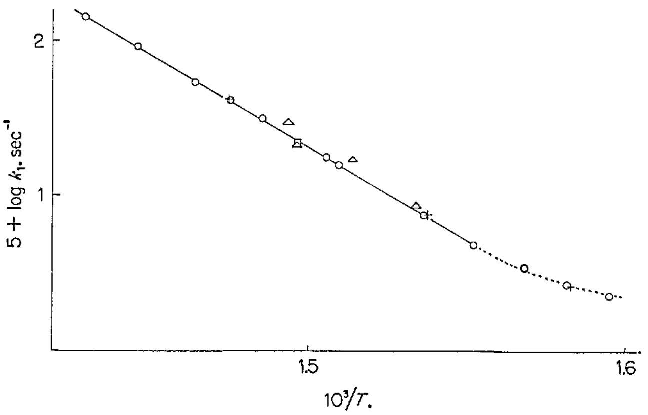
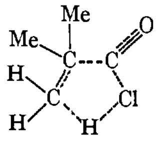
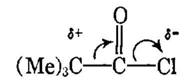


Figure 2. Arrhenius plot for temperatures 354–426°; +, without additives; ○, with cyclohexene; □, with isobutylene; △, in packed vessel.

appears quite apt in terms of electron movements, but in this case a slightly smaller A factor would seem more



I



II

appropriate. If the decomposition is akin to those of the alkyl halides,[9] reaction would involve polarization of the molecule in the manner of II. Kinetic investigations with other acyl halides are required to obtain information on the effects of substitutions at significant molecular sites.

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(9) A. Maccoll, *Advan. Phys. Org. Chem.*, 3, 91 (1965).

Kinetic Study of the Reaction $CHI_3 + HI \rightleftarrows CH_2I_2 + I_2$. A Summary of Thermochemical Properties of Halomethanes and Halomethyl Radicals[1a]

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Received May 2, 1969

Abstract: The rate of the reaction $CHI_3 + HI \rightleftarrows CH_2I_2 + I_2$ has been followed spectrophotometrically from 158.1 to 206.1°. The rate constant for the reaction $I + CHI_3 \rightleftarrows CHI_2 + I_2$ fits the equation, $\log k_1\ (M^{-1}\ \text{sec}^{-1}) = (11.75 \pm 0.17) - (9.63 \pm 0.36)/\theta$. This value, combined with the assumption that $E_2 = 0 \pm 1$ kcal/mole, leads to $\Delta H_f°_{298}(CHI_2\cdot) = 79.9 \pm 2.3$, $DH°_{298}(CHI_2\text{–}I) = 45.7 \pm 1.2$, and $DH°_{298}(CHI_2\text{–}H) = 102.7 \pm 2.5$ kcal/mole, respectively. The heats of formation of (unmixed) halomethanes and halomethyl radicals are summarized and discussed in terms of Bernstein's interaction scheme and Pauling's bond-energy equations.

In previous papers, we have reported on studies of the equilibrium $2CH_3I \rightleftarrows CH_4 + CH_2I_2$,[2a] the kinetics of $CH_2I_2 + HI \rightleftarrows CH_3I + I_2$, and the iodine-catalyzed process $2CH_3I \rightleftarrows CH_4 + CH_2I_2$,[2b] in which the heats of formation, $\Delta H_f°(CH_2I_2)$ and $\Delta H_f°(CH_2I)$, and bond dissociation energies, $DH°(CH_2I\text{–}I)$ and $DH°(CH_2I\text{–}H)$, were determined.

The kinetics and thermochemistry of the reaction $CH_3I + HI \rightleftarrows CH_4 + I_2$ have already been reported.[3,4]

In this paper, the kinetics of $CHI_3 + HI \rightleftarrows CH_2I_2 + I_2$ is discussed. This terminates our studies of iodomethanes (CI_4 is not adaptable to study with these methods). A summary of the thermochemical properties of halomethanes and halomethyl radicals is presented, as well.

Experimental Section

Materials. Mallinckrodt reagent grade, resublimed, iodine was used. Matheson anhydrous hydrogen iodide was used after purification by distillation under vacuum. Eastman iodoform was purified by recrystallization in methanol and resublimation under vacuum. The purity of CHI_3 was determined to be greater than 99.5% by nmr measurements.

Apparatus. The slightly modified Cary 15 spectrophotometer, adapted for use with a quartz reaction vessel situated in an Al block oven, has been described in detail previously.[4]

Procedure. The mechanism of the reaction $RI + HI \rightleftarrows RH + I_2$ has been well explained by the scheme proposed by Benson and O'Neal[5]

$$I_2 \rightleftarrows 2I \qquad K_{I_2}\text{(equilibrium)}$$

$$RI + I \underset{2}{\overset{1}{\rightleftarrows}} R\cdot + I_2 \tag{1, 2}$$

$$R\cdot + HI \underset{4}{\overset{3}{\rightleftarrows}} RH + I \tag{3, 4}$$

where R is an alkyl or aryl radical. The rate of deiodination of RI

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(1) (a) This work was supported in part by Grant AP0053-04, Public Health Service, Division of Air Pollution; (b) Postdoctoral Research Associate.

(2) (a) S. Furuyama, D. M. Golden, and S. W. Benson, *J. Phys. Chem.*, 72, 4713 (1968); (b) *Intern. J. Chem. Kinetics*, 1, 283 (1969).

(3) M. C. Flowers and S. W. Benson, *J. Chem. Phys.*, 38, 882 (1963).

(4) D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, 87, 4053 (1965).

(5) S. W. Benson and E. O'Neal, *J. Chem. Phys.*, 34, 514 (1961).

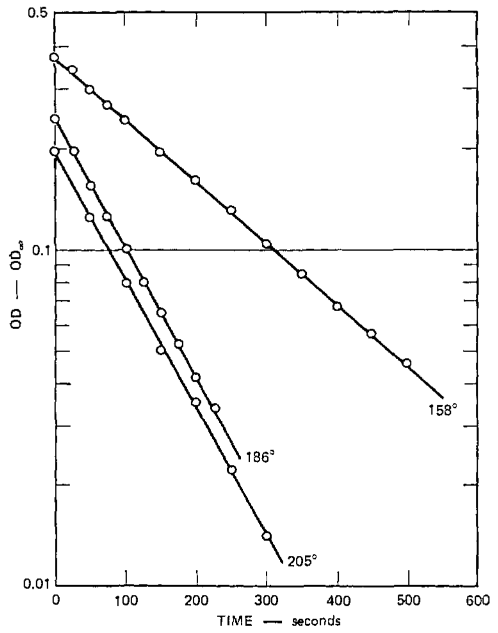

Figure 1. Plot of log (OD − OD$_\infty$) *vs.* time for $CHI_3 + HI \rightleftarrows CH_2I_2 + HI$. Values (in Torr) for three temperatures are given for $(CHI_3)_0$, $(HI)_0$, and $(I_2)_0$, respectively, as follows: (205°) 0.30, 4.42, 6.30; (186°) 0.28, 4.04, 11.83; (158°) 0.37, 116.2, 9.02.

with HI is expressed as

$$S \equiv \frac{-\mathrm{d(RI)}}{\mathrm{d}t} = \frac{k_1 K_{I_2}{}^{1/2}(I_2)^{1/2}(RI)}{\left\{1 + \dfrac{k_2(I_2)}{k_3(HI)}\right\}} \tag{5}$$

Equation 5 is transformed into a pseudo-first-order kinetic equation in a case where the pressures of HI and I_2 are so high in comparison with that of RI that they can be regarded as almost constant during the reaction.

$$S \equiv \frac{k_1 K_{I_2}{}^{1/2}(\bar{I}_2)^{1/2}(RI)}{\left\{1 + \dfrac{k_2(\bar{I}_2)}{k_3(\overline{HI})}\right\}} = k_{app}(RI) \tag{6}$$

Here $(\bar{I}_2)$ is $[(I_2)_0 + (I_2)_\infty]/2$, $(\overline{HI})$ is $[(HI)_0 + (HI)_\infty]/2$, and $(I_2)_0$, etc., are the initial, or final, pressures of I_2 and HI. (RI) can be equated with $\{OD - \alpha_{RH}(RI)_0 - \alpha_{I_2}(I_2) - \alpha_{HI}(HI)\}/(\alpha_{RI} - \alpha_{RH})$ which, to a good approximation, equals $(OD - OD_\infty)/(\alpha_{RI} - \alpha_{RH})$, where OD and OD_∞ are optical densities at time t and at equilibrium, respectively (RI = CHI_3, RH = CH_2I_2, here). The α's are the extinction coefficients at fixed wavelengths of the components indicated by the suffixes. By substituting this into eq 6, the usual first-order integrated equation is obtained.

$$\ln\left[\frac{OD_0 - OD_\infty}{OD - OD_\infty}\right] = k_{app}t \tag{7}$$

k_{app} was obtained by following OD — OD_∞ at 350 mμ.[6] k_2/k_3 and $k_1K_{I_2}{}^{1/2}$ were then determined from the intercept and the slope of a plot of $(\bar{I}_2)/(\overline{HI})$ against $(\bar{I}_2)^{1/2}/k_{app}$ by the equation

$$\frac{(\bar{I}_2)}{(\overline{HI})} = \frac{k_1k_3K_{I_2}{}^{1/2}(\bar{I}_2)^{1/2}}{k_2k_{app}} - \frac{k_3}{k_2} \tag{8}$$

Ca. 0.2–0.4 Torr of iodoform[7] ($OD_0 - OD_\infty$ was ~0.2–0.4 OD unit) was deiodinated to methylene iodide by excess hydrogen iodide (~4–120 Torr) in the presence of excess iodide (~6–20 Torr) at 158–206°.

It seems possible that the consecutive reaction, $CH_2I_2 + HI \rightleftarrows CH_3I + I_2$, might take place simultaneously during this experiment.

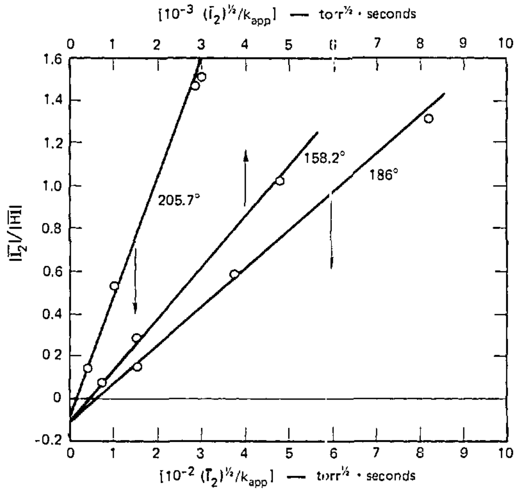

Figure 2. Plot of $(\bar{I}_2)/(\overline{HI})$ *vs.* $(\bar{I}_2)^{-1/2}/k_{app}$.

However, k_1 (for $CH_2I_2 + I \rightarrow CH_2I\cdot + I_2$) has been determined as $10^{11.45-15.11/\theta}$,[2b] which is about 240 times smaller than k_1 (for $CHI_3 + I \rightarrow CHI_2\cdot + I_2$). This was confirmed by the fact that increase of the pressure of iodine after the reaction was always comparable with the initial pressure of CHI_3, and $OD_\infty - OD_{I_2\infty} - OD_{HI\infty}$ was also the same as the expected $OD_{CH_2I_2}$.

Results

k_{app} was obtained from a plot of log $(OD - OD_\infty)$ *vs.* time. Typical plots are shown in Figure 1. $(\bar{I}_2)/(\overline{HI})$ was then plotted against $(\bar{I}_2)^{1/2}/k_{app}$ at 159, 186, and 205.5° in Figure 2. Good straight lines were obtained at each temperature where k_3/k_2 and $k_1K_{I_2}{}^{1/2}$ were determined directly from their intercepts and slopes. Data are summarized in Table I. All values of k_3/k_2 fall in the range ~0.10–0.12. Log (k_3/k_2) is $(-0.9 \pm 0.9) - (0.2 \pm 1.9)/\theta$, which agrees well with the relation log $(k_3/k_2) = (-0.5 \pm 1) - (1 \pm 1)/\theta$ ($\theta = 2.303RT$ kcal/mole) established for the analogous reactions in other systems.[3,8–10] $k_3/k_2 = 0.10$ at 158° coincides very closely with the estimated value from log $(k_3/k_2) = -0.5 - (1/\theta)$. This is probably the most reliable value because of the suitable reaction velocity for measurements (see Figure 1), and the excellent straight line of $(I_2)/(HI)$ *vs.* $(I_2)^{1/2}/k_{app}$ (see Figure 2) at this temperature. k_3/k_2 at 186–206° is corrected to obey log $(k_3/k_2) = -0.5 - (1/\theta)$ and substituted into eq 6 or 8, together with the known $K_{I_2}{}^{1/2}$ [11] to obtain k_1.

Log k_1, which is plotted against $1/T$ in Figure 3, is

$$\log k_1\,(M^{-1}\,\mathrm{sec}^{-1}) = (11.75 \pm 0.17) - (9.63 \pm 0.36)/\theta$$

where the errors are standard deviations.

k_1, which is directly obtained from the plots in Figure 2, is given by

$$\log k_1\,(M^{-1}\,\mathrm{sec}^{-1}) = (12.07 \pm 0.18) - (10.28 \pm 0.37)/\theta$$

The differences in the Arrhenius parameters of both k_1's are within the 95% confidence limits.

The bond dissociation energy, $DH°(CHI_2\text{–}I)$, is

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(6) α_{I_2} and α_{HI} are negligibly small at 350 mμ (ref 2).

(7) This is the highest vapor pressure of iodoform at ~100–200°.

(8) D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963).

(9) A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **89**, 4578 (1967).

(10) H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, **37**, 540 (1962).

(11) "JANAF Interim Thermochemical Tables," D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1963.

Table I. Kinetic Data for $CHI_3 + HI \rightleftarrows CH_2I_2 + I_2$ in the Presence of Excess HI and I_2

Temp, °C	$(CHI_3)_0$	$(HI)_0$	$(I_2)_0$	10^2k_{app},[a] sec^{-1}	k_3/k_2	$k_1K_{I_2}^{1/2}$, $M^{-1/2}\,sec^{-1}$	$10^{-7}k_1$, $M^{-1}\,sec^{-1}$	$(k_3/k_2)_{est}$[c]	$10^{-7}(k_1)_{corr}$,[d] $M^{-1}\,sec^{-1}$
206.1	0.33	27.55	14.32	3.66					2.43
205.8	0.20	7.77	11.63	1.12					2.10
205.7	0.22	36.55	5.04	5.30	0.10	9.70	2.46	0.111	2.35
205.2	0.30	4.42	6.30	0.877					2.16
201.4[b]	0.35	30.30	7.54	3.42	...	...	...	0.110	2.00
186.0	0.30	19.90	11.41	0.902					1.61
186.0	0.28	9.18	11.69	0.419	0.12	2.51	1.38	0.106	1.52
186.0	0.30	49.2	7.48	1.77					1.47
158.3	0.27	44.2	12.46	0.233					0.772
158.1	0.37	118.2	9.02	0.387	0.10	0.398	0.743	0.10	0.695
158.1	0.39	19.92	19.83	0.0970					0.745

[a] $k_{app} = k_1K_{I_2}^{1/2}(\overline{I_2})^{1/2}/(1 + k_2(\overline{I_2})/k_3(\overline{HI}))$. [b] The consecutive reaction $CH_2I_2 + HI \rightleftarrows CH_3I + I_2$ was followed after the reaction with addition of more HI. See ref 2b, Table III. [c] Estimated values from the equation $\log (k_3/k_2) = -0.5 - (1/\theta)$. [d] Corrected value, using $(k_3/k_2)_{est}$.

related to heats of formation by

$$DH_T°(CHI_2\text{–}I) \equiv \Delta H_f°_T(CHI_2\cdot) + \Delta H_f°_T(I) - \Delta H_f°_T(CHI_3) = \Delta H_{1.2}°(T) + DH_T°(I\text{–}I) \quad (9)$$

The usual assumption[2b,4] that $E_2 = 0 \pm 1$ kcal/mole leads to

$$\Delta H_{1.2}(455\,°K) = E_1 - E_2 \sim E_1 = 9.6 \pm 1 \text{ kcal/mole}$$

Using values of the appropriate thermochemical data listed in Table II

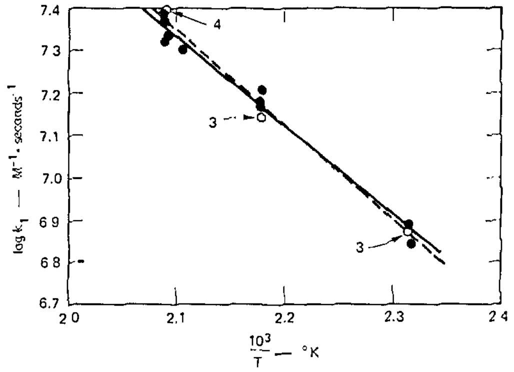

Figure 3. Arrhenius plot for the reaction $CHI_3 + I\cdot \rightarrow CHI_3 + I_2$: ○, ----, k_1 with experimental k_3/k_2; ●, ——, k_1 with estimated k_3/k_2.

$$DH°_{298}(CHI_2\text{–}I) = \Delta H_{1.2}(455\,°K) + DH°_{298}(I\text{–}I) + 0.16\overline{\Delta C_p°} = 45.7 \pm 1.2 \text{ kcal/mole}$$

where $\overline{\Delta C_p°} = (\Delta C_p°_{298} + \Delta C_p°_{455})/2 = -0.2 \pm 2$ cal/(mole deg). We cannot determine the precise value of $\Delta H_f°(CHI_2\cdot)$; however, it is possible to estimate it using the extrapolated value[2a] of $\Delta H_f°(CHI_3) = 59.8 \pm 2$ kcal/mole.

$$\Delta H_f°_{298}(CHI_2\cdot) = DH°_{298}(CHI_2\text{–}I) + \Delta H_f°_{298}(CHI_3) - \Delta H_f°_{298}(I) = 79.9 \pm 2.3 \text{ kcal/mole}$$

Thus, $DH°_{298}(CHI_2\text{–}H) = \Delta H_f°_{298}(CHI_2) + \Delta H_f°_{298}(H) - \Delta H_f°_{298}(CH_2I_2) = 102.7 \pm 2.5$ kcal/mole.

Table II. Gas-Phase Thermochemical Data

	$\Delta H_f°$, kcal/mole 298°	$S°$, gibbs/mole 298°	$C_p°$, gibbs/mole 298°	400°	500°
CHI_2	79.8[a]	75.28[b]	13.38[b]	14.90[b]	16.31[b]
I_2[c]	14.924	62.281	8.814	8.901	8.948
I[c]	25.537	43.184	4.968	4.968	4.968
CHI_3	59.8[a]	85.37[d]	17.11[d]	19.44[d]	21.73[d]

[a] Estimated in this work. [b] $S°$ and $C_p°$ of CHI_2 are determined as follows. When CHI_2 is produced from CH_2I_2 by abstraction of one hydrogen atom, three modes of vibration, that is, C–H stretching ($\nu \sim 3000$ cm^{-1}), H–C–H bending ($\nu \sim 1350$ cm^{-1}), and H–C–I bending ($\nu \sim 1100$ cm^{-1}), are lost: E. K. Plyler and W. S. Benedict, *J. Res. Nat. Bur. Std.*, **47**, 202 (1951). $S°(CHI_2)$ and $C_p°$ are then given by $S°(CH_2I_2) - \Sigma S°(\text{vib}) - 4.58(\Sigma \log \sigma - \log 2)$ and $C_p°(CH_2I_2) - \Sigma C_p°(\text{vib})$, respectively. σ = symmetry. Log 2 arises from the degeneracy of the electronic state. $S°(\text{vib})$ and $C_p°(\text{vib})$ are obtained from S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1968, p 208. [c] Reference 11. [d] $S°(CHI_3)$ is approximated by $2S°(CH_2I_2) - S°(CH_3I) + 4.58\Sigma \log$ (symmetry change). $C_p°(CHI_3) \simeq 2C_p°(CH_2I_2) - C_p°(CH_3I)$. $C_p°$ and $S°$ of CH_2I_2 and CH_3I are obtained from E. Gelles and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5259 (1953).

Discussion

$DH°_{298}(CHI_2\text{–}I) = 45.7 \pm 1.2$ kcal/mole obtained here agrees within the error with a value of 50 ± 4 kcal/mole obtained from a study of radical reactions in diffusion flames of alkali metals with organic halides.[12]

Log A_1 of the step $RI + I \rightarrow R\cdot + I_2$ for CHI_3 obtained here is 11.75, which is of comparable size to that for CH_3I (11.40)[3] and for CH_2I_2 (11.45).[2b] The A factor may be expressed in terms of collision theory as

$$A = pZe^{1/2}$$

where p is a steric factor, and Z is the collision frequency. (The $e^{1/2}$ arises as a result of the $T^{1/2}$ dependence in Z.) By taking the mean collision diameter, σ, 5.0 Å[13,14] for a CHI_3–I pair, $\log Ze^{1/2} = 11.42$ at 500°K, so that $p \cong 1$. For the case of CH_3I, $\log Ze^{1/2} = 10.96$, when σ is taken as 2.7 Å. This is slightly smaller than the experimental value of Flowers and Benson;[3] however, $p \cong 1$ within experimental error. For the case of CH_2I_2, $\log Ze^{1/2}$ is 11.33, when σ is taken as 4.4 Å. This agrees well with the experimental value, $\log k_1 = 11.45$, which means $p \cong 1$. In the cases of RI = C_2H_5I,[8] C_6H_5I,[9] and CH_3COI,[10] the steric factors are also almost unity. A value of p near unity implies little need for orientation in the collision pair and corre-

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(12) W. J. Miller and H. B. Palmer, *J. Chem. Phys.*, **40**, 701 (1964).

(13) Covalent radii of C and I = 0.77 and 1.33 Å.[14]

(14) C. A. Coulson, "Valence," Clarendon Press, Oxford, 1953, p 180.

sponds to a loose transition state in the language of transition-state theory.[15] Reactions of $RI + I \rightleftarrows R\cdot + I_2$ probably pass through the same type of transition state for all R's which are not resonance stabilized. This might suggest that the reaction $CI_4 + I \rightleftarrows CI_3 + I_2$ would proceed through a loose transition state, too. Therefore, log A_1 for the reaction would probably be 11.8 because log $Ze^{1/2}$ calculated at 500°K by taking $\sigma = 5.0$ Å is 11.40.

Considering that the activation energies, E_1's, for CH_3I,[3] CH_2I_2,[2b] and CHI_3 are 20.5, 15.5, and 9.6 kcal/mole, respectively, it may be plausible to predict by a simple extrapolation that E_1 for $CI_4 + I \rightleftarrows CI_3 + I_2$ would be 4 ± 1 kcal/mole. Combining this with A_1 estimated above, log k_1 for CI_4 would be $(11.8 \pm 0.2) - (4 \pm 1)/\theta$.

An activation energy of 4 kcal/mole implies $DH_T°$-(CI_3–I) $\sim DH°_{298}$(CI_3–I) ≈ 40 kcal/mole. This, together with an extrapolation of the double difference scheme applied in ref 2a, to yield $\Delta H°_{298}(CI_{4,g}) \cong 95$ kcal/mole, yields a value of $\Delta H_f°_{298}(CI_{3,g}) \cong 110$ kcal/mole. The latter value would mean that $DH°_{298}(CI_3\text{–}H) \cong 102$ kcal/mole.

Summary of Thermochemical Data for Halomethanes and Halomethyl Radicals

Table III summarizes the known thermochemical properties of the (unmixed) halomethanes and halomethyl radicals.

Bernstein[16] has developed an interaction scheme for predicting the properties of fluoro-, chloro-, and bromoethanes. This scheme may be expanded to include iodomethanes and the various halomethyl radicals. According to Bernstein's scheme, $\Delta H_f°(CH_{4-n}X_n)$ may be expressed as

$$\Delta H_f°(CH_{4-n}X_n) = n\overline{CX} + (4-n)\overline{CH} + n(4-n)\Delta XH \quad (10)$$

where $\overline{CX}$ and $\overline{CH}$ are the effective bond contributions of C–X and C–H and correspond to $\Delta H_f°(CX_4)/4$ and $\Delta H_f°(CH_4)/4$, respectively. ΔXH is the effective interaction between X and H, and corresponds to $-\Delta[\Delta(\Delta H_f°)]/2$.[17] $\overline{CH}$, $\overline{CX}$, and ΔXH may be defined in terms of

$$\Delta H_f°(CX_4)/4 = \overline{CX} = CX + \frac{3}{2}XX \quad (11)$$

$$\Delta H_f°(CH_4)/4 = \overline{CH} = CH + \frac{3}{2}HH \quad (12)$$

$$-2\Delta[\Delta(\Delta H_f°)]/2 = 2\Delta XH = 2XH - XX - HH \quad (13)$$

where CX and CH are implicit bond contributions, and XX, HH, and XH are implicit interactions between X and X, and so on.

Implicit bond contributions and interactions are obtained as follows. CA (A = X or H) is defined in terms of

$$CA = (1/4)\Delta H_f°(CA_4{*}) = (1/4)\Delta H_f°[C(g)] + \Delta H_f°[A(g)] - (1/4)\Delta H_a°(CA_4{*}) \quad (14)$$

Table III. The Heat of Formation[a] and the Bond Dissociation Energy[a] of Halomethanes CH_3X, CH_2X_2, CHX_3, and CX_4 and of Their Radicals

	F				Cl				Br				I			
RX(R'H)	$\Delta H_f°$(RX)	$\Delta H_f°$(R)	$DH°$(R–X)	$DH°$(R'–H)	$\Delta H_f°$(RX)	$\Delta H_f°$(R)	$DH°$ (R'–X)	$DH°$ (R'–H)	$\Delta H_f°$(RX)	$\Delta H_f°$(R)	$DH°$ (R–X)	$DH°$ (R–H)	$\Delta H_f°$(RX)	$\Delta H_f°$(R)	$DH°$ (R–X)	$DH°$ (R–H)
$CH_3X(CH_2XH)$	−56.0[b]	34.1[c]	109.0	≤102.8[d]	−20.7[b]	34.1[c,f]	83.7	100.9	−8.4[g]	34.1[c]	69.2	102.0	3.28[c]	34.1[c]	56.3[c]	103.8[l]
$CH_2XX(CHX_2H)$	−107.2[b]	≥−5.3	≤120.8	≤103.3[d]	−22.8[b]	28.1[f]	79.8	99.0	3[h]	41.5[i]	65.2	103.7	29.2[k]	55.0[l]	51.3[l]	(102.7)[l]
$CHX_2X(CX_3H)$	−166.6[b]	≥−57.0	≤127.0	106.2[e]	−24.7[b]	24.1[f]	77.7	95.5	19[h]	54.3	62[j]	(105)[n]	(59.8)[k]	(79.9)[l]	45.7[m]	(112)[n]
CH_3X	−223.0[b]	−112.5	129.4		−22.9[b]	18.7[b,f]	70.5	...	38[h]	(72)[n]	(61)[n]	...	(95.1)[n]	(110)[n]	(40)[n]	...

[a] In kcal/mole at 25°. If there is no indication, the value is calculated, using other thermochemical properties in the table. The following values are also used for calculation: $DH°(CH_3\text{–}H) = 104.1$ (ref 4); $\Delta H_f°(CH_4) = -17.8$, $\Delta H_f°(H) = 52.1$, $\Delta H_f°(F) = 18.9$, $\Delta H_f°(Cl) = 28.9$, $\Delta H_f°(Br) = 26.7$, $\Delta H_f°(I) = 25.5$ kcal/mole (ref 11). Values in parentheses are estimated. [b] Reference 11. [c] Reference 4. [d] A. M. Tarr, J. W. Coomber, and E. Whittle, *Trans. Faraday Soc.*, **61**, 1182 (1965). [e] J. C. Amphlett. J. W. Coomber. and E. Whittle. *J. Phys. Chem.*. **70**. 593 (1966). [f] Calculated value from kinetic data $E(RCl + Cl \rightarrow R + Cl_2) = 25.0, 21.4, 21.0$, and 18.9 kcal/mole for CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 tabulated in G. Chiltz, P. Goldfinger, G. Huybrechts, G. Martens, and G. Verbrecke, *Chem. Rev.*, **63**, 355 (1963), and R. Eckling, P. Goldfinger, G. Huybrechts, G. Martens, L. Myers, and S. Smoes, *Chem. Ber.*, **93**, 3014 (1960). $E(R + Cl_2 \rightarrow RCl + Cl)$ were reported as 2.3, 3.0, 4.0, and 6.0 kcal/mole for RCl = CH_3Cl, CH_2Cl_3, $CHCl_3$, and CCl_4, respectively, in Chiltz, *et al.* However, they are taken as −0.9, −0.2, 0.8, and 16.2 kcal/mole in the present paper for consistency with other thermochemical data. [g] National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," U. S. Government Printing Office, Washington, D. C., Jan 1968. [h] Estimated values by Bernstein.[16] According to the most recent NBS Table (footnote *g*), $\Delta H_f°(CHBr_3) = 4$ and $\Delta H_f°(CBr_4) = 9$ kcal/mole. If we adopt these values, $\Delta[\Delta(\Delta H_f°)]$ scatters in $\sim -3.5\text{–}5$ kcal/mole. We expect that the NBS values are wrong. [i] Calculated value from the kinetic data of G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944), which was corrected by G. C. Fettis and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, **81**, 5260 (1959). [j] The authors in ref 12 obtained $DH°(CHBr_2\text{–}Br) = 66 \pm 4$ kcal/mole. We adopted a minimum value here for the following reasons: (1) $DH°(CHBr_2\text{–}Br)$ should be 1 or 2 kcal/mole smaller than $DH°(CH_2Br\text{–}Br) = 65$ kcal/mole. (2) $DH°(CHBr_2\text{–}H)$ calculated by using $DH°(CHBr_2\text{–}Br) = 66$ kcal/mole is 107.7 kcal/mole which seems to be too large compared with $DH°(CH_3\text{–}H) = 104.1$ kcal/mole. (3) $DH°(CHI_2\text{–}I)$ obtained by the same authors in the same study is 50 ± 4 kcal/mole, which is also about 4 kcal/mole larger than the value 45.7 kcal/mole obtained by us in this study (see text). [k] Reference 2a. [l] Reference 2b. [m] This study. [n] Estimated value in this paper.

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(15) S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 271–281.

(16) H. J. Bernstein, *J. Phys. Chem.*, **69**, 1550 (1965).

(17) For example, $\Delta[\Delta(\Delta H_f°)] = [\Delta H_f°(CH_4) - \Delta H_f°(CH_3X)] - [\Delta H_f°(CH_3X) - \Delta H_f°(CH_2X_2)]$.

Table IV. Bond or Interaction Contributions to $\Delta H_f°$ (at 25° in Gas)[a]

Atom A	$\Delta H_f°$-(A)[b]	D(AA)[c]	x_A[c]	D(C–A)[c]	$\overline{\text{CA}}$	ΔXH	$\overline{\text{CA}}'$	ΔXH′	CA	AA	AH	CA′	AA′	AH′
H	52.1	104.2	2.1	98.8	−4.5		11.4		−4.0	−0.3		11.7	−0.3	
F	18.9	37.8	4.0	117.2[d]	−55.7	1.1[e]	−37.5	1.9[f]	−55.6	−0.1	0.9	−39.9	2.4	2.9
Cl	28.9	57.8	3.0	78.5	−5.7	−0.8	6.2	0.4	−6.9	0.3	−0.8	8.8	−2.6	−1.1
Br	26.7	46.0	2.8	65.9	9.5	−1.6	24.0	−2.6	4.5	3.3	−0.1	20.2	3.8	−0.9
I	25.5	36.1	2.5	57.4	23.8	−2.4	36.4	−2.0	10.8	8.7	1.8	26.5	9.9	2.8
C	170.9	83.1	2.5	83.1										

[a] All in kcal/mole, except for x_A in column 4. [b] Reference 11. [c] References 18 and 19. [d] Calculated value in the present paper (see text). [e] $\Delta H_f°(CH_4)$ is omitted to calculate $\Delta FH = -\Delta[\Delta(\Delta H_f°(RX))]/2$ (see text). [f] $\Delta H_f°(CH_3)$ is omitted to calculate $\Delta FH' = -\Delta[\Delta(\Delta H_f°(R\cdot))]/2$ (see text).

where CA_4^* is a hypothetical methane (or halomethane) gas which has no nonbonded interactions and $\Delta H_a°$ is the heat of atomization. $\Delta H_a°(CA_4^*)/4$ is identical with the "bond energy" of C–A, D(C–A). (14) is transformed into

$$CA = (1/4)\Delta H_f°[C(g) + \Delta H_f°[A(g)] - D(C\text{–}A) \quad (15)$$

D(C–A) may be calculated from Pauling's empirical equations[18,19]

$$D(C\text{–}A) = [D(C\text{–}C)D(A\text{–}A)]^{1/2} + 30(x_c - x_A)^2 \quad (16)$$

or

$$D(C\text{–}A) = \frac{1}{2}[D(C\text{–}C) + D(A\text{–}A)] + 23(x_c - x_A)^2 \quad (17)$$

where D(A–A) is the bond dissociation energy of A_2 gas, and x is the electronegativity value of the elements indicated by the suffix. D(C–C) is the bond dissociation energy of a typical C–C bond between sp^3 carbon atoms. Pauling uses 83.1 kcal/mole.[18,19]

Substituting D(C–A) obtained by Pauling[18] into (15), CA is calculated for A = H, F, Cl, Br, and I. XX and HH are, then, obtained by substituting CA's into eq 11 and 12. Finally, XH is calculated from relation 13.

The data are summarized in Table IV. The result that II = 8.7 and BrBr = 3.3 kcal/mole, while HH, FF, and ClCl ~ 0 kcal/mole, does not seem unreasonable.

The heat of formation of the halomethyl radical may be expressed in a similar way as (10)

$$\Delta H_f°(\cdot CH_{3-n}X_n) = n\overline{CX}' + (3 - n)\overline{CH}' + n(3 - n)\Delta XH' \quad (18)$$

where the definitions of CX′, etc., are the same as those for halomethanes and correspond to $\Delta H_f°(CX_3\cdot)/3$, $\Delta H_f°(CH_3\cdot)/3$, and $-\Delta[\Delta(\Delta H_f°)]/2$, respectively. $\overline{CX}'$, etc., are then given by

$$\Delta H_f°(\cdot CX_3)/3 = \overline{CX}' = CX' + XX' \quad (19)$$

$$\Delta H_f°(\cdot CH_3)/3 = \overline{CH}' = CH' + HH' \quad (20)$$

$$\Delta[\Delta(\Delta H_f°)] = 2\Delta XH' = 2XH' - XX' - HH' \quad (21)$$

where the definitions of CX′, etc., are the same as those for halomethanes.

Similarly, CA′ can be expressed as

$$CA' = (1/3)\Delta H_f°(\cdot CA_3^*) = (1/3)\Delta H_f°[C(g)] + \Delta H_f°[A(g)] - D(C\text{–}A) \quad (22)$$

$$D(\dot{C}\text{–}A) = [D(\dot{C}\text{–}\dot{C}) + D(A\text{–}A)]/2 + 23(x_{C\cdot} - x_A)^2 \quad (23)$$

where the definitions are analogous to those in (14)–(16). $D(\dot{C}\text{–}\dot{C})$ is then the hypothetical bond dissociation energy of a bond between carbons in the case where a radical center would exist at each carbon, but the dissociation products would be neither stabilized nor destabilized. This is clearly equal to D(C–C) and the same reasoning requires $D(C\text{–}A) = D(\dot{C}\text{–}A)$. Here we may make use of the following two approximations: (a) HH′ = HH, (b) CH − CH′ = CX − CX′. (a) seems reasonable as there is cause to suspect that the small H–H interaction will be even smaller in the radical. (b) seems reasonable, based on the following considerations. From (17) and (23)

$$CH - CH' = (1/2)[D(C\text{–}C) - D(\dot{C}\text{–}\dot{C})] + 23[x_C^2 - 2x_Cx_H - x_{C\cdot}^2 + 2x_{C\cdot}x_H]$$

$$CX - CX' = (1/2)[D(C\text{–}C) - D(\dot{C}\text{–}\dot{C})] + 23[x_C^2 - 2x_Cx_H - x_{C\cdot}^2 + 2x_{C\cdot}x_H]$$

$$\Delta = (CH - CH') - (CX - CX') = 46(x_X - x_H)(x_C - x_{C\cdot}) = 0 \text{ kcal/mole}$$

As $x_X \neq x_H$, (b) requires $x_{C\cdot} = x_C$ (=2.5). This, in turn, leads to $D(\dot{C}\text{–}\dot{C})$ = 83.2 ± 0.5 kcal/mole by (22) and (23) (where A = H, taking into account assumption a), which is the same as D(C–C) = 83.1 kcal/mole, which is expected. (a) and (b) lead to

$$CH' = \overline{CH}' - HH - 11.7 \text{ kcal/mole} \quad (24)$$

and

$$CX' = CX - CH + CH' = CX + 15.7 \text{ kcal/mole} \quad (25)$$

From the known data, CX′, XX′, and XH′ are calculated by (24), (19), and (21). The results are summarized in Table IV.

It is interesting to note that any XX′ or XH′ is quite close to the corresponding XX or XH (except for, perhaps, FF′ and ClCl′). Comparing the structure of $CH_{4-n}X_n$ with that of $\cdot CH_{3-n}X_n$, the distance between X and X (or X and H) in the radical is only a maximum

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(18) We have used D(C–A) from Tables 3–4, p 85 of ref 19, except for D(C–F), which is listed in this table as 105.4 kcal/mole. Calculations using eq 16 and 17 yield values of 111.7 and 122.6 kcal/mole, respectively. We have used the average value of 117.2 kcal/mole, since this value also fits well the heats of formation of some fluorinated ethanes. The difference in the values given by (16) and (17) may reflect, in part, some of the difficulties of fitting fluorine-containing compounds into a simple scheme.

(19) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 79–95.

of 7% longer than that in the molecule. It is reasonable to expect, therefore, that XX (or XH) is close to XX′ (or XH′). The coincidence between XX and XX′ (or XH and XH′) obtained here seems to be quite satisfactory and shows that the approximations a and b are not unreasonable.

It should be noted that the second differences in the fluorocarbon series (both molecule and radical) are not nearly as constant as the other halocarbons. Discussion of the interaction parameters for these compounds is therefore somewhat tenuous.

In the previous papers[2] it has been observed that

$$\Delta H°(2CH_3I \rightleftarrows CH_4 + CH_2I_2) = 4.7\ \text{kcal/mole} \quad (26)$$

$$DH°(CH_3\text{-}H) - DH°(CH_2I\text{-}H) = \Delta H°(CH_4 + \cdot CH_2I \rightleftarrows CH_3I + \cdot CH_3) = 0.3\ \text{kcal/mole} \quad (27)$$

and

$$DH°(CH_3\text{-}I) - DH°(CH_2I\text{-}I) = \Delta H°(CH_3I + \cdot CH_2I \rightleftarrows CH_2I_2 + \cdot CH_3) = 5\ \text{kcal/mole} \quad (28)$$

Since (26) is derived from (27) and (28), a problem is why $\Delta H°_{26}$ follows a simple bond additivity rule, while $\Delta H°_{27}$ does not. Generally

$$DH°(CH_{3-n}I_n\text{–}H) - DH°(CH_{3-n-1}I_{n+1}\text{–}H) \simeq 1\ \text{kcal/mole} \quad (29)$$

while

$$DH°(CH_{4-n}I_{n-1}\text{–}I) - DH°(CH_{4-n-1}I_n\text{–}I) \simeq 6\ \text{kcal/mole} \quad (30)$$

This can be explained as follows. Both (29) and (30) are expressed in terms of CX, XX, etc., through the relations in (10)–(13) and (18)–(21). They are finally approximated by (29) ≈ IH and (30) ≈ II − IH, since II ≈ II′ and IH ≈ IH′. Both IH ≈ 2, and II − IH ≈ 7 kcal/mole agree with (29) = 1 and (30) = 6 kcal/mole, respectively.

The data for II, II′, IH, and IH′ come from the same sources as eq 26–30, so this agreement is not surprising. However, formulation of (29) and (30), in terms of the interaction parameters of the Bernstein scheme, makes the differences in BDE's physically understandable.

For difference in bond strengths, such as (30), the number of I–I interactions change so that the difference is far from zero. For differences like (29), where only the transfer of a hydrogen atom occurs, it is the number of I–H interactions (a quantity much smaller than I–I) which changes and the difference is small.

The Thermal Decomposition of 6-Methyl-3,4-dihydro-2H-pyran[1]

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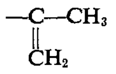
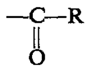
Abstract: The gas-phase thermal decomposition of 6-methyl-3,4-dihydro-2H-pyran (6-MDHP) into ethylene and methyl vinyl ketone has been investigated over the temperature range 330–370° and at initial pressures of 5–25 mm. The reaction is a first-order homogeneous process and is not affected by the addition of nitric oxide or propylene. An activation energy of 51.2 ± 0.5 kcal/mole has been found and the first-order rate constant is $k = 2.82 \pm 0.09 \times 10^{14} \exp(-51{,}200/RT)\ \text{sec}^{-1}$. 6-MDHP has been found by gas chromatography to be among the products formed in the decomposition of methyl cyclobutyl ketone.

The thermal decomposition of several derivatives of cyclopropane and cyclobutane (*i.e.*, those derivatives with



$$\text{—}\underset{\underset{CH_2}{\|}}{C}\text{—}CH_3$$

and



$$\text{—}\underset{\underset{O}{\|}}{C}\text{—}R$$

where R is H and CH_3) have been found to yield corresponding five- and six-membered ring compounds. Isopropenylcyclobutane[3] gave nearly equal amounts of ethylene–isoprene and 1-methylcyclohexene. Roquitte[4] established that a small amount of 3,4-dihydro-2H-pyran was formed during the decomposition of cyclobutanecarboxaldehyde. In contrast, no ring-enlargement reaction was reported for the decomposition of methyl cyclobutyl ketone.[5] Our present reinvestigation of the decomposition products of this compound by means of gas chromatography indicates the presence of a very small amount of a ring-enlargement product, 6-methyl-3,4-dihydro-2H-pyran (6-MDHP). Subsequently, the decomposition of 6-MDHP has been studied in some detail.

Experimental Section

Materials. Two methods were used to prepare 6-methyl-3,4-dihydro-2H-pyran (6-MDHP). Sample I was obtained by de-

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[1] This work was supported by a grant from the National Science Foundation.

[2] Abstracted by C. S. Caton from her M.S. thesis written under the supervision of the late W. D. Walters, University of Rochester, 1967. Address correspondence to author at 255 Dolly Varden Blvd., #38, Scarborough 722, Ontario, Canada.

[3] R. J. Ellis and H. M. Frey, *Trans. Faraday Soc.*, **59**, 2076 (1963).

[4] B. C. Roquitte and W. D. Walters, *J. Am. Chem. Soc.*, **84**, 4049 (1962).

[5] L. G. Daignault and W. D. Walters, *ibid.*, **80**, 541 (1958).