Kinetics and Thermochemistry of the CH₃CO Radical: Study of the CH₃CO + HBr \rightarrow CH₃CHO + Br Reaction

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The kinetics of the reaction between CH₃CO and HBr has been studied using a heatable tubular reactor coupled to a photoionization mass spectrometer. CH₃CO was produced homogeneously by laser photolysis in the presence and absence of HBr. Radical decays were monitored in time-resolved experiments. Rate constants were determined at five temperatures in the range 300-400 K and fitted to the Arrhenius expression, $6.4 (\pm 3.6) \times 10^{-13} \exp[4.45 (\pm 1.50) \text{ kJ mol}^{-1}/RT]$ cm³ molecule⁻¹ s⁻¹. This kinetic information was combined with known rate constants and Arrhenius parameters for the reverse reaction to obtain the heat of formation of CH₃CO. Both second law and third law procedures were used to obtain this thermochemical information from these rate constants. The two determinations of this heat of formation of -10.0 ± 1.2 kJ mol⁻¹ at 298 K which is 14 kJ mol⁻¹ higher than the value in common use. The current results imply a CH₃-CO bond enthalpy of 45.1 (± 1.5) kJ mol⁻¹ which is 14 kJ mol⁻¹ lower than currently believed and a CH₃CO heats of formation associated with the equilibrium systems studied to obtain this thermochemical information is 14 kJ mol⁻¹ lower than currently believed and a CH₃CO heats of formation associated with the

Introduction

Surprisingly, the heats of formation of few organic free radicals are established within today's desired "chemical accuracy" (i.e., within $\pm 4 \text{ kJ mol}^{-1}$). For example, only recently have disparities in reported heats of formation of the simple alkyl radicals, from which the primary, secondary, and tertiary C-H bond energies are derived, been resolved.¹⁻⁷ These disparities had been as large as 12 kJ mol⁻¹.

A large number of the heats of formation of polyatomic radical intermediates that are in common use come from thermochemical studies of equilibria involving these organic free radicals (**R**) and the hydrogen halides (HX), particularly HBr and HI^{8-11}

$$\mathbf{R} + \mathbf{H}\mathbf{B}\mathbf{r} \leftrightarrow \mathbf{R}\mathbf{H} + \mathbf{B}\mathbf{r} \tag{1}$$

$$\mathbf{R} + \mathbf{H}\mathbf{I} \Leftrightarrow \mathbf{R}\mathbf{H} + \mathbf{I} \tag{2}$$

Older studies, which are still the basis of many of the heats of formation in current use, combined *measured* activation energies of the X + RH reactions with *assumed* activation energies of the R + HX reactions to obtain reaction enthalpies and, via these enthalpies, the radical heats of formation.

Recently, in kinetic studies of R + HX reactions, we discovered that the formerly assumed activation energies of R + HX reactions were in error (by as much as 12 kJ mol⁻¹) and were usually the source of the disparities between heats of formation derived from studies of reactions 1 and 2 and those obtained from studies of other equilibria or physical processes.^{1-5,12} These negative activation energies in R + HX reactions have now also been found by others.^{6,7}

In a study still in progress of the unimolecular decomposition of the acetyl radical (CH₃CO), we have found that the unimolecular rate constants, including their fall-off behavior, are inconsistent with the recommended heat of formation of this radical, $-24 \pm 2 \text{ kJ mol}^{-1,11,13}$ This value is derived from older studies of reaction 2. Suspecting significant error in this value, we have now extended our investigation of R + HX reactions to include one of reaction 3 in order to obtain a new and more direct determination of the heat of formation of the acetyl radical, an important intermediate both in combustion processes and in atmospheric transformations.

$$CH_3CO + HBr \Leftrightarrow CH_3CHO + Br$$
 (3)

This reaction is essentially thermoneutral. Accurate rate constants for the reverse reaction have already been reported by Nicovich et al.¹⁴ We have measured rate constants as a function of temperature for the forward reaction and combined this information with that obtained by Nicovich et al. to obtain equilibrium constants of reaction 3. From these equilibrium constants, we obtained the CH₃CO heat of formation without the use of assumptions required in the prior studies discussed above. Second law and third law analyses of the data yielded values of the radical heat of formation that differed by less than 1 kJ mol⁻¹. All results taken together indicate a heat of formation of CH₃CO at 298 K of -10.0 ± 1.2 kJ mol⁻¹ which is substantially higher than the widely accepted value.

Prior determinations of the CH₃CO heat of formation have varied widely, from -4 to -26 kJ mol^{-1,8,9,15} Large disparities exist between heats of formation of CH₃CO obtained from studies of different kinds of chemical equilibria (see Table I). Former studies of reaction 1 or 2 (as represented by critical data assessments in Table I) have yielded values near the bottom of the range of determinations, and other values based on investigations of dissociation/recombination processes have yielded values near the high end of the range. Most prior determinations have been reviewed^{8,9} or tabulated.^{10,11,13,15,20}

The experimental investigation of reaction 3 and the thermochemical calculations of the CH_3CO heat of formation are presented here along with a discussion of other determinations of the heat of formation of CH_3CO .

Experimental Section

The apparatus used²³ and experimental procedures¹⁻⁴ have been described previously. Briefly, gas flowing through a tubular Pyrex reactor contained the CH₃CO source (see below), HBr in varying amounts, and an inert carrier gas in large excess (He, >99%). Reaction was initiated by laser photolysis which results in the rapid production of CH₃CO. Reactors having three different inner diameters were used, 0.67, 1.05, and 2.2 cm. The flow velocity was $\approx 5 \text{ m s}^{-1}$ when the two smaller reactors were used and $\approx 3 \text{ m s}^{-1}$ when the largest was employed. These velocities were adequate to completely replace gases in the reactor between laser pulses.

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TABLE I: Selected Determinations of the CH₃CO Heat of Formation (Energies in kJ mol⁻¹)^{*a*}

authors		Δ Η° _{f,298K}	
Based on Studies of CH ₃ CO + H Golden and Benson, 1969 ^b McMillen and Golden, 1982 ^c	Equilibria Involving $I \Leftrightarrow CH_3CHO + I$ (critical evaluation) (critical evaluation)	HX -22 ± 4 -24 ± 2	
CH ₃ CO + HB current study	$r \Leftrightarrow CH_3CHO + Br$ second law third law recommended	-10.3 ± 1.6 -9.9 ± 1.1 -10.0 ± 1.2	
Based on Studies of Dissoci CH ₃ CO of Kerr, 1966 ^d Watkins and Word, 1974 ^e	ation/Recombination ⇒ CH ₃ + CO (critical evaluation) second law third law	Equilibria -9 -14 ± 3 -11 ± 3	
3-methylpentan-2-one \Leftrightarrow CH ₃ CO + sec-C ₄ H ₉ , and hexan-2-one \Leftrightarrow CH ₃ CO + n-C ₄ H ₉ Tsang, 1984/ -13.8 \pm 8			
Based on Studies of Ionization Phenomer Fragmentation Thresholds Murad and Inghram, 1964 ^g Holmes and Lossing, 1984 ^h		na -21 ± 8 -19 ± 8	
Electron Affinity Determination Nimlos, Soderquist, and Ellison, 1989'		-22.6 ± 9	

^aError limits are those cited by the authors. ^bReference 9. ^cReference 11. ^dReference 8. Originally reported value (-12.5) revised to take into account current knowledge of CH₃ heat of formation needed in the thermochemical computation. ^cReference 18. Originally reported value (-17.4) based on second law determination revised for reason given in footnote d. Additional third law determination provided here based on equilibrium constant given in the reference and entropies used in the current study. ^fReference 19. ^gReference 20. ^hReference 21. ^fReference 22.

Gas emerging from a small sampling orifice in the wall of the reactor was formed into a molecular beam and analyzed continuously using a photoionization mass spectrometer (PIMS). Ionizing radiation in the PIMS was provided by atomic resonance lamps: CH₃CO with 8.9-9.1-eV radiation (Cl lamp), HBr using 11.6-11.8-eV light (Ar lamp), and CH₃COC₂H₅ using 10.2-eV radiation (H lamp).

The decay of CH₃CO was monitored in time-resolved experiments in the absence and the presence of HBr. Experiments were conducted under pseudo-first-order conditions (HBr in large excess). Initial conditions were chosen to essentially isolate the CH₃CO reaction of interest from other possible gas-phase reactions involving this free radical. With the initial concentration of CH₃CO kept low ($<5 \times 10^{10}$ molecules cm⁻³), radical-radical and radical-atom reactions had negligible rates compared to that of the elementary reaction of interest.

 CH_3CO was prepared by direct photolysis. Pulsed, unfocused 248-nm radiation from a Lambda Physik 201 MSC laser was directed along the axis of the tubular reactor and was used to photodecompose methyl ethyl ketone. The photolysis route of interest was

$$CH_3COC_2H_5 \rightarrow CH_3CO + C_2H_5$$
 (4)

Other photolysis products (including CH₃) are produced by photolysis at this wavelength but were of no concern in the current study because of the negligible rates of radical-radical reactions. The laser fluence used was ≈ 40 mJ cm⁻². Under these conditions the percent of ketone and HBr which decomposed was undetectable, <0.4%.

Under the pseudo-first-order conditions used in these experiments CH_3CO^+ ion signal decays, $I(CH_3CO^+)_t$, were exponential in shape as expected (see Figure 1). Decay profiles were fitted to the function $I(CH_3CO^+)_t = I(baseline) + I(CH_3CO^+)_0$ exp(-k't). k' was determined as a function of [HBr]. What was anticipated under the experimental conditions used was a linear



Figure 1. Plot of exponential decay constants k' of CH₃CO⁺ ion signals measured at 300-302 K vs [HBr] for two experiments using different wall coatings. Insert is actual ion signal profile recorded during one of the experiments whose decay constant is plotted here (indicated by arrow). For this experiment, [HBr] = 1.13×10^{14} molecules cm⁻³. The first-order decay constant is 514 ± 20 s⁻¹.



Figure 2. Plot of k' vs [HBr] for four sets of experiments using different reactor wall conditions. The reactor used was the same for all experiments, 1.05 cm diameter.

dependence of k' vs [HBr].^{1,2} Such dependence arises when the only reactions occurring in the system that consume CH₃CO are the expected ones, reaction 3 and a first-order heterogeneous wall loss process

$$CH_3CO \rightarrow heterogeneous loss$$
 (5)

For this case, $k' = k_3$ [HBr] + k_5 , and k_3 is simply obtained from the slope of the line established by the data on the k' vs [HBr] plot. This linear behavior was not what was observed. Instead there was curvature of the data on such a plot indicating at least one additional radical loss process.

Suspecting an additional heterogeneous process, additional experiments were conducted using reactors of three different internal diameters (to vary the surface/volume ratio significantly) as well as with and without wall coatings (to change surface reactivity). The coatings used were Halocarbon Wax, HW, and poly(dimethylsiloxane),²⁴ PDMS (the latter being used in our laboratory for the first time). The pattern of behavior of the data obtained on plots of k' vs [HBr] for the different wall conditions is displayed in Figure 2. There is a sharp increase of k' with the initial additions of HBr relaxing to a less steep linear increase with further [HBr] additions. The slope of the first increase vs k[HBr] (determined in separate experiments from those shown in Figure 2 in which only low HBr concentrations were used) depended on the nature of the wall coating while that of the second does not. This behavior is indicated by the lines through the data.

The dependence of the initial slope on the k' vs [HBr] plot on the reactor diameter (D) using the same wall coating material (PDMS) was also investigated. Such initial slopes (obtained using only very low HBr concentrations) were determined as a function of reactor diameter using the three reactors with diameters 0.67, 1.05, and 2.2 cm. Sets of such experiments were conducted at



Figure 3. Plot of k_3 (squares) and $k_{3,initial}$ (circles) vs (reactor diameter)⁻¹ for two sets of experiments conducted at different temperatures using PDMS-coated tubular reactors. Dotted lines indicate that extrapolating $k_{3,initial}$ determinations to infinite tube diameter (infinite volume/surface ratio) yields the measured value of k_3 .

both 300 and 400 K. This initial slope, termed $k_{3,initial}$, when extrapolated to infinite tube diameter (using a plot of $k_{3,initial}$ vs D^{-1} , see Figure 3) yields a value of k_3 that is the same as that obtained from the late slope (at higher [HBr] concentrations).

This observed behavior of CH₃CO loss as a function of reactor diameter and reactor wall coating clearly indicates the presence of a second-order CH₃CO heterogeneous wall-loss process. Several possibilities exist, e.g., one involving surface-adsorbed HBr

$$CH_3CO + [HBr]_{surface} \rightarrow heterogeneous loss$$
 (6)

At very low HBr concentrations, when the reactor walls are far from saturation, $[HBr]_{surface}$ is proportional to the HBr concentration in the gas phase. Hence the first-order rate constant for CH₃CO loss, k', increases linearly with [HBr] due to the combined increases in rates of the homogeneous and heterogeneous bimolecular reaction of CH₃CO with HBr, reactions 3 and 6. When wall saturation develops, further increase of k' with [HBr] is due only to increase in the homogeneous reaction, reaction 3.

It can be seen in Figure 2 that the contribution of the undesired heterogeneous bimolecular reaction (as manifested by the early portion of the plotted data with large slope) is greatest for a freshly cleaned quartz reactor, is less for a quartz reactor used for several days, and is almost unnoticeable using either the HW- or PDMS-coated reactors.

On the basis of this interpretation of our experimental observations, we derived all our k_3 values only from late slopes. Further, we obtained rate constants only from experiments conducted using the coated reactors where the "late" linear portion of the k' vs [HBr] plot is dominant. This dominance is most apparent in Figure 1 where k' values are plotted vs [HBr] from two sets of experiments conducted to obtain k_3 at 300 and 302 K, sets in which the two different coatings were used. As can be seen in this figure, the early portion of the k' vs [HBr] plot, that with the larger slope, is restricted to the small region between the point with no HBr present and the data point with the smallest amount of HBr added. The linear dependence of k' vs [HBr] after an initial small addition of HBr is apparent in this figure. This situation was typical of what was observed in all sets of experiments performed to determine k_3 .

Rate constants for reaction 3 were determined at five temperatures between 300 and 400 K. Higher temperatures could not be used because additional loss of CH_3CO by unimolecular decomposition becomes a significant process above 400 K.

Additional experimental parameters not expected to affect the rate constant determination were varied at selected temperatures. They include the total gas density and the laser fluence (affecting $[CH_3CO]_0$). The measured rate constants were independent of these variables as expected from the mechanism for CH_3CO loss used here to reduce the data. The reaction conditions used and the results obtained are presented in Table II. The rate constants vs temperature are plotted in Figure 4.

Reagents used were obtained from Aldrich ($CH_3COC_2H_5$ 99.7% and HBr >99%). Helium was obtained from Matheson

TABLE II: Reaction Conditions and Rate Constants Obtained in the Study of the $CH_3CO + HBr$ Reaction

T,ª K	10^{-16} [He], molecule cm ⁻³	10^{-12} [HBr], molecule cm ⁻³	reactor coating ^b	$10^{12}k_{3}$, cm ³ cm ³ molecule ⁻¹ s ⁻¹
_	k	$x_1 = 6.4 (\pm 3.6) \times$	10-13	
	exp{(4.45(±1.5	0) kJ mol ⁻¹ / RT)	cm ³ molecu	le ⁻¹ s ⁻¹
302	17.9	10.9-158	HW	3.87 ± 0.20
343	18.0	53.3-240	НW	2.94 ± 0.48
300	17.8	15.4-156	PDMS	4.17 ± 0.37
320	17.8	13.8-211	PDMS	3.09 ± 0.18
343	17.8	9.29-137	PDMS	3.07 ± 0.10
373	17.9	57.5-164	PDMS	2.96 ± 0.29
400	17.8	58.9-227	PDMS	2.44 ± 0.13

^aTemperature uncertainty ± 3 K. ^bHW, halocarbon wax; PDMS, poly(dimethylsiloxane). ^cErrors presented are 1σ and refer to random uncertainties only. Overall uncertainty estimated to be $\pm 20\%$.



Figure 4. Semilog plot of k_3 vs 1000 K/T. The line fitted through the plotted points by linear least-squares analysis was used to obtain the Arrhenius parameters for k_3 given in Table II.

(He, 99.995%). The ketone was degassed using freeze-pump-thaw cycles and used without further purification. Helium was used as provided. The HBr was repeatedly distilled to remove traces of H_2 and Br_2 (in the case of Br_2 to below detectable limits, <0.03%) and then stored in dark Pyrex bulbs. The purity of HBr was maintained by daily distillations.

Thermochemical Calculations

Nicovich et al. measured k_{-3} at five temperatures between 255 and 400 K from which they derived the Arrhenius expression k_{-3} = (1.51 ± 0.20) × 10⁻¹¹ exp((-364 ± 41)/T) cm³ molecule⁻¹ s⁻¹.¹⁴ The values we obtained for k_3 were combined with this kinetic information on the reverse reaction to obtain the CH₃CO heat of formation using both second law and third law procedures. Detailed examples of this kind of thermochemical calculations have been published in connection with our prior investigations of the thermochemistry of other free radicals,¹⁻⁴ and hence, the current calculations are presented here only in summary. Reported error limits are estimates or calculations of 1 σ values.

A. Second Law Determination of the CH_3CO Heat of Formation. a. In the second law calculation, rate constants and activation energies for the forward and reverse reactions are required at a single temperature. For maximum accuracy, we have selected the midpoint of the overlapping temperature range of our study and that of Nicovich, 343 K,¹⁴ as this temperature.

The enthalpy change for reaction 3 at 343 K is obtained directly from the difference of Arrhenius activation energies for the forward and reverse reactions

$$\Delta H^{\circ}_{343} = E_3 - E_{-3} = -4.45 \ (\pm 1.50) - 3.03 \ (\pm 0.34) = -7.5 \pm 1.6 \ \text{kJ}$$

b. The free energy change at the same temperature was obtained from the equilibrium constant at this temperature, $K_3 = k_3/k_{-3}$ (rate constant units used are cm³ molecule⁻¹ s⁻¹)

$$\Delta G^{\circ}_{343} = -RT \ln (k_3/k_{-3}) = -R \times 343 \ln (3.1 \times 10^{-12}/5.2 \times 10^{-12}) = 1.5 \pm 0.8 \text{ kJ}$$

 TABLE III: Calculated Thermodynamic Functions of CH₃CO (Standard State 1 bar)^a

	C° ",	$ S^{\circ}(T) - S^{\circ} $	$(0)\}, \{H^{\bullet}(T) - H^{\bullet}(0)\},$		
<i>T</i> , K	J K ⁻¹ mol ⁻¹	J K ⁻¹ mol	⁻¹ kJ mol ⁻¹		
150	40.296	236.94	5.717		
200	43.067	248.89	7.798		
250	46.714	258.88	10.042		
298.15	50.769	267.46	12.388		
300	50.933	267.77	12.481		
350	55.396	275.96	15.140		
400	59.872	283.64	18.027		
450	64.189	290.95	21.131		
500	68.283	297.92	24.445		
550	72.123	304.61	27.959		
600	75.715	311.05	31.656		
650	79.063	317.24	35.525		
700	82.190	323.22	39.558		
800	87.809	334.57	48.077		
900	92.675	345.20	57.121		
1000	96.874	355.18	66.612		
1100	100.499	364.59	76.494		
1200	103.625	373.47	86.711		
1300	106.318	381.87	97.218		
1400	108.649	389.84	107.976		
1500	110.670	397.40	118.956		
1600	112.427	404.60	130.118		
CH ₁ CO Molecular Parameters:					
molecular ma	ISS		43.0454		
external rota	tional constants:		$A = 2.943 \text{ cm}^{-1}, B = 0.334 \text{ cm}^{-1}, C = 0.318 \text{ cm}^{-1}$		

	cm^{-1} , $C = 0.318 cm^{-1}$
product of external moments of inertia	$7.01768 \times 10^{-137} \text{ kg}^3 \text{ m}^6$
reduced moment of inertia - internal	$2.66199 \times 10^{-47} \text{ kg m}^2$
rotation	$(B_{int} = 10.515892 \text{ cm}^{-1})$
barrier to internal rotation ^b	92.0 cm ⁻¹
vibration frequencies	2904, 2903, 2826, 1886,
•	1405, 1402, 1325, 1025,
	925, 817, 454 (all cm ⁻¹)
symmetry numbers	
external rotation	1
internal rotation	3
degeneracies	
electronic	2

^a Bond distances, bond angles, and vibration frequencies of CH₃CO taken from ref 22. ^bBarrier calculated from torsional frequency (94 cm⁻¹) and assumed three-cycle sinusoidal internal rotation barrier. Contributions to thermodynamic functions for hindered rotor taken from Pitzer, K. S.; Gwinn, W. D. J. Chem. Phys. **1942**, 10, 428.

c. The reaction entropy change at this same temperature was derived from the above information

$$\Delta S^{\circ}_{343} = (\Delta H^{\circ}_{343} - \Delta G^{\circ}_{343}) / 343 \text{ K} = -26.4 \pm 5.1 \text{ J K}^{-1}$$

d. By use of calculated heat capacities²⁵ for reactants and products based on partition functions (including those of CH₃CO obtain in the current study using recently obtained structural information and vibration frequencies of this radical²²—see Table III), small corrections to ΔH°_{343} and ΔS°_{343} were calculated and used to obtain the values of these thermodynamic variables at 298 K

$$\Delta H^{\circ}_{298} = -7.3 \pm 1.6 \text{ kJ}$$
 $\Delta S^{\circ}_{298} = -25.8 \pm 5.1 \text{ J K}^{-1}$

e. Finally, using the known molar heats of formation and entropies of HBr, CH_3CHO , and Br,²⁵ the values of these same properties for the CH_3CO radical were obtained from the reaction variables:

$$\Delta H^{\circ}_{f,298}(CH_3CO) = -10.3 \pm 1.6 \text{ kJ mol}^{-1}$$

S°₂₉₈(CH₃CO) = 266 ± 5 J K⁻¹ mol⁻¹

B. Third Law Determination of the CH₃CO Heat of Formation. Both k_3 and k_{-3} were measured at ambient temperature. Their values at 298 K were obtained from these determinations. Hence the free energy change of reaction 3 at this temperature is obtained directly from the data. The entropy change is obtained from calculated molecular entropies. Combining this information provides the enthalpy change of reaction 3 as well as the CH_3CO heat of formation at 298 K.

a. The free energy change at 298 K was obtained from the equilibrium constant for reaction 3, $K_3 = k_3/k_{-3}$. k_3 (298 K) was obtained from the Arrhenius expression for k_3 in Table I and k_{-3} (298 K) from the Arrhenius expression for k_{-3} reported by Nicovich et al.¹⁴

$$\Delta G^{\circ}_{298} = -R \times 298 \ln \left[(3.9 \pm 0.8) \times 10^{-12} \right]$$

(4.45 ± 0.9) × 10⁻¹²] = 0.35 ± 0.70 kJ

b. The entropy change of reaction 3 was obtained from calculated molar entropies (Table III and ref 25) of reactants and products.

$$\Delta S^{\circ}_{298} = -27 \pm 3.0 \text{ J K}^{-1}$$

c. The enthalpy change of reaction 3 (ΔH°_{298}) was obtained from the information in a and b, and finally the heat of formation of CH₃CO from this result and the known heats of formation of the other reactant and the products of this reaction (CH₃CHO, HBr, and Br):²⁵

$$\Delta H^{\circ}_{298} = -7.7 \pm 1.1 \text{ kJ}$$
$$H^{\circ}_{f,298}(CH_3CO) = -9.9 \pm 1.1 \text{ kJ mol}^{-1}$$

Discussion

Δ

A. Kinetics of Reaction 3. There are no prior reported values of the rate constants of reaction 3. The magnitudes of k_3 and the small yet significant negative activation energy found for this rate constant (-4.45 kJ mol⁻¹) are both consistent with what we¹⁻⁵ and others^{6,7} have observed for exothermic reactions of other polyatomic free radicals with the hydrogen halides.

Reaction 3 is essentially thermoneutral. $\Delta H^{\circ}_{298} = -7.6 \text{ kJ}$ mol⁻¹. In spite of this fact, there appears to be no potential energy barrier to reaction. The reduction of energy barriers in H-atom transfer reactions induced by "polar effects", $^{30-32}$ i.e., reductions resulting from attractive forces between the polar H-atom donors (such as HX) and polar or polarizable radicals, is well-known. That these attractive forces can also lead to "negative barriers", potential energy wells along the reaction coordinate before the H-atom transfer transition state is reached, appears increasingly indicated. It is supported by the kinetic behavior of reaction 3 as it was earlier by the kinetic behavior of the reactions between alkyl radicals and HBr or HI.¹⁻⁷

The relatively small but significant negative activation energies and the small Arrhenius A factors (compared to typical H-atom transfer reactions) of these reactions cannot be accounted for by a simple metathesis mechanism. However, both these kinetic properties can be quantitatively reproduced by considering the chemical reaction as a three-step process, the reversible formation of a bound complex and the alternative irreversible decomposition of the complex by a step which completes the H-atom transfer. Such potential energy wells have recently been reported in a theoretical study of the potential energy along the CH₃ + HBr and CH₃ + HCl reaction paths,³³ and reported Arrhenius A factors and negative activation energies for two R + HX reactions have been reproduced in RRKM calculations using this three-step mechanism (CH₃ + HBr and t-C₄H₉ + HI).^{34,35}

We have found that for a homologous series of these exothermic reactions (R + HX), a linear free energy relationship exists with the ionization potential of the free radical (IP).¹² Linear plots of the logarithm of the room temperature rate constant (the measure of the free energy of activation) vs IP for a series of R + HX reactions have now been published.¹² The room temperature rate constant of reaction 3 complies well with the linear free energy relationship established by the alkyl radicals plus HBr reactions.

B. Thermochemistry of CH_3CO . The two separate determinations of the CH_3CO heat of formation obtained from the second and third law analyses of the forward and reverse kinetics of reaction 3 are in excellent agreement, differing by only 0.4 kJ

mol⁻¹. This extreme closeness supports the assessment of the accuracy of the final determination, -10.0 ± 1.2 kJ mol⁻¹. It is a weighted average of the two values. The current determination is the most precise reported to date and its derivation involves no assumptions to obtain the desired thermochemical information.

In this study we have again been able to eliminate a former disparity between reported heats of formation for a free radical, a disparity that was associated with the particular kind of equilibrium studied to obtain this thermochemical information. The widely quoted value, -24 kJ mol^{-1} ,¹¹ is linked with a study involving a hydrogen halide molecule, in the current case, CH₃CO + HI \leftrightarrow CH₃CHO + I. Investigations of dissociation/recombination equilibria have generally yielded higher values (see Table I). In particular, studies of reaction 7

$$CH_3CO \Leftrightarrow CH_3 + CO$$
 (7)

have yielded values close to -12 kJ mol^{-1} (within 4 kJ mol⁻¹)^{8,18} while investigations of reactions 9 and 10¹⁹

> 3-methylpentan-2-one \Leftrightarrow CH₃CO + sec-C₄H₉ (8)

hexan-2-one
$$\Leftrightarrow$$
 CH₃CO + *n*-C₄H₉ (9)

have provided a value of -13.8 ± 8 kJ mol⁻¹ (see Table I).

In earlier thermochemical investigations of the iodination and reverse iodination of acetaldehyde on which the currently recommended^{11,13} CH₃CO heat of formation is based, assumptions were made regarding the activation energies of the $CH_3CO + I_2$ and $CH_3CO + HI$ reactions, the latter being assumed to be 4.2 kJ mol⁻¹ (a generic value assigned to all R + HI reactions¹⁰). In prior kinetic studies, we have found that the activation energy of a particular \mathbf{R} + HI reaction is usually slightly lower (i.e., slightly more negative) than that of the corresponding R + HBr reaction.^{3,4,12} Presuming this to be also the case for the pair of reactions, $CH_3CO + HBr$ and $CH_3CO + HI$, an activation energy of the latter reaction is indicated that is <-4.5 kJ mol⁻¹ which indicates that the difference between the assumed and actual values of the activation energies for the $CH_3CO + HI$ reaction is >8.7 kJ mol⁻¹. This error in the $CH_3CO + HI$ activation energy used in earlier thermochemical calculations accounts for most of the 12 kJ mol⁻¹ disparity between the value of CH₃CO heat of formation derived from the old study of reaction 2 and values obtained from studies of dissociation/recombination equilibria. The present study, using measured activation energies for both forward and reverse reactions yields a CH₃CO heat of formation from a study of an $R + HX \Leftrightarrow RH + X$ equilibrium that is in close agreement with the values obtained from studies of dissociation/recombination equilibria.

Measurements of ionization phenomena, including threshold determinations, have also been used to obtain the CH₃CO heat of formation. All tend to yield values below the current value. This is not unexpected from threshold determinations since they rigorously provide only an upper limit to the radical heat of formation. Murad and Inghram²⁰ measured the photoionization thresholds for two fragmentation processes

$$CH_3COCOCH_3 \rightarrow CH_3CO + CH_3CO^+$$
 (10)

$$CH_3COCOC_2H_5 \rightarrow CH_3CO + C_2H_5CO^+$$
(11)

This information was combined with additional threshold determinations and thermochemical information to derive their reported value of $-21 \pm 8 \text{ kJ mol}^{-1}$ for the CH₃CO heat of formation. Holmes and Lossing,²¹ who measured the electron bombardment energy needed to first produce CH₃CO in fragmentation processes, e.g.

$$CH_3CH(OH)CH_2OH \rightarrow CH_3CO + CH_3OH_2^+$$
 (12)

obtained a value of -19 ± 8 kJ mol⁻¹ from their results. Thresholds of this sort, particularly ones derived from fragmentation of large polyatomic species at ambient temperature, are difficult to establish with accuracy. The error limits for the radical heat of formation indicated by the authors, $\pm 8 \text{ kJ mol}^{-1}$, essentially place our determination within their relatively large uncertainty limits. More recently, Nimlos et al.²² measured the electron affinity

of CH₃CO and deduced a radical heat of formation of $-22.6 \pm$ 9 kJ mol⁻¹ using this electron affinity and other thermochemical information including the gas-phase acidity of CH₃CHO. Their value is 12.6 kJ mol⁻¹ below our own, a difference which is slightly larger than can be accounted for by the combined error limits of the two determinations. The study of Nimlos et al. does not involve a threshold measurement. Hence the fact that their value lies below our own cannot be ascribed to the known difficulty of establishing thresholds for fragmentation processes accurately. No explanation for this difference is apparent.

The CH₃CO heat of formation obtained here provides accurate determinations of the CH₃-CO and CH₃CO-H bond enthalpies at 298 K, DH^o_{298K}: for CH₃-CO, 45.1 \pm 1.5 kJ mol⁻¹; for CH₃CO-H, 373.8 \pm 1.5 kJ mol⁻¹. The former is lower and the latter higher (by 14 kJ mol⁻¹) than is implied by the lower heat of formation of CH₃CO (-24 kJ mol⁻¹) now in common use.^{11,13}

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Registry No. Acetyl, 3170-69-2; hydrogen bromide, 10035-10-6; 2butanone, 78-93-3.

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(24) (a) Halocarbon Wax is a product of the Halocarbon Wax Corp. Hackensack, NJ. (b) Poly(dimethylsiloxane), 200 fluid was obtained from Aldrich.

(25) Standard State Molar Thermodynamic Functions of CH₁CO, CH₁-CHO, HBr and Br used in the thermochemical calculations were obtained from the following sources: (1) all heat capacity functions, ref 26; (2) heats of formation at 298 K (kJ mol⁻¹), all from ref 27, CH₃CHO (-165.8), HBr (-36.38), Br (111.86); (3) entropies at 298 K (J mol⁻¹ K⁻¹), CH₃CHO

(-36.36), Br (111.86); (3) entropies at 298 K (J mol * K), CH₃CHO (263.95, ref 28), HBr (198.7, ref 29), Br (175.0, ref 29).
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Long Range Electron Transfers between Very Slowly Diffusing Tetracyanoquinodimethane and Its Radical Anion in Poly(ether) Solutions

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The homogeneous electron self-exchange rate between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its radical anion (TCNQ⁻), dissolved in the poly(ethylene oxide) (PEO) polymer electrolyte solvents network PEO and MW 600000 linear PEO, is measured by detecting the enhancement of the apparent diffusion rate of TCNQ⁻ by the electron exchange reaction. We report results for the physical diffusion constant D_{phys} ($D_{app,1/2}$) of TCNQ⁻ and the product $k_s \delta^2$ of the TCNQ^{-/0} electron self-exchange rate constant k_{δ} and the square of the center-to-center electron-transfer reaction distance δ . D_{phys} is made to vary from 3 $\times 10^{-7}$ to 5×10^{-12} cm²/s by choice of temperature and electrolyte concentration. Remarkably, $k_{\delta}\delta^2$ changes in a nearly proportional manner over this $>10^5$ -fold range of values. The explanation is not the trivial one of diffusion control of the rate of contact-collisions leading to reaction. The D_{phys} vs $k_{\delta}\delta^2$ correlation is interpreted in terms of a (D_{phys}) diffusion rate-dependent reaction distance; electron transfers between very slowly diffusing donor and acceptor occur at distances (δ) larger than collision-contact distances (Δ). Estimates of edge-to-edge electron-transfer distances yield values from contact up to ca. 16 Å and of self-exchange rate constants k_{δ} that range from 4×10^9 to 1×10^3 M⁻¹ s⁻¹ for the maximum and minimum values observed for D_{phys} , respectively. The interpretation is supported by estimates of time constants $\tau_{et,\delta}$ for the long range TCNQ^{-/0} electron transfer that give values within a factor of 2 of the sum of the time constants τ_{diff} and $\tau_{et,\Delta}$ for, respectively, diffusion together of TCNQ⁻ and TCNQ⁰ over the same long distance ($\delta - \Delta$) followed by electron transfer at collision. That is, in mixed valent solutions around electrodes, when D_{phys} is very small and the time constant τ_{diff} for physical diffusion correspondingly large, then even the slower electron transfers characteristic of long distance reactions can deliver charges on comparable timescales, $\tau_{et,\delta}$.

As part of a study¹ of electron-transfer dynamics of donor/ acceptor solutes in macroscopically rigid and semirigid solvents, we have investigated^{1a} the rate of homogeneous electron self-exchanges between 7,7,8,8-tetracyanoquinodimethane (TCNQ⁰) and its radical anion TCNQ⁻ dissolved in a "polymer electrolyte"² solvent, the cross-linked poly(ethylene oxide) "network PEO".3 In acetonitrile solvent,⁴ this donor/acceptor couple has a very large self-exchange rate constant ($k_{ex} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). In network PEO, TCNQ^{-/0} electron self-exchanges in the mixed valent solution around the electrode act to enhance the apparent diffusivity of TCNQ⁻ during its electrochemical oxidation to TCNQ. This coupling of physical diffusion and electron-transfer, called "transfer diffusion",⁵ occurs when the time $\tau_{diff} = \delta^2/D_{phys}$ needed for a TCNQ⁻ donor to physically diffuse over a distance δ with a diffusion constant D_{phys} is larger than or comparable to the time constant for delivery of an electron from a TCNQ⁻ donor to a TCNQ acceptor over the same distance, which is $\tau_{et,\delta} = 1/k_{\delta}C$, where k_{b} is the electron self-exchange rate constant at distance δ and C is the donor plus acceptor concentration. The enhanced, or apparent, TCNQ⁻ diffusion coefficient $D_{app,1/0}$ is according to the Dahms-Ruff relationship⁵ a summation of the two transport modes

$$D_{\text{app},1/0} = D_{\text{phys}} + \frac{k_{\delta}\delta^2 C}{6}$$
(1)

We measure D_{phys} separately, as the diffusion coefficient $D_{app.1/2}$ of TCNQ⁻ during its *reduction* to TCNQ²⁻. (The TCNQ^{-/2-} electron self-exchange rate is much smaller than that of TCNQ^{-/0};

experimentally we find^{1a} $D_{app,1/0} > D_{app,1/2}$.) The kinetic result $k_{\delta}\delta^2$ is obtained from the slope of a plot of $D_{app,1/0} - D_{app,1/2}$ against TCNQ⁻ concentration, $C_{\text{TCNQ}^{-}}$.

In ordinary fluid solvents, physical diffusivity typically exceeds 10^{-6} cm²/s so that transfer diffusion effects are small or insignificant even when the electron self-exchange rate constant k_5 is large. In network PEO solvent, however, D_{phys} (e.g., $D_{app,1/2}$ of TCNQ⁻) is much smaller with values ranging down to 5×10^{-12} cm²/s at room temperature and high electrolyte concentration. This slow physical diffusion, combined with the facile electron-transfer dynamics for the TCNQ^{-/0} couple, results in significant transfer diffusion enhancement^{1a} during electrochemical TCNQ⁻ oxidation.

The Dahms-Ruff relation has been applied by several groups,⁶ starting with the classical work of Buttry and Anson,^{6a,b} to other fast electron-transfer couples in polymeric media. These prior reports, and indeed the original theory papers,⁵ assume that electron transfer occurs upon donor/acceptor collision, i.e., that the reactant separation δ is the collision-contact sum Δ of donor and acceptor radii. In our earlier report, ^{1a} we speculated that this need not be the case, based on the reasoning that when (due to small D_{phys}) the time constant τ_{diff} for physical diffusion over a separation distance $\delta - \Delta$ to affect a collision-contact reaction is large, then even an electron-transfer rate slowed by occurring at long distance $\delta - \Delta$ is able to transport charge over the distance δ on a time scale $\tau_{\text{et},\delta}$ that is comparable to τ_{diff} .

We present evidence in this report that supports the role of long distance electron transfers in TCNQ^{-/0} transfer diffusion, namely, measurements of the TCNQ⁻ diffusion rates $D_{app,1/0}$ and $D_{app,1/2}$ (e.g., D_{phys}) in network PEO polymer solvent and in another polymer solvent, linear MW 600 000 poly(ethylene oxide), under conditions (varied LiClO₄ electrolyte concentration and temperature) that cause the value of D_{phys} to vary widely. Remarkably,

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