J. Phys. Chem. 1992, 96, 5401-5405

Kinetics of the CH_2OH + HBr and CH_2OH + HI Reactions and Determination of the Heat of Formation of CH_2OH

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(Received: December 26, 1991; In Final Form: March 10, 1992)

The reactions between CH_2OH and HBr (1) and CH_2OH and HI (2) have been studied using excimer laser flash photoylsis coupled with time-resolved photoionization mass spectrometry over the temperature range 298–538 K giving $k_1 = 8.7\ (\pm 3.2) \times 10^{-13} \exp\{3.7\ (\pm 1.3)\ \text{kJ mol}^{-1}/RT\}$ and $k_2 = 2.7\ (\pm 0.5) \times 10^{-12} \exp\{4.8\ (\pm 0.5)\ \text{kJ mol}^{-1}/RT\}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$. This kinetic information was combined with rate constants for the reverse reactions taken from the literature to obtain the heat of formation of CH_2OH. Both second law and third law procedures were used to obtain this thermochemical information from these rate constants. Three independent determinations of this heat of formation were in close agreement (differing at most by 1.0 kJ mol^{-1}). The results taken together indicate a CH_2OH heat of formation of −8.9 ± 1.8 kJ mol^{-1} at 298 K. The kinetic behavior of reactions 1 and 2 is comparable to that of other polyatomic free radicals with HBr and HI, radicals which have ionization potentials similar to that of CH_2OH. The significantly higher CH_2OH heat of formation obtained in the current investigation implies a stronger C–H bond energy in CH_3OH than currently believed and has implications in the modeling of the kinetics of methanol pyrolysis and oxidation, both of which are discussed.

Introduction

The increasing interest in methanol as a fuel or fuel additive has stimulated interest in modeling the chemical kinetics of its pyrolysis[1-4] and oxidation.[5-9] Mechanisms of ever-increasing sophistication have been compiled to account for the behavior of this fuel in various oxidation environments. To be used for predictive purposes, these models require both accurate rate constants of key elementary steps and quantitative knowledge of the thermochemistry of the molecules and free radicals involved in the methanol oxidation process.

Of central importance in the oxidation of this fuel is the role of the hydroxymethyl radical, CH_2OH, a principal intermediate.[5-9] Surprisingly, a significant uncertainty (±(8–12) kJ mol^{-1}) persists in the heat of formation of this labile intermediate. To date, determinations of this heat of formation have generally required significant assumptions or estimates of other thermochemical properties to derive its value from the results of experiments. Values of the CH_2OH heat of formation obtained in prior investigations are presented in Table I.

We have been able to obtain accurate heats of formation of selected polyatomic free radicals from our investigations of the kinetics of these radicals in their reactions with hydrogen halides (HCl, HBr, and HI).[16-21] Our measured rate constants, when combined with those for the reverse reactions (obtained either by ourselves or from prior investigations conducted by others), provide enthalpy and/or free energy changes for the overall reactions under study from which the heat of formation of the free radical can be obtained. These studies do not require the use of the assumed or estimated information needed in prior investigations which limited the accuracy of their thermochemical calculations.

We have now investigated the chemical kinetics of two equilibria involving the CH_2OH radical:

$$CH_2OH + HBr \Leftrightarrow CH_3OH + Br \qquad (1)$$

$$CH_2OH + HI \Leftrightarrow CH_3OH + I \qquad (2)$$

Rate constants for the forward reactions were determined as a function of temperature. This information was combined with kinetic information for the reverse reactions taken from the literature to obtain the CH_2OH heat of formation using both second and third law procedures. Very similar values were obtained for this thermochemical property using data from either equilibrium and for both of the data reduction procedures employed. The results indicate that the CH_2OH heat of formation is −8.9 ± 1.6 kJ mol^{-1}. The kinetics of reactions 1 and 2 and the thermochemical calculations used to obtain the CH_2OH heat of formation are presented here.

TABLE I: Determinations of the CH_2OH Heat of Formation (Energies in kJ mol^{-1})[a]

authors	$\Delta H^{\circ}_{f,298K}$
Buckley and Whittle (1962)[b]	<−34
Cruickshank and Benson (1969)[c]	≥−20 ± 8
Golden and Benson (1969, a review)[d]	−26 ± 8
Tsang (1976)[e]	−17.6 ± 8
Holmes and Lossing (1984)[f]	−24 ± 8
Ruscic and Berkowitz (1991)[g]	≤−15.5 ± 3
current study (three determinations)	
reaction 1, third law	−9.1 ± 1.7
reaction 2, second law	−8.7 ± 7.6
reaction 2, third law	−8.1 ± 8.0
recommended	−8.9 ± 1.8[h]

[a] Error limits are those reported by the authors. [b] Reference 10. [c] Reference 11. [d] Reference 12 (a compromise between the Buckley and Whittle and the Cruickshank and Benson determinations). This same value is recommended again by one of the same authors (D.M. G.): McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. [e] Reference 13. [f] Reference 14. [g] Reference 15. [h] Weighted average of three determinations (see text).

Experimental Section

The apparatus used[22] and experimental procedures[16-21] have been described previously. Briefly, gas flowing through the 1.05-cm (or 2.20-cm) i.d. Pyrex tubular reactor contains the CH_2OH source (see below), the second reactant in varying amounts, and an inert carrier gas in large excess (He, >99%). Reaction was initiated by laser photolysis which results in the rapid production of CH_2OH. The flow velocity (≈5 m s^{-1} when the small reactor was used and ≈2 m s^{-1} when the larger one was employed) was adequate to completely replace gases in the reactor between laser pulses.

Gas emerging from a small sampling orifice in the wall of the reactor is formed into a molecular beam and analyzed continuously using a photoionization mass spectrometer (PIMS). CH_2OH was monitored using 10.2 eV ionizing radiation in the PIMS and 11.6–11.8-eV radiation was used to detect HI and HBr.

The decay of CH_2OH was monitored in time-resolved experiments in the absence and presence of the second reactant (whose concentration was varied) to obtain the reaction rate constant. Experiments were conducted under pseudo-first-order conditions (HBr or HI in large excess). Initial conditions were chosen to essentially isolate the reaction of interest. By keeping the initial

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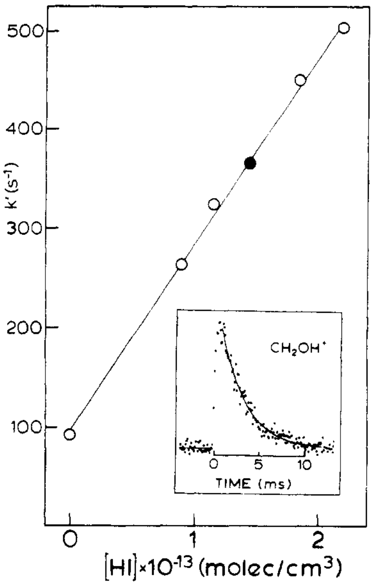

Figure 1. Plot of exponential decay constants of CH_2OH^+ ion signals measured at 298 K vs [HI]. Insert is actual ion signal profile recorded during one of the experiments whose decay constant is plotted here (dark circle). For this experiment, [HI] = 1.50×10^{13} molecules cm^{-3}. The first-order decay constant is 366 ± 10 s^{-1}.

concentration of CH_2OH low (typically $<5 \times 10^{10}$ molecules cm^{-3}), radical–radical and radical–atom reactions had negligible rates compared to the elementary reaction of interest.

CH_2OH was prepared indirectly. Pulsed, unfocused radiation from a Lambda Physik 201 MSC laser (193 or 248 nm) directed along the axis of the tubular reactor was used to photodecompose a Cl atom source:

$$CCl_4 \xrightarrow{193\ \text{nm}} CCl_3 + Cl,\ \text{or} \qquad (3)$$

$$C_2Cl_4 \xrightarrow{248\ \text{nm}} C_2Cl_3 + Cl \qquad (4a)$$

$$ \xrightarrow{\phantom{248\ \text{nm}}} C_2Cl_2 + Cl_2\ (\text{or } 2Cl) \qquad (4b)$$

The laser fluences used were ≈8 mJ cm^{-2} at 193 nm and ≈40 mJ cm^{-2} at 248 nm. Under these conditions the CCl_4 decomposed only slightly, ≈0.1%, the C_2Cl_4 more extensively, ≤2%. The concentration of C_2Cl_4 used was in the range $(2–7) \times 10^{12}$ molecules cm^{-3} and that of CCl_4 in the range $(6–9) \times 10^{13}$ molecules cm^{-3}.

The chlorine atoms produced by photolysis rapidly reacted with CH_3OH to produce only CH_2OH:[23]

$$Cl + CH_3OH \rightarrow CH_2OH + HCl \qquad (5)$$

Adequate CH_3OH concentrations were used, $(2–9) \times 10^{13}$ molecules cm^{-3}, to complete the conversion of Cl to CH_2OH in a time which was short (<1 ms) compared to the half-life of the subsequent reaction of this radical with HBr and HI (typically 10–20 ms).

Initial concentrations of the Cl atom source were chosen to yield low initial concentrations of CH_2OH, $(1–10) \times 10^{10}$ radicals cm^{-3}. Under these conditions reactions of CH_2OH with the other photolysis products and with itself had negligible rates compared to the rate of the reaction under study. CH_2OH was lost by only two reactions, the one of interest and a heterogeneous loss process which was kinetically first order:

$$CH_2OH \rightarrow \text{heterogeneous loss} \qquad (6)$$

Measurements of the CH_2OH exponential decay constant as a function of the concentration of the second reactant yielded the rate constant of interest. A sample measured decay profile of CH_2OH and a plot of the decay constants vs [HI] from one set of experiments to measure k_2 are shown in Figure 1.

Two different wall coatings were employed on the interior surface of the tubular reactor, Halocarbon Wax and poly(tetrafluoroethylene) (PTFE).[24] Use of either yielded the same results.

TABLE II: Reaction Conditions and Rate Constants Obtained in the Study of the CH_2OH + HI and CH_2OH + HBr Reactions

T,[a] K	10^{-16}[He], molecules cm^{-3}	10^{-12}[HX], molecules cm^{-3}	k_6, s^{-1}	wall-coating material[b]	$10^{12}k_{1\text{ or }2}$, cm^3 molecule^{-1} s^{-1}
		CH_2OH + HBr Reaction (k_1)			
298	7.84	27.7–122	38	HW	3.71[c]
300	3.95	33.7–126	42	HW	3.76[c]
302	15.0	21.4–101	81	T	4.24[c]
324	7.87	25.5–91.8	36	HW	3.13[c]
358	7.87	25.2–98.6	39	HW	2.89[c]
365	7.77	27.9–140	61	T	3.25[c]
409	7.70	27.2–128	53	T	2.70[c]
464	7.68	49.8–145	71	T	2.27[c]
538	7.66	15.8–48.1	85	T	2.22[d]
538	7.66	45.8–142	57	T	1.75[c]
$k_1 = 8.7\ (\pm 3.2) \times 10^{-13} \exp\{3.7\ (\pm 1.3)\ \text{kJ mol}^{-1}/RT\}$ cm^3 molecule^{-1} s^{-1}					
		CH_2OH + HI Reaction (k_2)			
298	5.78	8.92–21.9	93	HW	18.7
298	19.8	9.13–21.1	90	HW	19.6
300	3.18	5.46–11.6	29	HW	19.5[c]
319	5.80	11.4–22.1	95	HW	16.6
348	5.82	12.7–31.2	90	HW	14.1
349	5.82	7.59–32.9	99	T	14.1
382	5.84	7.37–33.3	109	T	11.9
422	5.84	8.02–43.4	101	T	10.9
471	5.83	7.75–43.7	104	T	9.64
536	5.83	7.57–47.3	92	T	8.08
$k_2 = 2.7\ (\pm 0.5) \times 10^{-12} \exp\{4.8\ (\pm 0.5)\ \text{kJ mol}^{-1}/RT\}$ cm^3 molecule^{-1} s^{-1}					

[a] Temperature uncertainty: ±1 K (296–422 K), ±3 K (464–538 K), and ±7 K (615–719 K). [b] Wall-coating materials used: HW (Halocarbon Wax) and T (Teflon). [c] CH_2OH produced in 2.20-cm-diameter reactor using 248-nm photolysis of C_2Cl_4 (the Cl source). [d] CH_2OH produced in 2.20-cm-diameter reactor using 193-nm photolysis of CCl_4 (the Cl source). Other experiments were performed using the 1.05-cm-diameter reactor using 193-nm photolysis of CCl_4.

The decay constant (k_6) was typically 100 s^{-1} (when the 1.05-cm.-i.d. reactor was used) and 50 s^{-1} (when the 2.20-cm.-i.d. reactor was used). Rate constants for reaction 1 were determined at 6 temperatures and those of reaction 2 at 7 temperatures in the range 298–538 K.

Experimental parameters not expected to affect the rate constant determination were varied at selected temperatures. They include the total gas density, the flow velocity, the wall coating, the reactor diameter, the Cl atom source, and the laser photolysis wavelength. The measured rate constants were independent of all of these variables as expected from the two-step mechanism for CH_2OH loss used to reduce the data. The range of conditions used and a summary of the results obtained are presented in Table II. The rate constants vs temperature are plotted in Figure 2.

Some reagents used were obtained from Aldrich (CH_3OH, >99.9%; CCl_4, >99.9%; C_2Cl_4, >99%). Gases were obtained from Matheson (He, 99.995%, HBr, 99.8%; HI, 98%). The reagents mentioned were degassed using freeze–pump–thaw cycles and used without further purification. Helium was used as provided. The HBr and HI were repeatedly distilled to remove traces of H_2, Br_2, and I_2 and then stored in dark Pyrex bulbs. The purified HBr and HI were checked frequently for signs of additional decomposition, and the purification procedure was repeated if evidence of this process was found.

Thermochemical Calculations

The CH_2OH heat of formation was obtained from the measured forward and reverse rate constants of reactions 1 and 2. Both a second law calculation (based on the Arrhenius activation energies of both the forward and reverse rate constants of reaction 2) and third law calculations (based on measured rate constants at a single temperature and *calculated* entropies of reactants and products of both reactions 1 and 2) were performed.

Detailed examples of the kind of thermochemical calculations presented below have been published in connection with our prior investigations of the thermochemistry of other free radicals,[15–17] and hence the current calculations are described here only briefly. Error limits reported below are estimates or calculations of 1σ values.

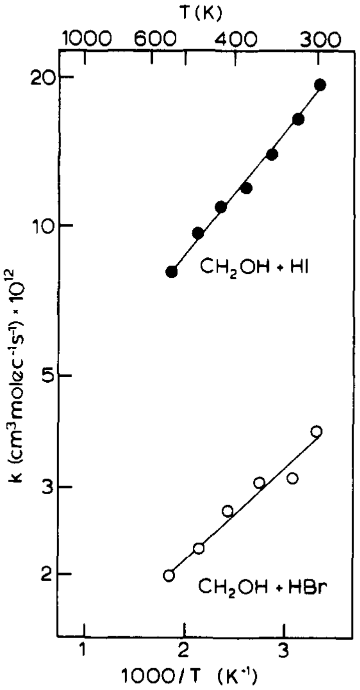

Figure 2. Semilog plot of measured rate constants vs 1000/T. The lines fitted through the plotted points by linear least-squares analysis were used to obtain the Arrhenius parameters for k_1 and k_2 given in Table II.

Thermochemistry of Reaction 1. Only a third law determination of the heat of formation of CH_2OH was done because reliable kinetic information on the reverse reaction is available only at one temperature. Buckley and Whittle studied the photobromination of methanol, extensively at 349 K but only to a limited degree at 367 K.[10] Enough primary data were available in their paper to recalculate k_{-1} at 349 K using their published results. Current knowledge of Br atom recombination rate constants needed to reduce the data was employed. Careful attention was paid to the composition of the gas mixture used by Buckley and Whittle to calculate an appropriate third-order Br + Br + M rate constant at 349 K. The recalculated value of k_{-1} at this temperature, $(1.03 \pm 0.28) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, is surprisingly close to the originally reported value obtained from their Arrhenius expression for k_{-1}, $(1.08 \pm 0.28) \times 10^{-16}$.

(1) The free energy change of reaction 1 at 349 K was obtained from the equilibrium constant for reaction 1, $K_1 = k_1/k_{-1}$. k_1(349 K) comes from our Arrhenius expressions for k_1 (Table II) and k_{-1} (349 K) from the study of Buckley and Whittle (see above):

$$\Delta G^\circ_{349} = -R \times 349 \times \ln\,[(3.12 \pm 1.14) \times 10^{-12}/(1.03 \pm 0.28) \times 10^{-16}] = -29.9 \pm 1.3 \text{ kJ}$$

(2) The free energy change at 298 K was obtained from ΔG°_{349} (from (1) above), ΔS°_{298} for the reaction (obtained using published calculated molar entropies[25]), and tabulated heat capacities of reactants and products of reaction:[25]

$$\Delta G^\circ_{298} = -32.0 \pm 1.3 \text{ kJ} \qquad \Delta S^\circ_{298} = -39.3 \pm 3.0 \text{J K}^{-1}$$

(3) The enthalpy change of reaction 1 (ΔH°_{298}) was obtained from the information in (1) and (2), and finally the heat of formation of CH_2OH from this result and the known heats of formation of the other reactant and the products of this reaction (CH_3OH, HBr, and Br):[25]

$$\Delta H^\circ_{298} = -43.7 \pm 1.6 \text{ kJ}$$

$$\Delta H^\circ_{f,298}(CH_2OH) = -9.1 \pm 1.7 \text{ kJ mol}^{-1}$$

Thermochemistry of Reaction 2. (*1*) *Second Law Calculation.* Cruickshank and Benson studied the iodination of methanol from which they obtained determinations of k_{-2} between 547 and 630 K.[11] The Arrhenius expression they report is $k_{-2} = 10^{11.5\pm0.7} \exp(-26 \pm 1.8 \text{ kcal mol}^{-1}/RT)$ L mol^{-1} s^{-1}. The values we obtained for k_2 were combined with this information to obtain the CH_2OH heat of formation using both second law and third law procedures.

(a) The temperature ranges of our study and that of Cruickshank and Benson do not overlap. In the second law calculation, rate constants and activation energies for the forward and reverse reactions are required at a single temperature. We have selected the midpoint of the temperature range of the Cruickshank and Benson study (586 K) as this temperature. This choice was made to obtain the highest accuracy possible in the rate constant and activation energy of reaction −2 which has a large activation energy. Reaction 2 has a very low activation energy, and extrapolating the Arrhenius expression for k_2 to this somewhat higher temperature adds little uncertainty to its value and Arrhenius activation energy.

The enthalpy change for reaction 2 at 586 K is obtained directly from the difference of Arrhenius activation energies for the forward and reverse reactions:

$$\Delta H^\circ_{586} = -4.8\ (\pm 0.5) - 108.6\ (\pm 7.5) = -113.4 \pm 7.5 \text{ kJ}$$

(b) The free energy change at 586 K was obtained from the equilibrium constant:

$$\Delta G^\circ_{586} = -RT \ln\,(k_2/k_{-2}) = -R \times 586 \ln\,(7.35 \times 10^{-12}/1.09 \times 10^{-19}) = -87.8 \pm 7.8 \text{ kJ}$$

(c) The reaction entropy change at this same temperature was derived from the above information:

$$\Delta S^\circ_{586} = (\Delta H^\circ_{586} - \Delta G^\circ_{586})/586 \text{ K} = -43.7 \pm 18.6 \text{ J K}^{-1}$$

(d) Using tabulated heat capacities[24] for reactants and products, ΔH°_{586} and ΔS°_{586} were corrected to yield their values at 298 K:

$$\Delta H^\circ_{298} = -112.0 \pm 75 \text{ kJ} \qquad \Delta S^\circ_{298} = -40.3 \pm 18.6 \text{ J K}^{-1}$$

(e) Finally, using the known molar heats of formation and entropies of HI, CH_3OH, and I,[24] the values of these same properties for the CH_2OH radical were obtained from the reaction variables:

$$\Delta H^\circ_{f,298}(CH_2OH) = -8.7 \pm 7.6 \text{ kJ mol}^{-1}$$

$$S^\circ_{298}(CH_2OH) = 254 \pm 19 \text{ J K}^{-1} \text{ mol}^{-1}$$

(2) Third Law Calculation. (a) The entropy change for reaction 2 at 298 was determined using calculated molar entropies for reactants and products:[24]

$$\Delta S^\circ_{298} = -41.4 \pm 3.0 \text{ J K}^{-1}$$

(b) The free energy change at 298 K was obtained from the value at 586 K (see above), the entropy change at 298 K in 2a, and tabulated heat capacities for reactants and products of reaction 2:[24]

$$\Delta G^\circ_{298} = -100.3 \pm 7.9 \text{ kJ}$$

(d) The reaction enthalpy at 298 K is obtained from the functions obtained in 2a and 2b:

$$\Delta H^\circ_{298} = \Delta G^\circ_{298} + 298\Delta S^\circ_{298} = -112.6 \pm 7.9 \text{ kJ}$$

Again, using the known heats of formation of HI, CH_3OH, and I,[25] the value for the heat of formation of CH_2OH was obtained from ΔH°_{298}:

$$\Delta H^\circ_{f,298}(CH_2OH) = -8.1 \pm 8.0 \text{ kJ mol}^{-1}$$

The results of all these thermochemical calculations are included in Table I.

Discussion

Kinetics of Reactions 1 and 2. There are no prior reported values of the rate constants of reactions 1 and 2. The magnitudes of k_1 and k_2 and the small yet significant negative activation energies found for these rate constants (≈ -4 kJ mol^{-1}) are both consistent with what we[16-19,20] and now others[28,29] have observed for other exothermic reactions of polyatomic free radicals with the hydrogen halides. The CH_2OH + HI reaction rate constant is faster (by a factor between 4 and 8) and has a slightly more negative activation energy than the $CH_2OH + HBr$ reaction. These differences are very similar to those observed in the case of other reactions of polyatomic free radicals with HBr and HI.[16-18,20,21]

We have found that for a homologous series of these exothermic reactions ($R + HX$), a linear free energy relationship exists with the ionization potential of the free radical (IP).[21] Linear plots of the logarithm of the room-temperature rate constant (the measure of the free energy of activation) vs IP for a series of $R + HX$ reactions have now been published.[21] The room-temperature rate constants of reactions 1 and 2 comply well with the linear free energy relationship established by the alkyl radicals plus HBr and HI reaction rate constants, respectively.

Thermochemistry of CH_2OH. The three separate determinations of the CH_2OH heat of formation obtained from the kinetic studies of two different equilibria involving this radical are extremely close in value, differing at the most by 1.0 kJ mol^{-1}. This fact strongly supports the result obtained and the stated accuracy of our final recommended value, -8.9 ± 1.8 kJ mol^{-1}, which is based on a weighted average of the three determinations. The largest weight was given to the more accurate third law determination using kinetic data from reaction 1.

The two heats of formation for this radical obtained from the kinetic studies of reaction 2, while in close agreement with the determination obtained from the study of reaction 1, have significantly larger uncertainty limits (±8 vs ±1.5 kJ mol^{-1}). We have chosen to still include these latter two determinations (with reduced weighting) in determining the recommended CH_2OH heat of formation because we strongly suspect that these larger error estimates are too high. They derive almost entirely from the large uncertainty limits in the Arrhenius parameters of k_2 (for the $I + CH_3OH$ reaction) reported by Cruickshank and Benson[11] (i.e., ±7.5 kJ mol^{-1} in the activation energy). It is highly probable that these Arrhenius parameters are significantly more accurate than indicated by the authors. This suspicion comes from the fact that the second and third law determinations of the CH_2OH heat of formation, which were both obtained using their Arrhenius expression of k_{-2}, agree so closely. The second law determination provides both the enthalpy of formation and the entropy of CH_2OH. The former can be regarded as being obtained directly from the slope of a straight line through the rate constant data on a modified van't Hoff plot, and the latter from the extrapolated intercept of the same line to infinite temperature ($1/T = 0$). The fact that the extrapolated intercept of the line is very accurate (as indicated by the nearly exact matching of the experimental entropy with its high uncertainty (254 ± 19 J mol^{-1} K^{-1}) with the calculated value (255 J mol^{-1} K^{-1})) is a strong indication that the slope of the line (and hence the CH_2OH heat of formation) is also very accurately determined.

The sources of some of the disagreements between our determination of the CH_2OH heat of formation and those reported in prior studies are easy to identify. The earliest reported values, those of Buckley and Whittle[10] (1962) and of Cruickshank and Benson[11] (1969), are second law determinations in which measured activation energies for the Br (or I) + CH_3OH reactions were combined with *estimated* activation energies for the reverse reactions ($CH_2OH + HBr$ (or HI)) in order to obtain the enthalpy changes of reaction 1 or 2 (directly from the difference in activation energies). The estimated activation energies were in error. Buckley and Whittle[10] estimated the $CH_2OH + HBr$ activation energy to be "greater than 8.4 kJ mol^{-1}" (the measured value is -3.7 kJ mol^{-1}). Cruickshank and Benson[11] assumed that the $CH_2OH + HI$ reaction has an activation energy of 4.2 kJ mol^{-1} (the measured activation energy is -4.8 kJ mol^{-1}). Our determinations of the CH_2OH heat of formation in fact use the rate constant measurements of both Buckley and Whittle and Cruickshank and Benson (for the Br (or I) + CH_3OH rate constants). However in our determinations we use *measured* $CH_2OH + HBr$ (or HI) rate constants (or activation energies) and not estimated values for these properties. We trusted only on the *magnitude* of the $Br + CH_3OH$ rate constant reported by Buckley and Whittle at 349 K, the temperature used in most of their study. We did not trust their reported activation energy for this reaction whose determination relied on just a few additional measurements done at a nearby temperature, 367 K. It is very likely that the additional disparity between our determination of the CH_2OH heat of formation and that of Buckley and Whittle, that which cannot be accounted for by the difference between estimated and measured $CH_2OH + HBr$ activation energies, is caused by the inaccuracy of the activation energy of the $Br + CH_3OH$ reaction obtained by these authors.

The difference between our CH_2OH heat of formation and that reported by Tsang,[13] ≈9 kJ mol^{-1}, cannot be regarded as significant. This difference is essentially within the uncertainty limits Tsang associates with his value, ±8 kJ mol^{-1}. Our two values lie within the overlapping error limits from both determinations.

The difference between our CH_2OH heat of formation and that reported by Holmes and Lossing[14] is more significant, ≈15 kJ mol^{-1}. Their determination is based on measurement of fragmentation thresholds of electron bombardment processes, those which produce an ion and CH_2OH as a neutral fragment, e.g.

$$CH_3CH(OH)CH_2OH \rightarrow CH_2OH + CH_3CHOH^+ \quad (7)$$

The measured thresholds were combined with estimates or reported determinations of the heats of formation of the parent molecule and the ionic fragment to obtain the heat of formation of CH_2OH. It is our opinion that the estimated error suggested by Holmes and Lossing for a determination of the heat of formation of a neutral fragment formed during such a process, ±8.4 kJ mol^{-1} (or 0.09 eV), is too low. The threshold determination alone would be expected to have an uncertainty of at least this magnitude. When the uncertainties in the heats of formation of the precursor molecule and the fragment ion are included in an error analysis, an overall uncertainty in the CH_2OH heat of formation derived by such an experiment of 12–15 kJ mol^{-1} would seem more appropriate.

Most recently, Ruscic and Berkowitz combined two threshold determinations of ionic processes to obtain an upper limit for the CH_2OH heat of formation, $\leq -15.5 \pm 3$ kJ mol^{-1}.[15] A literature-derived upper limit for heat of formation of CH_2OH^+ (obtained from thresholds for the formation of this ion by photodissociative ionization from CH_3OH and C_2H_5OH) was combined with their determination of the adiabatic ionization potential of the radical CD_2OH, 7.54 ± 0.006 eV. This upper limit is 6.6 kJ mol^{-1} (0.07 eV) below our determination, a difference which is just outside the combined uncertainty limits of our two investigations. The error estimate of the Ruscic and Berkowitz determination comes entirely from their suggested error limits of the CH_2OH^+ appearance potential. Their basis for assigning ±3 kJ mol^{-1} (±0.03 eV) error limits to this threshold energy was not explained. We cannot suggest a possible source of the small difference between their upper limit and our determination of the CH_2OH heat of formation.

C–H Bond Energy. The CH_2OH heat of formation obtained in our investigation is higher than previously reported values. This indicates a stronger C–H bond energy (DH($H-CH_2OH$) in CH_3OH (410 kJ mol^{-1}) than is currently thought to exist (393 kJ mol^{-1}) based on Benson and Golden's[12] widely quoted recommended CH_2OH heat of formation. Both of these values indicate that the C–H bond energy in methane (439 kJ mol^{-1}) is weakened when an OH group replaces a hydrogen atom in methane. However the results of our investigation show that this weakening is less than previously believed (a reduction of 29 kJ mol^{-1} instead of 45 kJ mol^{-1}).

Implications in Modeling of Methanol Combustion. In the combustion of C/H as well as C/H/O fuels, the principal fate of important polyatomic free-radical intermediates is loss by pyrolysis or by oxidation. In methanol combustion, CH_2OH is a principal intermediate, and important properties of the combustion of this alcohol determined the relative importance of these two processes:[5-9,30]

$$CH_2OH \rightarrow CH_2O + H \quad (8)$$

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2 \quad (9)$$

Reaction 8 leads to chain branching (since the H atoms which are produced react largely with O_2 to produce two new free radicals, $H + O_2 \rightarrow OH + O$). On the other hand, reaction 9 yields the relatively unreactive hydroperoxyl radical, and hence, in some circumstances, is regarded as a chain-terminating process. The rate constant for reaction 8 has never been measured, and in combustion models, k_8 is typically derived from the presumed thermochemistry of the overall reaction and some information on the kinetics of the reverse process. It is apparent from the results of the current investigation that the thermochemistry of CH_2OH has been in error. The heat of formation is 17 kJ mol^{-1} above the commonly used value recommended by Golden and Benson,[12] a value derived from indirect studies in which erroneous assumptions were made (discussed above). Substituting the new, directly determined CH_2OH heat of formation for the old value increases k_8 nearly an order of magnitude (a factor of 8) at 1000 K when calculated in the same manner, i.e., from kinetic information on the reverse reaction and the heats of formation of reactants and products. Future use of the current thermochemistry for CH_2OH in modeling studies of the oxidation of methanol will significantly enhance the importance of the pyrolysis of CH_2OH over its oxidation.

Summary

The kinetics of the $CH_2OH + HBr$ (and HI) reactions have been characterized. Both reactions are relatively rapid and have small negative activation energies. The kinetic behavior is not unlike that of the isoelectronic $C_2H_5 + HBr$ (and HI) reactions which have been studied previously.[18,19] The rate constants obtained for reactions 1 and 2 were combined with those for the reverse reactions obtained from the chemical literature to obtain the heat of formation of CH_2OH. Three separate determinations are in close agreement supporting the recommended value and the suggested uncertainty limits, -8.9 ± 1.8 kJ mol^{-1} (at 298 K). Explanations for the disagreements between this determination and prior reported values were provided or suggested. The implications of this significantly higher CH_2OH heat of formation on the C–H bond energy in methanol and in the modeling of the combustion of methanol were discussed.

Acknowledgment. Support for this research was provided by the National Science Foundation, Chemistry Division, under Grant CHE-9102038. We thank Dr. Irene R. Slagle for her advice, help and assistance. J.A.S. thanks the Natural Science Council of the Academy of Finland and the Finnish Cultural Foundation for fellowships.

Registry No. HBr, 10035-10-6; HI, 10034-85-2; methanol, 67-56-1; hydroxymethyl, 2597-43-5.

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An Infrared Laser Study of the O(^{3}P) + CS_2 Reaction

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(Received: December 30, 1991; In Final Form: March 16, 1992)

The reaction of ground-state oxygen atoms with carbon disulfide was studied using time-resolved diode laser spectroscopy. CO and OCS products were detected under vibrationally relaxed conditions in order to directly obtain the product branching ratios. Results indicate that the OCS + S channel contributes 8.5 ± 1.0% to the total reaction rate, and CO + S_2 contributes 3.0 [illegible] 1.0%. The undetected CS + SO channel contributes the balance. In addition, the energy disposal dynamics into the ν_1 antisymmetric stretch vibrational mode of OCS was measured. We determine an upper limit of 0.47 ν_1 quanta per OCS product molecule. This result is consistent with a nonstatistical mechanism in which the carbon–oxygen bond length changes very little as the reaction proceeds from the transition state to products, and most of the reaction exoergicity is deposited into other degrees of freedom.

Introduction

The kinetics and dynamics of oxygen atom reactions are topics of great interest. Atomic oxygen plays a crucial role in both atmospheric and combustion chemistry. Accurate modeling of these processes requires the knowledge of elementary rate constants and product branching ratios. Many previous studies have been devoted to measurements of rate constants of ground-state oxygen atom reactions with numerous small molecules, including CH_2O, CS_2, C_2H_2, C_2H_4, and other hydrocarbons.[1-3] The kinetic data base on O(^{3}P) chemistry is therefore reasonably complete with