

# The Thermochemistry of the Gas Phase Equilibrium $I_2 + CH_4 \rightleftharpoons CH_3I + HI$ and the Heat of Formation of the Methyl Radical<sup>1</sup>

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With the aid of a Cary spectrophotometer, modified for use with high-temperature gas systems, it has been possible to obtain the equilibrium constant for the reaction  $CH_4 + I_2 \rightleftharpoons CH_3I + HI$  at 605, 630, and 667°K. From the measured value at 630°K. of  $K_{eq} = 2.32 \pm 0.09 \times 10^{-4}$  and the known values,  $\Delta S^\circ_{630} = 3.64$  gibbs/mole and  $\Delta C_p^\circ = +0.63$  gibbs/mole,<sup>2a,b</sup> the heat of reaction at 298°K. is found to be  $\Delta H^\circ_{298} = 12.56 \pm 0.13$  kcal./mole. Combining this with known values<sup>2a</sup> of the heats of formation of  $CH_4$ ,  $I_2$ , and  $HI$  yields the value  $\Delta H_f^\circ_{298}(CH_3I(g)) = 3.28 \pm 0.16$  kcal./mole. These results together with the kinetic parameters of Flowers and Benson<sup>3</sup> lead to  $\Delta H_f^\circ_{298}(CH_3(g)) = 34.1 \pm 0.5$  kcal./mole,  $DH^\circ_{298}(CH_3-H) = 104.1 \pm 0.5$  kcal./mole, and  $DH^\circ_{298}(CH_3-I) = 56.3 \pm 0.5$  kcal./mole, in good agreement with recent data on these quantities.

## Introduction

The kinetic parameters and equilibrium constants of reactions of the type  $RH + I_2 \rightleftharpoons RI + HI$  may be conveniently and accurately determined in the temperature range 250 to 400°, even though the extent of reaction is small and the equilibria are well to the left. This is made possible with spectrophotometric techniques. If R is a resonance-stabilized radical such as allyl or benzyl, lower temperatures are used. From the equilibrium constants one can obtain the free energies of formation of the iodides, which are not well known, to better than  $\pm 0.1$  kcal./mole. When the entropy of the iodide is known to  $\pm 0.2$  gibb/mole, this may be used to obtain a value of the heat of formation of the iodide to an accuracy of the order of  $\pm 0.15$  kcal./mole. When the entropy is not known to the above limits, it can be estimated to  $\pm 2$  gibbs/mole or it may be determined by measurement of the equilibrium constant over a reasonable temperature range. In this case the uncertainty in  $\Delta H_f^\circ(RI)$  would be  $\sim 0.8$  kcal. From the heat of formation of the iodide and the kinetic parameters, the heat of formation of the radical R may be determined.

Flowers and Benson<sup>3</sup> have already studied the kinetics of the system where R is  $CH_3$  (starting from  $CH_3I$  and  $HI$ ) and in this work the equilibrium constant for the same system has been measured. In addition we

shall present some kinetic observations which support the rate data of Flowers and Benson.

## Experimental

(a) *Materials.* Phillips research grade methane (99.98% pure) and reagent grade resublimed iodine were used. Matheson anhydrous hydrogen iodide and Eastman methyl iodide, both further purified by distillation under vacuum, were used for calibration purposes. (Dow Corning silicone grease was used on all stopcocks.)

(b) *Apparatus.* Experiments were carried out in a 400-cm.<sup>3</sup> quartz vessel made up of two unequal cylindrical absorption cells with Supersil windows. The larger cylinder, consisting of the bulk of the volume, was about 10 cm. long and 8 cm. in diameter. The smaller cylinder, an appendix on the larger one connected by two 15-mm. diameter tubes, was about 2 cm. long and 3 cm. in diameter. (The end plates were 3-cm. diameter Supersil windows.) The vessel was placed in a uniformly heated and well-insulated aluminum block furnace. The temperature was maintained to within 0.3° during any experiment (as indicated by a copper-constantan thermocouple situated in a well in the larger cylinder of the vessel) by a proportional controller acting upon 10% of the total load. The temperature gradient in the vessel was less than 1°.

The vessel could be isolated from the gas-handling system by a heated stopcock at a point which left a dead space of  $< 5$  cm.<sup>3</sup>. This stopcock and the glass lead into the vessel were kept at  $\sim 140^\circ$ . Gases were admitted to the vessel through an 18-cm.<sup>3</sup> volume (kept at  $\sim 110^\circ$ ) which included a  $\pm 0.1$  p.s.i.d. Pace pressure transducer used as a null device for pressure measurement.

The vessel and oven were placed vertically above the sample compartment of a Cary Model 15 spectrophotometer (modified to have an essentially collimated emergent beam) so that the light beam when deflected upward by  $\sim 90^\circ$  passed through either the smaller or the larger cylinder of the vessel to identical mirrors at the top and then back through the vessel to the sample compartment of the spectrophotometer where it was once again turned by  $\sim 90^\circ$  onto the photomultiplier. Since the light path described above is 100 cm. in length and since the beam diverges by 4°, the mirrors above the vessel were spherical with a 50-cm. focal length to avoid extreme energy losses. (All mirrors were front-surfaced aluminum with thin  $MgF_2$  coating to preserve them.)

The flat mirrors, used to turn the beam out of the sample compartment and to turn the returning beam back on to the photomultiplier, were mounted on a

(1) This investigation was supported in part by Public Health Service Research Grant 5235 from the Air Pollution Division, Public Health Service.

(2) (a) "JANAF Interim Thermochemical Tables," D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1963; (b) E. Gelles and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5259 (1953).

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

moveable triangular block (in a manner which allowed for slight adjustment of their positions relative to the block). Movement of this block, by a rack and pinion arrangement, allowed the reproducible choice of whether the beam traversed the short or long cylinder of the vessel, which differed by a factor of  $\sim 5$  in optical path length.

The sensitivity of the instrument was such as to permit detection of  $10^{-3}$  torr of HI,  $\text{CH}_3\text{I}$ , or  $\text{I}_2$ . At our temperatures this corresponded to  $\sim 3 \times 10^{-8}$  mole/l.

(c) *Procedure.* Before any run the reaction vessel was evacuated to  $10^{-5}$  torr, and the absorbance of the empty cell was recorded at 500, 350, 257, 245, and 235  $m\mu$ . (The 350- $m\mu$  wave length was found to be an optical window for this system and therefore the base line at 350  $m\mu$  served as a reference point whenever lamps or optical paths were changed.)

$\text{I}_2$  was admitted to the reaction system to the desired pressure, determined by nulling the transducer with air whose pressure was measured on a silicone oil manometer. At this point the isolating stopcock was closed and the  $\text{I}_2$  was removed from the remaining 18-cm.<sup>3</sup> volume. (This latter step was to prevent the methane from sweeping more  $\text{I}_2$  into the vessel and to prevent the reaction of small amounts of  $\text{I}_2$  with the stainless steel transducer.) The  $\text{I}_2$  absorption was then recorded at 500, 257, 245, and 235  $m\mu$  using 350  $m\mu$  as a window as described above.  $\text{CH}_4$  was then admitted to the reaction system at the desired pressure, and the isolating stopcock was closed. (Several experiments were performed without an isolating stopcock. It was found that these results were somewhat erratic and seemed to show a dependence on the  $\text{CH}_4$  pressure. This was found to be due to the reaction of HI with the stainless steel transducer.)

The absorbance at the above wave lengths was checked from time to time until it was apparent from the lack of change in absorbance that equilibrium had been reached. At this point the isolating stopcock was opened and the transducer deflection observed to determine if there had been a pressure change during the reaction. Reactants and products were then removed from the vessel and the base lines were recorded once again. (In some runs, after recording the absorbances at equilibrium, more  $\text{CH}_4$  was added and this new mixture was allowed to come to equilibrium before evacuating the vessel. Thus, two values for the equilibrium constant, with two different  $\text{CH}_4$  pressures, could be obtained.)

For calibration purposes HI and  $\text{CH}_3\text{I}$  were admitted to the vessel individually at various pressures and their absorption coefficients were determined at 257, 245, and 235  $m\mu$  for each temperature used (neither absorbs at 500  $m\mu$ ). Beer's law was obeyed to better than 3% for pressures up to 30 torr. (HI and  $\text{CH}_3\text{I}$  could also be calibrated accurately at 225  $m\mu$ , but this is not a useful wave length for these experiments since it was found that the absorption due to  $\text{I}_2$  at 225  $m\mu$  is affected by total pressure.) No other indications of pressure effects were observable with varying pressures of both  $\text{N}_2$  and  $\text{CH}_4$  for  $\text{I}_2$ , HI, or  $\text{CH}_3\text{I}$  at this or any other wave length. Teranishi and Benson,<sup>4</sup> however, have reported such pressure broad-

ening effects in similar studies, but these were undoubtedly due to the sweeping of  $\text{I}_2$  from dead spaces on admitting pressurizing gas into the system.

At equilibrium the  $\text{I}_2$  pressure was directly obtainable from the absorbance at 500  $m\mu$ , the ratio of final to initial absorbance multiplied by the initial pressure yielding the final pressure of  $\text{I}_2$ . The ratio of absorbances at 500  $m\mu$  was also multiplied by the initial  $\text{I}_2$  absorbances at 257, 245, and 235  $m\mu$  to determine the contributions of  $\text{I}_2$  to the final absorbances at these wave lengths.

Equilibrium pressures of HI and  $\text{CH}_3\text{I}$  were then obtained by subtracting the contributions due to  $\text{I}_2$  from the final total absorbance and then distributing the remaining contributions at 257, 245, and 235  $m\mu$  between HI and  $\text{CH}_3\text{I}$ . This distribution involved the solution of three possible sets of two simultaneous equations. These yielded three values for the final pressures of both HI and  $\text{CH}_3\text{I}$ . Since the three values for either component were found to agree to within 3 or 4% in all but one case, the average values were used.

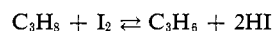
The final  $\text{CH}_4$  pressure was determined by subtracting the pressure of  $\text{CH}_3\text{I}$  from the initial methane pressure.

Equilibrium constants were determined by dividing the product of final  $\text{CH}_3\text{I}$  and HI pressures by the product of final  $\text{I}_2$  and  $\text{CH}_4$  pressures.

In three runs the absorbances at 257 and 225  $m\mu$  were recorded at various time intervals over the first 30% of the reaction and these were used to check the measurements of Flowers and Benson<sup>3</sup> on the kinetics of this system.

## Results

In order to test the apparatus, it was first used to determine the equilibrium constant for the reaction



The equilibrium constant for this system has been carefully measured<sup>5</sup> over the temperature range 308–340°, and the results with this apparatus, obtained at 300 and at 330°, were within  $\sim 10\%$  of Benson and Nangia's values.

The results of the equilibrium measurements using  $\text{CH}_4$  and  $\text{I}_2$ , mostly obtained at 630°K. where the rate of attainment of equilibrium is reasonably rapid (4–15 hr.), are summarized in Table I; the subscript "0" refers to initial pressures while "eq" stands for equilibrium quantities. While, from stoichiometric considerations, the concentrations of  $\text{CH}_3\text{I}$  and HI should be the same at equilibrium, the differences (which, though  $< 0.3$  torr, are certainly real) are unimportant as long as equilibrium is achieved. This is amply demonstrated by the 65-fold variation in the ratio of  $(\text{CH}_3\text{I})_0/(\text{I}_2)_0$ . The over-all  $\text{I}_2$  mass balance was checked by comparing the depletion of  $\text{I}_2$  measured at 500  $m\mu$  with one-half the sum of HI and  $\text{CH}_3\text{I}$  pressures determined from the ultraviolet absorbances. These agree to better than 0.1 torr in most cases with a maximum disagreement of 0.23 torr. The possible presence of small quantities of  $\text{CH}_2\text{I}_2$  was not overlooked. However, from a knowledge of its spectrum, it was estimated that as little as 0.03 torr of  $\text{CH}_2\text{I}_2$  could have been detected in the presence of HI and

(4) H. Teranishi and S. W. Benson, *J. Chem. Phys.*, **40**, 2946 (1964).

(5) P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2770 (1964).

**Table I.** Equilibrium Data for the Gaseous System<sup>a</sup> CH<sub>4</sub> + I<sub>2</sub> ⇌ CH<sub>3</sub>I + HI

Temp., °K.	Time, hr. <sup>b</sup>	[I <sub>2</sub> ] <sub>0</sub>	[CH <sub>4</sub> ] <sub>0</sub>	[I <sub>2</sub> ] <sub>eq</sub>	[CH <sub>4</sub> ] <sub>eq</sub>	[CH <sub>3</sub> I] <sub>eq</sub>	[HI] <sub>eq</sub>	K × 10 <sup>4</sup>
630.1	12.2, 21.5 <sup>c</sup>	7.96	105.1	7.54	104.6	0.451	0.394	2.26
630.2	4, 6.5 <sup>c</sup>	7.96	580.8	7.02	579.7	1.132	0.869	2.42
631.2	10.5	31.8	100.9	31.0	100.1	0.800	0.877	2.26
631.2	11.5	31.8	554.2	29.9	552.3	1.948	1.969	2.32
630.4	6, 21.5 <sup>c</sup>	19.95	59.0	19.52	58.5	0.510	0.425	1.897 <sup>d</sup>
630.1	6.7	19.95	290.8	18.83	289.7	1.187	1.125	2.45
630	18.2	25.7	100.9	24.8	100.2	0.714	1.037	2.98 <sup>d</sup>
629.8	18	36.8	64.6	35.9	64	0.652	0.807	2.28
630.8	6	5.36	599.5	4.55	598.7	0.797	0.779	2.28
666.5	2, 2.5 <sup>c</sup>	22.29	108.2	21.25	107.3	0.855	1.242	4.64
667.2	1.5	22.29	562.5	20.07	560.5	1.958	2.48	4.30
605.6	24, 28.2 <sup>c</sup>	7.77	463.3	7.10	462.6	0.670	0.710	1.45

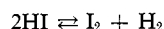
<sup>a</sup> All pressures in torr. <sup>b</sup> Rough measurements showed that times required to establish equilibrium were proportional to [CH<sub>4</sub>]<sup>1/2</sup>. <sup>c</sup> These runs were used to check that equilibrium was established in the expected time by leaving the reaction mixture several hours longer and observing no change in composition. <sup>d</sup> These two values were not used for averaging purposes since they differ by more than 3 standard deviations from the mean value of K<sub>p</sub> at 630°K.

**Table II.** Thermodynamic Data

Temp., °K.	K	ΔG°, kcal./mole	ΔS°, <sup>b</sup> gibbs/mole	ΔH°, kcal./mole	ΔC <sub>p</sub> , <sup>c</sup> gibb/mole	ΔH <sub>298</sub> °, kcal./mole
630.4	2.32 ± 0.09	+10.48 ± 0.05	+3.64 ± 0.2	+12.77 ± 0.13	+0.63	+12.56 ± 0.13
666.9	4.48 <sup>a</sup> ± 0.45	+10.22 ± 0.12	+3.72 ± 0.2	+12.70 ± 0.18	+0.53	+12.59 ± 0.18
605.6	1.45 <sup>a</sup> ± 0.15	+10.64 ± 0.13	+3.60 ± 0.2	+12.82 ± 0.19	+0.63	+12.63 ± 0.19

<sup>a</sup> These values estimated to be good to ±10%. <sup>b</sup> Calculated from JANAF Tables<sup>2a</sup> and Gelles and Pitzer.<sup>2b</sup> <sup>c</sup> ΔC<sub>p</sub>° defined as 1/2 (ΔC<sub>p</sub>°<sub>T</sub> + ΔC<sub>p</sub>°<sub>298</sub>); C<sub>p</sub>° values obtained from JANAF<sup>2a</sup> Tables and Gelles and Pitzer.<sup>2b</sup>

CH<sub>3</sub>I; therefore, the presence of CH<sub>2</sub>I<sub>2</sub> could be disregarded. Hydrogen was unlikely to occur as an impurity since the maximum quantity required to satisfy the equilibrium



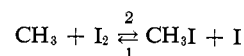
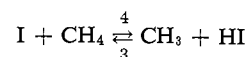
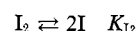
under the conditions of these experiments was ~10<sup>-5</sup> torr.

A reliable estimate of the standard error in K<sub>p</sub> could only be made at 630°, where sufficient data were obtained. A rough estimate of ±10% was placed on values of the error in K<sub>p</sub> at the other temperatures. These equilibrium constants and the thermodynamic data derived from them at each temperature are listed in Table II. Column 5 of this table, ΔH°, was calculated from the observed free energy change and the entropy change computed from the listed entropies.<sup>2a</sup> The enthalpy change at room temperature, ΔH°<sub>298</sub>, shown in column 7 of Table II, was obtained by correcting ΔH for an average specific heat change. This method of measuring ΔH°<sub>298</sub> is extremely accurate, as can be seen from the quoted standard error limits. These errors originated from two sources, the first being the experimental uncertainty in ΔG°, the other being that estimated for the TΔS° term. This latter arose primarily from the uncertainty in the entropy of CH<sub>3</sub>I (estimated by Gelles and Pitzer<sup>2b</sup> to be not greater than ±0.2 gibb/mole). Compared with this, errors in S° for CH<sub>4</sub>, I<sub>2</sub>, and HI are negligible, since the molecular geometry and vibration frequencies for these compounds are very well known.

As a further check of internal consistency of the data of Table II, a van't Hoff plot of log K<sub>p</sub> against 1/T was made and this yielded (from measurement of the slope and intercept) ΔH°<sub>636</sub> = 14.6 ± 2.0 kcal./mole and ΔS°<sub>636</sub> = 6.45 ± 3.2 gibbs/mole. Within

error limits these results are in agreement, with the more accurate values quoted in Table II.

Using the best value for ΔH°<sub>298</sub> of 12.56 ± 0.13 kcal./mole in conjunction with the known ΔH<sub>f</sub>° values for CH<sub>4</sub>, I<sub>2</sub>, and HI,<sup>2a</sup> leads to a value at 298°K. of ΔH<sub>f</sub>°(CH<sub>3</sub>I(g)) = +3.28 ± 0.16 kcal./mole assuming the combined errors in the tabulated ΔH<sub>f</sub>° values do not exceed ±0.1 kcal./mole (not an unreasonable assumption for such well studied molecules). The kinetic measurements were interpreted according to the mechanism proposed by Flowers and Benson,<sup>3</sup> viz.



A steady-state treatment of this mechanism shows that

$$\frac{d[\text{HI}]}{dt} = \frac{d[\text{CH}_3\text{I}]}{dt} = k_4 K_{12}^{1/2} [\text{I}_2]^{1/2} [\text{CH}_4] \times \left\{ 1 - \frac{[\text{HI}][\text{MeI}]}{[\text{HI}]_{\text{eq}}[\text{MeI}]_{\text{eq}}} \right\} \quad (1)$$

To obtain a rough value for k<sub>4</sub> (all that was required to verify Flowers and Benson's estimate), the approximate expression

$$\frac{\Delta x}{\Delta t} = k_4 K_{12}^{1/2} [\text{I}_2]^{1/2} [\text{CH}_4] \left\{ 1 - \frac{x^2}{x_{\text{eq}}^2} \right\} \quad (2)$$

was used, where x<sup>2</sup> = [HI][MeI] and Δx/Δt is the rate of formation of x at less than 30% conversion. Three experiments were done to measure Δx/Δt and resulting

values of  $k_4$  are shown in Table III. It is hardly surprising that this crude approach gives two somewhat different values of  $k_4$  at one temperature. Nevertheless, they bracket the value calculated using Flowers and Benson's data, while the agreement between this work and theirs is surprisingly good at 605°K. These results confirm the value of Flowers and Benson's global rate constant ( $k_1k_3/k_2$ ). No attempt was made in this work to check the Arrhenius parameters. [Note. There is a serious typographical error in ref. 3 (p. 888) where a value is quoted for  $k_4$ . This should read  $\log k_4 = 11.70 - (33,500/4.575T)$ . A subsequent value of  $E_4$  on the same page should read  $E_4 = 33.2$  kcal./mole. However, using the value of  $K_{eq}$  reported in the present work together with their  $k_1k_3/k_2$ , we obtain  $\log k_4 = 11.70 - (34,100/4.575T)$ .]

Table III. Kinetic Parameters

Temp., °K.	$k_4$ obsd., l./mole sec.	$k_1k_3/k_2$ calcd., <sup>a</sup> l./mole sec.	$k_4$ calcd., <sup>b</sup> l./mole sec.
630.4	0.489	$3.63 \times 10^3$	0.843
630.0	0.975	$3.63 \times 10^3$	0.843
605.6	0.263	$1.82 \times 10^3$	0.264

<sup>a</sup> Obtained from  $\log k_1k_3/k_2 = 10.90 - 21.3/\theta$ .<sup>b</sup> Obtained from  $k_4 = (k_1k_3/k_2) K_{eq}$ , where  $K_{eq}$  is value reported in this paper.

The rate constant for reaction 1 obtained by Flowers and Benson<sup>3</sup> at a mean temperature of 560°K. is

$\log k_1$  (l./mole sec.) =  $(11.40 \pm 0.20) - (20.5 \pm 0.5)/\theta$   
where  $\theta = 2.303RT$  in kcal./mole.

Assuming that  $E_2$  is zero (an assumption which puts the following discussion on the same basis as one by Fettes and Trotman-Dickenson<sup>6</sup>), then  $\Delta H_{1,2}^\circ(560^\circ\text{K.}) = 20.5 \pm 0.5$  kcal./mole.

Using a value of  $\Delta C_p^\circ$  obtained from the JANAF Tables<sup>2a</sup> and Gelles and Pitzer<sup>2b</sup> of 1.22 gibbs/mole,  $\Delta H_{1,2}^\circ(298^\circ\text{K.}) = 20.2 \pm 0.5$  kcal./mole.

From the value of  $\Delta H_f^\circ(298^\circ\text{K.})$  for  $\text{CH}_3\text{I}$  determined in this work together with the values tabulated in JANAF Tables<sup>2a</sup> for I and  $\text{I}_2$ , the heat of formation of the methyl radical at 298°K. is  $\Delta H_f^\circ(\text{CH}_3(\text{g})) = +34.1 \pm 0.5$  kcal./mole.

Thus, using the tabulated<sup>2a</sup> heats of formation of H and I, the following bond dissociation energies at 298°K. may be obtained.

$$\begin{aligned} DH_{298}^\circ(\text{CH}_3\text{-H}) &= \Delta H_f^\circ(\text{CH}_3(\text{g})) + \Delta H_f^\circ(\text{H}(\text{g})) - \\ &\quad \Delta H_f^\circ(\text{CH}_4(\text{g})) \\ &= 104.1 \pm 0.5 \text{ kcal./mole} \end{aligned}$$

$$\begin{aligned} DH_{298}^\circ(\text{CH}_3\text{-I}) &= \Delta H_f^\circ(\text{I}(\text{g})) + \Delta H_f^\circ(\text{CH}_3(\text{g})) - \\ &\quad \Delta H_f^\circ(\text{CH}_3\text{I}(\text{g})) \\ &= 56.3 \pm 0.5 \text{ kcal./mole} \end{aligned}$$

On the basis of these data the rate parameters for reactions 2 and 3 become  $\log k_2 = 10.00$  and  $\log k_3 = 9.50 - 0.8/\theta$ .

## Discussion

Previous values for  $\Delta H_f^\circ(298^\circ\text{K.})$  for  $\text{CH}_3\text{I}(\text{g})$  lie within the range  $+(2-4)$  kcal./mole<sup>7-9</sup> and are in good agreement with the results of this work.

(6) G. C. Fettes and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3037 (1961).

Values obtained in this work for the important bond dissociation energies  $DH_{298}^\circ(\text{CH}_3\text{-H})$  and  $DH_{298}^\circ(\text{CH}_3\text{-I})$  are subject to the following qualifications: (a) they will be less by the amount that  $E_2$ , the activation energy for the reaction of methyl radical with  $\text{I}_2$ , is greater than zero; (b) they depend strongly on the value of  $E_1$ . The value of  $k_1$  used agrees with Benson and O'Neals'<sup>10</sup> reinterpretation of Ogg's<sup>11</sup> data for the same system; however, Boyd, *et al.*,<sup>12</sup> report a rate constant some 20% lower for the same reaction with an activation energy of 19.2 kcal./mole. Unfortunately, the temperature and error limits are not stated.

Concerning qualification (a), the evidence is indirect but does seem to point to the zero value. Christie's value<sup>13</sup> for the rate constant  $k_2$  ( $10^{10.0}$  l./mole sec.) at room temperature is almost the same as the  $A_2$  factor calculated from Flowers and Benson's value of  $A_1$  ( $10^{11.4}$  l./mole sec.) and a value for  $\Delta S_{1,2}^\circ(560^\circ\text{K.})$  of 6.2 gibbs/mole.<sup>2a,b</sup> (If  $\log A_1$  differs from 11.4 it is only likely to be lower, implying, if there were an activation energy of even as great as 0.5 kcal./mole, that Christie's value would have to be in error by a factor of three or four.) Thus Benson and Flower's Arrhenius parameters are strongly supported by Christie's results and this also tends to remove qualification (b).

From the thermal and photochemical studies of the bromination of  $\text{CH}_4$ , Kistiakowsky and Van Artsdalen<sup>14</sup> reported a value for  $DH_{298}^\circ(\text{CH}_3\text{-H})$ , which when corrected for more recent values for  $DH_{298}^\circ(\text{H-Br})$  and using Arrhenius rather than collision theory activation energies, becomes 102.9 kcal./mole. (This yields  $\Delta H_f^\circ(298^\circ\text{K.})$  for  $\text{CH}_3(\text{g}) = +32.9$  kcal./mole.)

Trotman-Dickenson<sup>15</sup> and co-workers have carefully remeasured the activation energy for Br attack on  $\text{CH}_4$  and further have measured<sup>6</sup> the activation energy of the reaction of  $\text{CH}_3$  with HBr (relative to that of  $\text{CH}_3$  with  $\text{I}_2$ , which they have taken to be zero). Their results led to  $DH_{298}^\circ(\text{CH}_3\text{-H}) = 103.9 \pm 1$  kcal./mole and  $\Delta H_f^\circ(298^\circ\text{K.})$  for  $\text{CH}_3(\text{g}) = 33.9 \pm 1$  kcal./mole, in excellent agreement with the values reported in this work. Their quoted error limits may be a bit small because of the uncertainty in the activation energy for Br atom recombination on which their values depend (see Fettes and Knox<sup>16</sup>).

Measurements of  $\Delta H_f^\circ(298^\circ\text{K.})$  for  $\text{CH}_3(\text{g})$  by electron impact methods yield values in the range of  $32 \pm 1.5$  kcal./mole,<sup>17,18</sup> but errors involved in this method have often been underestimated.

An important consequence of using the value of 34.1 kcal./mole for the heat of formation of the methyl radical is that those reported values of bond strengths

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which are based on a value of +32 for  $\Delta H_f^\circ{}_{298}(\text{CH}_3(\text{g}))$  are all too low. Thus, for example,  $DH^\circ{}_{298}(\text{CH}_3-\text{CH}_3) = 88.4 \pm 0.7$  kcal./mole<sup>19</sup>;  $DH^\circ{}_{298}(\text{C}_2\text{H}_5-\text{CH}_3) = 84.2 \pm 1.3$  kcal./mole.<sup>19,20</sup>

In addition, fixing the value of  $\Delta H_f^\circ{}_{298}(\text{CH}_3(\text{g}))$  sheds some light on the question of  $\Delta H_f^\circ{}_{298}(\text{CH}_3\text{CO}(\text{g}))$ . Those values which depend on  $\Delta H_f^\circ{}_{298}(\text{CH}_3(\text{g}))^{21-23}$  lead to a value of  $-2.9 \pm 1.5$  kcal./mole. A value which is independent of the methyl heat of formation and the extrapolations to high pressure limits, which add uncertainty to the above value, was obtained by studying the kinetics of the reaction between HI and acetyl iodide.<sup>24</sup> This leads to a value of  $\Delta H_f^\circ{}_{298}(\text{CH}_3\text{CO}(\text{g})) = -6.3 \pm 2.0$  kcal./mole, where the uncertainties are in measuring an activation energy, in taking the activation energy of the reaction between

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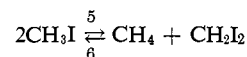
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$\text{CH}_3\text{CO}$  and  $\text{I}_2$  to be zero, and in the value of  $\Delta H_f^\circ{}_{298}(\text{CH}_3\text{COI}(\text{g}))$ . The latter value is probably not off by much more than its standard error of 2 kcal./mole, but the weight of evidence does seem to favor the lower value, so the suggested value is, in agreement with Kerr and Calvert,<sup>22</sup>  $\Delta H_f^\circ{}_{298}(\text{CH}_3\text{CO}(\text{g})) = -4$  (+1 or -2) kcal./mole.

The absence of  $\text{CH}_2\text{I}_2$  enables us to set an upper limit on the equilibrium constant for the reaction



Taking the maximum pressure of  $\text{CH}_2\text{I}_2$  as 0.03 torr (see Results) it can be calculated that  $K_{5,6} \leq 3.6$  at 630°K. Using the same procedure outlined in the Results section to obtain  $\Delta H^\circ{}_{298}$  and taking the data on  $S^\circ$  and  $C_p^\circ$ ,<sup>2</sup> the following value is obtained:  $\Delta H^\circ{}_{298} \geq -2.86$  kcal./mole. In conjunction with  $\Delta H_f^\circ(\text{CH}_4)$ ,<sup>2a</sup> and the value of  $\Delta H_f(\text{CH}_3\text{I}(\text{g})) = 3.28$  kcal./mole measured in the present work, this leads to  $\Delta H_f(\text{CH}_2\text{I}_2(\text{g})) \geq +21.6$  kcal./mole. This has not previously been measured.

## Matrix Infrared Studies of OF Compounds.

### II. The $\text{O}_2\text{F}$ Radical<sup>1</sup>

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*The  $\text{O}_2\text{F}$  radical has been produced during the photolysis of  $\text{OF}_2\text{-O}_2$  or  $\text{F}_2\text{-O}_2$  mixtures in  $\text{O}_2$ ,  $\text{N}_2$ , or argon matrices at 4°K. The radical in argon has infrared absorptions at 584 and 1494  $\text{cm}^{-1}$  which disappear during thermal cycling of the matrix to the diffusion temperature. The products of diffusion,  $\text{O}_2\text{F}_2$  and  $\text{O}_4\text{F}_2$ , are formed by combination of  $\text{O}_2\text{F}$  with atomic fluorine and by dimerization of  $\text{O}_2\text{F}$ , respectively. Parallel work using  $\text{O}^{18}$ -substituted  $\text{O}_2$  gave isotopic infrared absorptions which were in good agreement with calculated values. The stretching force constants derived for  $\text{O}_2\text{F}$  and  $\text{O}_4\text{F}_2$  indicate relatively short O-O bonds compared to peroxide type compounds and relatively long O-F bonds compared to  $\text{OF}_2$ . These results are in general agreement with the previously established structure of  $\text{O}_2\text{F}_2$ .*

#### Introduction

During a study of the effects of a radiofrequency glow discharge on  $\text{OF}_2$ , evidence was obtained for the existence of OF and  $\text{O}_2\text{F}$  radicals. The evidence was based on the formation of new absorptions in the infrared following the matrix (Ar or  $\text{N}_2$  at 4°K.) deposition of radiofrequency-discharged  $\text{OF}_2$ . When the matrix was thermally cycled to its diffusion temperature, the

new infrared absorptions disappeared with the formation of  $\text{O}_2\text{F}_2$ ,  $\text{O}_4\text{F}_2$ , and recovered  $\text{OF}_2$ . It was apparent from the complexity of the spectra that specific assignment of infrared absorptions to radical species would require the selective production of each species for individual study. In this respect the technique of matrix photolysis gave some measure of control not common to other methods of activation. For example, the restricting nature of the matrix allowed only limited migration of atoms during the photolysis step. Thus the choice of a matrix, the photolysis temperature, the range of radiation, and the size of the atom generated during photolysis all had to be considered as factors contributing to successful radical isolation. Ample evidence for the importance of these factors was found in a subsequent study of the matrix photolysis of  $\text{OF}_2$  to obtain the OF radical.

The matrix isolation of the OF radical and its identification by infrared spectroscopy<sup>2</sup> was the first direct evidence of a species related to the family of radicals containing only oxygen and fluorine. In contrast to the much discussed OF radical, the other members of this family, namely,  $\text{O}_2\text{F}$ ,  $\text{O}_3\text{F}$ , and  $\text{O}_4\text{F}$ , have received relatively little attention. This stems partly from the fact that the initial preparation<sup>3</sup> of two of the parent

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