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we find that it fails completely, emphasizing once again the difficulties one encounters in explaining the experimental results. One possibility for extending the scope of the BEBO model to embrace these reactions is to assume that the two parameters of the Sato triplet function, the Morse parameter β , and Si-O electronic dissociation energy, E_{is} , which are interconnected, are dependent on methylation. Taking $E_{\text{is}} = 540$ kJ/mol and $\beta = 2.1 \text{ \AA}^{-1}$ for $\text{O} + \text{SiH}_4$, and $E_{\text{is}} = 520$ kJ/mol and $\beta = 2.25 \text{ \AA}^{-1}$ for $\text{O} + \text{Me}_3\text{SiH}$, (for other parameters see ref 1) one obtains the results presented in Table VI. The trend in the rate constants with methylation can be satisfactorily reproduced but the Arrhenius parameters and kinetic isotope effects are in much worse agreement with the corresponding experimental values than is the

case for the $\text{O} + \text{alkane}$ system.²¹

Finally, it should be mentioned that the peculiar behavior of silanes is not limited toward oxygen atoms; it has also been observed in a diminished form in reactions with H ,¹⁷ OH ,²⁸ SiH_2 ,²⁹ and Me_2Si .³⁰

Acknowledgment. We thank Prof. A. Streitwieser for valuable discussions on the reaction mechanism.

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Kinetics of the Reaction of $\text{CCl}_3 + \text{Br}_2$ and Thermochemistry of CCl_3 Radical and Cation

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The rate constant of the $\text{CCl}_3 + \text{Br}_2 \rightarrow \text{CCl}_3\text{Br} + \text{Br}$ reaction was determined as a function of temperature between 300 and 532 K and fit to an Arrhenius expression: k_1 ($\text{L mol}^{-1} \text{s}^{-1}$) = $(1.8 \pm 0.4) \times 10^8 \exp[(-1.43 \pm 0.29) \text{ kcal mol}^{-1}/RT]$. The reaction was studied in a tubular flow reactor by using laser photolysis to produce the CCl_3 reactant and photoionization mass spectrometry to monitor CCl_3 in time-resolved experiments. Previously published kinetic data were reevaluated to obtain k_{-1} , the rate constant for the reverse reaction, and recent spectroscopic data were used to calculate accurate entropies and heat capacities. The values of k_{-1} , k_1 , and these calculated thermodynamic properties were used in a third law determination to obtain $\Delta H^\circ_{f,298.15}(\text{CCl}_3) = 17.0 \pm 0.6 \text{ kcal mol}^{-1}$ and $\Delta H^\circ_{f,0}(\text{CCl}_3) = 16.7 \pm 0.6 \text{ kcal mol}^{-1}$. This information was combined with spectroscopic data on CCl_3^+ to obtain $\Delta H^\circ_{f,298.15}(\text{CCl}_3^+) = 205.2 \pm 0.6 \text{ kcal mol}^{-1}$ and $\Delta H^\circ_{f,0}(\text{CCl}_3^+) = 203.7 \pm 0.6 \text{ kcal mol}^{-1}$. Bond energies of several relevant compounds and tables of thermodynamic functions for CCl_3 and CCl_3^+ are presented. An improved heat of formation for the CCl_3O_2 radical, $\Delta H^\circ_{f,298.15}(\text{CCl}_3\text{O}_2) = 2.7 \pm 1.1 \text{ kcal mol}^{-1}$, is also reported.

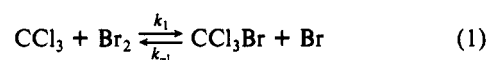
Introduction

The kinetic and thermochemical properties of chlorine-containing free radicals are receiving renewed interest because of their roles in chemical processes of environmental and commercial importance. The trichloromethyl (CCl_3) radical is particularly important. The production of CCl_3 radicals during the burning of industrial waste can account for the CHCl_3 that evolves from incinerators.¹ In the upper atmosphere, CCl_3 radicals formed by photolysis of freons eventually degrade yielding chlorine atoms that accelerate ozone depletion.² The etching of gallium arsenide (GaAs) microelectronic chips with RF discharges in CCl_4 gas may involve reactions of CCl_3 radicals with the semiconductor surface.^{3,4} Accordingly, reliable kinetic and thermochemical information on the CCl_3 radical is needed to accurately model these chemical processes.

During our recent experimental and theoretical investigations of CCl_3 species,^{5,6} we found that published thermochemical values for CCl_3 and CCl_3^+ are inconsistent with the observed properties for these species. For example, the differences between the reported heats of formation of CCl_3 and CCl_3^+ do not predict the adiabatic ionization potential of the CCl_3 radical. Furthermore, although it is now well-established that the CCl_3 radical has a pyramidal structure,^{5,7} the existing tabulations, such as the JANAF tables,⁸ were calculated by presuming that the CCl_3 radical is planar, similar to BCl_3 , and has a harmonic ν_2 umbrella vibration.

As will be shown, this presumption has introduced significant errors into calculated thermochemical properties.

The most commonly cited heat of formation for CCl_3 radical,^{8,9} $\Delta H^\circ_{f,298.15}(\text{CCl}_3) = 19.0 \pm 1 \text{ kcal mol}^{-1}$, is a thermochemical determination by Benson,^{10,11} which is based, in part, on estimated A factors for the reaction



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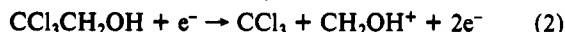
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More recently, Holmes and Lossing¹² reported $\Delta H^\circ_{f,298.15}(\text{CCl}_3) = 18.0 \pm 2 \text{ kcal mol}^{-1}$ based upon the measured appearance threshold of the electron impact process



The thermochemical calculation of $\Delta H^\circ_{f,298.15}(\text{CCl}_3)$ required some estimated information (e.g., $\Delta H^\circ_{f,298.15}(\text{CCl}_3\text{CH}_2\text{OH})$) as well as the assumption that the nascent fragments of reaction 2 are formed at ambient temperature.

The heat of formation of CCl_3^\bullet is still uncertain. Measurements of (1) the ionization potential of the CCl_3 radical,¹³ (2) the appearance potential of CCl_3^+ ,¹⁴⁻¹⁷ and (3) the presence and absence of ion-molecule reactions¹⁸ that produce CCl_3^+ provide a set of conflicting values of $\Delta H^\circ_{f,0}(\text{CCl}_3^\bullet)$ that range between 192 and 209 kcal mol⁻¹.

In this work, we provide new determinations of thermodynamic properties for the CCl_3 radical and cation. We report on determinations of k_1 that we have combined with redetermined values of k_{-1} to obtain the equilibrium constant for reaction 1. From the equilibrium constant at a single temperature, we have used the third law method to derive $\Delta H^\circ_{f,298.15}(\text{CCl}_3)$. Finally, we have combined this $\Delta H^\circ_{f,298.15}(\text{CCl}_3)$ with recent spectroscopic information to obtain more accurate thermochemical properties of CCl_3^\bullet .

Experimental Apparatus and Procedures¹⁹

The experimental facility²⁰ (located at CUA) and its use for studies of this kind²¹⁻²⁴ have been described. Briefly, the apparatus consists of a heatable, coated Pyrex tubular reactor (1.05-cm i.d.) coupled to a photoionization mass spectrometer. Pulsed, unfocused 248-nm radiation from a Lambda Physik EMG 201MSC excimer laser is directed along the axis of the reactor to produce the radical of interest. Gas flows through the tube at $\sim 5 \text{ m s}^{-1}$, which is a rate sufficient to ensure that the sample is completely replaced between laser pulses. In these experiments, the flowing gas mixture contained CCl_3Br (the CCl_3 precursor; typically 0.0001%), Br_2 (in varying amounts), and the carrier gas (He) in large excess (>98%). Gas was sampled continuously through a 0.4-mm-diameter hole (located at the end of a nozzle in the wall of the reactor) and was formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and then mass selected. By use of a multichannel scaler, temporal ion signal profiles were recorded from a short time before each laser pulse to as long as 40 ms following the pulse. Only data from the first 26 ms following the laser pulse were used in the data analysis. Gas sampled during this period originates from the uniformly heated portion of the reactor. Data from 2000–20 000 repetitions of the experiment were accumulated before the data were analyzed. The photoionization energies used in the mass spectrometer were 11.6–11.8

TABLE I: Conditions and Results of Experiments That Measured Rate Constants of $\text{CCl}_3 + \text{Br}_2 \rightarrow \text{CCl}_3\text{Br} + \text{Br}$

$T, ^\circ\text{K}$	$10^5[\text{He}], \text{mol L}^{-1}$	$10^8[\text{Br}_2], \text{mol L}^{-1}$	k_w, s^{-1}	wall coating material ^c	$10^{-7}k_1(T), \text{L mol}^{-1} \text{s}^{-1}$
300	7.99	8.87–151	1.5	HW	2.12
358	7.76	42.2–155	2.0	HW	1.87
358	3.72	18.3–132	1.3	HW	2.34
358	7.77	43.7–176	2.3	PTFE	2.28
399	7.81	47.5–146	1.8	PTFE	2.89
456	7.86	37.7–169	1.7	PTFE	4.00
532	7.94	25.2–126	3.5	PTFE	5.32

^a Temperature uncertainty: $\pm 2 \text{ K}$ (300–358 K), $\pm 4 \text{ K}$ (399–456 K), and $\pm 5 \text{ K}$ (532 K). ^b k_w is the measured first-order CCl_3 heterogeneous loss rate constant (determined with no Br_2 in the reactor). ^c Wall coating materials: HW (halocarbon wax) and PTFE (poly(tetrafluoroethylene)). ^d $k_1(\text{L mol}^{-1} \text{s}^{-1}) = (1.8 \pm 0.4) \times 10^8 \exp[(-1.43 \pm 0.29)\text{kcal mol}^{-1}/RT]$.

TABLE II: Physical Properties of the CCl_3 Radical and Cation Used To Derive Thermodynamic Values

physical property ^a	CCl_3 radical	CCl_3 cation
electronic state	$\tilde{X}^2A_1(C_{3v})$	$\tilde{X}^1A_1(D_{3h})$
symmetry number	6	6
ground-state degeneracy	2	1
$r_e(\text{C-Cl}), \text{\AA}$	1.7142	1.6437
$\angle(\text{Cl-C-Cl}), \text{deg}$	117.1	120.0
$I_{\text{ad}}I_{\text{c}} \times 10^{-14}, \text{g}^3 \text{cm}^6$	31.03 ^b	26.06 ^b
$B_{\text{inv}}, \text{cm}^{-1}$	460	0
$\omega_1(a_1') \text{ C-Cl}_3 \text{ sym str}, \text{cm}^{-1}$	487	544
$\omega_2(a_2'') \text{ umbrella bend}, \text{cm}^{-1}$	0, 1.58, 251, ^c 290, ^c 466, ^c 611, ^c 793, 991, 1205, 1433, 1674, 1927, 2191, 2465, 2749, 3042, 3344, 3654, 3972, 4298, 4631, 4971, 5317, 5671, 6031, 6397, 6769, 7147, 7530, 7919, 8314, 8714, 9119, 9529, 9943, 10363, 10787, 11216, 11650, 12089, 12531, 12978, 13433, 13895, 14364, 14829, 15329, 15893 ^d	509
$\omega_3(e') \text{ deg str}, \text{cm}^{-1}$	898 ^e	1037 ^e
$\omega_4(e') \text{ deg def}, \text{cm}^{-1}$	266	302
zero-point energy, cm^{-1}	1609	1824
IP, eV	8.109	

^a Unless noted otherwise, physical properties are from ref 5. Only values for $^{12}\text{C}^{35}\text{Cl}_3$ species are listed. ^b Calculated from the ab initio structure of ref 5. ^c Experimental energy from ref 5. ^d Unmarked energy levels were calculated from the potential energy surface of ref 5. ^e Infrared Ar matrix data from ref 26.

eV to detect Br_2 and 8.9–9.1 eV to detect CCl_3 .

The gases used were obtained from Aldrich (CCl_3Br , 97%; Br_2 , >99%) and Matheson (He, 99.995%). CCl_3Br and Br_2 were degassed by repeated freeze-pump-thaw cycles and used without further purification. Helium was used as provided.

Experimental Results

Table I lists the experimental conditions used and rate constants obtained for reaction 1. Experiments were conducted under pseudo-first-order conditions with Br_2 in great excess. Initial CCl_3 concentrations were sufficiently low (typically $1 \times 10^{10} \text{ molecule cm}^{-3}$) that the reaction rates between CCl_3 radicals and between CCl_3 and Br were negligible compared to those of reaction 1. Measurements of the exponential decay constants of CCl_3 vs $[\text{Br}_2]$ yielded the rate constant of reaction 1. A typical plot of decay constant k vs $[\text{Br}_2]$ and a recorded CCl_3 decay profile are shown in Figure 1. Additional details of the experimental procedure and tests conducted to verify that reaction 1 was appropriately isolated for direct study are in the report of our prior investigation of the kinetics of the alkyl radical + Br_2 , which was conducted on the same apparatus.²⁵ Rate constants have an uncertainty of $\pm 20\%$ (1 σ).

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TABLE III: Thermochemical Properties of the CCl₃ Radical in JANAF Format at Reference Pressure of 0.1 MPa

T, K	$C_{p,T}^{\circ}$ J (mol K) ⁻¹	S°_{T} J (mol K) ⁻¹	$-[G^{\circ} - H^{\circ}(T_r)]/T$, J (mol K) ⁻¹	$H^{\circ} - H^{\circ}(T_r)$, kJ mol ⁻¹	$\Delta H^{\circ}_{f,T}$, kJ mol ⁻¹	$\Delta G^{\circ}_{f,T}$, kJ mol ⁻¹	log K_f
0	0.000	0.000	infinite	-13.958	69.870	69.870	
100	41.934	245.559	353.761	-10.820	70.727	74.617	-38.980
150	50.014	264.178	320.988	-8.522	70.657	76.217	-26.544
200	55.788	279.401	308.783	-5.876	70.760	78.485	-20.500
250	60.163	292.340	304.251	-2.978	70.937	80.394	-16.799
298.15	63.521	303.235	303.235	0.000	71.128	82.196	-14.402
300	63.636	303.628	303.235	0.118	71.136	82.265	-14.325
350	66.420	313.655	304.029	3.369	71.340	84.103	-12.553
400	68.652	322.676	305.811	6.746	71.539	85.912	-11.220
450	70.443	330.869	308.151	10.223	71.725	87.696	-10.180
500	71.885	338.369	310.807	13.781	71.894	89.461	-9.347
550	73.055	345.277	313.632	17.405	72.044	91.090	-8.652
600	74.011	351.676	316.539	21.082	72.175	92.953	-8.093
700	75.456	363.201	322.404	28.558	72.373	96.400	-7.194
800	76.472	373.347	328.151	36.157	72.502	99.824	-6.518
900	77.210	382.399	333.686	43.842	72.574	103.235	-5.992
1000	77.762	390.564	338.972	51.592	72.596	106.639	-5.571
1100	78.186	397.997	344.006	59.390	72.576	110.046	-5.226
1200	78.519	404.815	348.793	67.226	72.518	113.454	-4.939
1300	78.784	411.111	353.349	75.091	72.426	116.868	-4.696
1400	79.001	416.958	357.686	82.981	72.304	120.292	-4.489
1500	79.179	422.415	361.822	90.890	72.152	123.724	-4.309
1600	79.328	427.530	365.771	98.815	71.973	127.167	-4.152
1700	79.454	432.343	369.546	106.755	71.767	130.622	-4.014
1800	79.561	436.888	373.162	114.706	71.535	134.091	-3.892
1900	79.654	441.192	376.631	122.666	71.276	137.576	-3.783
2000	79.733	445.280	379.962	130.636	70.990	141.071	-3.685

* Derived by using the entropies listed in ref 8 for the reference species.

Calculation of Thermodynamic Properties

Third Law Approach to the Derivation. The equilibrium constant of reaction 1 at a specific temperature, $K_{eq,T} = k_1/k_{-1}$, is related to the Gibbs free energy of reaction 1 and to the reaction enthalpy through the equations

$$\Delta G^{\circ}_{r,T} = -RT \ln (K_{eq,T})$$

$$\Delta H^{\circ}_{r,T} = T\Delta S^{\circ}_{r,T} + \Delta G^{\circ}_{r,T}$$

From the determinations of k_1 and k_{-1} , $\Delta G^{\circ}_{r,T}$ was obtained. Then, by using knowledge of the thermochemical properties of the other reactants and products, $\Delta H^{\circ}_{f,T}(\text{CCl}_3)$ was calculated.

Because the temperature ranges of the studies that measured k_1 and k_{-1} did not overlap significantly, a second law determination of $\Delta H^{\circ}_{f,T}(\text{CCl}_3)$ was not conducted. The temperature range covered by the measurements of k_{-1} was only 35 K. Hence, the measured activation energy of the reverse reaction, E_{-1} , is not expected to be highly accurate.

Calculation of $S^{\circ}_{T}(\text{CCl}_3)$ and $C^{\circ}_{p,T}(\text{CCl}_3)$. The entropy $S^{\circ}_{T}(\text{CCl}_3)$, and heat capacity, $C^{\circ}_{p,T}(\text{CCl}_3)$, of the CCl₃ radical were calculated from knowledge of the CCl₃ structure and vibrational frequencies. Table II lists the molecular parameters adopted in these calculations. The moments of inertia used to calculate the rotational partition function are based upon the ab initio structure of the CCl₃ radical optimized at the UHF/6-31G* level of theory.⁵ To compute the vibrational partition functions of the harmonic modes, we adopted the experimental frequency, ω_3 (e') = 898 cm⁻¹,²⁶ and the scaled ab initio frequencies of the ν_1 (a₁') and ν_4 (e') modes.⁵ Because the ν_2 (a₂'') umbrella mode potential energy surface is far from harmonic, the ν_2 (a₂'') vibrational partition function was calculated by an explicit summation over the first 48 energy levels of the ν_2 umbrella mode manifold (Table II). These energy levels are eigenvalues of the quartic potential that describes the $\nu_2'' = 1, 2, 3, 4$ hot bands observed in the REMPI spectrum of the ¹²C³⁵Cl₃ radical.⁵ We have weighted the translational and rotational contributions to $S^{\circ}_{T}(\text{CCl}_3)$ and $C^{\circ}_{p,T}(\text{CCl}_3)$ by the isotopic distributions of carbon and chlorine and have included the usual entropy contribution for electron spin degeneracy. Since the wavefunctions of the CCl₃

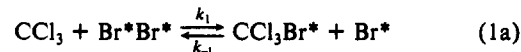
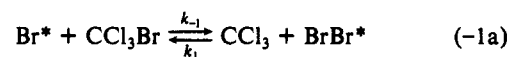
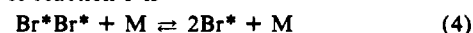
radical and cation belong to the D_{3h} point group, the symmetry number (σ) used to calculate the entropy equals 6.²⁷⁻²⁹

Table III lists the calculated entropies, $S^{\circ}_{T}(\text{CCl}_3)$, and heat capacities, $C^{\circ}_{p,T}(\text{CCl}_3)$, as a function of temperature. These values differ significantly from previous tabulations which were calculated on the assumption that the ν_2 umbrella mode of the CCl₃ radical is harmonic. Calculations based upon a harmonic assumption significantly underestimate $S^{\circ}_{T}(\text{CCl}_3)$. For example, because the $\nu_2'' = 0$, 1 levels lie only 1.6 cm⁻¹ apart, this practical degeneracy adds $\sim R \ln 2$ to the entropy. The tendency of higher $\nu_2 = 2n$, $2n + 1$ vibrational levels to lie close together in energy further enhances the magnitude of $S^{\circ}_{T}(\text{CCl}_3)$. Our calculations yield $S^{\circ}_{450}(\text{CCl}_3) = 330.869 \text{ J mol}^{-1} \text{ K}^{-1}$ (Table III). The JANAF thermochemical table for the CCl₃ radical, which is based upon a harmonic, ν_2 umbrella mode, gives the value, $S^{\circ}_{450}(\text{CCl}_3) = 324.785 \text{ J mol}^{-1} \text{ K}^{-1}$.⁸ In the following calculations, the use of the JANAF values for $S^{\circ}_{T}(\text{CCl}_3)$ and $C^{\circ}_{p,T}(\text{CCl}_3)$ would have caused an underestimate of $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3)$ by $\sim 0.6 \text{ kcal mol}^{-1}$.

Determination of $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3)$. Table IV traces the derivation of $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3)$ from the kinetic data available for reaction 1. The forward rate constant, k_1 , is from the current study (Table I). The reverse rate constant, k_{-1} , is derived from the study of Davidson and Sullivan,³⁰ who measured the rate of exchange of radioactive bromine with CCl₃Br



The mechanism of reaction 3 is



The authors determined k_3 , the overall exchange rate constant. Between 420 and 455 K the exchange rate is described by log

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TABLE IV: Third Law Determination of $\Delta H^\circ_{f,298.15}(\text{CCl}_3)$ Based upon the Equilibrium $\text{CCl}_3 + \text{Br}_2 \rightleftharpoons \text{CCl}_3\text{Br} + \text{Br}$

parameter	data from expt and theory	intermed calcd result	final calcd thermochem prop.
Temperature = 437 K			
$k_1,^a \text{ L (mol s)}^{-1}$	Derivation of Forward Rate (3.5 ± 0.7) $\times 10^7$		
$k_3,^b \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$	Derivation of Reverse Rate (1.54 ± 0.9) $\times 10^{-4}$		
$K_{4p},^c \text{ atm}$	2.38×10^{-18}		
$K_{4c} = K_{4p}/RT, \text{ L}^{-1} \text{ mol}$	6.63×10^{-20}		
$k_{-1} = k_3/K_{4c}^{1/2}, \text{ L (mol s)}^{-1}$		(6.0 ± 3.5) $\times 10^5$	
Calculation of Gibbs Free Energy of Reaction			
$K_{eq,437} = k_1/k_{-1}$		58 ± 30	
$\Delta G_{r,437} = -RT \ln K_{eq,437}, \text{ kcal mol}^{-1}$			$-(3.5 \pm 0.5)$
Heat Capacity of Reaction, cal (mol K) ⁻¹			
$C^\circ_{p,437}(\text{CCl}_3\text{Br})^d$	22.60		
$C^\circ_{p,437}(\text{Br})^e$	4.97		
$C^\circ_{p,437}(\text{Br}_2)^e$	8.81		
$C^\circ_{p,437}(\text{CCl}_3)^e$	16.73		
$\Delta C^\circ_{p,437}$		2.03	
$C^\circ_{p,298.15}(\text{CCl}_3\text{Br})^d$	20.36		
$C^\circ_{p,298.15}(\text{Br})^e$	4.97		
$C^\circ_{p,298.15}(\text{Br}_2)^e$	8.62		
$C^\circ_{p,298.15}(\text{CCl}_3)^e$	15.18		
$\Delta C^\circ_{p,298.15}$		1.53	
$\Delta C^\circ_{p,\text{ave}} = 0.5(\Delta C^\circ_{p,437} + \Delta C^\circ_{p,298.15})$			1.8 ± 0.2
Entropies, cal (mol K) ⁻¹			
$S^\circ_{298.15}(\text{CCl}_3\text{Br})^d$	79.70		
$S^\circ_{298.15}(\text{Br})^e$	41.83		
$S^\circ_{298.15}(\text{Br}_2)^e$	58.64		
$S^\circ_{298.15}(\text{CCl}_3)^e$	72.48		
$\Delta S^\circ_{r,298.15}$		$-(9.6 \pm 0.5)$	
Enthalpy of Reaction, kcal mol ⁻¹			
$\Delta H^\circ_{r,298.15} = \Delta G_{r,437} - \Delta C^\circ_{p,\text{ave}}(T - 298.15) + T[\Delta S^\circ_{r,298.15} + \Delta C^\circ_{p,\text{ave}} \ln(T/298.15)]$			$-(7.6 \pm 0.5)$
Enthalpies of Formation, kcal mol ⁻¹			
$\Delta H^\circ_{f,298.15}(\text{CCl}_3\text{Br})^f$	$-(10.0 \pm 0.3)$		
$\Delta H^\circ_{f,298.15}(\text{Br})^e$	26.74 ± 0.01		
$\Delta H^\circ_{f,298.15}(\text{Br}_2)^e$	7.39 ± 0.03		
Third Law Result, kcal mol ⁻¹			
$\Delta H^\circ_{f,298.15}(\text{CCl}_3) = \Delta H^\circ_{f,298.15}(\text{CCl}_3\text{Br}) + \Delta H^\circ_{f,298.15}(\text{Br}) - \Delta H^\circ_{f,298.15}(\text{Br}_2) - \Delta H^\circ_{r,298.15}$			17.0 ± 0.6

^a From the Arrhenius expression in Table I. ^b From ref 30. ^c From ref 8. ^d From ref 32. ^e From Table III. ^f From ref 11.

$k_3(\text{L}^{1/2} \text{ mol}^{-1/2} \text{ sec}^{-1}) = (-33\,120 \pm 400)/(4.574T) + 12.75 \pm 0.20$. The reverse reaction rate is $k_{-1} = k_3/K_{4c}^{1/2}$ where $K_{4c} = K_{4p}/RT$ and K_{4p} is the equilibrium constant for reaction 4.

The midpoint of the overlapping portions of the temperature range of the current study of k_1 and of the exchange rate study of k_3 is 437 K. Evaluating k_{eq} for reaction 1 at 437 K yields $\Delta H^\circ_{r,298.15} = -7.6 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta H^\circ_{f,298.15}(\text{CCl}_3) = 17.0 \pm 0.6 \text{ kcal mol}^{-1}$ ($71.1 \pm 2.5 \text{ kJ mol}^{-1}$) (Table IV). Table III lists the thermodynamic properties of the CCl_3 radical with the same format and reference states as adopted for the JANAF tables.⁸ The calculation of Table III obtains $\Delta H^\circ_{f,0}(\text{CCl}_3) = 16.7 \pm 0.6 \text{ kcal mol}^{-1}$ ($69.9 \pm 2.5 \text{ kJ mol}^{-1}$).

Table IV also lists the thermochemical values for Br, Br₂, and CCl_3Br used to calculate $\Delta H^\circ_{f,298.15}(\text{CCl}_3)$. We have reevaluated $\Delta H^\circ_{f,298.15}(\text{CCl}_3\text{Br})$ using equilibrium constants measured for Br₂ with CHCl_3 ³¹ and Br₂ with CCl_4 .¹¹ In agreement with Mendenhall et al.¹¹ these calculations gave $\Delta H^\circ_{f,298.15}(\text{CCl}_3\text{Br}) = -10.0 \pm 0.3 \text{ kcal mol}^{-1}$.

Thermodynamic Properties of the CCl_3 Cation. The heat of formation of the CCl_3 cation is calculated by using the relationship

$$\Delta H^\circ_{f,0}(\text{CCl}_3^+) = \Delta H^\circ_{f,0}(\text{CCl}_3) + \text{IP}_a(\text{CCl}_3)$$

The spectroscopic study of Hudgens et al.⁵ reports the adiabatic ionization potential $\text{IP}_a(\text{CCl}_3) = 8.109 \pm 0.005 \text{ eV}$. The calcu-

lation using $\Delta H^\circ_{f,0}(\text{CCl}_3)$ from this study (Table III) and $\text{IP}_a(\text{CCl}_3)$ yields $\Delta H^\circ_{f,0}(\text{CCl}_3^+) = 203.7 \pm 0.6 \text{ kcal mol}^{-1}$ ($852.3 \pm 2.5 \text{ kJ mol}^{-1}$).

Table V tabulates the thermodynamic properties of CCl_3^+ with the same format and reference states as adopted for the JANAF tables.⁸ Because all vibrational modes in the cation are essentially harmonic, the calculation of the vibrational entropy and heat capacity of CCl_3^+ from the molecular parameters listed in Table II is straightforward. To keep Table V consistent with other thermodynamic tables,^{8,32} the thermal electron convention³³ was adopted for the calculation of thermodynamic properties for CCl_3^+ . The thermal electron convention leads to $\Delta H^\circ_{f,298.15}(\text{CCl}_3^+) = 205.2 \pm 0.6 \text{ kcal mol}^{-1}$ ($858.5 \pm 2.5 \text{ kJ mol}^{-1}$).

Discussion

Rate Constant of $\text{CCl}_3 + \text{Br}_2$ Reaction. There have been no prior determinations of k_1 . At room temperature the reaction rate, k_1 , is $\sim 10^3$ times slower than the reaction rates of alkyl radicals with Br₂. This lower reactivity of CCl_3 with Br₂ is manifested

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TABLE V: Thermochemical Properties of CCl₃ Cation in JANAF Format at Reference Pressure of 0.1 MPa

T, K	$C_p^{\circ}(T_r)^{-1}$ J (mol K) ⁻¹	$S^{\circ}(T_r)^{-1}$ J (mol K) ⁻¹	$-(G^{\circ} - H^{\circ}(T_r))/T_r$ J (mol K) ⁻¹	$H^{\circ} - H^{\circ}(T_r)$ kJ mol ⁻¹	$\Delta H^{\circ}_{f,T_r}$ kJ mol ⁻¹	$\Delta G^{\circ}_{f,T_r}$ kJ mol ⁻¹	log K_f
0	0.000	0.000	infinite	-12.939	852.282	852.282	
100	37.946	231.827	331.024	-9.920	854.838		
150	44.742	248.496	300.846	-7.853	855.577		
200	50.852	262.230	289.543	-5.463	856.464		
250	55.949	274.142	285.313	-2.793	857.451		
298.15	60.048	284.358	284.358	0.000	858.458	868.900	-152.242
300	60.192	284.730	284.360	0.111	858.498	868.964	-151.314
350	63.714	294.282	285.113	3.209	859.587	870.622	-129.945
400	66.624	302.986	286.819	6.467	860.708	872.121	-113.898
450	69.018	310.976	289.069	9.858	861.847	873.479	-101.400
500	70.987	318.353	291.637	13.358	862.996	874.709	-91.389
550	72.612	325.197	294.382	16.948	864.153	875.751	-83.180
600	73.957	331.575	297.220	20.613	865.310	876.840	-76.343
700	76.019	343.139	302.973	28.116	867.612	878.580	-65.567
800	77.486	353.391	308.649	35.794	869.899	879.990	-57.463
900	78.559	362.583	314.140	43.599	872.167	881.115	-51.143
1000	79.362	370.903	319.407	51.496	874.416	881.987	-46.075
1100	79.976	378.498	324.440	59.464	876.643	882.637	-41.917
1200	80.456	385.478	329.240	67.486	878.851	883.084	-38.443
1300	80.836	391.933	333.817	75.551	881.037	883.347	-35.497
1400	81.143	397.935	338.184	83.651	883.203	883.446	-32.965
1500	81.394	403.543	342.358	91.778	885.348	883.386	-30.765
1600	81.601	408.802	346.347	99.928	887.472	883.185	-28.836
1700	81.774	413.755	350.169	108.097	889.574	882.852	-27.129
1800	81.920	418.433	353.832	116.282	891.655	882.398	-25.609
1900	82.045	422.866	357.350	124.480	893.712	881.828	-24.245
2000	82.152	427.077	360.732	132.690	895.744	881.149	-23.015

^a Derived by using entropies listed in ref 8 for the reference species.

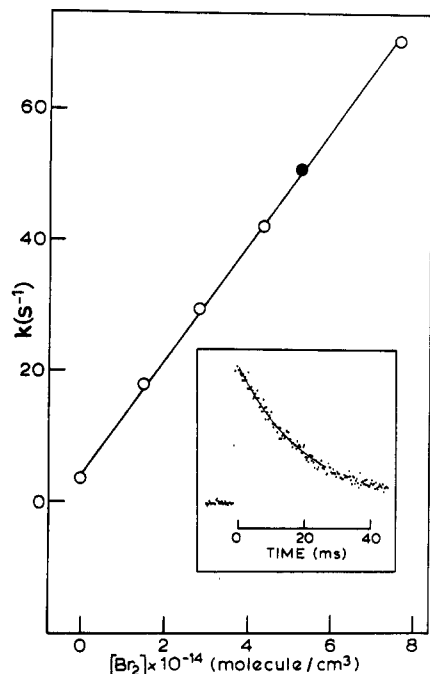
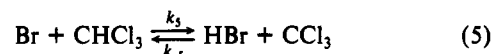


Figure 1. Plot of experimental decay constants of the CCl₃⁺ ion signal (measured at 532 K) vs [Br₂]. Insert is the actual CCl₃⁺ ion signal profile recorded during one of the experiments (solid circle) whose results are plotted here ([Br₂] = 5.26 × 10¹⁴ molecule cm⁻³). The line through the data is that of the experimental function fitted by a nonlinear least-squares procedure. The first-order decay constant (k) for CCl₃⁺ is 51 ± 1 s⁻¹.

in both a lower Arrhenius A factor ($\sim 10^2$ times lower) and a higher activation energy (~ 2 kcal mol⁻¹ higher) than typical values in alkyl radical + Br₂ rate constant Arrhenius expressions. A higher activation energy is expected considering that reaction 1 is only slightly exothermic ($\Delta H^{\circ}_{f,298.15} = -7.6$ kcal mol⁻¹) while alkyl radical + Br₂ reactions are highly exothermic processes (typically $\Delta H^{\circ}_{f,298.15} \approx -25$ kcal mol⁻¹).

Heat of Formation of CCl₃ Radical. This experimental study has obtained a heat of formation of the CCl₃ radical of

$\Delta H^{\circ}_{f,298.15}(\text{CCl}_3) = 17.0 \pm 0.6$ kcal mol⁻¹. The less accurate value of 18 ± 2 kcal mol⁻¹ reported by Holmes and Lossing¹² is in agreement with this heat of formation. A reevaluation of Benson's thermochemical calculation^{10,11} of $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3)$ using the entropies and heat capacities of the CCl₃ radical from Table III also supports our lower value. Benson's estimate of $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3) = 19.0 \pm 1$ kcal mol⁻¹ used data³¹ for the equilibrium at 442 K



The basis of Benson's second law determination of $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3)$ was the result, $\Delta H^{\circ}_{f,442} = E_5 - E_{-5} = 8.3$ kcal mol⁻¹. A prior study of reaction 5 by Sullivan and Davidson³⁰ had reported the Arrhenius rate equation, $\log k_5$ (L mol⁻¹ s⁻¹) = $\log A_5 - E_5/4.574T$, where $\log A_5 = 9.36$ and $E_5 = 9.30$ kcal mol⁻¹. Benson's estimate of E_{-5} requires among other things a calculation of $\Delta S^{\circ}_{f,T_r}$. His calculated value of $S^{\circ}_{442}(\text{CCl}_3)$ is based upon a planar CCl₃ structure that has a harmonic ν_2 umbrella vibration. When Benson's analysis of reaction 5 is repeated with the correct CCl₃ structure, $\Delta S^{\circ}_{f,442}$ decreases from 6.9 to 5.0 cal (mol K)⁻¹, E_{-5} at 442 K increases from 1.0 to 1.9 kcal mol⁻¹, and $\Delta H^{\circ}_{f,442}$ decreases from 8.3 to 7.4 kcal mol⁻¹. The recalculated heat of formation of the CCl₃ radical, $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3) = 18.1 \pm 1$ kcal mol⁻¹, is consistent with our direct determination.

This study's experimental $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3)$ also agrees with the results of ab initio calculations. Melius⁶ has obtained $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3) = 16.6 \pm 2.0$ kcal mol⁻¹ from a BAC-MP4 calculation. Using an atom-equivalent method to calibrate for different substituents, Luke et al.³⁴ simultaneously fit several substituted C₁ compounds at the MP2/6-31G*/HF/3-31G level of ab initio theory and obtained $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3) = 17.9 \pm 1.2$ kcal mol⁻¹.

Table VI lists bond dissociation energies, $\text{DH}^{\circ}_{298.15}$, for compounds in the series of Y-CCl₃ and Y-CH₃. These values are based upon the $\Delta H^{\circ}_{f,298.15}(\text{CCl}_3)$ obtained here and the known values of $\Delta H^{\circ}_{f,298.15}$ of other species.^{8,35-43} The right most column

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TABLE VI: Comparison of Bond Dissociation Energies (kcal mol⁻¹) of Methyl- and Corresponding Trichloromethyl-Containing Molecules

bond	DH° _{298.15} ^a	bond	DH° _{298.15} ^a	DH°(X - CCl ₃) - DH°(X - CH ₃)
H-CCl ₃	93.8 ± 0.6	H-CH ₃	104.8 ± 0.2	-11
F-CCl ₃	104.0 ^b ± 0.8	F-CH ₃	112 ^c ± 1	-8
Cl-CCl ₃	68.9 ± 0.7	Cl-CH ₃	83.5 ± 0.2	-14.6
Br-CCl ₃	53.7 ^d ± 0.6	Br-CH ₃	70.7 ^e ± 0.4	-17
I-CCl ₃	40 ^f ± 5	I-CH ₃	57.0 ^g ± 0.4	-17
O ₂ -CCl ₃	19.7 ^h ± 0.9	O ₂ -CH ₃	32.4 ⁱ ± 0.7	-12.7
CH ₃ -CCl ₃	86.3 ^j ± 0.7	CH ₃ -CH ₃	89.9 ^k ± 0.2	-3.6
CF ₃ -CCl ₃	80 ^{l,m} ± 2	CF ₃ -CH ₃	103.7 ⁿ ± 1.4	-24
CCl ₃ -CCl ₃	69 ^o ± 1.7	CCl ₃ -CH ₃	87.0 ^p ± 0.7	-18

^a Unless noted otherwise, $\Delta H^\circ_{298.15}$ is derived by using values of $\Delta H^\circ_{f,298.15}$ from ref 8. ^b Derived by using $\Delta H^\circ_{f,298.15}$ (CCl₃F) from ref 35. ^c Derived by using $\Delta H^\circ_{f,298.15}$ (CH₃F) from ref 36. ^d Derived by using $\Delta H^\circ_{f,298.15}$ (CCl₃Br) from ref 11. ^e Derived by using $\Delta H^\circ_{f,298.15}$ (CH₃Br) from ref 37. ^f Derived by using an estimated value of $\Delta H^\circ_{f,298.15}$ (CCl₃I) from ref 39. ^g Derived by using $\Delta H^\circ_{f,298.15}$ (CH₃I) from ref 41. ^h Corrected $\Delta H^\circ_{f,298.15}$ of CCl₃ + O₂ → CCl₃O₂ from data of ref 6. See text. ⁱ $\Delta H^\circ_{f,298.15}$ of CH₃ + O₂ → CH₃O₂ from ref 40. ^j Derived by using $\Delta H^\circ_{f,298.15}$ (C₂H₅Cl₃) from ref 38. ^k Derived by using $\Delta H^\circ_{f,298.15}$ (C₂H₆) from ref 42. ^l Derived by using $\Delta H^\circ_{f,298.15}$ (CF₃) from ref 43. ^m Derived by using an estimated value of $\Delta H^\circ_{f,298.15}$ (C₂F₃Cl₃) from ref 38. ⁿ Derived by using $\Delta H^\circ_{f,298.15}$ (CH₃CF₃) from ref 38. ^o Derived by using $\Delta H^\circ_{f,298.15}$ (C₂Cl₆) from ref 42.

of Table VI shows the reduction in bond strength that results when CCl₃ is substituted for CH₃ at one end of the bond. In Table VI, this substitution reduces the average bond energy by ~16 kcal mol⁻¹. The systematic weakening of bonds caused by Cl substitution of this nature was first discussed by Weisman and Benson.⁴⁴

In our earlier study of the equilibrium, CCl₃ + O₂ ⇌ CCl₃O₂, thermochemical calculations were conducted that required values of $S^\circ_f(\text{CCl}_3)$.⁶ The calculated entropy, $S^\circ_{298}(\text{CCl}_3) = 74 \text{ cal mol}^{-1}$

K⁻¹,⁶ was too high due to the use of an incorrect symmetry number, $\sigma = 3$. Repeating the third law calculations of the thermodynamic properties of this equilibrium with the correct $S^\circ(\text{CCl}_3)$ yields $\Delta S^\circ_{f,298.15} = -34.4 \pm 2.3 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $\Delta H^\circ_{f,298.15} = -19.7 \pm 0.9 \text{ kcal mol}^{-1}$, the latter number being the bond enthalpy, $\text{DH}^\circ_{298.15}(\text{O}_2\text{-CCl}_3)$. Our earlier study⁶ also reported the heat of formation of CCl₃O₂ based on the bond enthalpy and $\Delta H^\circ_{f,298.15}(\text{CCl}_3)$. Using the current values of these two thermodynamic properties yields an improved value, $\Delta H^\circ_{f,298.15}(\text{CCl}_3\text{O}_2) = -2.7 \pm 1.1 \text{ kcal mol}^{-1}$.

Heat of Formation of CCl₃ Cation. This study has found that $\Delta H^\circ_{f,0}(\text{CCl}_3^+) = 203.7 \pm 0.6 \text{ kcal mol}^{-1}$ and $\Delta H^\circ_{f,298.15}(\text{CCl}_3^+) = 205.2 \pm 0.6 \text{ kcal mol}^{-1}$. Our value is the first based upon a spectroscopic measurement of $\text{IP}_a(\text{CCl}_3)$.⁵ $\text{IP}_a(\text{CCl}_3)$ was calculated by the extrapolation of several Rydberg series. Because a spectroscopic analysis ascertained that each Rydberg series member used in the calculation of $\text{IP}_a(\text{CCl}_3)$ corresponds to an energy difference between a vibrationless Rydberg state and the vibrationless ground state radical, this measurement of $\text{IP}_a(\text{CCl}_3)$ was affected neither by the initial temperature of the radicals nor by instrument sensitivity. Since all current evidence indicates that $\Delta H^\circ_{f,0}(\text{CCl}_3)$ is now accurately known, the thermodynamic values for CCl₃⁺ presented in Table V appear to be established with a high degree of accuracy.

Prior experimental measurements of $\Delta H^\circ_{f,0}(\text{CCl}_3^+)$ vary between 192 and 209 kcal mol⁻¹.^{13-16,18} These values are derived from the appearance threshold of an ion signal. Accuracy of such threshold measurements often depends upon instrument sensitivity. In addition, the interpretation of threshold measurements can be biased by improper accounting of the vibrational temperature of the target molecules and the fragment ions, by the presence of undetected ion processes, and by the kinetic energy released into the atomic and molecular fragments. We note good agreement with the results of Golovin et al.¹⁵ They reported $\Delta H^\circ_{f,0}(\text{CCl}_3^+) = 204.1 \pm 3 \text{ kcal mol}^{-1}$ based upon photoion-photoelectron measurements of CCl₃⁺ produced from CCl₄ in which the kinetic energy of the fragments was taken into account.

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