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THE THERMOCHEMISTRY OF THE GAS PHASE REACTION: $CF_3CH_2Br + I_2 = CF_3CH_2I + IBr$. POLARITY EFFECTS IN THERMOCHEMISTRY

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ABSTRACT

The gas phase equilibria in the reaction $CF_3CH_2Br + I_2 = CF_3CH_2I + IBr$ have been studied over the temperature range 614—726 K. A third law treatment of the data gave ΔH_r° (298 K) = 6.6 ± 0.5 kcal $mole^{-1}$. This result led to $\Delta H_f^\circ(CF_3CH_2Br, g, 298) = -166.0 \pm 0.5$ kcal $mole^{-1}$ and $DH^\circ(CF_3CH_2—Br) = 69.2 \pm 1$ kcal $mole^{-1}$.

These results were combined with previous data to obtain the enthalpies of reaction for the series

$CF_3CF_3 + XCH_2CH_2X = 2\ CF_3CH_2X$

in which X = H, I, and Br. It was found that the enthalpies of reaction became progressively less negative as the electronegativity of the substituent, X, increased. These experimental enthalpy changes are shown to be in excellent agreement with the net change in electrostatic interaction energy which was calculated assuming that the CF_3 and CH_2X groups in the reactant and product molecules were polarizable dipoles. The good agreement supports the hypothesis that polarity does play an important role in gas phase thermochemistry.

INTRODUCTION

According to group additivity principles, the enthalpy change for the disproportionation reaction

$$CF_3CF_3 + CH_3CH_3 \rightarrow 2\ CF_3CH_3 \qquad (1)$$

should be essentially zero [1,2]. The observed change, however, is —16.1 kcal $mole^{-1}$ [3]. Dipole—dipole interaction of the CX_3 moeities has been suggested as a major factor in this discrepancy [3,4]. The repulsive interaction of two CF_3 groups in CF_3CF_3 combined with the attractive interaction of the CF_3 and CH_3 groups in CF_3CH_3 accounted for most of the observed deviation.

In order to investigate further the effect of dipole—dipole interaction energies on the enthalpy change for disproportionation reactions, the series

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of reactions

$$CF_3CF_3 + XH_2CCH_2X \rightarrow 2\ CF_3CH_2X \qquad (2)$$

where $X = H$, I, Br, and Cl are considered. The observed enthalpy change, where available, in each of these reactions differs from the zero expected from group additivity. Classical calculations of the dipole—dipole interaction energy for each species gives an estimation of the significance of dipole effects in these reactions.

Experimental data are available for reaction (2) where $X = H$ and I, but are lacking for CF_3CH_2X where $X = Br$ and Cl. This experimental work was undertaken to obtain enthalpy of formation data for CF_3CH_2Br. A third law treatment applied to the equilibrium data for the reaction

$$CF_3CH_2Br + I_2 \rightarrow CF_3CH_2I + IBr \qquad (3)$$

yields the required $\Delta H_f^\circ(CF_3CH_2Br, g, 298)$. Thermodynamic functions of I_2 and IBr are readily available [5] and those for CF_3CH_2Br and CF_3CH_2I have been calculated using standard techniques [4]. Equilibrium in reaction (3) has been confirmed by approaching it from both directions.

EXPERIMENTAL

Research grade CF_3CH_2I and CF_3CH_2Br were obtained from Penninsular Chemical Research Company and both were distilled under vacuum several times before use. Reagent grade I_2 was obtained from J.T. Baker Chemical Company and was resublimed just before use. Research grade Br_2 was obtained from Mallinckrodt Chemical Company and was distilled under vacuum.

The experimental apparatus has been described in detail previously [6]. Basically, it consists of a heated 475 ml Pyrex static reactor vessel connected to a "hot box" maintained between 98 and 108°C to facilitate the handling of up to 40 torr iodine. Pressure measurements are conducted inside the "hot box" using a Pace-Wiancko pressure transducer as a null device. Pressures are read either on a dibutylphthalate manometer ($P < 60$ torr) or on a mercury manometer ($P > 60$ torr). The "hot box" is connected to a series of cold traps to sample the reaction cell mixture for gas chromatographic analysis. The reaction cell was placed inside a wire-wound aluminum block oven which was temperature controlled to ±0.25°C by means of a variable autotransformer and E.P.C. 1300 series proportional controller.

In order to initiate an equilibrium study, bromine was measured into the reaction cell. Addition of a larger pressure of iodine converted essentially all Br_2 to IBr ($K_{eq} \cong 38$ [5]). The desired mixture of CF_3CH_2Br and CF_3CH_2I was then expanded into the reaction cell and the total pressure measured. After sufficient time had been allowed for equilibrium to be attained, the contents of the reaction cell were passed through an Ascarite trap submerged in ice water to remove I_2 and IBr. The remaining halocarbon mixture was then expanded into a second trap and subjected to gas—liquid chromatographic analysis. A 0.6 × 305 cm column (6 mm i.d.) packed with 10% Carbowax 550 on Chromosorb G-DMCS was run at 58°C with a helium flow rate of 40 ml min^{-1}. The air peak occurred at 1.5 min and the retention times relative to air for CF_3CH_2Br and CF_3CH_2I were 3.9 and 10.5, respectively. The accuracy of the gas—liquid chromatographic analysis was ±2% and was determined from standard mixtures analyzed under simulated experimental conditions. Peak areas were determined by the peak width at half-height method.

RESULTS

Data for the equilibrium study of reaction (3) are presented in Table 1. Assuming that all Br_2 initially present is converted to IBr, the initial pressure of IBr is given as twice the pressure of Br_2 introduced. The pressure of I_2 remaining after formation of IBr is then

$$P^{i}_{I_2} = P^{o}_{I_2} - P_{Br_2}$$

where $P^{o}_{I_2}$ is the pressure of iodine introduced. After reaction, the final, or equilibrium, pressures of IBr (P^{e}_{IBr}) and I_2 ($P^{e}_{I_2}$) are given by

$$P^{e}_{IBr} = P^{i}_{IBr} + \Delta P_{RI}$$

$$P^{e}_{I_2} = P^{i}_{I_2} - \Delta P_{RI}$$

where

$$\Delta P_{RI} = P_T \left[1 + \left(\frac{P_{RBr}}{P_{RI}}\right)^{i}\right]^{-1} - P_T \left[1 + \left(\frac{P_{RBr}}{P_{RI}}\right)^{e}\right]^{-1}$$

TABLE 1

Experimental data for $CF_3CH_2Br + I_2 \rightleftharpoons CF_3CH_2I + IBr$

T (K)	Run no.	$P^{0}_{I_2}$ (torr)	$P^{0}_{Br_2}$ (torr)	P_T (torr)	$\left(\frac{P_{RBr}}{P_{RI}}\right)^{i}$	Time (h)	$\left(\frac{P_{RBr}}{P_{RI}}\right)^{e}$
614	4	19.11	3.62	19.27	4.60	7.08	19.00
	9	19.75	1.65	38.08	7.90	13.58	8.95
	8	18.60	0.90	23.50	5.80	12.75	6.70
	5	18.30	0.90	17.35	6.80	8.92	7.60
	24	17.85	3.15	16.00	28.42	3.33	39.43
	25	21.46	1.04	23.00	28.42	3.92	12.49
	26	21.42	1.08	2.50	28.42	4.17	15.13
	28	22.50	2.00	16.00	42.61	4.25	17.37
	29	23.27	3.23	3.00	42.61	10.83	31.71
658	16	20.09	1.31	23.60	11.11	1.00	9.52
	17	20.70	1.69	21.11	11.11	2.00	12.00
	18	20.96	1.23	23.31	5.48	1.00	7.70
	19	20.50	1.19	23.21	5.48	2.00	7.28
726	21	20.77	1.23	16.73	11.11	0.25	8.40
	20	20.31	1.31	21.88	5.48	0.25	7.62
	31	25.88	2.62	6.00	13.56	0.25	11.07
	30	22.00	2.50	11.00	13.56	0.25	11.91

and

$P_T = P_{RBr} + P_{RI}$

Table 2 gives the values for $-RT\ln Q$ in which Q is the ratio of the partial pressures of the products to reactants for both the initial, Q_i, and the equilibrium, Q_e, reaction mixtures. One expects that $Q_e = K_p$ for this reaction; however, it is evident from the values of $-RT\ln Q_e$ in Table 2 that there is considerable scatter in the values of Q_e, of the order of 20—40%. This large variance is most likely due to side reactions, quite probably the slower bromination of CF_3CH_2Br and/or CF_3CH_2I. In order to show that Q_e does indeed approximate K_p, the initial pressures ratios of $(P_{RBr}/P_{RI})^i$ were adjusted so that reaction (3) took place in both directions thus assuring that the Q_i values bracketed K_p.

Equilibria data with a variance of 20—40%, such as determined here, can not be used in a van't Hoff plot to calculate ΔS_r° and ΔH_r° accurately; however, the Gibbs Free Energy changes, ΔG_r°, can be determined to ±0.5 kcal mole^{-1} and if ΔS_r° is known, ΔH_r° can be obtained. The ideal gas thermodynamic functions for IBr and Br_2 are known [5] and those for the two halocarbons have been calculated for this work [4]. Table 3 summarizes the important thermochemical data.

Experimental values of ΔH_i and ΔH_e are given in Table 2. They were ob-

TABLE 2

Results of the equilibrium study of $CF_3CH_2Br + I_2 \rightleftharpoons CF_3CH_2I + IBr$

T (K)	ΔS_r^0 cal mole^{-1} K^{-1}	Run No.	$-RT \ln Q_i$ (kcal mole^{-1})	$-RT \ln Q_e$ (kcal mole^{-1})	ΔH_i [a] (kcal mole^{-1})	ΔH_e [b] (kcal mole^{-1})
614	1.60	4	2.79	5.21	>3.8	6.2
		9	4.63	5.04	>5.6	6.0
		8	4.92	5.40	>5.9	6.4
		5	5.10	5.40	>6.1	6.4
		24	5.12	5.56	>6.1	6.6
		25	6.87	5.36	<7.9	6.4
		26	6.82	6.00	<7.8	7.0
		28	6.57	5.30	<7.6	6.3
		29	5.96	5.59	<6.9	6.6
658	1.62	16	5.73	5.70	~6.8	6.8
		17	5.42	5.46	~6.5	6.5
		18	4.96	6.02	>6.0	7.1
		19	4.97	5.90	>6.0	7.0
726	1.63	21	5.30	6.34	>6.5	7.5
		20	6.45	6.41	<7.6	7.6
		31	5.91	5.59	<7.1	6.8
		30	5.72	5.50	<6.9	6.7

[a] $\Delta H_i = -RT \ln Q_i + T\Delta S$; > or < indicates that ΔH_r^0 is > or < ΔH_i^0.

[b] $\Delta H_e = -RT \ln Q_e + T\Delta S$; an estimate of ΔH_r^0.

TABLE 3

Thermochemical data

	ΔH_f^0(g, 298) (kcal mole^{-1})	S^0(g, 298) (cal mole^{-1} K^{-1})	C_p^0(g, 298) (cal mole^{-1} K^{-1})	C_p^0(g, 700) (cal mole^{-1} K^{-1})
CF_3CH_2Br		80.6 [4]	21.6 [4]	33.5 [4]
I_2	14.9 [5]	62.3 [5]	8.8 [5]	9.0 [5]
CF_3CH_2I	—154.3 [7]	82.5 [4]	21.8 [4]	33.6 [4]
IBr	9.76 [5]	61.9 [5]	8.7 [5]	9.0 [5]

tained by adding $T\Delta S$ to the appropriate $-RT\ln Q$ values. The ΔH_i values are upper or lower limits to ΔH_r° depending on whether the reaction of the initial mixture proceeds to the right or left, respectively. For example, in run 5 of Table 2, the reaction obviously proceeds to greater partial pressures for the reactants so that $Q_i > K_p$ and therefore $\Delta H_r^\circ > \Delta H_i$ as indicated in Table 2. Similarly, in run 29, $Q_i < K_p$ so that $\Delta H_r^\circ < \Delta H_i$.

The average value for ΔH_e is 6.7 ± 0.5 kcal mole^{-1} and this value is consistent with the upper and lower limits set by the ΔH_i's so that we can conclude that $\Delta H_r^\circ(3,\ 650) = 6.7 \pm 0.5$ kcal mole^{-1} and since $\langle \Delta C_p^\circ \rangle \cong 0.13$ cal mole^{-1} K^{-1}, then $\Delta H_r^\circ(3, 298) = 6.6 \pm 0.5$ kcal mole^{-1}.

DISCUSSION

The result $\Delta H_r^\circ(3, 298) = 6.6 \pm 0.5$ kcal mole^{-1} may be combined with the data of Table 3 to yield $\Delta H_f^\circ(CF_3CH_2Br, g, 298) = -166.0 \pm 0.5$ kcal mole^{-1}. This result will also yield the C—Br bond dissociation energy in CF_3CH_2Br as

$$\Delta H_r^\circ(3, 298) = DH^\circ(CF_3CH_2{-}Br) + DH^\circ(I{-}I) - DH^\circ(CF_3CH_2{-}I) - DH^\circ(I{-}Br)$$

Since $DH^\circ(I{-}I) = 36.1$ [5], $DH^\circ(I{-}Br) = 42.4$ [5], and $DH^\circ(CF_3CH_2{-}I) = 56.3$ [8] kcal mole^{-1}, then the above equation gives $DH^\circ(CF_3CH_2{-}Br) = 69.2 \pm 1$ kcal mole^{-1}.

Group additivity [1,2] predicts that the enthalpy, intrinsic entropy, and heat capacity changes for disproportionation reactions of the type

$$RXXR + SXXS \rightarrow 2\ RXXS \tag{4}$$

should be essentially zero. However, Table 4 lists some disproportionation reactions involving halogens in which the enthalpy of reaction is not zero. Past explanations of deviations from additivity have centered around "non-near neighbor interactions", but the magnitude of the energy differences between the *gauche* and *trans* isomers in the 1,2-dihaloethanes [9] make it unlikely that such steric terms can account for the deviations observed in Table 4.

Rodgers and Ford [3,4] had earlier suggested that the deviation found for the first reaction in Table 4 could be due to dipole—dipole and dipole—induced dipole interactions associated with the very polar CF_3 group. Clas-

TABLE 4

Enthalpies of reaction, ΔH_r^0, and net electrostatic interaction energies for five disproportionation reactions

No.	Reaction	ΔH_r^0 (kcal mole^{-1})	ΔU_d (kcal mole^{-1})
1	$CF_3CF_3 + CH_3CH_3 \rightarrow 2\ CF_3CH_3$	−16.1	−17.7
2	$CF_3CF_3 + CH_2ICH_2I \rightarrow 2\ CF_3CH_2I$	−3.6	−2.4
3	$CF_3CF_3 + CH_2BrCH_2Br \rightarrow 2\ CF_3CH_2Br$	−1.5	−1.1
4	$CF_3CF_3 + CH_2ClCH_2Cl \rightarrow 2\ CF_3CH_2Cl$		0.0
5	$CF_3CF_3 + CH_2FCH_2F \rightarrow 2\ CF_3CH_2F$		0.4

sical electrostatic calculations [10] were carried out for this reaction with the results shown in Table 4. The good agreement obtained in these calculations stimulated our interest to test this hypothesis further. The experimental data reported here and in our previous studies [7] have resulted in experimental values for the enthalpy changes in reactions 2 and 3 in Table 4 so that we can now extend the comparison between experiment and calculation to two more reactions.

In these calculations, the CF_3 and CH_3 groups are treated as single resultant dipoles lying along the C—C axis at the midpoint of the projection of the C—X bond length on the C—C axis. The CH_2X groups are also treated as single dipoles but lying along the C—X bond with center at the midpoint of that bond. The polarizability of each dipole is estimated from molar refractivity [11] and is assumed to act only along the dipole axis, i.e. only the parallel component of the polarizability is used. Finally, the 1,2-dihaloethanes were assumed to be in the *trans* configuration. A summary of the initial dipole moments and their polarizabilities are given in Table 5. The calculated dipole—dipole interaction energy for each molecule, U_d, is given in the last two columns of Table 5. This energy is a result of two terms, the first is the electrostatic interaction of the two resultant induced dipoles at

TABLE 5

Data and results for dipole—dipole interaction energy calculations

R	$d_{C—X}$ [a] (Å)	μ_r [b] (D)	α_R [c] ($\times 10^{-24}$ cm^3)	$U_{CF_3—R}$ (kcal mole^{-1})	$U_{R—R}$ (kcal mole^{-1})
$—CF_3$	1.33	1.4	2.3	4.5	4.5
$—CH_3$	1.10	0.4	2.0	−6.4	0.4
$—CH_2I$	2.14	1.19	7.1	1.4	0.7
$—CH_2Br$	1.93	1.38	5.1	2.3	1.2
$—CH_2Cl$	1.78	1.46	4.0	3.0	1.5
$—CH_2F$	1.38	1.4	2.1	3.3	1.7

[a] Distances taken from ref. 13. The C—C distance was taken as 1.52 Å in CF_3CH_3 and 1.54 Å in all others. All C—C—X angles were 110°.

[b] Bond moment from ref. 11.

[c] Polarizability calculated from electron group refractions in ref. 11.

their bond distance, and the second is the work of polarization [10]. The net change in electrostatic interaction energy, ΔU_d, for each reaction has been obtained from these data and is summarized in the last column in Table 4.

Again, the comparison between the experimental values and ΔU_d for the first three reactions in Table 4 is excellent and supports the hypothesis that electrostatic interactions play a significant role in the gas phase thermochemistry of polar compounds. Indeed, Benson and Luria [12] have found that electrostatic interactions may be important in the thermochemistry of hydrocarbons, i.e. non-polar compounds, as well. However, our calculations differ from theirs in that we must include polarization effects directly. This is most likely a result of the very polar and polarizable nature of the halogens.

The good agreement obtained between $\Delta H_r^\circ(298)$ and ΔU_d for reactions 1—3 in Table 4 make it reasonable to assume that $\Delta H_r^\circ(298) \cong \Delta U_d$ for reactions 4 and 5 too. Thus, one can calculate $\Delta H_f^\circ(CF_3CH_2Cl, g, 298) = -176 \pm 1.5$ kcal mole^{-1} based upon $\Delta H_r^\circ \cong 0$, $\Delta H_f^\circ(CF_3CF_3, g, 298) = -320.6$ [14], and $\Delta H_f^\circ(CH_2ClCH_2Cl, g, 298) = -30.7$ [15] kcal mole^{-1}. From reaction 5 of Table 4, one can calculate $\Delta H_f^\circ(CH_2FCH_2F, g, 298) = -107 \pm 2.5$ kcal mole^{-1} based upon $\Delta H_r^\circ \cong 0.4$ and $\Delta H_f^\circ(CF_3CH_2F, g, 298) = -214 \pm 2$ [14] kcal mole^{-1}.

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REFERENCES

1 S.W. Benson and J.H. Buss, J. Chem. Phys., 29 (1958) 546.
2 S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E. O 'Neal, A.S. Rodgers, R. Shaw and R. Walsh, Chem. Rev., 69 (1969) 279.
3 A.S. Rodgers and W.G.F. Ford, Int. J. Chem. Kinet., 5 (1973) 965.
4 W.G.F. Ford, Ph.D. Dissertation, Texas A & M University, 1975.
5 Dan Stull (Ed.), JANAF Thermochemical Tables, U.S. Department of Commerce, PB 168370 and supplements.
6 A.S. Rodgers and M.C.R. Wu, J. Chem. Thermodyn., 3 (1971) 591.
7 E.C. Wu and A.S. Rodgers, J. Phys. Chem., 78 (1974) 2315.
8 E.C. Wu and A.S. Rodgers, Int. J. Chem. Kinet., 5 (1973) 1001.
9 P. Klaboe and J.R. Nielsen, J. Chem. Phys., 33 (1960) 1764.
10 C.J.F. Böttcher, Theory of Electric Polarization, Elsevier, Amsterdam, 1952, p. 147.
11 C.P. Smyth, Dielectric Behavior and Structure, McGraw-Hill, New York, 1955.
12 S.W. Benson and M. Luria, J. Am. Chem. Soc., 97 (1975) 704, 3337, 3342.
13 G.A. Crowder, J. Fluorine Chem., 3 (1973) 125.
14 S.S. Chen, A.S. Rodgers, J. Chao, R.C. Wilhoit and B.J. Zwolinski, J. Phys. Chem. Ref. Data., 4 (1975) 441.
15 D.R. Stull, E.F. Westrum, Jr. and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.