J. Am. Chem. Soc. **1989**, *111*, 3977-3980 3977

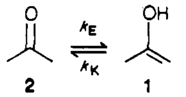
Temperature Coefficients of the Rates of Acid-Catalyzed Enolization of Acetone and Ketonization of Its Enol in Aqueous and Acetonitrile Solutions. Comparison of Thermodynamic Parameters for the Keto-Enol Equilibrium in Solution with Those in the Gas Phase

Y. Chiang, A. J. Kresge,* and N. P. Schepp

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada. *Received August 19, 1988*

Abstract: Rates of hydrogen ion catalyzed enolization of acetone and ketonization of acetone enol were measured over a range of temperatures in water and in acetonitrile solution. The data give $\Delta H^{\ddagger} = 20.0 \pm 0.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -12.1 \pm 0.3$ cal K^{-1} mol^{-1}, and $\Delta H^{\ddagger} = 20.1 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.8 \pm 1.7$ cal K^{-1} mol^{-1}, for enolization in water and acetonitrile, respectively, and $\Delta H^{\ddagger} = 9.7 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -8.6 \pm 1.4$ cal K^{-1} mol^{-1}, and $\Delta H^{\ddagger} = 11.4 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = 1.6 \pm 0.8$ cal K^{-1} mol^{-1}, for ketonization in water and acetonitrile, respectively. These values lead to $\Delta H^{\circ} = 10.3 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\circ} = -3.5 \pm 1.5$ cal K^{-1} mol^{-1}, for the keto-enol equilibrium in water, and $\Delta H^{\circ} = 8.7 \pm 0.6$ kcal mol^{-1}, $\Delta S^{\circ} = -7.4 \pm 1.9$ cal K^{-1} mol^{-1}, for the equilibrium in acetonitrile. This is the first determination of thermodynamic parameters for a simple ketone-enol equilibrium in solution; the results are remarkably similar to the thermodynamic parameters for this reaction in the gas phase. A mechanism involving acid catalysis of the bromination of acetone enol by *N*-bromosuccinimide, the process used to monitor enolization in acetonitrile solution, is ruled out.

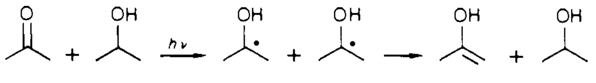
The gas-phase heat of formation of acetone enol (**1**) has recently been determined,[1] and that, in combination with the known heat of formation of acetone itself[2] (**2**), makes available the standard enthalpy change for the keto-enol equilibrium, eq 1, in the gas



2 **1** (1)

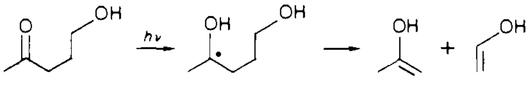
phase. It is of interest to compare this value with the enthalpy change for the same process in solution, and to that end we have measured the temperature coefficients of the specific rates of the forward, k_E, and reverse, k_K, reactions in water and acetonitrile solvents. These results lead to the temperature coefficient of the equilibrium constant K_E, through the relationship $K_E = k_E/k_K$, and thus provide the standard enthalpy change for the reaction in solution. Our work also gives a standard entropy change for the reaction in solution, which may be compared with gas-phase values either estimated by Benson's rules[3] or calculated from the gas-phase free energy change.[4] To the best of our knowledge, thermodynamic parameters for a simple ketone-enol equilibrium in solution have never been determined before, and such a comparison of gas phase with solution values has therefore not been possible.

We measured rates of enolization by using bromine to scavenge the enol as it formed. Determination of ketonization rates required production of the enol in greater than equilibrium amounts, and this we accomplished either by photooxidation of isopropyl alcohol, eq 2,[5] or by Norrish type II photoelimination of 5-hydroxy-2-



(2)

pentanone, eq 3.[6] All of the ketonization reactions were very rapid, and measurement of their rates required flash photolytic techniques.



(3)

Experimental Section

Materials. All materials employed were best available commercial grades and were used as received. Aqueous solutions were prepared with deionized water purified further by distillation, and acetonitrile solutions were made with HPLC grade solvent.

Kinetics. Rates of both enolization and ketonization were measured in dilute mineral acid solutions. The enolization reaction was slow under these conditions, and an initial rate method was therefore used to make kinetic measurements. For determinations in aqueous solution, the rapid reaction of enol with bromine was employed to monitor enol formation. This was done spectrophotometrically in the presence of bromide ion using the strong absorbance of tribromide ion at $\lambda = 320$ nm. Initial stoichiometric bromine concentrations were ca. 3×10^{-4} M, and acetone concentrations were $(6-8) \times 10^{-3}$ M; reactions were followed for about 0.5% consumption of acetone. Hydrobromic acid was used as the catalyst, and ionic strength was maintained at 0.10 M with sodium bromide.

In a typical run, 3.0 mL of aqueous HBr solution contained in a cuvette was allowed to equilibrate with the thermostated spectrometer (Cary 118) cell compartment for at least 10 min. A total of 10 μL of an aqueous stock solution of acetone was then added, and an absorbance reading was taken at $\lambda = 264$ nm, from which the concentration of acetone was calculated ($\epsilon_{264} = 20.2$ M^{-1} cm^{-1}).[7] A total of 5 μL of aqueous bromine was then added, and the decrease in absorbance at $\lambda = 320$ nm was recorded for at least 30 min. Observed first-order rate constants were calculated from zero-order rates of decrease of absorbance, $-\mathrm{d}A/\mathrm{d}t$, using eq 4 with $\epsilon_{320} = 5\,515$ M^{-1} cm^{-1} [7] and $K_{\mathrm{ass.}}$ (the $\mathrm{Br_2 + Br^- = Br_3^-}$ association constant) = 16.7 M^{-1}.[8]

$$k_{\mathrm{obs}} = \frac{-\mathrm{d}A/\mathrm{d}t}{[\mathrm{acetone}]\epsilon_{320}}\left(1 + \frac{1}{K_{\mathrm{ass.}}[\mathrm{Br}^-]}\right) \tag{4}$$

Rates of enolization of acetone in acetonitrile solution were also determined by bromine scavenging, but, in order to avoid the need to know

---

[1] (a) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2648–2649. (b) Turecek, F.; Havlas, Z. *J. Org. Chem.* **1986**, *51*, 4066–4067.

[2] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986; p 116.

[3] Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968.

[4] Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4845–4846.

[5] Keeffe, J. R.; Kresge, A. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1988**, *110*, 1993–1995.

[6] Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000–4009.

[7] Keeffe, J. R., unpublished determination.

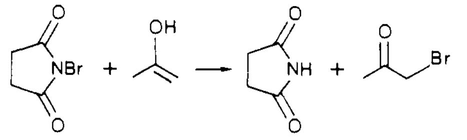
[8] Keeffe, J. R.; Kresge, A. J.; Toullec, J. *Can. J. Chem.* **1986**, *64*, 1224–1227.

0002-7863/89/1511-3977$01.50/0

Table I. Rate Constants for the Hydronium Ion Catalyzed Enolization of Acetone in Aqueous Solution

T/°C	$k^E_{H^+}/10^{-5}$ M^{-1} s^{-1}	ref	T/°C	$k^E_{H^+}/10^{-5}$ M^{-1} s^{-1}	ref
0	0.117	9	25	2.77	this work
0	0.112	10	27	3.60	9
24	2.53	9	35	8.81	9
25	2.86	9	35	8.49	11
25	2.75	10	45	24.3	11
25	2.76	11			

the $Br_2 + Br^-$ association constant in this medium, *N*-bromosuccinimide was used as the brominating agent: reaction of this substance with acetone enol produces succinimide as the other product, eq 5, and bromide ion is therefore not formed. Reactions were followed spectrophotometrically by monitoring the decrease in absorbance of *N*-bromosuccinimide at λ = 218 nm; succinimide itself has negligible absorbance at this wavelength. Initial concentrations of *N*-bromosuccinimide were 4 × 10^{-5} to 4 × 10^{-4} M, and acetone concentrations were 2.5 × 10^{-3} to 1.5 × 10^{-2} M; reactions were again followed for about 0.5% consumption of acetone. Perchloric acid (0.003–0.010 M) was used as the catalyst, and ionic strength was maintained at 0.10 M with sodium perchlorate. The perchloric acid was supplied by adding 1 vol of aqueous $HClO_4$ solution to 99 vol of acetonitrile, and the reaction mixtures therefore contained 1% water by volume.


(5)

In a typical run, 1.00 mL of acetonitrile (1% water) perchloric acid solution was allowed to come to temperature equilibrium with the spectrometer cell compartment. A few microliters of *N*-bromosuccinimide stock solution was then added, and the absorbance at λ = 218 nm was recorded, from which the *N*-bromosuccinimide concentration was calculated (ϵ_{218} = 2.27 × 10^3 M^{-1} cm^{-1}, independent of temperature over the range employed). A total of 10 μL of acetone stock solution of accurately known concentration was then added, and the decrease in absorbance at λ = 218 nm was recorded for 60–250 s. Observed first-order rate constants were calculated using eq 6.

$$k_{obs} = -(dA/dt)/[\text{acetone}]\epsilon_{218} \qquad (6)$$

Rates of ketonization were measured using the conventional flash photolysis apparatus already described.[6] Reactions were carried out in a 10-cm jacketed cuvette whose temperature was controlled by water circulating from a constant temperature bath; reaction temperatures were measured with a calibrated thermometer immersed directly in the reaction solution. Acetone enol was generated in aqueous solution by the photooxidation reaction shown in eq 2, with isopropyl alcohol and acetone concentrations = 0.05 M, and in acetonitrile solution (1% water) by the Norrish type II reaction of eq 3 with 5-hydroxy-2-pentanone concentration = 0.01 M. Decay of the enol transient was monitored at λ = 210 nm in aqueous solution and at λ = 215 nm in acetonitrile solvent. Perchloric acid was used as the catalyst in both solvents, and in both cases the ionic strength was maintained at 0.10 M with sodium perchlorate.

Results

Aqueous Solutions. The rate of enolization of acetone in dilute aqueous mineral acid solutions has been determined accurately before at temperatures ranging from 0 to 45 °C (Table I),[9-11] and only one set of measurements, at 25 °C, was therefore carried out here. The data, covering the acid concentration range [HBr] = 0.02–0.10 M, are summarized in Table S1,[12] given in the supplementary material.

These presently determined first-order rate constants are accurately proportional to acid concentration, and linear least-squares analysis gives the hydrogen ion catalytic coefficient k_{H^+} = (2.77 ± 0.05) × 10^{-5} M^{-1} s^{-1}. This agrees well with previous results (see Table I). As Figure 1 shows, all of the data give an accurately linear relationship when plotted according to the Eyring equation.

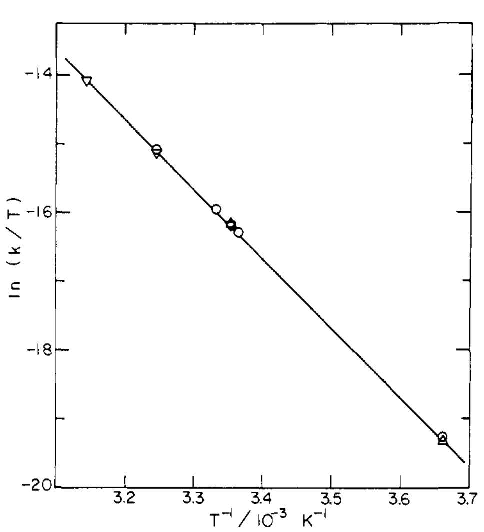


Figure 1. Eyring plot for the enolization of acetone in aqueous solution.

Table II. Rate Constants for the Perchloric Acid Catalyzed Ketonization of Acetone Enol in Aqueous Solution[a]

T/°C	$k^K_{H^+}/10^3$ M^{-1} s^{-1}	T/°C	$k^K_{H^+}/10^3$ M^{-1} s^{-1}
15.1	3.44 ± 0.02	44.5	17.1 ± 0.20
25.0	5.38 ± 0.08[b]	54.0	28.4 ± 0.50
34.5	10.7 ± 0.10		

[a] Ionic strength = 0.10 M ($NaClO_4$). [b] Reference 5.

Least-squares analysis leads to the activation parameters $\Delta H^\ddagger$ = 20.05 ± 0.08 kcal mol^{-1}, $\Delta S^\ddagger$ = −12.1 ± 0.3 cal K^{-1} mol^{-1}, and the rate constant at 25 °C $k^E_{H^+}$ = (2.79 ± 0.02) × 10^{-5} M^{-1} s^{-1}.

Rates of ketonization of acetone enol in dilute aqueous perchloric acid solutions were measured here at four temperatures from 15 to 54 °C. At each temperature, at least five different acid concentrations, varying by at least a factor of 5, were used. These data are summarized in Table S2 of the supplementary material.[12]

Observed first-order ketonization rate constants determined at each temperature were accurately proportional to acid concentration, and least-squares analysis gives the hydrogen ion catalytic coefficients shown in Table II. These, together with a value for 25 °C, reported before,[6] give a linear Eyring plot, which provides the activation parameters, $\Delta H^\ddagger$ = 9.74 ± 0.44 kcal mol^{-1}, $\Delta S^\ddagger$ = −8.6 ± 1.4 cal K^{-1} mol^{-1}, and the rate constant at 25 °C $k^K_{H^+}$ = (5.95 ± 0.23) × 10^3 M^{-1} s^{-1}.

Combination of these activation parameters for enolization and ketonization gives ΔH° = 10.31 ± 0.45 kcal mol^{-1} and ΔS° = −3.5 ± 1.5 cal K^{-1} mol^{-1} for the keto–enol equilibrium reaction. The 25 °C rate constants provided by the two Eyring relations give K_E = (4.69 ± 0.19) × 10^{-9}, pK_E = 8.33 ± 0.02, which is more accurate than pK_E = 8.22 ± 0.08 reported before.[13]

Acetonitrile Solutions. Rates of reaction of acetone with *N*-bromosuccinimide catalyzed by perchloric acid in acetonitrile solution (containing 1% water) were measured at five temperatures over the range 14–56 °C. Both perchloric acid and *N*-bromosuccinimide concentrations were varied, the former from 0.003 to 0.010 M and the latter from 0.00004 to 0.00040 M. These data are summarized in Table S3 of the supplementary material.[12]

Observed first-order rate constants proved to be somewhat dependent upon the concentration of *N*-bromosuccinimide: they sometimes dropped off slightly with decreasing concentration at the lower end of the concentration range employed; an example is shown in Figure 2. This indicates that the reaction of acetone enol with *N*-bromosuccinimide was not always sufficiently faster than its reversion back to ketone to make enolization fully rate-determining, i.e., that *N*-bromosuccinimide was not always functioning as a sufficiently efficient enol scavenger. This is unlike

---

(9) Rice, F. O.; Kilpatrick, M. *J. Am. Chem. Soc.* **1923**, *45*, 1401–1412.

(10) Smith, G. F. *J. Chem. Soc.* **1934**, 1744–1750.

(11) Baliga, B. T.; Whalley, E. *Can. J. Chem.* **1964**, *42*, 1835–1850.

(12) Supplementary material; see paragraph at the end of this paper regarding availability.

(13) Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *J. Am. Chem. Soc.* **1984**, *106*, 460–462.

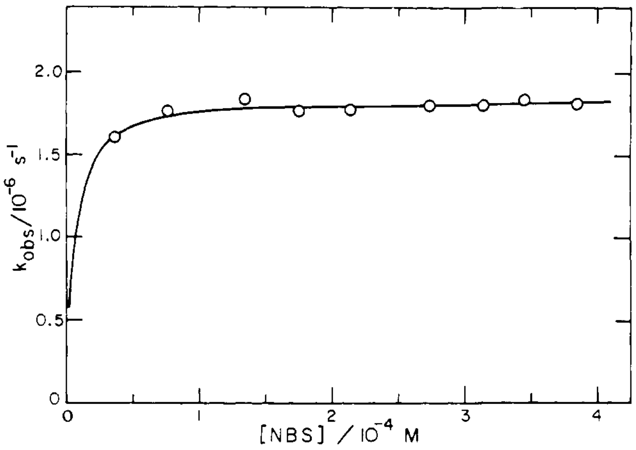


Figure 2. Dependence of observed rate constants upon *N*-bromosuccinimide concentration for the reaction of acetone in acetonitrile solution (1% water) at 56 °C. The line is drawn according to eq 8 with parameters obtained by least-squares fit to eq 9.

Table III. Rate Constants for the Perchloric Acid Catalyzed Enolization of Acetone ($k^{E}_{H^+}$) and Reaction of the Enol with *N*-Bromosuccinimide (k_2) in Acetonitrile Solution Containing 1% Water[a]

T/°C	$k^{E}_{H^+}/10^{-3}$ M^{-1} s^{-1}	$k_2/10^{8}$ M^{-1} s^{-1}
14.0	0.159 ± 0.005	
25.0	0.643 ± 0.032	1.2 ± 0.4, 1.2 ± 0.8
34.8	1.92 ± 0.08	1.9 ± 0.3, 4.2 ± 2.3
46.4	5.62 ± 0.06	2.3 ± 0.8, 5.9 ± 3.7
56.4	18.8 ± 0.9	5.1 ± 1.0

[a] Ionic strength = 0.10 M ($NaClO_4$).

Table IV. Rate Constants for the Perchloric Acid Catalyzed Ketonization of Acetone Enol in Acetonitrile Solution Containing 1% Water[a]

T/°C	$k^{K}_{H^+}/10^{4}$ M^{-1} s^{-1}	T/°C	$k^{K}_{H^+}/10^{4}$ M^{-1} s^{-1}
9.0	1.74 ± 0.05	25.0	5.74 ± 0.09
15.2	2.81 ± 0.09	33.8	9.77 ± 0.37
19.9	3.84 ± 0.10		

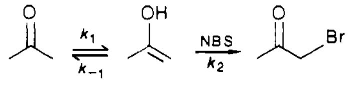
[a] Ionic strength = 0.10 M ($NaClO_4$).

Table V. Summary of Thermodynamic Parameters for Acetone Keto–Enol Interconversion

	water	acetonitrile	gas
	Enolization		
$\Delta H^{\ddagger}$/kcal mol^{-1}	20.0 ± 0.1	20.1 ± 0.5	
$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	−12.1 ± 0.3	−5.8 ± 1.7	
	Ketonization		
$\Delta H^{\ddagger}$/kcal mol^{-1}	9.7 ± 0.4	11.4 ± 0.2	
$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	−8.6 ± 1.4	1.6 ± 0.8	
	Equilibrium		
ΔH°/kcal mol^{-1}	10.3 ± 0.4	8.7 ± 0.6	12.0 ± 2.0
ΔS°/cal K^{-1} mol^{-1}	−3.5 ± 1.5	−7.4 ± 1.9	−7 ± 10
pK_E	8.33 ± 0.02	7.96 ± 0.02	10.3 ± 2.0

the situation with bromine scavenger in aqueous solution. The reaction of acetone enol with bromine in aqueous solvent is very fast, nearly encounter-controlled,[14] and, at the concentrations employed here, the scavenging reaction in that medium was always at least 2 orders of magnitude faster than reketonization.

This insufficiently efficient scavenging in acetonitrile solution was taken into account by treating the data in terms of a two-step reaction as shown in eq 7 (NBS = *N*-bromosuccinimide). The



(7)

rate law for this process is given in eq 8, and eq 9 shows that a plot of $1/k_{obs}$ vs 1/[NBS] should be linear with the desired enolization rate constant as the intercept. The data did obey this

$$k_{obs} = \frac{k_1 k_2[\mathrm{NBS}]}{k_{-1} + k_2[\mathrm{NBS}]} \tag{8}$$

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2[\mathrm{NBS}]} \tag{9}$$

relationship, although in some cases the variation of $1/k_{obs}$ with 1/[NBS] was less than the experimental uncertainty and least-squares analysis failed to give a significant value of the slope parameter, k_{-1}/k_1k_2; the intercept $1/k_1$, however, was in all cases well determined.

Values of k_1 obtained in this way proved to be accurately proportional to acid concentration over the range employed,[15] and least-squares analysis gave the hydrogen ion catalytic coefficients for enolization listed in Table III. These provided an accurately linear Eyring plot, which led to the activation parameters $\Delta H^{\ddagger}$ = 20.1 ± 0.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −5.8 ± 1.7 cal K^{-1} mol^{-1} and the 25 °C rate constant $k^{E}_{H^+}$ = (6.15 ± 0.31) × 10^{-4} M^{-1} s^{-1}.

In those cases where least-squares analysis of the relationship between $1/k_{obs}$ and 1/[NBS] led to determined values of the slope k_{-1}/k_1k_2, division of this slope by the intercept $1/k_1$ gave the ratio k_{-1}/k_2, and from that, since k_{-1} is known (vide infra), k_2 could be calculated; values obtained in this way are listed in Table III. These results are of limited accuracy, but they nevertheless give a reasonable Eyring plot, which in turn provides the activation parameters $\Delta H^{\ddagger}$ = 8.1 ± 2.8 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 6 ± 9 cal k^{-1} mol^{-1} and the 25 °C rate constant k = (1.4 ± 0.4) × 10^{8} M^{-1} s^{-1}. The latter is more than 1 order of magnitude below the specific rate of reaction of acetone enol with bromine in aqueous solution, k_2 = 4 × 10^{9} M^{-1} s^{-1},[14] in keeping with the decreasing efficiency of *N*-bromosuccinimide as an enol scavenger.

Rates of ketonization of acetone enol in acetonitrile solution (1% water) catalyzed by perchloric acid were measured at five temperatures from 9 to 34 °C. Acid concentrations were varied over the range 0.002–0.010 M; these data are summarized in Table S4 of the supplementary material.[12]

Observed first-order ketonization rate constants again proved to be accurately proportional to acid concentration, and least-squares analysis led to the hydrogen ion catalytic coefficients listed in Table IV. An Eyring plot constructed with these data was nicely linear and gave $\Delta H^{\ddagger}$ = 11.4 ± 0.2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 1.6 ± 0.8 cal K^{-1} mol^{-1} and the 25 °C rate constant $k^{K}_{H^+}$ = (5.56 ± 0.07) × 10^{4} M^{-1} s^{-1}.

Combination of these activation parameters for ketonization with those for enolization in acetonitrile solution gives ΔH° = 8.7 ± 0.6 kcal mol^{-1} and ΔS° = −7.4 ± 1.9 cal K^{-1} mol^{-1} for the keto–enol equilibrium reaction in this solvent. The two 25 °C rate constants provided by Eyring relations lead to K_E = (1.11 ± 0.06) × 10^{-8}, pK_E = 7.96 ± 0.02.

Discussion

Thermodynamics. Two determinations of the heat of formation of acetone enol in the gas phase have recently been made: ΔH°_f = −38 ± 2 kcal mol^{-1} [1a] and ΔH°_f = −42 ± 2 kcal mol^{-1}.[1b] The average of these values, when combined with ΔH°_f = −52 kcal mol^{-1} for acetone itself,[2] gives ΔH° = 12 ± 2 kcal mol^{-1} for the acetone keto–enol equilibrium reaction in the gas phase. This value is remarkably close to ΔH° = 10.3 ± 0.4 kcal mol^{-1} obtained here for the same reaction in aqueous solution, and it is also close to the present result for acetonitrile solution, ΔH° = 8.7 ± 0.6 kcal mol^{-1}. These similarities imply that the heats of solvation of the keto and enol forms of acetone in water are quite similar and that

---

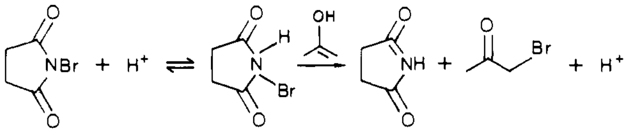
(14) (a) Hochstrasser, R. A.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1988**, *110*, 7875–7876. (b) Dubois, J. E.; El-Alaoui, M.; Toullec, J. *J. Am. Chem. Soc.* **1981**, *103*, 5393–5401.

(15) Acid concentrations were limited to [$HClO_4$] ≤ 0.01 M because at about [$HClO_4$] = 0.03 M rates began to increase more rapidly than in direct proportion to [$HClO_4$]. This effect is reminiscent of the "acidity function behavior" commonly observed in concentrated aqueous acids, which would be expected to become apparent at lower acidities in the nonaqueous medium used here.

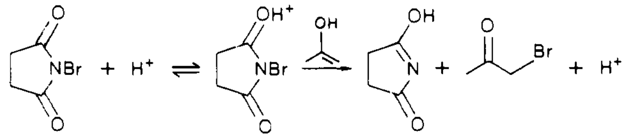
the corresponding values for acetonitrile solution are not very different as well.

An estimate of the standard entropy of acetone enol, $S° = 66$ cal K^{-1} mol^{-1}, may be made using Benson's additivity scheme,[3] and this, when combined with $S° = 71$ cal K^{-1} mol^{-1} for acetone itself,[2] gives $\Delta S° = -5$ cal K^{-1} mol^{-1} for the keto–enol equilibrium reaction in the gas phase. This value is consistent with $\Delta S° = -7 \pm 10$ cal K^{-1} mol^{-1}, which may be obtained from the free energy change for this reaction at 25 °C determined in an ICR experiment, $\Delta G° = 14 \pm 2$ kcal mol^{-1},[4] and the gas-phase enthalpy change derived above, $\Delta H° = 12 \pm 2$ kcal mol^{-1}. These results once again show the gas-phase reaction to be remarkably similar to the solution process, for which $\Delta S° = -3.5 \pm 1.5$ cal K^{-1} mol^{-1} in water and $\Delta S° = -7.4 \pm 1.9$ cal K^{-1} mol^{-1} in acetonitrile.

Mechanism of the Reaction of Acetone Enol with *N*-Bromosuccinimide. There is some evidence that the bromination of aromatic compounds by *N*-bromoamides is subject to acid catalysis,[16] and it is of interest to inquire whether acid catalysis could have been operating in the present reaction of *N*-bromosuccinimide with acetone enol. Such catalysis could facilitate transfer of bromine by prior formation of either a nitrogen protonated species, eq 10, or an oxygen protonated species, eq 11, each of which would be expected to be a better source of electrophilic bromine than *N*-bromosuccinimide itself.



(10)



(11)

Such mechanisms require the k_{-1}/k_2 ratio of eq 7 to be acid independent, since both the forward, bromination, and the reverse, ketonization, reactions of the enol are now acid-catalyzed. A mechanism involving unprotonated *N*-bromosuccinimide as the brominating agent, on the other hand, would give k_{-1}/k_2 ratios, which increased with increasing acidity, for in this case only the numerator (k_{-1}) of this fraction would be influenced by acid. The data do show a tendency for k_{-1}/k_2 to increase with increasing acidity, thus supporting an uncatalyzed mechanism.

Additional evidence for this conclusion can be obtained from the magnitude of the operational bromination rate constant k_2. For either of the acid-catalyzed reaction schemes (eq 10 or 11), this rate constant is equal to the specific rate of the actual bromination step k_{Br} divided by the acidity constant of protonated *N*-bromosuccinimide, K_a, times acid concentration $= k_2 = (k_{Br}/K_a)[H^+]$. Rearranging this expression and inserting $k_2 = 1.4 \times 10^8$ M^{-1} s^{-1} determined here and $[H^+] = 0.003–0.010$ M as the range of acid concentrations used gives $k_{Br} = (1–5) \times 10^{10}K_a$ M^{-1} s^{-1}. The acidity constant of protonated *N*-bromosuccinimide is not known, but it is likely to be considerably greater than 1: simple aliphatic amides have $K_a \cong 10$,[17] and introduction of an *N*-halo substituent as well as a second carbonyl group, both strongly acid-strengthening groups, is certain to increase this value by many orders of magnitude. This puts k_{Br} well above the acceptable limit for a bimolecular reaction in solution, $k \cong 10^{10}$ M^{-1} s^{-1}, and rules out an acid-catalyzed reaction mechanism.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Shell Development Co. for financial support of this work.

Registry No. I, 29456-04-0; **2**, 67-64-1; *N*-bromosuccinimide, 128-08-5.

Supplementary Material Available: Tables S1–S4 of rate data (9 pages). Ordering information is given on any current masthead page.

---

(16) de la Mare, P. B. D.; Ridd, J. H. *Aromatic Substitution Nitration and Halogenation*; Academic Press: New York, 1959; pp 110, 120. March, J. *Advanced Organic Chemistry*; McGraw-Hill: New York, 1977; p 483.

(17) Liler, M. *Reaction Mechanisms in Sulfuric Acid and Other Strong Acid Solutions*; Academic Press: New York, 1971; p 105.