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Direct Kinetic Studies of the Reactions Br + CH_3OH and CH_2OH + HBr: The Heat of Formation of CH_2OH

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The chemical equilibrium Br + $CH_3OH \rightleftharpoons$ HBr + CH_2OH (1, −1) has been studied by investigating the kinetics of the forward and reverse reactions. Excimer laser photolysis coupled with Br atom resonance fluorescence detection was used over the temperature range 439−713 K to obtain $k_1 = (3.41 \pm 0.89) \times 10^9 T^{1.5} \exp[-(29.93 \pm 1.47)\ \mathrm{kJ\ mol^{-1}}/RT]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$. The reverse reaction was studied with the fast flow technique, in the temperature range 220−473 K, using laser magnetic resonance for monitoring the CH_2OH radicals. Thus, $k_{-1} = (1.20 \pm 0.25) \times 10^{12} \exp[(3.24 \pm 0.44)\ \mathrm{kJ\ mol^{-1}}/RT]$ was obtained. The kinetic results were compared with available literature data and possible causes of the deviations were discussed. Kinetic information on the foward and back reactions was combined to obtain the heat of formation for CH_2OH. Both second-law and third-law procedures were used in the derivations, giving a recommended value of $\Delta_f H^\circ_{298}(CH_2OH) = -16.6 \pm 1.3\ \mathrm{kJ\ mol^{-1}}$, which corresponds to the C−H bond dissociation energy of $DH^\circ_{298}(H-CH_2OH) = 402.3 \pm 1.3\ \mathrm{kJ\ mol^{-1}}$. These thermochemical data obtained from kinetic equilibrium studies agree within the error limits with current photoionization mass spectrometric and *ab initio* theoretical results.

1. Introduction

The importance of an accurate knowledge of the thermochemistry of free radicals lies in the fact that thermochemical kinetic estimation is sometimes the only possibility of obtaining rate constants or branching ratios for reactions of reactive intermediates that are used in modeling of combustion and atmospheric processes. An example for this is provided by the competing reactions of the hydroxymethyl radical, CH_2OH,

$$CH_2OH + M \rightarrow CH_2O + H + M$$

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2$$

which occur in methanol combustion, where the decomposition step leads to chain branching (via reaction H + $O_2 \rightarrow$ OH + O), while the oxidation reaction causes termination (since unreactive HO_2 is formed, which may decay without propagating the chain). Lacking experimental rate constants for CH_2OH decomposition, an error in the heat of formation may easily lead to an over- or underestimation of the decomposition relative to the oxidation process.

The major source of the heat of formation for polyatomic free radicals has been the investigation of the kinetics of halogenation reactions of the type

$$X + RH \rightleftharpoons HX + R$$

where X = Cl, Br, or I. In most of the early studies of this kind, the reaction enthalpy was obtained as the difference of the measured activation energy for the forward reaction and an assumed activation energy for the reverse one.[1−4] The activation energy assumed in these determinations was 8 ± 4 and 4 ± 4 kJ $\mathrm{mol^{-1}}$ for R + HBr and R + HI reactions, respectively. The heats of formation derived for the alkyl free radicals in halogenation studies were about 10−15 kJ $\mathrm{mol^{-1}}$ lower than those obtained from the investigation of bond dissociation and radical combination processes.[5,6]

In recent direct studies of the alkyl radical + hydrogen halide reactions, negative activation energies were determined.[7−14] With these negative activation energies, higher heats of formation were obtained, which essentially resolved the discrepancies in the alkyl radical heats of formation existing between the results of halogenation and dissociation−combination studies.

However, significant uncertainties still exist in the thermochemistry of oxygen-containing free radicals, among which important oxidation intermediates are found. One of these is the hydroxymethyl free radical, for which heats of formation of around −9 kJ $\mathrm{mol^{-1}}$ were obtained in kinetic equilibrium studies,[15−17] while photoionization mass spectrometric determinations[18−21] appear to support a value that is lower by 6−10 kJ $\mathrm{mol^{-1}}$. In an attempt to resolve this problem, we have investigated the chemical equilibrium

$$Br + CH_3OH \rightleftharpoons HBr + CH_2OH \qquad (1, -1)$$

by direct kinetic techniques. Rate constants for both the forward and the reverse reactions were determined in wide temperature ranges that partly overlap. Carefully selected thermochemical data were used to derive the heat of formation for CH_2OH from our own kinetic results and to re-evaluate data available from the literature.

2. Experimental Section

Kinetic studies of reaction 1 were conducted at a laser flash photolysis/resonance fluorescence (LP/RF) facility in Budapest.

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The reverse reaction, i.e. reaction −1, was studied in a fast flow/far infrared laser magnetic resonance (DF/LMR) apparatus in Göttingen.

The apparatus and methodology applied in the LP/Br atom resonance fluorescence experiments were of the standard type, which are documented well in the literature (see, for example, refs 22−25); therefore, only special features of the experimental technique are discussed here.

The reactor was made of stainless steel and heated electrically. The reaction temperature was measured in the middle of the cell with a retractable thermocouple. It was found to be stable within ±2 K throughout the temperature range studied. Optical windows were attached to the reactor through water-cooled flanges.

Br atoms were generated by pulsed excimer laser (Lambda Physik LPX 105) photolysis of CF_2Br_2 at 248 nm. The bromine atom resonance radiation was obtained by flowing a premixed Br_2(0.1%)/He mixture through a microwave discharge. The resonance light was slightly focused into the middle of the reactor by two CaF_2 lenses. The resonantly scattered photons were detected by a solar blind photomultiplier (Thorn EMI 9423B) at right angles through a BaF_2 filter ($\lambda \geq 135$ nm). Absorption of the fluorescence light by O_2 was prevented by flowing dry N_2 in front of the photomultiplier tube.

Experiments were carried out under "slow flow" conditions; He was the carrier (buffer) gas. The concentrations of CH_3OH and CF_2Br_2 in the reaction mixture were determined from measurements of the partial flows and the overall pressure. The partial flow rates were determined by measuring the pressure rise in calibrated volumes. The gas flows were regulated by needle valves, and the overall pressure was measured by a precision Bourdon-type pressure gauge (Texas Instruments).

Bromine atom decay signals were detected, digitalized, and transferred to a 386 PC by a 100 MHz digital storage oscilloscope (Gould DSO Model 7404). Typically 500−1000 decays were averaged in the computer.

The FD/LMR technique applied to study the reaction between the hydroxymethyl radical and HBr has been described previously in detail.[26] Various experimental aspects of studies of CH_2OH reactions have also been dealt with.[17,27,28]

Two important modifications were accomplished in the experimental setup compared to that of the analogous CH_2OH + HCl investigations:[17] First, a reactor with thermostating jacket was installed, which allowed the experiments to be carried out below room temperature by circulating cooled methanol from a cryostat. The temperature was constant within ±1 K along the reaction zone.

Secondly, the LMR-spectrometer was mounted with a new, liquid helium cooled Si bolometer (Infrared Laboratories, Model LN-6/C). This resulted in an increased sensitivity of the CH_2OH detection (the new detection limit was less than 1×10^9 cm^{-3}). Consequently, there was no need to apply the $CH_2OH + O_2 \rightarrow HO_2 + CH_2O$ conversion[17,28] to detect the hydroxymethyl radical in the form of hydroperoxyl; the CH_2OH radicals were monitored directly by LMR at a wavelength of 118.8 μm and a magnetic flux density of 0.05 T.[29]

The inner surface of the 3.6 cm i.d. quartz reactor was coated with Teflon and was equipped with a movable injector. The CH_2OH radicals were generated inside the injector by spatially separated consecutive reactions: $F + HCl \rightarrow Cl + HF$ followed by $Cl + CH_3OH \rightarrow CH_2OH + HCl$. This clean source of CH_2OH was tested in separate kinetic investigations[30] and was used in previous studies of other CH_2OH reactions as well.[16,17,27,28]

Gases were used in the experiments as provided by the suppliers: He (99.9999%, Praxair; in the LP/RF studies 99.996%, Matheson), HCl (5% in He 99.9999%, Praxair), F_2 (1% in He 99.999%, Messer-Griesheim). CH_3OH (≥99%, Merck) and CF_2Br_2 (≥98%, Fluka) were degassed by freeze−pump−thaw cycles prior to use. HBr (99.8%, Praxair) was subjected to repeated low-temperature bulb-to-bulb distillations to remove traces of H_2 and Br_2. The distilled HBr was stored at liquid N_2 temperature and was metered into the reactor from the container warmed up to 195 K. The sample was repurified every 3 or 4 days. Purified frozen samples were colorless, and no residual pressure could be detected after freezing. Carefully cleaned glassware was used, and metal parts were entirely excluded from the HBr line that led into the reactor.

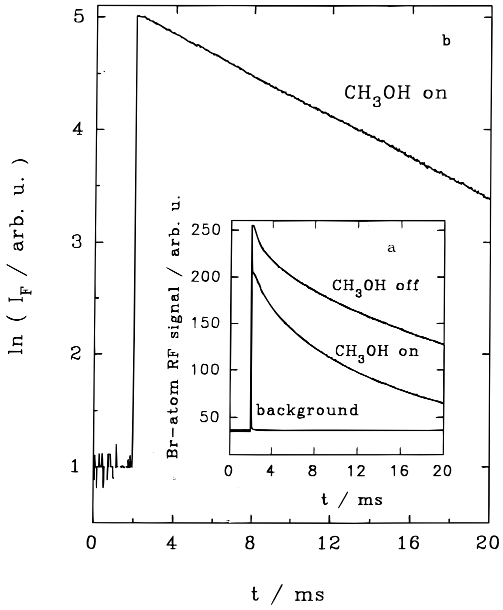

Figure 1. Representative background corrected Br-atom resonance fluorescence decays obtained for reaction 1 at $T = 503$ K.

3. Results and Discussion

3.1. Kinetics of the Reaction of Br + CH_3OH. The kinetics of the bromination equilibrium in the forward direction, i.e. reaction 1, was studied by the excimer laser photolysis/time-resolved Br atom resonance fluorescence detection technique in the temperature range 439−713 K, at 14 temperatures. The total pressure, made up by the reactants and the He bath gas, was typically around 170 mbar. The usual bromine atom concentration was (2−3) × 10^{-12} mol cm^{-3}, and methanol was applied in large excess over Br.

A. Derivation of the Kinetic Parameters. Bromine atom concentration−time profiles were monitored by recording its resonance−fluorescence. The Br atom concentration decays were found of single-exponential character, $I_F = C \exp(-k'_1 t)$, where I_F is the background-corrected resonance fluorescence signal strength, k'_1 is the exponential decay constant, t is the reaction time, and C is a constant. Representative Br atom resonance fluorescence decays are presented in Figure 1 as obtained after averaging multiple oscilloscope traces and are in the form of a semilogarithmic plot. The latter is seen to display linearity with reaction time. The decay constant k'_1, was obtained from the linearized form of the exponential expression given above using linear least squares analysis. Under the pseudo-first-order conditions employed, k'_1 is given by $k'_1 = k_1^{ov}[CH_3OH] + k_d$, where k_1^{ov} is the second-order rate constant of the overall reaction between Br and CH_3OH and k_d is the decay constant due to diffusional loss of Br out of the detection zone. The overall rate coefficient was obtained from

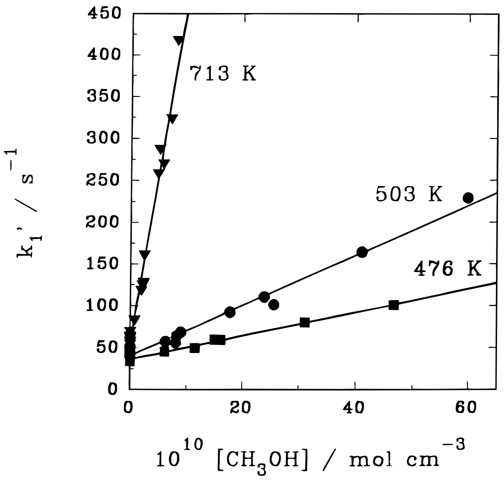

Figure 2. Plot of the pseudo-first-order decay constant, k'_1, *vs* methanol concentration at 476, 503, and 713 K.

the slope of the plot of k'_1 *vs* methanol concentration using a weighted linear least squares fit to the data. Such plots are given for three temperatures in Figure 2. The intercepts of the plots were, under wide experimental conditions, equal to the diffusional loss rate coefficients of bromine atoms measured in the absence of methanol. (Note that in experiments made in the absence of CH_3OH the decay of the RF signal closely followed exponential decay kinetics.) This may be taken as an indication for the unimportance of secondary reactions. Finally, the overall rate coefficient was identified with k_1; that is, it was assumed that the only reaction channel occurring was the H atom abstraction from the methyl group of the methanol molecule (see below).

Since the LP/RF apparatus had been newly installed, it was tested for instrumental errors, i.e. errors arising from temperature and concentration measurements, data acquisition, etc. To assess for instrumental errors, test experiments were performed with ethane. These supplied a rate coefficient of $k(Br+C_2H_6) = (3.9 \pm 0.9) \times 10^9$ cm^3 mol^{-1} s^{-1} at 601 K, which agrees well with the recent value of $(3.4 \pm 1.2) \times 10^9$ cm^3 mol^{-1} s^{-1} reported by Seakins et al. from direct measurements.[24]

To test for the presence of interfering parallel and secondary reactions, the following experimental parameters were varied: (i) the initial Br atom concentration from 1×10^{-13} up to 8×10^{-12} mol cm^{-3} by varying both the laser flash energy and the CF_2Br_2 precursor concentration; (ii) the laser repetition rate between 1 and 4 Hz; (iii) the overall flow rate by a factor of 3; and (iv) the overall pressure between 85 and 527 mbar. None of the tests resulted in a systematic variation of the bimolecular rate coefficient, indicating that the reaction of interest had been kinetically isolated from potential side reactions. (The use of low CH_3OH concentrations is not favorable to the occurrence of side reactions.) The observed invariance makes probable also that the spin–orbit-excited $Br(^2P_{1/2})$, formed in the photolysis of CF_2Br_2 beside the ground state $Br(^2P_{3/2})$, relaxed rapidly to the ground state and did not interfere. (The relaxation rate of $Br(^2P_{1/2})$ is known to be fast even with simple molecules.[31])

The rate of reformation of Br atoms via the reverse reaction −1 increases with decreasing temperature, which may lead to an underestimation of k_1. It can be shown, however, that under standard experimental conditions (even at the lowest temperature of 439 K) the reformation of bromine atom amounts to less than 2% of the rate of the forward, Br-consuming reaction. No correction for such an effect was made.

Reaction conditions used and kinetic results obtained in the study of the Br + CH_3OH reaction are summarized in Table 1.

TABLE 1: Summary of Kinetic Data Obtained in the Laser Flash Photolysis/Resonance Fluorescence Study of the Br + CH_3OH Reaction

T (K)	*P* (mbar)	[CH_3OH] (10^{-10} mol cm^{-3})	k'_1 (s^{-1})	k_1[a] (10^{10} cm^3 mol^{-1} s^{-1})	no. of experiments
439	174	5.45−106.0	52−143	0.84 ± 0.09	24
453	157	5.85−80.0	58−155	1.27 ± 0.05	17
476	154	6.11−46.7	45−101	1.40 ± 0.04	10
491	177	4.49−36.9	65−124	1.92 ± 0.14	13
503	156	6.29−59.9	57−229	3.00 ± 0.10	15
519	176	7.37−54.9	67−229	3.28 ± 0.19	10
535	165	4.39−12.9	65−188	5.74 ± 1.80	9
559	527	3.90−13.9	52−121	6.70 ± 0.67	4
563	85	3.50−50.6	109−487	7.67 ± 0.69	12
581	176	3.85−10.0	80−131	7.93 ± 0.58	10
623	192	6.20−18.7	51−95	16.70 ± 1.07	4
659	152	1.28−17.4	146−512	24.46 ± 1.70	9
674	170	3.72−20.2	160−652	31.61 ± 0.87	16
713	166	0.75−8.17	82−417	40.00 ± 1.34	20

[a] Errors are 1σ statistical uncertainties.

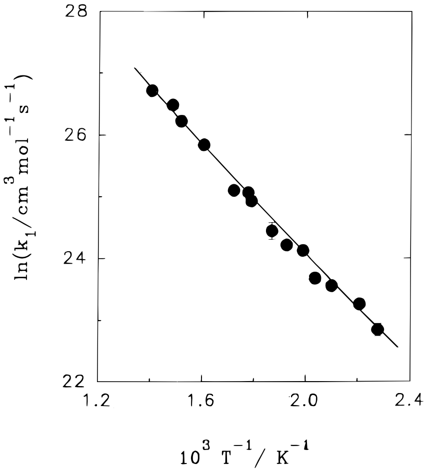

Figure 3. Temperature dependence of the rate coefficient for reaction 1. The solid line corresponds to the three-parameter rate coefficient equation (see text).

The selected CH_3OH concentration ranges were considered to be the best compromises since (i) the use of lower [CH_3OH] would have decreased the contribution of k_1^{ov} to k'_1 and (ii) the use of higher [CH_3OH] was restrained by the fact that CH_3OH is an efficient absorbing medium for the resonance radiation and it is an efficient quencher of the electronically excited Br atoms.

The Arrhenius plot of the rate coefficients is presented in Figure 3. The temperature dependence of the rate coefficient for reaction 1 can be described reasonably well by an Arrhenius equation, as is seen in Figure 3, where the ln k_1 *vs* $1/T$ data lie on or are near to a straight line. A closer inspection of the data reveals, however, that there is a small but definite upward curvature in the Arrhenius graph. The most straightforward explanation of the upward curvature in Figure 3 is that the H atom abstraction from the OH group of the methanol molecule by Br begins to play an increasing role at higher temperature, while its contribution to the overall rate is negligible at lower temperature. It can be shown, however, that this is not the case here: the share of the hydrogen abstraction from the OH site is negligible throughout the temperature range studied. Namely, it is less than 0.4% even at 713 K, which is the highest temperature of the investigation. This estimation is based on the assumption that the activation energy of the H atom abstraction from the OH group is higher than that from the CH_3 group of methanol by 38 kJ mol^{-1} (which is the difference between the heats of formation of CH_3O and CH_2OH), and the preexponential factors are taken equal in the two abstraction reactions. That is, the estimation implies the assumption that both reverse reactions, i.e. $CH_2OH + HBr$ and $CH_3O + HBr$, occur essentially without activation barriers (see sections 3.2 and 3.3). As a conclusion, it can be stated that the slightly curved Arrhenius graph in Figure 3 represents real temperature dependence for the rate coefficient of the elementary reaction 1.

Non-Arrhenius behavior of elementary bimolecular reactions is expected from theory and has been found experimentally in recent years as a result of the application of high-precision experimental techniques and due to the extension of the temperature range of the investigations.[32] Therefore, the temperature dependence of the rate coefficient is preferably described by the three-parameter expression of the form $k(T) = BT^n \exp(-C/RT)$, which is also applied in our data analysis below.

First, all three parameters were varied in a nonlinear least squares fitting procedure, which resulted in the values of 4.23×10^9 cm^3 mol^{-1} s^{-1}, 1.47, and 30.07 kJ mol^{-1} for B, n, and C, respectively. Since the three parameters are strongly correlated, they were obtained from the three-parameter estimation with very large error limits. Therefore, the procedure was repeated with a fixed value of $n = 1.5$, varying only the other two parameters at a time. In this way, the recommended three-parameter rate coefficient expression has been obtained for reaction 1 in the temperature range 439−713 K:

$$k_1 = (3.41 \pm 0.89) \times 10^9 T^{1.5} \times \exp[(-29.93 \pm 1.47)\ \mathrm{kJ\ mol^{-1}}/RT]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

where the error limits represent 1σ statistical uncertainties.

The goodness of fits was found to be almost the same when fixing the n values in the range 1.1−1.8. This can be understood since the sum of squares of residuals is not sensitive[32] to the value of the exponent n. On the other hand, the chi-squared values and statistical tests for the weighted nonlinear fits showed slight but perceptible preference of the three-parameter equation with $n = 1.5$ compared to the two-parameter Arrhenius equation ($\chi^2 = 0.980 \times 10^{20}$ and 1.041×10^{20}, respectively). Similarly, the fitted parameters were obtained with smaller error limits from the estimations in the first case. The choice of $n = 1.5$ has been based on both the result of the unrestricted fits (i.e. $n = 1.47$) and the guidance of theoretical considerations. This procedure is in accordance with the recommendations of using three-parameter kinetic expressions.[32d,e]

Three-parameter rate coefficient expressions with temperature exponents around 1.5 have been found experimentally in numerous other atom + molecule type hydrogen abstraction reactions[33] and have been preferred by critical data evaluations in many cases. For example, the review of Baulch et al.[34] recommends $n = 1.56$ for the reaction $O + CH_4$, which is one of the best known bimolecular reactions of all. Theoretical considerations also support similar n values: Cohen has suggested an estimation method to calculate the temperature exponent by applying the thermochemical kinetics formulation of conventional transition state theory.[35] In this way, n values in the range 1.35−1.50 can be calculated for reaction 1. (In the estimation, anharmonicity was neglected and the activated complex properties were obtained from the results of *ab initio* calculations for similar reactions.[36,37])

The conventional Arrhenius parameters derivable from the experimental kinetic results of the $Br + CH_3OH$ reaction are $A_1 = (2.43 \pm 0.66) \times 10^{14}$ cm^3 mol^{-1} s^{-1} and $E_1 = 37.73 \pm 2.27$ kJ mol^{-1}. These parameters allow direct comparison with the literature data and an assessment of the effect of non-Arrhenius behavior of the CH_2OH heat of formation derived.

B. Comparison with Previous Studies. There has been no prior kinetic investigation of reaction 1 by direct techniques. Buckley and Whittle studied the photobromination chain reaction of methanol by conventional stationary photolysis.[38] Using spectrophotometric analysis to monitor the consumption of Br_2 in the initial stages of the reaction, the authors determined the reaction order and the corresponding overall rate coefficient. Both were found to depend on the chemical composition and pressure of the system. This was attributed to the change in the nature of the termination reaction involving Br atoms, i.e. heterogeneous recombination, homogeneous recombination, or combination with other radicals. The rate coefficients for reaction 1 were derived from experimental results that were obtained under conditions (i.e. at $[CH_3OH]/[Br_2] \approx 1/2$ and in the presence of about 400 Torr CO_2) where the chain termination reaction was assumed to be the homogeneous recombination, $Br + Br + M \rightarrow Br_2 + M$. From temperature dependence studies carried out between 349 and 408 K, with a literature value for the rate coefficient of the assumed termination process, Buckley and Whittle derived a preexponential factor of $A_1 = 7.64 \times 10^{11}$ cm^3 mol^{-1} s^{-1} and an activation energy of $E_1 = 27.36$ kJ mol^{-1} for reaction 1.

The Arrhenius parameters reported by Buckley and Whittle[38] are much smaller than those obtained in the present investigation, and by inference, the rate coefficient values are about 10 times smaller in the 349−408 K temperature range. We note furthermore that the magnitude of the preexponential factor determined in the photobromination study is apparently incompatible with what is currently known from the literature for H atom abstraction reactions of Br atoms.[33]

One possible reason for the discrepancy between the two determinations is that the chain termination mechanism was more complicated than assumed by Buckley and Whittle: wall recombinations and Br + radical reactions may have played a role besides the homogeneous recombination of Br atoms. If this was the case, the derived k_1 values were probably underestimated to an unknown degree. Interestingly, the activation energies of the overall reactions reported by Buckley and Whittle under conditions where different termination mechanisms prevailed agree quite well with each other and also with the activation energy obtained in the present study for reaction 1. (The average of the overall activation energies reported in the photobromination study is 34.3 kJ mol^{-1}.) This can be understood provided that reaction 1 was the rate-limiting step in the photobromination mechanism and the termination reactions that effectively occurred had activation energies close to zero. The significantly lower activation energy of 27.4 kJ mol^{-1} proposed by Whittle and Buckley for reaction 1 was arrived at by the assumption that the termination step had an activation energy of −8.4 kJ mol^{-1}.

The kinetic parameters obtained in the present investigations are in line with those determined recently for the hydrogen abstraction reactions by Br atoms in direct experimental studies.[13,24] The preexponential factor that can be calculated for one abstracted C−H hydrogen atom in methanol, $A_m = 8.1 \times 10^{13}$ cm^3 mol^{-1} s^{-1}, is similar to the corresponding value for a tertiary H atom abstracted from hydrocarbons, $A_t = 9.7 \times 10^{13}$ cm^3 mol^{-1} s^{-1}.[24] The activation energy obtained for reaction 1 resembles that of a secondary H atom abstraction reaction, $E_s = 36.4$ kJ mol^{-1}.[24] Comparison with the $Br + CH_4$ reaction[25] indicates that substitution of an H atom in the methane molecule for an OH group both loosens the tran-

TABLE 2: Summary of Kinetic Data Obtained in the Fast Flow/Laser Magnetic Resonance Study of the CH_2OH + HBr Reaction

T (K)	P (mbar)	[HBr] (10^{-11} mol cm^{-3})	k'_{-1} (s^{-1})	$k_{-1}{}^{a}$ (10^{12} cm^3 mol^{-1} s^{-1})	no. of experiments
220	1.3−2.3	0.49−1.62	95−159	6.71 ± 1.09	5
252	1.5−3.0	0.53−2.08	37−145	6.25 ± 0.48	7
295	1.2−3.0	0.52−2.94	37−131	4.53 ± 0.41	11
373	1.4−3.4	0.43−2.59	19−85	3.24 ± 0.45	6
473	1.6−2.6	0.76−2.18	26−59	2.59 ± 0.54	5

[a] Errors are 1σ statistical uncertainties.

sition state and drastically reduces the activation barrier of the reaction.

3.2. Kinetics of the Reaction of CH_2OH + HBr. Kinetic behavior of the reverse reaction −1 between the hydroxymethyl radical and hydrogen bromide was investigated by the fast flow/LMR technique. Experiments were carried out between 220 and 473 K, at five temperatures. The total pressure, made up with helium, was around 2 mbar. The initial CH_2OH concentration was typically about 2×10^{-13} mol cm^{-3}. The measurements were performed under pseudo-first-order conditions with a more than 20 fold excess of HBr concentration over that of the hydroxymethyl radicals.

A. Derivation of the Kinetic Parameters. The overall rate coefficient, $k_{-1}{}^{ov}$, was determined by monitoring the consumption of CH_2OH radicals with the LMR spectrometer along the reaction distance z, varied by the position of the moveable injector in the reactor tube. Under pseudo-first-order conditions, the exponential decay constant, $k'_{-1} = k_{-1}{}^{ov}[\mathrm{HBr}]$, can be obtained from the expression $-\ln(S^{CH_2OH}_{+HBr}/S^{CH_2OH}_{-HBr}) = k'_{-1}(z/v)$, where $S^{CH_2OH}_{+HBr}$ and $S^{CH_2OH}_{-HBr}$ are the LMR signal strenghts of the hydroxymethyl radical in the presence and absence of HBr, respectively, and v is the average flow velocity.[39] Corrections for the viscous pressure drop and axial diffusion were taken into account by known formulas.[39b] The maximum correction was less than 6%. From k'_{-1}, the bimolecular rate coefficient $k_{-1}{}^{ov}$ is obtained by varying [HBr].

The experimental conditions and kinetic results for reaction −1 are summarized in Table 2. A upper limit for the HBr concentration was set by the attainable linear flow rate, and the lower limit was determined by the rate of wall loss. Representative pseudo-first-order CH_2OH decays at 252 K are presented as semilogarithmic plots in Figure 4a and k'_{-1} *vs* [HBr] data for the same temperature are plotted in Figure 4b. Linear least squares analyses of plots similar to those shown in Figure 4a,b supplied the decay constant k'_{-1} and the bimolecular rate coefficient $k_{-1}{}^{ov}$, respectively, at different temperatures. The $S^{CH_2OH}_{-HBr}$ data as a function of reaction time also gave straight lines. The slopes provided rate coefficients for the heterogeneous wall loss of CH_2OH in the range 9−16 s^{-1}, independent of the reaction temperature and the initial hydroxymethyl concentration. $k_{-1}{}^{ov}$ provides k_{-1} since abstraction of Br is endothermic.

The good sensitivity of the LMR-spectrometer allowed the kinetics of reaction −1 to be studied essentially in isolation from the reaction Br + CH_3OH and the interfering radical−radical reactions. This is indicated by the linearity and zero intercept of the pseudo-first-order plots of the experimental data (see for instance Figure 4a,b). To further assess the significance of possible systematic errors, the initial CH_2OH concentration was varied between 6×10^{-14} and 3.7×10^{-13} mol cm^{-3} and the linear flow rate in the range 9.0−36.5 m s^{-1}. The rate coefficients determined in the experiments were invariant to these changes. Systematic errors due to H_2 and Br_2 contaminations were eliminated by careful purification and handling of HBr as described in the Experimental Section. In situ formation of contaminants on the reactor surface cannot be excluded with absolute certainty, but the short contact time and Teflon wall coating make heterogeneous processes quite improbable. In case of a substantial heterogeneous formation of Br_2, especially in the low-temprature experiments, one would expect some "memory" or hysteresis effect to occur in the CH_2OH wall loss when switching off the HBr flow. No such phenomena were, however, observed.

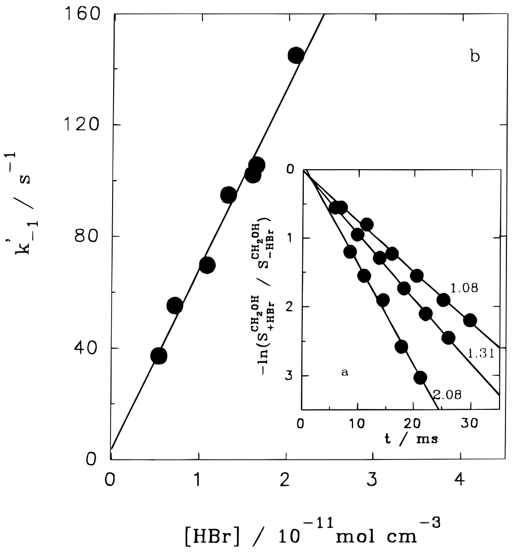

Figure 4. Representative pseudo-first-order plot and hydroxymethyl LMR decay obtained for reaction −1 at T = 252 K. The numbers in inset a are the HBr concentrations in 10^{-11} mol cm^{-3} units.

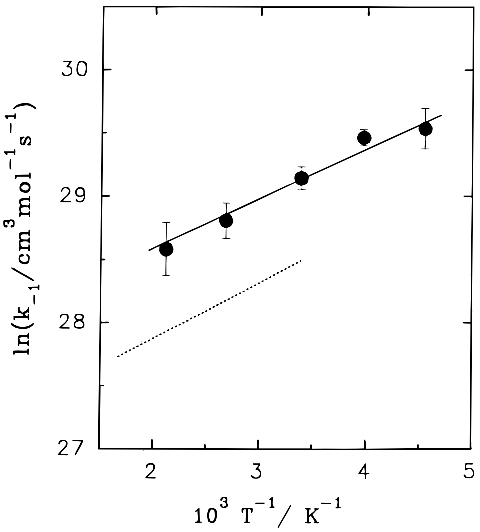

Figure 5. Temperature dependence of the rate coefficient for reaction −1. Full line: this work. Dotted line: from ref 15.

The measured second-order rate coefficients are plotted according to the Arrhenius equation in Figure 5. In the temperature range 220−473 K, the rate equation obtained for reaction −1 by nonlinear least squares analysis of the k_{-1} *vs* *1/T* data is

$$k_{-1} = (1.20 \pm 0.25) \times 10^{12} \times \exp[(3.24 \pm 0.44)\ \mathrm{kJ\ mol^{-1}}/RT]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

where the error limits denote 1σ statistical uncertainties. The Arrhenius preexponential factor and activation energy in the above expression were obtained by weighted nonlinear least squares analyses of the k_{-1} *vs* T data. A smaller weight than the statistical one was given to the k_{-1} value at the lowest temperature, i.e. at 220 K. This can be justified by the small nonzero intercept of the k'_{-1} *vs* [HBr] plot observed at this temperature, which is an indication for the different wall activity in the presence and absence of HBr and consequently also for a reduced accuracy of the bimolecular rate coefficient derived.

B. Comparison with Previous Studies. Seetula and Gutman[15] studied the kinetics of the reaction between CH_2OH and HBr using excimer laser flash photolysis coupled with time-resolved photoionization mass spectrometry. Their experiments were carried out over the temperature range 298−538 K at a few mbar pressure of helium. CH_2OH radicals were generated by excimer laser photolysis of CCl_4 at 193 nm or C_2Cl_4 at 248 nm in the presence of CH_3OH, i.e. by the reaction of Cl + CH_3OH. The rate coefficient of reaction −1 was determined by monitoring the decay of CH_2OH under pseudo-first-order conditions with HBr in large excess. Thus, Seetula and Gutman obtained

$$k_{-1} = (5.23 \pm 1.92) \times 10^{11} \times \exp[(3.7 \pm 1.3)\ \mathrm{kJ\ mol^{-1}}/RT]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$$

The straight line calculated according to this equation is also shown in Figure 5 together with our results.

The most striking feature of the results of both investigations is that the rate coefficients increase with decreasing temperature; that is, the activation energy is negative. Moreover, the activation energies obtained by Seetula and Gutman and by us agree well with each other. That is, the negative temperature dependence is confirmed by different direct experimental techniques over a wide combined temperature range 220−538 K. It appears that by now small yet significantly negative activation energies have been well established for reactions of carbon-centered radicals with HBr and HI. (For a thorough discussion of the subject see the very recent review paper by Berkowitz et al.[40] and references therein.)

It is apparent from Figure 5 that the *A* factors and the rate coefficients obtained in the present investigation are systematically higher by about a factor of 2 than those reported by Seetula and Gutman. No straightforward explanation can be given for this deviation. Similar differences between earlier and more recent direct measurements were found also for the alkyl radical reactions with HBr.[13,24] This was attributed to the presence of a large amount of H_2 in the HBr reactant, which acted as an unreactive diluent and resulted in a systematic underestimation of the R + HBr rate coefficients in the earlier studies. This argument seems to fail, however, in this case since the HBr samples were apparently carefully purified to remove H_2 and Br_2 contaminations in both investigations of the CH_2OH + HBr reaction. No homogeneous side reactions are evident either that could be made responsible for the observed deviations. To reveal the possible reasons, further investigations are required. Such studies should clarify especially the role of heterogeneous processes in both the fast flow and laser flash photolysis systems and the interference caused by secondary photolysis and nonthermalized radicals in the latter case.

C. Mechanism of the CH_2OH + HBr Reaction. Characteristics of reaction −1 are the small negative temperature dependence and the relatively small Arrhenius *A* factor. Such counterintuitive kinetic behavior has been observed experimentally in recent years also for H atom abstraction reactions of other carbon-centered radicals with HBr[13,24] and HI.[11,14] The theoretical interpretation of these observations can be given in terms of a chemical activation mechanism[36,41] in contrast to direct metathesis. For the reaction series R + HX (where R = CH_3, fluorinated CH_3, or C_2H_5, while X = F, Cl, Br, or CH_3) Tschuikow-Roux and co-workers[36,37,42] calculated *ab initio* potential energy surfaces at a high level of theory and derived RRKM rate parameters by the proposed mechanism that reproduced well the experimental findings including the magnitude of the negative activation energy for the reaction of C_2H_5 with HBr[37] (note that C_2H_5 is isoelectronic with CH_2OH). On this basis, it is reasonable to assume that the reaction CH_2OH + HBr also proceeds through the formation of a weakly bound hydrogen-briged complex. The complex is formed in a barrierless process via a loose transition state, TS1, and decomposes into products via a second transition state, TS2, which is tighter and lower in energy compared to TS1. The occurrence of a potential energy well and the lowering of the energy barrier can be attributed to a significant extent to the presence of polar (inductive) effects, a manifestation of which is the linear free energy correlation between ln *k* and the ionization potential, IP, of the free radicals in the reaction series of hydrocarbon radicals with HBr, as shown in Figure 6. This type of correlation has been observed and rationalized in many other reactions involving polar or polarizable reactants (see, for example, refs 43−46).

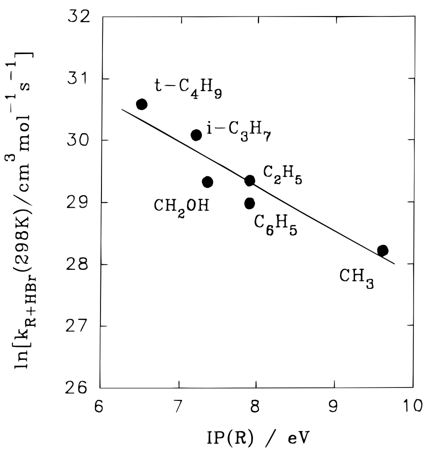

Figure 6. Correlation between ln *k*(298 K) and the ionization potential of the radical R in the reaction series R + HBr.

3.3. Derivation of the Heat of Formation of CH_2OH. The heat of formation of CH_2OH was derived from the rate constants for the forward and reverse reactions by performing both second-law and third-law calculations. Kinetic parameters relating to 450 K were used in all thermodynamic calculations; 450 K is near the midpoint of the overlapping temperature range in the studies of forward and reverse reactions and is also close to the middle of the whole temperature range covered in the investigations.

The sources of thermochemical data (heats of formation, entropies, and heat capacities) of reactants and products required in the calculations were as follows: the JANAF Thermochemical Tables[47] for Br and HBr, the TRC Thermodynamic Tables[48] for CH_3OH, and finally the very recent spectroscopic data and *ab initio* calculations of Johnson and Hudgens[49] for the CH_2OH entropy and heat capacity.

The error limits of the derived thermochemical quantities represent the 1σ level originating from the statistical uncertainties of the kinetic results, as well as the estimated systematic errors of the thermochemical data used in the derivations.

In the *second-law derivation* of the CH_2OH heat of formation, the enthalpy change for reaction 1 was obtained as the difference of the activation energies of the forward and reverse reactions calculated in the following way:

$$\Delta_r H°_{450} = RT^2\left(\frac{\partial \ln k_1}{\partial T} - \frac{\partial \ln k_{-1}}{\partial T}\right) = 38.78 \pm 1.53 \text{ kJ mol}^{-1}$$

Here $RT^2(\partial \ln k_1/\partial T)_{450} = 35.54 \pm 1.47$ kJ mol^{-1} and $RT^2(\partial \ln k_{-1}/\partial T)_{450} = 3.24 \pm 0.44$ kJ mol^{-1} are by definition the empirical or so-called Arrhenius activation energies for reactions 1 and −1, respectively, at 450 K.

The free energy change for the reaction was calculated from the equilibrium constant at 450 K:

$$\Delta_r G°_{450} = -RT \ln(k_1/k_{-1}) = 20.82 \pm 1.98 \text{ kJ mol}^{-1}$$

Next, the entropy change in the reaction was determined:

$$\Delta_r S°_{450} = (\Delta_r H°_{450} - \Delta_r G°_{450})/T = 39.91 \pm 5.56 \text{ J mol}^{-1} \text{ K}^{-1}$$

The molar heat capacities, taken from the indicated literature sources, gave $\Delta_r C°_p = 11.696$ J mol^{-1} K^{-1} (at 298.15 K), 11.072 J mol^{-1} K^{-1} (at 350 K), 10.484 J mol^{-1} K^{-1} (at 400 K), and 9.486 J mol^{-1} K^{-1} (at 450 K), with an estimated error of ±0.3 J mol^{-1} K^{-1}. With these heat capacities, the room temperature thermochemical data for reaction 1 were calculated:

$$\Delta_r H°_{298} = \Delta_r H°_{450} - \int_{298}^{450} \Delta_r C°_p \, dT = 37.10 \pm 1.53 \text{ kJ mol}^{-1}$$

$$\Delta_r S°_{298} = \Delta_r S°_{450} - \int_{298}^{450} \Delta_r C°_p \, d \ln T = 35.32 \pm 5.56 \text{ J mol}^{-1} \text{ K}^{-1}$$

Finally, the heat of formation and the entropy for the CH_2OH radical at 298.15 K were derived from $\Delta_r H°_{298}$ and $\Delta_r S°_{298}$, respectively, using literature thermochemical data for Br, HBr, and CH_3OH:

$$\Delta_f H°_{298}(CH_2OH) = -15.54 \pm 1.56 \text{ kJ mol}^{-1}$$

$$S°_{298}(CH_2OH) = 251.52 \pm 5.57 \text{ J mol}^{-1} \text{ K}^{-1}$$

The *third-law derivation* sets out from the equilibrium constant of reaction 1 at 450 K,

$$K = k_1/k_{-1} = (3.38 \pm 2.02) \times 10^{-3}$$

which yields for the free energy change of the reaction:

$$\Delta_r G°_{450} = -RT \ln(k_1/k_{-1}) = 20.82 \pm 1.98 \text{ kJ mol}^{-1}$$

Then, the reaction entropy of $\Delta_r S°_{450} = 32.58 \pm 1.52$ J mol^{-1} K^{-1}, obtained with the recent entropy for CH_2OH reported by Johnson and Hudgens[49] and the entropies for Br, HBr, and CH_3OH taken from the literature, was used to derive the enthalpy change of reaction 1 at 450 K:

$$\Delta_r H°_{450} = \Delta_r G°_{450} + T\Delta_r S°_{450} = 35.48 \pm 2.09 \text{ kJ mol}^{-1}$$

which gave the room temperature value of

$$\Delta_r H°_{298} = 33.80 \pm 2.09 \text{ kJ mol}^{-1}$$

Finally, from the reaction heat and the thermochemical data for Br, HBr, and CH_3OH, the third-law heat of formation for CH_2OH was derived:

$$\Delta_f H°_{298}(CH_2OH) = -18.84 \pm 2.12 \text{ kJ mol}^{-1}$$

When selecting a *recommended heat of formation,* we prefer to give more weight to the second-law value, because (i) the activation energies used in the second-law calculation both for the forward and for the back reactions are based on investigations made over wide temperature ranges; (ii) the activation energy for reaction 1 is derived from a large number of accurate direct measurements; and (iii) the activation energy obtained for reaction −1 in this work is in excellent agreement with the value determined in another experimental direct study[15] carried out with a different method, while there is no good agreement between the *A* factors reported in these two investigations. Thus, our recommended heat of formation of the CH_2OH radical is the weighted average of the second-law and third-law values, i.e.

$$\Delta_f H°_{298}(CH_2OH) = {}^2/_3\,(-15.54 \pm 1.56) + {}^1/_3\,(-18.84 \pm 2.12) = -16.6 \pm 1.3 \text{ kJ mol}^{-1}$$

which corresponds to a value of the C−H bond dissociation energy of

$$DH°_{298}(H{-}CH_2OH) = 402.3 \pm 1.3 \text{ kJ mol}^{-1}$$

Results of very recent photodissociation dynamic studies[50] provide an accurate value for the heat of formation of methoxy radical, which corresponds to the O−H bond dissociation energy of $DH°_{298}(CH_3O{-}H) = 440 \pm 1$ kJ mol^{-1}. This means that the O−H bond is by almost 40 kJ mol^{-1} stronger than the C−H bond in the methanol molecule:

$$DH°_{298}(CH_3O{-}H) - DH°_{298}\,(H{-}CH_2OH) = 38 \text{ kJ mol}^{-1}$$

Finally, the consequences of the non-Arrhenius representation of the rate coefficient for reaction 1 on the heat of formation of CH_2OH have to be considered. If the Arrhenius parameters, i.e. $A_1 = 2.43 \times 10^{14}$ cm^3 mol^{-1} s^{-1} and $E_1 = 37.73$ kJ mol^{-1}, are used in the derivation of the heat of formation, the third-law result ($\Delta_f H°_{298}(CH_2OH) = -18.3$ kJ mol^{-1}) changes only slightly, but the second-law value ($\Delta_f H°_{298}(CH_2OH) = -13.3$ kJ mol^{-1}) increases by more than 2 kJ mol^{-1} compared to the CH_2OH heat of formation obtained with the non-Arrhenius rate parameters for reaction 1. This indicates that due attention has to be paid to the use of the appropriate kinetic equation for the rate coefficients in the determination of the heat of formation by kinetic equilibrium studies.

3.4. Comparison of the Heat of Formation of CH_2OH with Literature Data. In this section the CH_2OH heat of formation determined in this work is compared with recent literature data obtained in the other kinetic equilibrium studies, in photoionization mass spectrometric investigations, and in *ab initio* calculations. For a review of earlier determinations, reference is made to the papers of Ruscic and Berkowitz.[18,19]

Heat of formation for CH_2OH obtained from kinetic equilibrium studies were reported recently by Seetula and Gutman.[15] They determined rate constants and Arrhenius parameters for reactions of CH_2OH with HBr and HI, respectively, using laser flash photolysis techniques coupled with time-resolved photoionization mass spectrometry. The CH_2OH heats of formation were obtained by combining their data with kinetic parameters for the reverse reactions (i.e. reactions X + CH_3OH, where X = Br and I, respectively), taken from the literature. With a recalculated rate constant at 349 K for the Br + CH_3OH reaction, obtained from the photobromination study of Buckley and Whittle,[38] a third-law value of $\Delta_f H°_{298}(CH_2OH) = -9.1 \pm 1.7$ kJ mol^{-1} was derived. Moreover, the combination of their kinetic results on reaction $CH_2OH + HI$ with the Arrhenius expression reported by Cruickshank and Benson[51] for reaction $I + CH_3OH$ resulted in second-law and third-law heats of formation of -8.7 ± 7.6 and -8.1 ± 8.0 kJ mol^{-1}, respectively.

These heats of formation derived from previous kinetic equilibrium studies appear to be higher by 7−9 kJ mol^{-1} than the results obtained in the present work. A smaller part of the difference comes from the use of different entropies for CH_2OH in the third-law derivations. If the CH_2OH entropy is taken from the recent experimental study and high-quality calculation of Johnson and Hudgens,[49] i.e. if $S°_{298}(CH_2OH) = 244.17$ J mol^{-1} K^{-1} is used, this decreases the third-law values of Seetula and Gutman to -12.7 kJ mol^{-1} ($CH_2OH + HBr$ system) and -12.1 kJ mol^{-1} ($CH_2OH + HI$ system). We believe, however, that much of the remaining difference in the heats of formation obtained in this work and in that of Seetula and Gutman arises from the uncertainty of the kinetic data used in the latter study for the $X + CH_3OH$ reactions.

The rate constant for the reaction of $Br + CH_3OH$ at 349 K was extracted by Seetula and Gutman from the kinetic investigation of the photobromination of methanol,[38] a complex reaction system where the dominant chain termination process was assumed to be the homogeneous recombination of bromine atoms (see section 3.1). Thus, the ± 1.6 kJ mol^{-1} error limit, attached by Seetula and Gutman to the third-law CH_2OH heat of formation derived from the investigation of the $CH_2OH + HBr \rightleftharpoons CH_3OH + Br$ equilibrium, is an obvious underestimation. Combining our kinetic data for reaction 1 with the results of Seetula and Gutman for the reverse reaction yields -15.1 and -20.5 kJ mol^{-1} second-law and third-law heats of formation, respectively, and a 258.5 J mol^{-1} K^{-1} entropy for the CH_2OH radical at 298.15 K. The low third-law heat of formation and the high second-law entropy are mainly due to the low A factor determined by Seetula and Gutman for reaction -1 and used in their derivation of the thermodynamic properties.

The kinetic parameters for the $I + CH_3OH$ reaction were obtained from a study[51] of the thermal reaction of $I_2 + CH_3OH$ that applied the initial rate method. As a consequence of the use of this technique, the statistical errors of the rate parameters were large, which resulted in ± 7.5 and ± 7.8 kJ mol^{-1} error limits for $\Delta_r H°_{586}$ and $\Delta_r G°_{586}$, respectively, of the reaction $CH_2OH + HI \rightleftharpoons CH_3OH + I$. Taking into account also the possible systematic errors in the kinetic measurements and errors of other data used in the derivation, the large error limits indicate that the CH_2OH heat of formation cannot be derived with a reasonable accuracy from the results available for the equilibrium of methanol iodination.

A kinetic equilibrium study of the $CH_2OH + HCl \rightleftharpoons CH_3OH + Cl$ reaction was carried out recently,[16,17] using the fast flow technique, to investigate the kinetics of the forward and reverse reactions in the range 500−812 K and at room temperature, respectively. To obtain the heat of formation of CH_2OH, a long-range extrapolation of the kinetic parameters of the $CH_2OH + HCl$ reaction had to be made and a 0 ± 4 kJ mol^{-1} activation energy was assumed for the reverse reaction in the second-law derivation. Thus, CH_2OH heats of formation of -13.2 ± 5.1 kJ mol^{-1} (revised third-law value, calculated with $S°_{298}(CH_2OH) = 244.17$ J mol^{-1} K^{-1} of Johnson and Hudgens[49]) and -8.5 ± 5.1 kJ mol^{-1} (second-law value) are obtained. These heats of formation are higher than the ones derived in the present work. In particular, the second-law value is high, which, however, becomes smaller if a small negative activation energy is used instead of zero for the reaction $Cl + CH_3OH$. This is not an unreasonable assumption for the reaction of the electronegative Cl atom with the CH_3OH molecule, where the polar effect and the formation of a reaction intermediate may play a significant role in the reaction.

Another group of published heats of formation for CH_2OH stems from mass spectrometric investigations and is based on the equation

$$\Delta_f H°_{298}(CH_2OH) = \Delta_f H°_{298}(CH_2OH^+) - \Delta_I H°_{298}(CH_2OH)$$

where $\Delta_f H°_{298}(CH_2OH^+)$ is the heat of formation of the radical cation CH_2OH^+ and $\Delta_I H°_{298}(CH_2OH)$ is the enthalpy of ionization of CH_2OH at 298 K:

$$\Delta_I H°_{298}(CH_2OH) = IP(CH_2OH) + (H°_{298} - H°_0)_{CH_2OH^+} - (H°_{298} - H°_0)_{CH_2OH}$$

The available adiabatic ionization potentials of CH_2OH are in good agreement with each other. Ruscic and Berkowitz[18] estimated $IP(CH_2OH) = 7.549 \pm 0.006$ eV from the measured value of $IP(CD_2OH) = 7.540$ eV and the zero-point energy difference between CH_2OH and CD_2OH. The IP for CD_2OH was measured by photoionization mass spectrometry[18] (PIMS) and is identical with a very recent value[21] obtained with the same technique. A somewhat higher value of 7.56 eV was also reported for $IP(CH_2OH)$, from PIMS[52] and photoelectron spectroscopic[53] (PES) investigations. *Ab initio* molecular orbital calculations[54] gave a lower ionization potential. Thus, the value of $IP(CH_2OH) = 7.549 \pm 0.006$ eV appears to be a good compromise.

The critical component in these determinations of $\Delta_f H°_{298}(CH_2OH)$ is the heat of formation of the radical cation CH_2OH^+. $\Delta_f H°_{298}(CH_2OH^+)$ values are available from two different sources: (i) the proton affinity (PA) of CH_2O and (ii) the appearance potential (AP) of CH_2OH^+.

The proton affinities of CH_2O found in the literature are rather scattered, and the data are characterized by very wide error limits. The basicity and proton affinity tables of Lias et al.[55] cite an experimental value of $PA(CH_2OH) = 718.0$ kJ mol^{-1} (without error limits indicated), while from the enthalpy change[56] in the proton transfer reaction $CH_2O + HCNH^+ \rightarrow CH_2OH^+ + HCN$, $\Delta_f H°_{298}(CH_2OH^+) = 706.3 \pm 11$ kJ mol^{-1} or $PA(CH_2O) = 708.6 \pm 11$ kJ mol^{-1}; that is, an approximately 10 kJ mol^{-1} lower proton affinity is derived.[21] A recent *ab initio* calculation at the G2 level[57] yielded 711.8 kJ mol^{-1} at 298 K, for which ± 8 kJ mol^{-1} error limit can be estimated. These data show that the uncertainties inherent in the literature data for proton affinities of CH_2O are large and are therefore not suitable for the derivation of an accurate $\Delta_f H°_{298}(CH_2OH^+)$ value.

The heat of formation of CH_2OH^+ can be obtained also from the appearance potential of CH_2OH^+ from CH_3OH, measured by photoionization mass spectrometry. Such determinations have recently been published by Traeger and Holmes[20] and by Ruscic and Berkowitz,[19] yielding $AP(CH_2OH^+/CH_3OH) = 11.578 \pm 0.007$ eV or $\Delta_f H°_{298}(CH_2OH^+) = 708.5 \pm 0.8$ kJ mol^{-1} and $AP(CH_2OH^+/CH_3OH) = 11.649 \pm 0.003$ eV or $\Delta_f H°_{298}(CH_2OH^+) = 715.2 \pm 0.4$ kJ mol^{-1}, respectively. Although the indicated error limits are small, the agreement of the data obtained in the two laboratories is modest. In an earlier work of Refaey and Chupka,[58] $AP(CH_2OH^+/CH_3OH) = 11.67 \pm 0.03$ eV was determined, which appears to support the higher appearance potential suggested by Ruscic and Berkowitz.

Among the physical methods used in the determination of the heat of formation of CH_2OH, preference is given to photoionization mass spectrometry. The ionization potential[18] of CH_2OH and the appearance potential[19] of CH_2OH^+ reported by Ruscic and Berkowitz are selected by us to represent the results obtained with this technique. Thus, using IP(CH_2OH) = 7.549 ± 0.006 eV and AP(CH_2OH^+/CH_3OH) = 11.649 ± 0.003 eV, the heat of formation of $\Delta_fH°_{298}(CH_2OH) = -16.6 \pm 0.9$ kJ mol^{-1} is obtained, which is full agreement with the results of the kinetic equilibrium studies reported in this work. (Note the significant deviation of the AP(CH_2OH^+/CH_3OH) values obtained in different laboratories, which indicates that the actual error limits are considerably larger than those originally suggested. Taking into account the AP results of two recent determinations,[19,20] an error limit of ±2.3 kJ mol^{-1} appears to be more reasonable for the CH_2OH heat of formation derived from PIMS studies.)

Theoretical studies are the third source of the heat of formation of CH_2OH. Curtiss et al.[54] used the Gaussian-2 procedure based on *ab initio* molecular orbital theory, while a modified coupled-pair functional (MCPF) method with a large basis set was applied in the computations of Bauschlicher et al.[59] In both studies a bond dissociation energy of $D_0(H-CH_2OH) = 402.5$ kJ mol^{-1} was suggested, which corresponds to $\Delta_fH°_{298}(CH_2OH) = -10.0$ kJ mol^{-1}.

Very recently two new theoretical heats of formation of the CH_2OH radical were published. One, reported by Espinosa-García and Olivares del Valle,[60] was based on MP4 computations and yielded a value of $\Delta_fH°_{298}(CH_2OH) = -15.6 \pm 1.5$ kJ mol^{-1}. The other theoretical work, carried out by Bauschlicher and Partridge,[61] dealt with the isodesmic reaction

$$CH_3 + CH_3OH \rightarrow CH_4 + CH_2OH$$

in which the number and kind of bonds in both the reactants and products are the same, and therefore many of the errors are expected to cancel. They used higher levels of theory than any of the previous studies. The best heat of reaction in the cc-pVTZ basis set was obtained using the CCSD(T) approach, which gave, with known thermodynamic quantities, $\Delta_fH°_{298}(CH_2OH) = -15.2 \pm 3.5$ kJ mol^{-1}. The most recent theoretical work dealing with the heat of formation of CH_2OH has been carried out by Johnson and Hudgens and is presented in the next paper.[49] All the recent heats of formation are significantly lower than the previous theoretical ones and agree within the error limits with the experimental heat of formation derived from kinetic equilibrium studies in this work as well as with that obtained from PIMS measurements by Ruscic and Berkowitz.[19]

4. Conclusion

In this work, the chemical equilibrium $Br + CH_3OH \rightleftharpoons HBr + CH_2OH$ has been studied by the investigation of the kinetics of the reaction in both directions. Second-law and third-law procedures (with a new entropy[49] for CH_2OH) were used to obtain $\Delta_fH°_{298}(CH_2OH) = -16.6 \pm 1.3$ kJ mol^{-1}. This is in perfect agreement with $\Delta_fH°_{298}(CH_2OH) = -16.6 \pm 2.3$ kJ mol^{-1} derived from photoionization mass spectrometric measurements[19] and agrees well with the results of theoretical studies.[49,60,61]

The agreement between recent kinetic, mass spectrometric, and theoretical results indicates that the discrepancy that seemed to exist between the heats of formation obtained for CH_2OH by different methods has by now practically vanished. The high value for the CH_2OH heat of formation reported in an earlier kinetic equilibrium study[15] of reaction 1 originated from the use of a rate constant for reaction 1 that appears to be too low compared with the present results. The underestimation of k_1 was only partly compensated for by a somewhat low k_{-1} value. In another kinetic study[16,17] of the equilibrium $CH_2OH + HCl \rightleftharpoons CH_3OH + Cl$, the long-range extrapolation of the rate constant for the reaction $CH_2OH + HCl$ and the arbitrary assumption of 0 ± 4 kJ mol^{-1} activation energy for the reverse reaction resulted in a considerable uncertainty in the heat of formation derived for CH_2OH. In addition, the overestimation of the entropy of CH_2OH in both previous kinetic equilibrium studies contributed another 2−3 kJ mol^{-1} to the derived third-law heat of formation.

Methods based on the determination of the difference $\Delta_fH°_{298}(CH_2OH^+) - \Delta_fH°_{298}(CH_2OH)$ formerly appeared to give lower values for the heat of formation of CH_2OH. However, a survey of available literature data shows considerable scatter for this difference, which is mainly due to the uncertainty in $\Delta_fH°_{298}(CH_2OH^+)$. Derivation of $\Delta_fH°_{298}(CH_2OH)$ from the appearance potential of CH_2OH^+ from CH_3OH,[19,20,58] apparently the best source of $\Delta_fH°_{298}(CH_2OH^+)$, indicates a possible range of the heat of formation for CH_2OH, which comprises the value obtained in the present kinetic equilibrium study.

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