \text{Br}) = 10^{15.0} \exp(-27390/T) \text{ s}^{-1}$$

However, in view of the fact that the size of isopropyl bromide and allyl bromide are similar and the lower *A* factor for the former may be compensated by the higher activation energy for the latter, we carried out additional experiments with methylcyclohexene decomposition as the internal standard. The results are sum-

TABLE II: Parameters for and Results of RRKM Calculations on 1,2-Dibromoperfluoroethane Decomposition

molecule			
$I_{\text{ABC}} = 8.2 \times 10^{-112} \text{ g cm}^2$ (bond distances from ref 15)			
$\nu^a = 50, 200 (2), 250 (3), 300 (2), 450 (2), 500 (3), 700, 800, 1100, 1200, 1250 \text{ cm}^{-1}$ (estimated from ref 16)			
transition state			
$I^+/I = 5.6 (967 \text{ K}); I^+/I = 5.4 (1051.5 \text{ K}); I^+/I = 5.3 (1136 \text{ K})$			
$\nu(\text{C}_2\text{F}_4\text{Br}) = 50, 200, 250 (2), 300 (2), 450 (2), 500 (2), 700, 800, 1100, 1200, 1250 \text{ cm}^{-1}$ (estimated from ref 15 and 19)			
$I(2\text{D C}_2\text{F}_4\text{Br})^b = 80 \times 10^{-38} \text{ g cm}^2$ reduced to $1.6\text{E} \times 10^{-38} \text{ g cm}^2$			
reaction degeneracy = 2			
collisional efficiency			
~0.06 with collisional diameter Ar-BrC <sub>2</sub> F <sub>4</sub> Br = 6 Å			
rate parameter	967 K	1051.5 K	1136 K
$A_\infty$	$1.9 \times 10^{15}$	$1.7 \times 10^{15}$	$1.6 \times 10^{15}$
$E_\infty$	64700	64500	64300
$k/k_\infty, \text{ mol/cm}^3$			
$10^{19}$	0.88	0.81	0.75
$3.1 \times 10^{19}$	0.94	0.91	0.86

<sup>a</sup> Absence of number next to frequency signifies single frequency. <sup>b</sup> Moment of inertia.

marized in Figure 1. At the lower pressure region, we find the comparative rate relation

$$\log k(\text{C}_3\text{H}_5\text{Br} \rightarrow \text{C}_3\text{H}_5 \cdot + \text{Br}) = (0.795 \pm 0.01) \times \log k(\text{CH}_3\text{C}_6\text{H}_9 \rightarrow 1,3\text{-C}_4\text{H}_6 + \text{C}_3\text{H}_6) + (2.22 \pm 0.006)$$

and the higher pressure

$$\log k(\text{C}_3\text{H}_5\text{Br} \rightarrow \text{C}_3\text{H}_5 \cdot + \text{Br}) = (0.807 \pm 0.01) \times \log k(\text{CH}_3\text{C}_6\text{H}_9 \rightarrow 1,3\text{-C}_4\text{H}_6 + \text{C}_3\text{H}_4) + (2.29 \pm 0.006)$$

Over the temperature range of these experiments, this is equivalent to a departure from the unimolecular limit is of the order of  $p^{0.14 \pm 0.07}$ . The rate expression is then at 1.9 atm

$$k(\text{C}_3\text{H}_5\text{Br} \rightarrow \text{C}_3\text{H}_5 \cdot + \text{Br}) = 10^{14.4} \exp(-26550/T) \text{ s}^{-1}$$

and at 4.7 atm

$$k(\text{C}_3\text{H}_5\text{Br} \rightarrow \text{C}_3\text{H}_5 \cdot + \text{Br}) = 10^{14.6} \exp(-26910/T) \text{ s}^{-1}$$

## Discussion

The small pressure dependences that have been observed make necessary extrapolation of the directly determined numbers in order to obtain high-pressure rate parameters. For this purpose we have treated the data on the basis of RRKM calculations.<sup>14</sup>

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TABLE III: Parameters for and Results of RRKM Calculations on Allyl Bromide Decomposition

molecules			
$I_{ABC} = 9.2 \times 10^{-114}$ g cm <sup>2</sup> (bond distances from ref 15)			
$\nu^a = 200, 290, 417, 580$ (2), 911, 930, 990, 1050, 1172, 1297, 1370, 1415, 1440 (2), 1640, 2950 (2), 3050 (3) cm <sup>-1</sup> (estimated from frequency assignments for propylene <sup>16</sup> and the effect of bromine substitution to hydrocarbon framework <sup>17</sup> )			
transition state			
$I^+/I = 5.4$ (894 K); $I^+/I = 5.3$ (950 K); $I^+/I = 5.2$ (1006 K)			
$\nu$ (allyl) = 360 (2), 800 (2), 900 (2), 1000 (2), 1100, 1200, 1400 (2), 1900, 3000 (3), 3100 (2) cm <sup>-1</sup> (estimated from frequency assignment for allene <sup>18</sup> )			
$I$ (2D, allyl) <sup>b</sup> = $9 \times 10^{-39}$ g cm <sup>2</sup> lowered to $0.54 \times 10^{-39}$ g cm <sup>2</sup> to obtain exp $A$ factor reaction degeneracy = 1			
collisional efficiency ~0.07 allyl Br-A, collision diameter ~4.5 Å			
rate parameters <sup>c</sup>	894 K	950 K	1006 K
log $A_\infty$	15.0	15.0	14.95
$E_\infty$	54800	54700	54600
$k/k_\infty$ , mol/cm <sup>3</sup>			
10 <sup>19</sup>	0.80	0.75	0.69
$3.1 \times 10^{19}$	0.90	0.87	0.83
rate parameters <sup>d</sup>	830 K	885 K	940 K
log $A_\infty$	15.0	15.0	15.0
$E_\infty$	54900	54800	54700
$k/k_\infty$ , mol/cm <sup>3</sup>			
10 <sup>19</sup>	0.85	0.80	0.75
$3.1 \times 10^{19}$	0.93	0.89	0.86
rate parameters <sup>e</sup>	735 K	800 K	865 K
$k_\infty$ , s <sup>-1</sup>	0.05	1.08	14.5
$k$ , s			
at $5 \times 10^{16}$ mol/cm <sup>3</sup>	0.035	0.64	7.4
at $1 \times 10^{16}$ mol/cm <sup>3</sup>	0.039	0.74	8.8
measd	0.037	0.52	5

<sup>a</sup> Absence of number next to parentheses signifies single frequency.<sup>b</sup> Moment of inertia. <sup>c</sup> With methylcyclohexene as internal standard.<sup>d</sup> With isopropyl bromide as internal standard. <sup>e</sup> Under conditions of ref 8 (collision diameter for toluene-allyl bromide = 6 Å; efficiency = 1).

The data and results for allyl bromide and 1,2-dibromoperfluoroethane are summarized in Tables II and III. For each case a set of  $A_\infty E_\infty$  and  $\beta$  (collision efficiency) was found that exactly reproduced the experimental rate constants over the entire temperature and pressure range studied. In the case of the isopropyl bromide we used the rate parameters given earlier and the  $\beta$  determined from these studies. An important question is the uniqueness of the rate parameters for the allyl bromide and 1,2-dibromoperfluoroethane decomposition. Fortunately, we are very close to the high-pressure limit. Thus minimal errors are

introduced by the extrapolational procedure. There is, however, an uncertainty of about a factor of 2 in the derived collision efficiency. It is known that no purely vibrator or rotor transition state for bond breaking can fit experimental results over the entire temperature range (300–1100 K) for bond-breaking reactions. We have accordingly followed Benson's prescription of a "hindered rotor" transition state.<sup>2</sup> This involves beginning with a Gorin type model and lowering the moment of inertia of the two-dimensional rotor until a satisfactory  $A_\infty$  factor is obtained. Our results for the isopropyl bromide using a vibrator model and with the rate expression for dehydrobromination given earlier suggest that under the present conditions it is virtually at the high-pressure limit,  $k/k_\infty \sim 0.98$ . This is equivalent to a pressure dependence of  $p^{0.02}$ . For allyl bromide decomposition under the same conditions the pressure dependence is  $p^{0.08}$ . Combining this and the experimental result would lead to a difference in pressure dependence of the order of  $p^{0.06}$ . As can be seen from Figure 1, this was not observable since it is within the uncertainty limits.

The rate constants for 1,2-dibromoperfluoroethane decomposition are two orders of magnitude higher than that estimated by Skinner<sup>4</sup> in his earlier study. This is largely due to his smaller  $A$  factor. It is clear that the  $A$  factors in the  $10^{13}$ -s<sup>-1</sup> range are not compatible with bond-breaking processes. For allyl bromide decomposition extrapolation of our high-pressure results to 600 K yield  $k(600) = 10^{-5}$ -s<sup>-1</sup>. This is about a factor of 5 smaller than the measurements of Maccoll.<sup>9</sup> As suggested by Benson and O'Neal<sup>3</sup> it is likely that the static study has an important chain component. The present results are in excellent agreement with the toluene carrier experiments,<sup>8</sup> when one takes into the account of the falloff behavior of allyl bromide. RRKM calculations based on the strong collision approximation can be found in Table III, where one finds  $k(800) = 1$  s<sup>-1</sup> as opposed to the measured quantity of  $k(800) = 0.5$  s<sup>-1</sup>. Indeed, if one use a slightly lower value of  $\beta$ , in the range of 0.4–0.7 an exact fit can be made. The accuracy of the experimental result probably does not justify such a conclusion. Nevertheless it is not unreasonable. However, unlike the rate constants the calculated rate expression is still considerably different from that reported. This is in line with previous observations.<sup>21,22</sup> That is, the toluene carrier studies do not yield accurate rate parameters. Finally, it should be noted that our experimental rates are about an order of magnitude larger than that predicted by Benson and O'Neal.<sup>3</sup> This is largely due to their assumption of a smaller rate of recombination than that which can be deduced from this study. This will be discussed in a subsequent section.

With respect to the measured activation energies, for 1,2-dibromoperfluoroethane this can be converted to the bond dissociation energy through the relation

$$\Delta H(298) = \text{BDE}(\text{BrC}_2\text{F}_4\text{-Br}) =$$

$$\text{activation energy} + R(1050) + \int_{298}^{1050} \Delta C_p dT$$

where we have assumed no temperature dependence for the reverse process. The high-pressure activation energy is 267.7 kJ. Assuming that the heat capacity of the brominated compound differs from that of the fluorinated analogue as perfluoromethyl bromide differs from perfluorinated methane (on a per bromine atom basis) leads to  $\Delta C_p = 1.32$  kJ/K and yields

$$\text{BDE}(\text{BrC}_2\text{F}_4\text{-Br}) = 278 \text{ kJ}$$

This is within 9 kJ of the value for the BDE(C<sub>2</sub>F<sub>5</sub>-Br) of 287 kJ.<sup>6</sup> The difference can be attributed to experimental uncertainty or possible effects arising from Br substitution on the  $\beta$ -position. The same process can be used to derive the heat of formation of allyl radical. Starting with

$$\Delta H(950) = \text{activation energy} + R(950) =$$

$$\Delta H_f(\text{allyl}) + \Delta H_f(\text{Br}) - \Delta H_f(\text{allyl bromide})$$

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TABLE IV: Experimental and Calculated Results on the Rate Constant for CX Bond Cleavage on Some Organic Halides

process <sup>k</sup>	exptl cond	rate const, s <sup>-1</sup>	
		exptl (at midpt)	calcd <sup>e</sup>
PhCH <sub>2</sub> Br → PhCH <sub>2</sub> · + Br <sup>f</sup> ΔS = 121, ΔH = 247	768–872 K, 8–15 torr of toluene	10 <sup>13</sup> exp(−25430/T) k(820) = 0.35	10 <sup>15.0</sup> exp(−28760/T) k(820) = 0.6
PhCH <sub>2</sub> Cl → PhCH <sub>2</sub> · + Cl <sup>g</sup> ΔS = 127.5, ΔH = 305	922–1020 K, 8–15 torr of toluene	10 <sup>14.83</sup> exp(−34240/T) k(970) = 0.16	10 <sup>15.4</sup> exp(−35740/T) k(970) = 0.12
CH <sub>3</sub> Br → CH <sub>3</sub> · + Br <sup>a,h</sup> ΔS = 132.6, ΔH = 300	977–1080 K, 4 torr of toluene	10 <sup>12.95</sup> exp(−33740/T) k(1030) = 0.054	10 <sup>15.6</sup> exp(−35140/T)(∞) k(1030) = 0.023, [0.017] <sup>e</sup>
	977–1080 K, 11 torr of toluene	10 <sup>13.2</sup> exp(−33740/T) k(1030) = 0.097	10 <sup>15.6</sup> exp(−35140/T)(∞) k(1030) = 0.055, [0.036] <sup>e</sup>
	977–1080 K, 20 torr of toluene	10 <sup>13.4</sup> exp(−33740/T) k(1030) = 0.15	10 <sup>15.6</sup> exp(−35140/T)(∞) k(1030) = 0.010, [0.05] <sup>e</sup>
allyl I → allyl· + I <sup>b,i</sup> ΔS = 126.8, ΔH = 129	742–1068 K, 169–1429 torr of argon	10 <sup>14</sup> exp(−20830/T) k(905) = 10 <sup>4</sup>	10 <sup>15.0</sup> exp(−21060/T)(∞) k(905) = 8400–23000, [2350–4100] <sup>e</sup>
EtI → Et· + I <sup>c,j</sup> ΔS = 136, ΔH = 236	704–774 K, 14 torr of toluene	10 <sup>11.9</sup> exp(−22700/T) k(739) = 0.04	10 <sup>15.8</sup> exp(−27440/T) k(739) = 0.14, [0.03] <sup>e</sup>

<sup>a</sup>Based on RRKM calculations. Molecular frequencies as in ref 17. Structure in ref 15. Rotor transition state. CH<sub>3</sub> frequencies and structure from ref 23.  $I^{\ddagger}/I = 5.5$ ; collision diameter  $5 \times 10^{-8}$ ; unit efficiency,  $k/k_{\infty} \sim 0.01$ . <sup>b</sup>Based on RRKM calculations. Molecular frequencies based on analogous molecules in ref 17. Structure from ref 15. Restricted rotor transition state.  $I^{\ddagger}/I = 5.3$ . Allyl structure and frequencies as in Table III. Two-dimensional allyl rotor reduced to  $2.3 \times 10^{-39}$  to match  $A$  factor in Table V. Collision diameter = 4.5 Å. Efficiency  $\approx 0.06$ ,  $k/k_{\infty} \sim 0.3$ . <sup>c</sup>Based on RRKM calculations. Molecular frequencies from ref 20. Structure from ref 15. Restricted rotor transition state.  $I^{\ddagger}/I = 5.7$ . Ethyl structure and frequencies as in ref 31. Two-dimensional rotor reduced to  $8 \times 10^{-40}$  to match  $A$  factor in Table V. Collision diameter = 5 Å. Efficiency = 1,  $k/k_{\infty} \sim 0.3$ . <sup>d</sup>Calculate rates and expressions are at 950 K and assuming combination rate is  $10^{14}$  cm<sup>3</sup>/(mol s). <sup>e</sup>Results with combination rate constant of  $10^{13}$  cm<sup>3</sup>/(mol s). <sup>f</sup>Reference 32. <sup>g</sup>Reference 33. <sup>h</sup>Reference 34. <sup>i</sup>Reference 35. <sup>j</sup>Reference 36. <sup>k</sup> $S, \Delta H_f$  for CH<sub>3</sub>, Cl, Br, and I from ref 23.  $S, C_p$  for PhCH<sub>2</sub>X estimated from properties of propene, allyl X, and toluene (ref 25).  $S, C_p$  for PhCH<sub>2</sub> from ref 22.  $\Delta H_f(\text{PhCH}_2\text{X})$  from ref 30.  $S, \Delta H_f$  for C<sub>2</sub>H<sub>5</sub> from ref 1 and 31.  $\Delta H_f$  for PhCH<sub>2</sub> from ref 1.  $\Delta S$  in units of J/K.  $\Delta H$  in units of kJ.

and upon substitution of  $\Delta H_f(\text{Br}) = 97.9$  kJ<sup>23</sup> and  $\Delta H_f(\text{allyl bromide}) = 20.3$  kJ<sup>24</sup> at 950 K, we find

$$\Delta H_f(\text{allyl}) = 159 \text{ kJ/mol}$$

Since the heat capacity of the allyl radical can be readily calculated this leads at 298 K to

$$\Delta H_f(\text{allyl}) = 173.6 \text{ kJ/mol}$$

This is very close to the value of 177.8 kJ/mol from other shock-tube experiments.<sup>1</sup> It is nevertheless larger than the number derived from iodination experiments of 163.3 kJ/mol<sup>25</sup> and recommended in a recent review, although the sum of the experimental uncertainties would appear to overlap.

The collisional efficiency of  $\sim 0.06 \pm 0.03$  required to fit the pressure dependence found in these experiments is in accord with the value of  $\sim 0.05$  found by Lewis and co-workers<sup>26</sup> in their extensive study on cyclopropane decomposition. We have used this value to reproduce experimental results on the shock-tube decomposition of allyl iodide (see below). Since we are very close to the high-pressure limit we expect the actual number (at the low-pressure limit) to be of the order of 0.1–0.15.<sup>27</sup> This suggests a downward step size of the order of  $6 \pm 3$  kJ. This is in accord with the work of King<sup>28</sup> with respect to the step size for energy transfer by argon at these temperatures. In addition we are also able to reproduce the toluene carrier experiments on small molecules with close to unit efficiency. Thus up to about 1100 K, it would appear that there is no abnormal kinetic behavior in the usual single-pulse shock-tube experiments. As one goes to higher temperatures falloff behavior should become more pronounced especially since the collision efficiency can be expected to decrease the increasing temperature.

The results on allyl bromide decomposition in combination with the calculated entropy of allyl radicals and the assumption that

the recombination process has no or small temperature dependence leads to a rate of  $10^{14.0}$  cm<sup>3</sup>/(mol s) for the latter process. This number can be compared with the collision rate value of  $10^{14.55}$  cm<sup>3</sup>/(mol s) where we have used as the collision cross section the position of the rotational barrier at 950 K, 4.64 Å. The difference is thus roughly a factor of 4. Since the spins must be opposed for any allyl and bromide atom collision to effect combination, it would appear that reaction is occurring at every possible collision. Note that the close correspondence between our measured and literature values for the heat of formation of allyl is consistent with negligible temperature dependence for combination. At worst this will lead to an error of a factor of 2. Benson and O'Neal<sup>3</sup> have suggested that recombination between an atom and a resonance-stabilized radical may be slower than the close to collisional value that they assigned for an ordinary radical and atom. An examination of their work leads to the conclusion that this was mainly a working hypothesis. It would appear from the present study that resonance-stabilized radicals behave no differently than ordinary hydrocarbon radicals. This is fully consonant with combination processes involving two polyatomic radicals<sup>29</sup> where rate constants for combination of all hydrocarbon radicals (irrespective of stabilization) appear to be consistently near  $1 \times 10^{13}$  cm<sup>3</sup>/(mol s). On this basis we have investigated for a number of simple organic halides ( $\text{RX} \rightarrow \text{R} + \text{X}$ ) the consequences of a recombination rate of  $1 \times 10^{14}$  cm<sup>3</sup>/(mol s). Results are summarized in Table IV, and one expects an uncertainty of about a factor of 3 in the  $A$  factor. This is a direct reflection of the uncertainty in the recombination rate. Thus in resonance-stabilized systems the "tighter" radical is reflected in lower  $A$  factors for decomposition. It should be noted that we have observed similar effects in the decomposition of alkynes<sup>1</sup> and in fact suggested the relationship<sup>1,29</sup>

$$k(\text{CH}_3=\text{CHCH}_2-\text{R}) = \frac{1}{(3 \pm 1.5)} \exp(5200/T) k(\text{CH}_3\text{CH}_2\text{CH}_2-\text{R})$$

between rate expressions for alkane and alkene decomposition, in close agreement with the results of the present calculations. It should be noted that the results for 1,2-dibromoperfluoroethane does not fit into this framework. The  $A$  factor per C–Br bond is  $10^{14.9}$  s<sup>-1</sup> or a factor 6 lower than that for comparable hydro-

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carbon. This may be a reflection of a lower recombination rates for halogenated organic radicals.<sup>2</sup>

Also included in Table IV are direct comparisons with literature values.<sup>32-36</sup> The latter are subject to all the usual uncertainties in kinetics studies. Nevertheless there is very satisfactory agreement in most cases. As perhaps would be expected the rate parameters are vastly different. However, in the case of benzyl bromide and benzyl chloride our rate parameters produce constants in extraordinarily good agreement with experiments. These rate parameters are in reasonable accord with the values given by Benson and O'Neal.<sup>3</sup> This is, however, fortuitous since their analysis was based on older thermodynamic data and on the assumption that the recombination rate was constant in pressure units. In the case of allyl iodide, methyl bromide, and ethyl iodide rates are slower than predicted. The small size of these molecules makes it worthwhile to look for falloff effects. In the case of methyl bromide and allyl iodide agreement between calculation and experiments becomes extraordinarily good. However, in the former case we are so far into the falloff region that practically all information on high-pressure behavior is lost. This can be seen by the invariance of the calculated unimolecular rates when the *A* factor is lowered by a factor of 10. In the case of allyl iodide we are in the region where the pressure dependence is  $p^{0.5}$ , the calculated rates still reflect to a considerable extent high-pressure unimolecular behavior. For ethyl iodide the data would seem to favor a slower combination rate. However, we feel that the measured rate is probably only a minimum value. This is because ethane is used as a marker for extent of reaction (derived from the abstraction of a hydrogen atom by ethyl from toluene). Unfortunately, on the basis of the work of Lin and Laidler<sup>37</sup> and rates of the abstraction process<sup>13</sup> we estimate that at 750 K and

14-torr toluene pressure the rate for the former is no more than a factor of 2 higher than the latter. Furthermore, there are numerous other channels for ethyl radical destruction. Overall, these data offer very strong support for high rates of combination between polyatomic organic radicals and a halogen atom. In the case of the resonance-stabilized species they would appear to be at least an order of magnitude higher than that suggested by Benson and O'Neal. This also means that there is no particular difference between resonance-stabilized and ordinary hydrocarbon radicals with respect to combination processes.

Finally, for completeness we have carried out RRKM calculations for cyclohexene decomposition. This is the fundamental standard for all our comparative rate studies. The calculations are made more realistic by the values of the collisional efficiency that have been obtained (see above). For the present purposes we use a value of 0.04. This is at the lower end of our range and is probably appropriate for the slightly higher temperatures of these calculations. On the basis of a vibrator model and with structure and vibrational frequencies for cyclohexene as given by Beckett and co-workers<sup>38</sup> leading to decomposition rate expression of  $10^{15.15} \exp(-33500/T) \text{ s}^{-1}$  we find that with our experimental conditions  $k(\text{cyclohexene}) < 1000 \text{ s}^{-1}$  and concentration range of  $6 \times 10^{18}$  to  $2 \times 10^{19}$  molecules/cm<sup>3</sup> we were never more than 5-6% away from the high-pressure limit. The consequence with respect to the activation energy and *A* factor is thus never more than 3 kJ or 30%, respectively. This is within the range of our other uncertainties. In the present case with 4-methylcyclohexene as the internal standard and the lower temperature employed, falloff effects from the internal standard cannot make any contributions.

**Registry No.** Br(CF<sub>2</sub>)<sub>2</sub>Br, 124-73-2; CH<sub>2</sub>=CHCH<sub>2</sub>Br, 106-95-6; CH<sub>2</sub>=CHCH<sub>2</sub>·, 1981-80-2; PhCH<sub>2</sub>Br, 28807-97-8; PhCH<sub>2</sub>Cl, 25168-05-2; MeBr, 74-83-9; CH<sub>2</sub>=CHCH<sub>2</sub>I, 556-56-9; EtI, 75-03-6; cyclohexene, 110-83-8; cyclopentane, 287-92-3.

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## Vibrationally Excited Carbon Dioxide Produced by Infrared Multiphoton Pyrolysis

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Vibrationally excited CO<sub>2</sub> has been observed in the infrared multiphoton pyrolysis (IRMP) of some organic molecules. The pyrolysis was induced by a high-power, pulsed CO<sub>2</sub> TEA laser. The vibrational excitation of CO<sub>2</sub> was investigated by time-delayed, intracavity probing with a weak flash photolysis CO<sub>2</sub> laser. The molecules 2-oxetanone ( $\beta$ -propiolactone), 3-butenic acid (vinylacetic acid), and 2-oxopropanoic acid (pyruvic acid) were all shown to produce vibrationally excited CO<sub>2</sub> as one of the photofragments. The excitation involved the symmetric stretching mode, as well as the asymmetric stretching mode, of CO<sub>2</sub>. The results provide information about the structural dynamics of each reaction as well as the geometry of the transition states.

### Introduction

Infrared multiple photon dissociation provides the means for instantaneous, high-yield photofragmentation of molecules. This has already been used extensively to study various aspects of unimolecular reactions. Of particular interest seems to be the energy distribution among the products. We here introduce a technique to measure vibrational excitation of selected photofragments. Specifically, we have probed the vibrational excitation

of CO<sub>2</sub> from the infrared multiphoton pyrolysis of three organic molecules: 2-oxetanone ( $\beta$ -propiolactone), 3-butenic acid (vinylacetic acid), and 2-oxopropanoic acid (pyruvic acid). The choice was in the case of 2-oxetanone based on a report<sup>1</sup> that equimolar CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> were the only products from normal pyrolysis. 3-Butenoic acid and 2-oxopropanoic acid have been shown to undergo laser-induced decarboxylation reactions by

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