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Time-Resolved Studies of the Kinetics of the Reactions of CHO with HI and HBr: Thermochemistry of the CHO Radical and the C−H Bond Strengths in CH_2O and CHO

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Time-resolved studies of formyl radical, CHO, generated by laser flash photolysis of acetaldehyde, have been carried out to obtain rate constants for its bimolecular reactions with HI and HBr. Each reaction was studied in the gas-phase at five different temperatures in the range 293−540 K. The pressure-independent rate constants gave the following Arrhenius equations: for CHO + HI, $\log(k_2/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = (-11.51 \pm 0.01) - (0.83 \pm 0.06\ \text{kJ mol}^{-1})/RT \ln 10$, for CHO + HBr, $\log(k_4/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = (-12.59 \pm 0.06) - (0.13 \pm 0.44\ \text{kJ mol}^{-1})/RT \ln 10$. The Arrhenius parameters are consistent with those for reactions of other free radicals with HI and HBr and support the idea of intermediate complexes in these processes. Combination with the known kinetic data on the reverse reactions leads to the thermodynamic estimate for $\Delta H_f°(\text{CHO}) = 44.29 \pm 0.43$ kJ mol^{-1} (third law method, 298 K value). Second law values are in reasonable agreement. This value corresponds to the bond dissociation energies $D(\text{H−CHO}) = 370.86 \pm 0.28$ kJ mol^{-1}, and $D(\text{H−CO}) = 63.18 \pm 0.46$ kJ mol^{-1}. These values are in close agreement with several previous determinations although more precise. A small unresolved discrepancy exists with the most recent value for the photodissociation threshold for CH_2O.

Introduction

The formyl radical, CHO, is of importance as a reactive intermediate in both atmospheric chemistry[1] and combustion.[2] Reliable values for $\Delta H_f°$(CHO) and the related bond dissociation energy D(H−CHO) are necessary in order to assess the kinetics of its elementary reactions. Recent years have seen a gradual refinement of the values of heats of formation of many organic free radicals through the application of a variety of techniques[3] such that, in many cases, uncertainties have diminished to as low as ±2 kJ mol^{-1}. As far as CHO is concerned, our interest in this radical began in 1966 when one of the present authors was involved in an earlier gas phase study[4] of the kinetics of the reaction:

$$\text{I} + CH_2O \rightarrow \text{CHO} + \text{HI} \qquad (1)$$

which led to a value of 30 ± 8 kJ mol^{-1} for $\Delta H_f°$(CHO). This determination was by no means the first value of this quantity, but it was a landmark in the sense that it served at the time to eliminate some earlier estimates as much as 50 kJ mol^{-1} lower in value and also threw some light on the photochemistry of CH_2O. The weakness in this determination was that it required an assumption about the activation energy of reaction 2, the reverse of reaction 1:

$$\text{CHO} + \text{HI} \rightarrow CH_2O + \text{I} \qquad (2)$$

In the intervening years there have been several determinations of $\Delta H_f°$(CHO) employing a variety of experimental techniques.[5−12] The values tend to cluster in the range 40−45 kJ mol^{-1}, mostly with uncertainties of at least ±4 kJ mol^{-1}. In the most recent study Chuang, Foltz, and Moore[12] have obtained a value of 41.8 ± 0.8 kJ mol^{-1} from a measurement of the threshold for onset of photodissociation of CH_2O, using the PHOFEX technique to monitor H atoms.

Despite the apparent precision of the current value, we feel that the importance of this quantity makes the experimental check of its value worthwhile. This is only true if the technique can yield a value of equivalent precision, which is the case with the work described here. Direct kinetic studies of reaction 2 offer this possibility since a combination of the rate constants of reactions 1 and 2, and their temperature dependencies, can be used to obtain $\Delta H_f°$ for the reaction and thereby $\Delta H_f°$(CHO). This would eliminate the assumption made earlier[4] and lead to the desired precision. The key to obtaining a reliable value is to ensure that the temperature ranges of study of (1) and (2) are as close as possible and to check that the thermodynamic data derived using both second and third law treatments are in close agreement. This approach follows closely that of Gutman and co-workers,[13] who have studied the kinetics of many radicals, R, with both HI and HBr and used the results to obtain $\Delta H_f°$(R). The kinetics of reaction (2) have not previously been studied.

Following earlier time-resolved investigations of CHO radical reactions,[14,15] we describe here studies in which CHO is created via excimer laser flash photolysis of acetaldehyde and monitored via its $\tilde{X}\ ^2A' \rightarrow \tilde{A}\ ^2A''$ vibronic transition. As well as reaction 2 with HI, the reaction of CHO with HBr, reaction 4, is also investigated here in order to gain a second handle on the desired thermochemistry by combination with the known rate data[16,17] for reaction 3, viz.,

$$\text{Br} + CH_2O \rightarrow \text{CHO} + \text{HBr} \qquad (3)$$

$$\text{CHO} + \text{HBr} \rightarrow \text{Br} + CH_2O \qquad (4)$$

The kinetics of reaction 4 have also not been studied previously.

Quite apart from the thermochemical application, reactions of CHO radicals with HI and HBr are of interest because the

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study of their kinetics can throw further light on the possible involvement of intermediate complexes in radical reactions with hydrogen halides.[18−26]

Experimental Section

The apparatus and equipment for these studies have been described in detail previously.[14,15] Only essential and brief details are therefore included here. CHO was produced by the 308 nm flash photolysis of acetaldehyde using an Oxford Lasers KX2 exciplex laser operating on XeCl emission. CHO concentrations were monitored in real time by means of a Coherent 699-21 single mode dye laser pumped by an Innova 90-5 argon ion laser and operating with Kiton Red. Experiments were carried out in a variable temperature quartz reactor with demountable windows.[27] The monitoring laser beam was multipassed 32 or 36 times through the reaction zone to give an effective path length of up to 1.5 m.

The monitoring laser was tuned to 614.66 nm, corresponding to a position slightly to the red of the $\tilde{A}\ ^2A''(0,9,0) \leftarrow \tilde{X}\ ^2A'(0,0,0)$ bandhead at 614.38 nm.[28] Small variations in wavenumber (within a spread of 0.5 cm^{-1}) were shown to make no difference to the results. Light signals were measured by a dual photodiode/differential amplifier combination, and the signal decays were stored in a transient recorder (Datalab 910) interfaced to a BBC microcomputer. This was used to average decays of up to 40 laser shots (at a repetition rate of 1 or 2 Hz). The averaged decay traces were processed by fitting the data to an exponential form using a nonlinear least-squares package. This analysis provided the values for the first-order rate constants, k_{obs}, for removal of CHO in the presence of known partial pressures of substrate gas.

Gas mixtures for photolysis were made up, containing 5 or 10 Torr of acetaldehyde, together with appropriate pressures of added substrate gas (either 1−5 Torr of HI or 10−50 Torr of HBr). In a few experiments SF_6 was added to test for pressure dependence. Pressures were measured by capacitance manometers (MKS Baratron). The gases used in this work were obtained as follows. Acetaldehyde was from Aldrich (99%). Hydrogen iodide was obtained by dehydration of aqueous hydriodic acid (Aldrich, 99.99% HI in water) using phosphoros pentoxide. Hydrogen bromide was from Fluka (purum grade). Sulfur hexafluoride (no GC detectable impurities) was from Cambrian Gases. All gases were degassed thoroughly prior to use. Additionally, the hydrogen halides were distilled at low pressure periodically to maintain their purity from contamination by decomposition to halogen. They were only used after checking they were pure white when condensed.

Results

Earlier work has demonstrated that the 308 nm photolysis of CH_3CHO provides a reliable source of CHO radicals,[14,15] via the reaction

$$CH_3CHO + h\nu \rightarrow CH_3 + CHO \tag{5}$$

The presence of CH_3 radicals does not perturb the kinetics of CHO decay in the presence of reactive substrates. Preliminary experiments demonstrated that signal decay in the absence of added substrate was not first order, as expected. Estimates from the known extinction coefficient,[14] suggested initial CHO concentrations were of the order of 3×10^{14} molecules cm^{-3}. Because of our previous study,[14] we did not seek to remeasure the CHO radical recombination constant. Although decay rates in the absence of added substrate were sensitive to initial CH_3CHO partial pressure and photolysis laser energy (50−100 mJ/pulse), the important point was established that, in the presence of reactive substrate, the decays became exponential and were not sensitive to these parameters. An example of such a decay trace is shown, inset, in Figure 1a. Signal size was dependent on CH_3CHO pressure, and higher pressures were needed at higher temperatures, because the CHO detection sensitivity decreases with increasing temperature. Signal decay constants in the presence of HI or HBr were insensitive to photolysis repetition rates and the number of photolysis shots, except for slight increases with number of shots at high HI and high temperature.

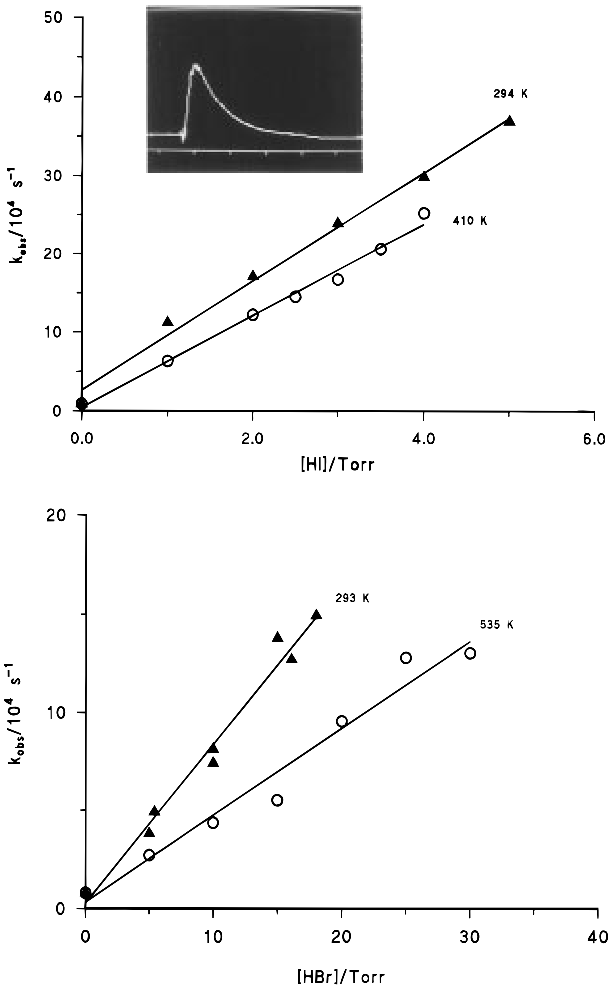


Figure 1. Second-order plots: examples of the dependence of the decay constants, k_{obs}, on pressure of (a) HI and (b) HBr. The inset photograph shows the decay trace for the [HI] = 3.0 Torr point at 294 K; the vertical scale shows absorbance, and the time base corresponds to 6.4 μs between divisions.

For both HI and HBr, a series of experiments were carried out at each of five temperatures in the range 293−540 K. At each temperature five or six runs, usually of 10 shots each, were carried out at different substrate pressures. A blank in the absence of substrate was also performed at the same excimer laser energy, and the decay was treated as a first-order process for fitting purposes. These experiments showed good linear dependencies of k_{obs} with partial pressure of substrate, as expected for second-order kinetics. This is illustrated in Figure 1 for reaction of CHO with both HI and HBr. The second-order rate constants, obtained by least-squares fitting to these plots, are collected in Table 1. The rate constants showed no variation with added SF_6. The error limits shown are single standard deviations. Arrhenius plots of the rate constants for

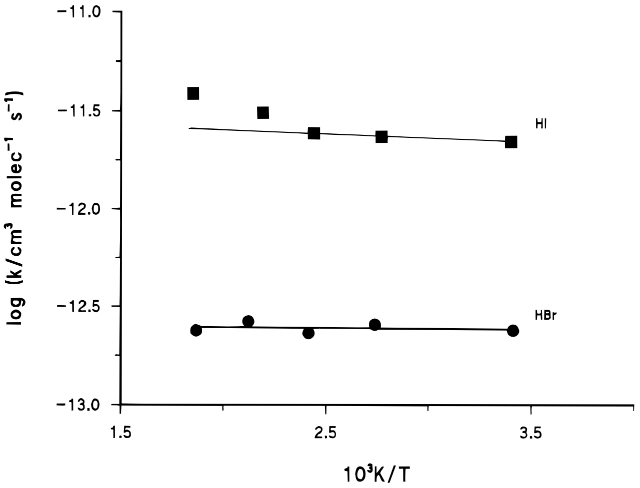


Figure 2. Arrhenius plots of the rate constants of reaction for CHO with HI and HBr.

TABLE 1: Experimental Rate Constants for the Reactions of Formyl

CHO + HI		CHO + HBr	
T/K	$k/10^{-12}$ cm^3 molecule^{-1} s^{-1}	T/K	$k/10^{-13}$ cm^3 molecule^{-1} s^{-1}
294	2.21 ± 0.07	293	2.38 ± 0.09
361	2.34 ± 0.12	365	2.55 ± 0.08
410	2.43 ± 0.06	414	2.31 ± 0.08
456	3.09 ± 0.07	471	2.65 ± 0.11
540	3.86 ± 0.17	535	2.38 ± 0.11

both reactions are shown in Figure 2. For reaction 4, CHO + HBr, the plot is linear with an almost zero gradient. For reaction 2, CHO + HI, the plot shows some curvature. We chose to put the Arrhenius line through the lower temperature points and make the assumption that the rate constants at 456 and 540 K were slightly too high. This can be justified as a perturbation arising from unavoidable formation of small quantities of I_2 at these temperatures. (Use of high pressures of HI led to curvature in the second-order plot at 540 K.) The Arrhenius parameters obtained from fitting the data of Figure 2 are

$$\log(k_2/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = (-11.51 \pm 0.01) - (0.83 \pm 0.06\ \text{kJ mol}^{-1})/RT \ln 10$$

$$\log(k_4/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = (-12.59 \pm 0.06) - (0.13 \pm 0.44\ \text{kJ mol}^{-1})/RT \ln 10$$

For reasons given later (see Discussion) we believe that the error limits for A_2 and $E_{a,2}$ should be 10 times larger, and therefore increased uncertainties are used in the calculations below.

Thermochemical Calculations

The availability of temperature-dependent rate constants for both reaction pairs (1), (2) and (3), (4) in substantially overlapping temperature ranges offers the opportunity for calculation of $\Delta H_f°$(CHO) using both second and third law procedures for each reaction pair. To facilitate the presentation, Arrhenius parameters for all four reactions are given in Table 2. For reaction 3 we have chosen to use the data of Nava et al.,[16] rather than that of Poulet et al.,[17] because it covers a wider temperature range.

A. Second Law Determination of the Enthalpy of Formation of Formyl. In this procedure enthalpy changes for these reactions are obtained directly from the differences of Arrhenius activation energies for the forward and reverse reactions, and the only problem is that of correcting them to 298 K. For this purpose midpoint temperatures of the overlapping ranges were chosen: viz 500 K for reaction pair (1), (2) and 385 K for reaction pair (3), (4). These give

TABLE 2: Arrhenius Parameters for Reactions 1−4

reaction	T range/K	log(A/cm^3 molecule^{-1} s^{-1})	E_a/kJ mol^{-1}	ref
I + CH_2O	453−574	−9.86 ± 0.04	72.93 ± 0.38	4
CHO + HI	294−540	−11.51 ± 0.09	0.83 ± 0.56	this work
Br + CH_2O	223−480	−10.84 ± 0.09	6.24 ± 0.47	16
CHO + HBr	293−535	−12.59 ± 0.06	0.13 ± 0.44	this work

TABLE 3: Thermodynamic Quantities for Species Involved in the Reactions of Interest

species	$\Delta H_f°$/kJ mol^{-1}	$S°$/J K^{-1} mol^{-1}
CH_2O	−108.57 ± 0.46[a]	218.95[b]
CHO	see text	224.65[b]
I[b]	106.76 ± 0.04	180.79
HI[b]	26.36 ± 0.21	206.59
Br[b]	111.86 ± 0.06	175.02
HBr[b]	−36.44 ± 0.17	198.70

[a] From ref 29. [b] From ref 10.

$$\Delta H°_{1,2}(500\ \text{K}) = (72.93 \pm 0.38) - (0.83 \pm 0.56) = 72.10 \pm 0.68\ \text{kJ mol}^{-1} \quad \text{(i)}$$

The tabulated enthalpy functions[10] $H°(T) - H°(298\ \text{K})$ for I, CH_2O, HI, and CHO are used to obtain $\Delta(H°(500\ \text{K}) - H°(298\ \text{K})) = 1.17$ kJ mol^{-1} and thereby $\Delta H°_{1,2}(298\ \text{K}) = 70.93 \pm 0.68$ kJ mol^{-1}. Combination of this value with the known enthalpies of formation[10,29] of I, HI, and CH_2O, shown for convenience in Table 3, leads to $\Delta H_f°$(CHO) = 42.76 ± 0.85 kJ mol^{-1}.

$$\Delta H°_{3,4}(385\ \text{K}) = (6.24 \pm 0.47) - (0.13 \pm 0.44) = 6.11 \pm 0.64\ \text{kJ mol}^{-1} \quad \text{(ii)}$$

The tabulated enthalpy functions[10] $H°(T) - H°(298\ \text{K})$ for Br, CH_2O, HBr, and CHO are used to obtain $\Delta(H°(385\ \text{K}) - H°(298\ \text{K})) = 0.58$ kJ mol^{-1} and thereby $\Delta H°_{3,4}(298\ \text{K}) = 5.53 \pm 0.64$ kJ mol^{-1}. Combination of this value with the known enthalpies of formation[10,29] of Br, HBr, and CH_2O, shown for convenience in Table 3, leads to $\Delta H_f°$(CHO) = 45.27 ± 0.81 kJ mol^{-1}.

The reaction entropy changes obtained using $\Delta S° = R \ln(A_f/A_r)$ with correction from reaction temperature to 298 K via use of tabulated C_p values[10] are

$$\Delta S°_{1,2}(298\ \text{K}) = 28.58 \pm 1.89\ \text{J K}^{-1}\ \text{mol}^{-1} \quad \text{(cf. 31.50 from Table 3)}$$

$$\Delta S°_{3,4}(298\ \text{K}) = 31.79 \pm 2.07\ \text{J K}^{-1}\ \text{mol}^{-1} \quad \text{(cf. 29.38 from Table 3)}$$

The small differences between the entropies obtained from the experiments and those from statistical calculations[10] lead one to believe that the values of $\Delta H_f°$(CHO) obtained must be close to the true value which will lie in the range 42−45 kJ mol^{-1}.

B. Third Law Determination of the Enthalpy of Formation of Formyl. In this procedure the Gibbs free energy changes for these reactions are obtained from the equilibrium constants, themselves calculated from the ratio of forward and reverse rate constants (i.e., k_1/k_2 or k_3/k_4) at the midpoint temperatures, and these are then corrected to 298 K using the free energy functions $(G°(T) - H°(298\ \text{K}))/T$.

Thus, for (1) and (2) at 500 K

$$K = k_1/k_2 = (1.32 \pm 0.11) \times 10^{-6}$$

$$\Delta G° = 56.28 \pm 0.35 \text{ kJ mol}^{-1}$$

Then from the tabulated functions[10] $(G°(T) - H°(298\text{ K}))/T$ for I, CH_2O, HI, and CHO, we obtain

$$\Delta(G°(500\text{ K}) - H°(298\text{ K}))/T = -32.25 \text{ J K}^{-1}\text{ mol}^{-1}$$

and therefore

$$\Delta(G°(500\text{ K}) - H°(298\text{ K})) = -16.13 \text{ kJ mol}^{-1}$$

This gives

$$\Delta H°(298\text{ K}) = 56.28 + 16.13 = 72.41 \pm 0.35 \text{ kJ mol}^{-1}$$

Combination of this value with the known enthalpies of formation[10,29] of I, HI, and CH_2O (Table 3) leads to $\Delta H_f°(\text{CHO}) = 44.24 \pm 0.62$ kJ mol^{-1}.

Also, for (3) and (4) at 385 K

$$K = k_3/k_4 = 8.34 \pm 0.85$$

$$\Delta G° = -6.79 \pm 0.32 \text{ kJ mol}^{-1}$$

Then from the tabulated functions[10] $(G°(T) - H°(298\text{ K}))/T$ for Br, CH_2O, HBr, and CHO, we obtain

$$\Delta(G°(385\text{ K}) - H°(298\text{ K}))/T = -29.62 \text{ J K}^{-1}\text{ mol}^{-1}$$

and therefore

$$\Delta(G°(385\text{ K}) - H°(298\text{ K})) = -11.40 \text{ kJ mol}^{-1}$$

This gives

$$\Delta H°(298\text{ K}) = -6.79 + 11.50 = 4.61 \pm 0.32 \text{ kJ mol}^{-1}$$

Combination of this value with the known enthalpies of formation[10,29] of Br, HBr, and CH_2O (Table 3) leads to $\Delta H_f°(\text{CHO}) = 44.34 \pm 0.59$ kJ mol^{-1}.

The third law method thus produces almost perfect agreement between the values obtained from the two reaction systems. It is intrinsically more precise than the second law method and leads to an averaged estimate:

$$\Delta H_f°(\text{CHO}) = 44.29 \pm 0.43 \text{ kJ mol}^{-1}$$

From this may be derived the following bond dissociation energies:

$$D(\text{H}-\text{CHO}) = 370.86 \pm 0.28 \text{ kJ mol}^{-1}$$

$$D(\text{H}-\text{CO}) = 63.18 \pm 0.46 \text{ kJ mol}^{-1}$$

Discussion

A. Kinetics. There are no previous studies of the kinetics of the reactions of CHO with HI or HBr. The laser flash photolysis technique provides direct and absolute measurements of the reaction rate constants. A number of aspects of the study provide assurance that there are no serious errors. The photolysis wavelength of 308 nm is not absorbed by either HI or HBr, and so adventitious and undesirable photolytic side reactions are avoided. CHO radical concentrations are probed centrally in the reactor, and decay times are of the order of 10 μs. At the pressures of study this is fast compared with diffusion times, and so the results should not be affected by diffusion or reaction vessel surface effects. In another type of check, tests showed that there was insignificant sample depletion by repetitive laser photolysis (up to 40 shots). The only problem encountered was an apparent enhancement in decay constants for HI left in the vessel at high temperatures and pressures. In the extreme, it was clear that rates were too fast, since at high [HI] (>4 Torr at 540 K), the decay constant was clearly higher than the second-order plot through lower [HI] values suggested. The most plausible explanation for this was the formation of small quantities of I_2 in the cell at the highest two temperatures. The rate constant for the reaction of CHO + I_2 is ca. 20 times greater than that for CHO + HI.[4] Thus, as little as 1% of I_2 will cause a 20% increase in decay constant. We thus suspect that, despite our efforts to purify HI rigorously, small quantities of I_2 are the cause of the apparently high rate constants for CHO + HI at 456 and 540 K. This was the reason for not including these constants in the Arrhenius fit. The consistency of the rate constants at the other three temperatures is remarkable. However, in view of this problem the uncertainties in the Arrhenius parameters must be considered larger than those quoted. Hence, we have increased these error limits by an order of magnitude; i.e., *A* is uncertain to $10^{\pm 0.09}$ cm^3 molecule^{-1} s^{-1} and E_a is uncertain to ±0.56 kJ mol^{-1}.

TABLE 4: Comparisons of Arrhenius Parameters for Radical Reactions with HI and HBr

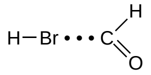
radical, R	$A/10^{-12}$ cm^3 molecule^{-1} s^{-1}	E_a/kJ mol^{-1}	ref
	(a) R + HI		
CH_3	4.5 ± 0.8	−1.2 ± 0.6	18
C_2H_5	4.5 ± 0.9	−3.2 ± 0.6	18
i-C_3H_7	3.9 ± 0.8	−5.1 ± 0.7	18
t-C_4H_9	3.1 ± 0.6	−6.3 ± 0.8	18
CHO	3.1 ± 0.6	+0.8 ± 0.6	this work
	(b) R + HBr		
CH_3	1.57 ± 0.26	−1.6 ± 0.6	19
C_2H_5	1.70 ± 0.55	−4.2 ± 1.2	19
i-C_3H_7	1.58 ± 0.38	−6.4 ± 0.9	19
t-C_4H_9	1.37 ± 0.47	−7.8 ± 1.4	19
CHO	0.26 ± 0.04	+0.1 ± 0.4	this work
CH_3CO	0.64 ± 0.36	−4.5 ± 1.5	20

It is interesting to compare the Arrhenius parameters obtained in this work with those of reactions of other radicals with HI and HBr.[18,19] These are shown in Table 4. For reactions of alkyl radicals with HI, *A* factors are typically ca. (3−5) × 10^{-12} cm^3 molecule^{-1} s^{-1}, which is very similar to the value obtained for CHO + HI. The small positive activation energy for CHO + HI apparently contrasts with the negative activation energies seen for alkyl radicals with HI. However, the values are generally small and are consistent with (although not a proof of) a reaction proceeding via an intermediate complex. For reactions of alkyl radicals with HBr, *A* factors are typically ca. (1.3−1.7) × 10^{-12} cm^3 molecule^{-1} s^{-1}, which is ca. 6 times the value obtained for CHO + HBr. Although this might seem like an unusually large difference for such apparently similar reactions, the *A* factor for the reverse reaction, Br + CH_2O (Table 2 and ref 16), is lower than those for Br atom reactions with alkanes[22] by a similar order of magnitude. The *A* factor for CH_3CO + HBr[20] is also lower than those for alkyl radicals + HBr but by a smaller factor. This suggests that for CHO + HBr, and likewise the Br + CH_2O reaction, the activated complex has a tighter structure than those for the alkyl radical + HBr reactions. A possible explanation for this could lie in the more polar character of the reactants in this case. The carbon atom of CHO is more positively charged than the odd-electron-bearing carbon atoms of alkyl radicals while HBr has a bigger

TABLE 5: Summary of Experimental Values of $\Delta H_f°$(CHO)/kJ mol^{-1} at 298 K

experiment	value	ref
kinetics of iodination of CH_2O (1966)	30 ± 8	4
photoionization threshold of CH_2O, HCOOH (1974)	42 ± 5	5, 6
photodissociation threshold in CH_2O (1978)	39 ± 4	7
direct photoionisation of CHO (1980)	28 ± 5	8
photodissociation threshold in CH_2O (1983)	44 ± 3	9
CHO radical recombination (1985)	43.5 ± 8	10
reevaluation (1987)	43.5 ± 4	11
photodissociation threshold in CH_2O (1987)	41.8 ± 0.8	12
kinetics of CHO + HI, HBr; third law value	44.29 ± 0.43	this work

dipole than HI. Therefore, the long-range interactions of these species should lead to initial formation of a complex of structure:



If the reorganization of this species is more difficult than that of the equivalent H−I···CHO complex due to stronger binding forces, then a tighter transition state could well arise. The activation energy is almost zero for CHO + HBr (just as for CHO + HI) compared with the negative values for alkyl + HBr, but this is still consistent with the involvement of an intermediate complex. For CH_3CO + HBr the activation energy is negative (but small).[20] This is not inconsistent with this idea if methyl groups can assist in lowering the secondary barriers of rearrangement of complexes of this type. This requires the second step of the process to be rate determining but is consistent with the trends of increasingly negative values for the activation energies of the alkyl radicals + HBr (and HI) with methyl substitution in the alkyl radical.[18,19] Interestingly, it is *also* consistent with methyl group substituent trends in the seemingly quite different reactions of silylene insertion into the Si−H bonds of methylsilanes (Me_nSiH_{4-n}, $n = 1$, 2, or 3). The evidence for involvement of intermediate complexes in this class of reactions is very strong.[30,31]

The results of the present work are therefore fully in tune with the long-held, well-known involvement of polar effects in alkyl radical H atom transfer reactions[32−34] and the more recently proposed arguments in favor of intermediate complexes.[18−26]

B. Thermochemistry of CHO and the Related Bond Dissociation Energies, D(H−CHO) and D(H−CO). Previous experimental values for $\Delta H_f°$(CHO) are listed in Table 5. Only data since 1966 have been considered as values prior to that were reviewed by Walsh and Benson.[4] The data shown have been obtained by five different types of measurement: iodine−formaldehyde kinetic studies, photoionization studies, photodecomposition studies, photoelectron spectroscopic studies, and formyl radical recombination studies. The kinetic study of reaction 1 carried out previously by Walsh and Benson[4] had two deficiencies as far as the determination of $\Delta H_f°$(CHO) is concerned. First, it required an estimate of $E_{a,2}$ (since this was not experimentally available), and second it was based on an older, less reliable value[35] for $\Delta H_f°(CH_2O)$ of −116 ± 6 kJ mol^{-1} compared with the more recent and precise flame calorimetric figure of −108.57 ± 0.46 kJ mol^{-1} obtained by Fletcher and Pilcher.[29] For some inexplicable reason, the JANAF tables[10] continue to prefer the older value. The present work rectifies these two defects as well as backing up the result via the additional study of the reaction pair (3), (4). The photoionization studies of Warneck[5,6] set out to measure threshold energies for formation of H^+ and OH^+ from CH_2O and HCOOH, respectively, where CHO is the neutral fragment. Without any corrections for nonthermal effects these lead to individual (298 K) values of 41 ± 7 and 43 ± 5 kJ mol^{-1}. Photodecomposition studies essentially attempt to obtain the threshold energy of the process

$$CH_2O \rightarrow CHO + H$$

which is a measure of D_0(CHO). This can be either corrected to 298 K or used to obtain $\Delta H_f°$(CHO) at 0 K, which can itself be corrected to 298 K. The difficulty in carrying out the experimental studies themselves lies in identifying the true threshold for dissociation without assistance from thermal or internal vibrational energy in CH_2O. Thus, typically values have tended to be slightly low in the past. Reilly et al.[7] cite the value of D_0(H−CHO) = 360 ± 4 kJ mol^{-1}, corresponding to $\Delta H_f°$(CHO) = 39 ± 4 kJ mol^{-1} (at 298 K), while Moortgat et al.[9] obtained D_0(H−CHO) = 364 ± 3 kJ mol^{-1}, corresponding to $\Delta H_f°$(CHO) = 44 ± 3 kJ mol^{-1} (at 298 K). More recently, Chuang, Foltz, and Moore[12] have identified the threshold by simultaneously monitoring absorption (photoacoustic spectrum) and H atom dissociation excitation (PHOFEX spectrum) in both CH_2O and CD_2O. The threshold is identified by breakoff in the PHOFEX spectrum. This result leads to D_0(H−CHO) = 362.21 ± 0.67 kJ mol^{-1}, corresponding to $\Delta H_f°$(CHO) = 41.80 ± 0.81 kJ mol^{-1} (at 298 K), by far the most precise value yet obtained.

In the photoelectron spectroscopic study, Dyke et al.[8] measured the vertical ionization energy of CHO directly and used it to estimate $\Delta H_f°$(CHO) = 28.0 ± 5.4 kJ mol^{-1}. It seems probable that the low value results from an incorrect assignment of the adiabatic ionization potential. The fifth method[36] involves observation of chemiluminescence from glyoxal, $(CHO)_2$, formed via CHO radical recombination, giving D_{298}(OHC−CHO) = 299.2 ± 1.3 kJ mol^{-1}. This was used by Fletcher and Pilcher[29] to obtain D_{298}(H−CHO) = 370.3 ± 3.8 kJ mol^{-1}, corresponding to $\Delta H_f°$(CHO) = 43.7 ± 3.8 kJ mol^{-1}. The JANAF tables[10] citing this last data give more conservative error limits of ±8 kJ mol^{-1}.

Some of these data were briefly reviewed earlier by Timonen et al.,[11] who suggested a consensus value of $\Delta H_f°$(CHO) = 43.1 ± 4 kJ mol^{-1} (at 0 K), corresponding to 43.5 ± 4 kJ mol^{-1} at 298 K. It thus appears that all values since 1974 (except those of ref 8) for $\Delta H_f°$(CHO) at 298 K lie in the range 40−45 kJ mol^{-1}. Error margins of all studies prior to that of Chuang, Folz, and Moore[12] cover this range. The discrepancy now is between the more precise values of the latter and the value derived in this work, the error margins of which do not overlap. We have looked carefully at the possible errors arising in this study. We focus first on the third law derived values, since these are the most precise. Errors in the rate constants (Table 1) are single standard deviations (68% confidence). An increase to two standard deviations (95% confidence) would lead to a final uncertainty of ca. ±0.6 instead of ±0.4 kJ mol^{-1}, not a large change. The thermodynamic functions of the species involved in reactions 1−4 should be reliable to a high degree of precision, since the structural parameters (geometries, vibrational wavenumbers) required for their calculation are well-established.[10] We estimate that uncertainties deriving from this source are unlikely to exceed ±0.1 kJ mol^{-1}. The second law derived values of $\Delta H_f°$(CHO), while inevitably less reliable, do not undermine confidence in the results obtained here. The values from the two reaction pairs (1), (2) and (3), (4) differ by 2.51 kJ mol^{-1}. While the error margins do not quite overlap at one standard deviation uncertain, they do at two. The values span the third law derived values. Small differences between second and third law derived values commonly arise. The second law values are usually less precise (and therefore less reliable). This is because a second law value relies on measurements of the values of the gradients of two Arrhenius plots. Small distortions (unknown systematic errors) in the rate constants at the temperature extremes of the kinetic study (always the most demanding) can easily give rise to errors of a few kJ mol^{-1} in activation energy values, even though rate constant values themselves may be reliable to ±5% in themselves. The judgment of the quality of a second-order value for $\Delta H°$ of a reaction rests on how well the $\Delta S°$ value derived from the A factor ratio fits the known or estimated $\Delta S°$ from thermodynamic considerations. For both reactions of this study the agreement is quite good, if not perfect. It is certainly comparable with the best obtained for the equivalent H abstraction reactions of I or Br atoms with alkanes.[18,19] Nevertheless the third law values are much more precise, especially in this case where ancillary thermodynamic quantities are so reliable. The puzzle that remains, therefore, is the origin of the discrepancy between this work and that of Chuang et al.[12] We can throw no more light on it except to indicate the implications. If our results are correct, it means that D_0(H−CHO) = 364.70 kJ mol^{-1}, corresponding to a photodissociation threshold for CH_2O of $\lambda = 328.0$ nm compared with 330.3 nm observed.[12] If Chuang, Foltz, and Moore[12] are correct, it means that either our measured rate constants are too large by ca. a factor of 2 (1.8 for k_2 at 500 K and 2.2 for k_4 at 385 K) or k_1 and k_3 from the published studies[4,16,17] are too small by equivalent factors. Since there are two studies of k_3 that are in close agreement (rate constant differences are ≤14% over the whole range 295−480 K), it seems unlikely that this value can be seriously in error. The consistency of the kinetics makes it appear unlikely that k_1 is also in error. There is thus a strong case for the reliability of the data based on kinetics.

Although it is not our prime consideration to review theoretical work in this area, it is worth noting that the considerable interest in the unimolecular dissociation of the CHO radical has led to high-level calculations of its dissociation surface. The most recent of these[37] gives D_0(H−CO) = 54.98 kJ mol^{-1}, corresponding to $\Delta H_f°$(CHO) = 47.61 kJ mol^{-1}. The agreement with experiment is reasonable, if we accept the the expressed uncertainties of ±4 kJ mol^{-1} of earlier theoretical calculations.[38,39]

It is also interesting to note the close similarity in values of D(H−CHO) and D(CH_3CO−H) for which the most recent values are 373.8 ± 1.5 kJ mol^{-1} (experiment[23]) and 374.9 ± 2.8 kJ mol^{-1} (theory[40]). It appears that Me-for-H replacement in formaldehyde marginally increases the remaining aldehydic C-H bond strength.

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