Kinetics of the Spontaneous and Catalysed Hydration of Chloral in Aqueous Dioxane

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Kinetic orders with respect to water, $n(c_w)$, as well as activation parameters have been determined for both the uncatalysed and catalysed hydration of chloral in mixtures of water and dioxane. The value of $n(c_w)$ for the uncatalysed reaction is found to vary from 4 to 2 when the molar concentration of water, c_w, is gradually changed from 0.25 to 46.3 M. This is interpreted as evidence for a cyclic transition state consisting of the carbonyl compound and four water molecules and the fall in $n(c_w)$ as c_w increases is explained on the basis of association phenomena in the solvent. This picture of the transition state is supported by activation entropy measurements, where large negative values are found in agreement with earlier observations; but the individual values are difficult to explain theoretically. Activation data for a series of acid catalysts seem to indicate a relation between acid strength and degree of association with water molecules and it is concluded that amine catalysts probably enter the cyclic transition state indirectly via associated water molecules.

The detailed mechanism for addition of water to the carbonyl group has been the subject of a number of investigations [1] and it has been suggested that the reaction proceeds via a cyclic transition state consisting of the carbonyl group and several water molecules. Thus, from hydration experiments with 1,3-dichloro-acetone in water-dioxane mixtures, Bell, Millington, and Pink [2] found the order of reaction with respect to water to be approximately three and later studies [3] of the activation parameters for the same reaction supported this picture of the transition state. The role of acid catalysts in the mechanism was investigated by Bell and Critchlow [4] and they concluded that one molecule of catalyst replaces one

water molecule in the transition state (for the uncatalysed reaction) in contrast to earlier suggestions [2] that two water molecules were replaced.

The aim of the present work is to investigate reaction orders with respect to water for the hydration of chloral (trichloroacetaldehyde) in water-dioxane mixtures over a wide range of water concentrations and also to look more closely at activation parameters for the process. It was also of interest to study some aspects of the catalysis of the reaction by Brønsted acids and bases, especially to see whether there was any difference between the function of secondary and tertiary amines, the former having one nitrogen bound hydrogen atom, which could form part of the cyclic transition state, like the $O-H$ group of, e.g., a carboxylic acid.

Because chloral is very strongly hydrated [5] over a wide range of water concentrations this compound is particularly suitable for hydration experiments, since the process can be regarded as effectively irreversible without large error.

EXPERIMENTAL

Materials. Chloral, BDH *lab.reag.*, was doubly distilled under dry nitrogen before use. The high risk of oxidation of chloral by atmospheric air was clearly demonstrated by an appreciable increase in the uncatalysed reaction rate if the above precautions were not taken. The following acid catalysts were used without further purification: Trichloroacetic acid, BDH *AnalaR*; dichloroacetic acid, Fluka, *puriss.*; monochloroacetic acid, Merck *purum cryst.*; cyanoacetic

acid, Fluka *puriss.*; glacial acetic acid, BDH *lab.reag.* and formic acid, Merck 98−100 % *krystalliserbar* were distilled before use. The following basic catalysts were purified by distillation before use: Triethylamine, Fluka *purum*; diethylamine, Fluka *purum*; piperidine BDH *lab.reag.*; 2,4,6-collidine, BDH *lab.reag.*; pyridine, Baker *analysed reag.* Dioxane, BASF *technical* was purified as described by Bell and Jensen.[6] This method gives a product which contains less than 0.08 % water, determined by the Karl Fischer titration method. Doubly distilled water was used throughout.

Uncatalysed reactions. The hydration process was followed spectrophotometrically at 294 nm where the carbonyl group has an absorption maximum. At the higher water concentrations ($c_w > ca.$ 0.6 M) the process was too fast to be followed by conventionel techniques and a Durrum-Gibson stopped-flow spectrophotometer was used, provided with an oscilloscope, X−Y recorder, and a paper tape read out system. Solutions of chloral in dioxane (*ca.* 5×10^{-2} M) and of water in dioxane were thermostated and rapidly mixed in the apparatus. The very high water concentrations were established by using a driving syringe of reduced volume for the chloral solution. A Beckman DB-GT spectrophotometer with recorder was used for measuring the reaction rates at water concentrations below 0.6 M. The reaction solution was prepared by injecting pure chloral from a microsyringe into the thermostated water-dioxane mixture in 1 cm silica cells.

Catalysed reactions. Catalytic experiments were only carried out in the region of water concentration where the stopped-flow instrument was used. The experimental procedure was analogous to that described above for the uncatalysed reaction. The catalyst was always dissolved in the water-dioxane mixture to prevent complications from possible side reactions between the catalyst and chloral before mixing.

RESULTS AND DISCUSSION

The observed kinetic curves were in all cases found to be of first order − c_w being much larger than the concentration of chloral − except for the very low values of c_w, where small corrections had to be made to the rate constants. Disturbances due to heat of mixing of water and dioxane in connection with the stopped-flow experiments were not observed. This is consistent with the fact that this enthalpy is a very small positive or negative quantity depending on the composition of the mixture,[7] and with the fact that the activation energy for the hydration is relatively low.

The molar concentrations of water in the reaction chamber of the stopped-flow instrument could be calculated from the dimensions of the driving syringes and the water content of the solutions mixed. For the experiments at low values of c_w, where a conventional technique was used there was good agreement between calculated and titrimetrically obtained values for the water concentration (Karl Fischer method).

Uncatalysed reactions. The results for uncatalysed hydration at some fifty water concentrations (c_w: 0.25−46.3 M) are shown in Fig. 1, where log k_{obs} is plotted against log c_w. Each point represents the mean of at least two experiments which agreed within ±5 %. The solid curve is a least squares fit of a second order polynomial to the points and is represented by the following expression:

$$\log k_{obs} = -2.379 + 3.582 \;\log c_w - 0.494(\log c_w)^2 \tag{1}$$

The order of reaction with respect to water, $n(c_w)$, is determined as the slope of this curve and is seen to vary from about 4.0 to about 2.0 in going from the lower to the higher water concentrations. The present results differ to some extend from those reported by Bell, Millington and Pink [2] (Fig. 1) who considered
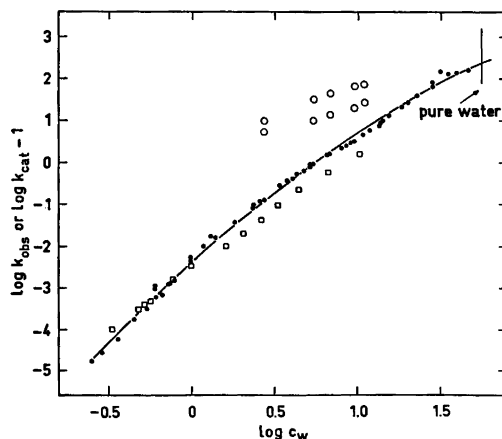

Fig. 1. Kinetic data for hydration of carbonyl compounds in mixtures of water and dioxan at 298.2 K. ● Chloral, present work. ○ Chloral catalysed by diethylamine (upper curve) and triethylamine, present work. □ 1,3-Dichloroacetone, Ref. 2 (log k_{obs}+3). k_{obs} in s⁻¹, k_{cat} in mol dm⁻³ s⁻¹, c_w in mol dm⁻³.

the analogous hydration of 1,3-dichloroacetone under very similar conditions. They found a nearly linear dependence of log k_{obs} upon log c_w and determined $n(c_w)$ to be approximately equal to three. However, if the composition of the transition state is independent of water concentration, and medium effects are ignored, it seems likely that a plot of log k_{obs} against log c_w* should show the type of curvature found in the present work. Thus it has been shown by, *e.g.*, cryoscopic measurements [8] that water is unassociated in dioxan only below water concentrations of about 0.3 M and it is easily shown that polymerization of the water leads to a fall in the order of reaction with respect to total water concentration, *i.e.* if the transition state is formed from substrate and four unassociated water molecules, $S + 4H_2O \rightarrow$ t.s., the reaction order with respect to water is clearly four, whereas if the water molecules are dimerized, $S + 2(H_2O)_2 \rightarrow$ t.s., leading to the same transition state, the rate expression is, $v = k[(H_2O)_2]^2[S] = k[\frac{1}{2}[H_2O]_{total}]^2[S]$, which gives a reaction order with respect to water (total concentration) of only two.

The failure of Bell *et al.*[2] to observe considerable curvature may be due to the fact that their water concentrations were not corrected for the presence of small amounts of water in the purified dioxane; *cf.* experimental section. Thus in later work Bell and Critchlow [4] found approximately 40 % lower values for the hydration rate constant of 1,3-dichloroacetone at $c_w = 1.06$ mol dm^{-3} but the range of water concentrations used in their work was too small for the curvature to be observed.

The reaction order with respect to water is approximately four in the concentration range where water exists mainly as a monomer in dioxane. This suggests four water molecules in the cyclic transition state as in (2).

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* A different curvature is found if mol fractions, x_w, are used instead of molar concentrations, *i.e.* the reaction order increases from four to approximately five in going from low to high water concentrations. Application of this concentration unit seems unreasonable in the present case since polymerization of the water on increasing its concentration should lead to lower reaction orders (see below), which is also confirmed by activation entropy measurements.
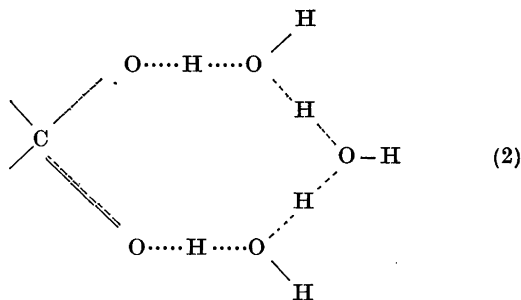
If the O···H···O bonds are considered to be linear the most stable configuration of (2) is a cyclohexane structure because of the tetrahedral disposition of the carbon and oxygen valencies. The formation of this structure therefore requires a minimum of break down of the ordinary water structure in concentrated water solutions, where, particularly according to a model by Bernal,[9] the so-called V-structure can be described as an irregular network of hydrogen bonded rings with varying numbers of water molecules and therefore varying distortion and stability.

Although the composition of the transition state suggested here may seem more attractive than one involving only three water molecules,[2-4] it is still doubtful whether it is really reasonable to suggest that a single structure operates over a wide range of water concentrations. It is also worth pointing out that it is still a hypothesis that the transition state is of cyclic nature at all and that a number of other questions such as, *e.g.*, the degree of concertedness of the proton transfers are still unsolved.

The type of inert solvent may be expected to affect the observed reaction orders, but it is interesting to see that for the present type of reaction only a small difference is observed if acetonitrile is used instead of dioxane.[2] A solvent such as dimethyl sulfoxide interacts very strongly with water by hydrogen bond formation and this might create a different behaviour for this solvent. Unfortunately there are no experimental data available at present for the hydration of carbonyl compounds in mixtures of water and dimethyl sulfoxide.[15]

Despite a comparatively high inaccuracy for k_{obs} at the very high water concentrations the stopped-flow technique applied in the present work seems to provide a method for obtaining

Table 1. Collected results from acid-base catalysis of the hydration of chloral at 298.2 K, c_w in mol dm^{-3}, k_{cat} in l mol^{-1} s^{-1}.

Compound No.	Catalyst	$-\log K_a{}^a$	c_w	Statistical factors p	q	k_{cat}	Linear regression coefficient (number of points)
9	Hydrochloric acid (H$_3$O$^+$)	-1.74	2.72	3	2	(32)	$-$ (2)
1	Trichloro-acetic acid	0.63	2.73	1	2	2.96 ± 0.06	0.999 (7)
2	Dichloro-acetic acid	1.48	2.73	1	2	2.13 ± 0.04	0.999 (7)
3	Cyanoacetic acid	2.47	2.73	1	2	1.62 ± 0.06	0.997 (7)
4	Monochloro-acetic acid	2.87	2.73	1	2	1.66 ± 0.04	0.998 (6)
5	Formic acid	3.75	2.73	1	2	0.89 ± 0.01	0.999 (8)
6	Acetic acid	4.76	2.73	1	2	0.99 ± 0.04	0.996 (8)
7	o-Chlorophenol	8.48	< 2.73	1	1	(0.08)	$-$ (3)
8	Water	15.74	2.73	2(3)	1(2)	0.05	$-$
10	Piperidine	11.13	2.73	2	1	5.8 ± 0.6	0.990 (3)
11	Diethylamine	11.00	2.73	2	1	100 ± 2	0.999 (7)
			5.45			353 ± 6	0.999 (7)
			6.81			446 ± 9	0.999 (6)
			9.57			690 ± 31	0.994 (7)
			10.95			739 ± 21	0.998 (6)
12	Triethylamine	10.73	2.73	1	1	55 ± 1	0.999 (7)
			5.45			47 ± 3	0.987 (6)
			6.81			132 ± 3	0.999 (6)
			9.57			197 ± 8	0.997 (6)
			10.95			268 ± 6	0.999 (5)
13	2,4,6-Collidine	7.45	2.73	1	1	2.0 ± 0.1	0.998 (6)
14	Pyridine	5.22	2.73	1	1	1.5 ± 0.1	0.994 (6)

[a] Taken from Kortüm, G., Vogel, W. and Andrussow, K. *Dissociation of Organic Acids in Aqueous Solution*, IUPAC, Butterworths, London 1961.

values for the hydration rate constants of strongly hydrated carbonyl compounds in pure water using short extrapolations. These constants can be combined with the much slower dehydration rate constants, measured by scavenger techniques, for calculating hydration equilibrium constants, which are unknown or known with little accuracy for many compounds. It is interesting in this context to note that k_{obs} for the hydration of chloral in pure water from Fig. 1, 232 s^{-1}, is comparable with a value, $(4.5 \pm 0.7) \times 10^2$ s^{-1}, determined recently in this laboratory [10] by a polarographic technique analogous to that described by Brdička,[11] making use of the literature value, $K_h = 2.8 \times 10^4$,[5] for the hydration equilibrium constant for chloral.

Catalysed reactions. Catalytic constants were found for a number of acids and bases. The results of these experiments are collected in Table 1 and it is seen from the linear regression coefficients that good linearity was obtained in most cases when the expression $k_{obs} = k_0 + k_{cat}[cat]$ was applied to the primary data. For the basic catalysts there was a risk of a side reaction between chloral and the amine. However, these reactions were shown to be much slower than the rate of hydration. For o-chlorophenol, very high concentrations had to be used to obtain a considerable contribution to k_{obs} from the catalysed reaction. This of course affects the water concentrations; this was allowed for, but the catalytic constant given in Table 1 for this compound is only approximate. The value given for HCl is based on a single experiment with 0.01 HCl.

The Brønsted plots for the acidic and basic catalysts are shown in Fig. 2. Because the pH-
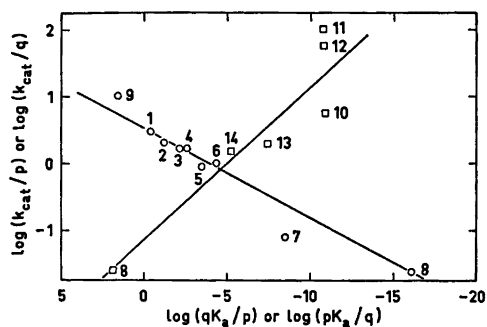
Fig. 2. Brønsted plots for catalysis of the hydration of chloral by a series of acids and bases. Data taken from Table 1. Temperature 298.2 K, $c_w = 2.73$ mol dm^{-3}. The figures are the compound numbers listed in Table 1.

values are not known in the mixed solvent (2.73 M water in dioxan) the values from aqueous solution are used. As was observed by Bell and Jensen [6] for hydration of 1,3-dichloroacetone (2.78 M water in dioxan), using 24 acids, the acid catalysts show good linearity and give an α-value of about 0.13 for the present system. Hydrochloric acid shows clear positive deviation from the plot and, as pointed out by Kresge,[12] this seems to be a typical feature of reactions where all the proton transfers take place between oxygen or nitrogen atoms. The pK-value for H_3O^+ has been used for HCl in the present case. This is reasonable because this species probably exists as the ion pair H_3O^+ Cl^- under the present conditions, and it has been shown [6] that replacement of Cl^- by other inorganic anions such as Br^- or ClO_4^- caused little change in catalytic activity, and that the changes observed were in the direction opposite to the order of strengths of the acids in aqueous solution.

For the basic catalysts, however, the points are very scattered. It may be reasonable, taking into account the point for water, to draw a line as shown in Fig. 2, giving a rough value for β of about 0.2. The values of α and β for the present reaction are somewhat lower than for the hydration of 1,3-dichloroacetone (α = 0.27, β = 0.5). This is in accord with the fact that the hydration of chloral is more exothermic ($\Delta H = -59$ kJ mol^{-1})[5] than that of 1,3-dichloroacetone ($\Delta H = -24$ kJ mol^{-1}).[13]

As seen from Table 1 the catalytic behaviour of diethylamine and triethylamine was examined at several water concentrations, and the logarithm of the observed catalytic constants are plotted against log c_w in Fig. 1. Least squares fits to these two sets of points give reaction orders with respect to water which are indistinguishable and approximately equal to 1.2. This is a considerable decrease compared with the uncatalysed reaction for which $n(c_w)$ is about 2.9 in this region and the value is also somewhat lower than that found by Bell, Millington and Pink [2] ($n(c_w) = 1.85$) for the catalysis of the hydration of 1,3-dichloroacetone by triethylamine. If a transition state similar to (2) is still assumed for the catalysed reaction the above data suggest that the amines are able to replace some of the water molecules in the cyclic transition state. However, since the behaviour of the tertiary and the secondary amine is very similar it seems reasonable to assume that the amine itself is not involved directly in the hydrogen bonded structure, which would be expected to create a difference in behaviour of the two, *cf.* the introduction, but that it operates *via* attached water molecules.

Activation parameters. Table 2 collects the activation parameters obtained by the method of least squares. No detectable curvature was observed within experimental error for any of the plots in contrast to what was reported by Bell and Sørensen [3] for the uncatalysed hydration of 1,3-dichloroacetone where considerable curvature was found. However, this discrepancy may only be apparent because of the comparatively narrow temperature range investigated in the present work.

Considering first the activation energies for the uncatalysed hydration, E_a tends to increase with increasing water concentration. This behaviour was also observed for 1,3-dichloroacetone [3] and can be attributed qualitatively to the increasing degree of association of the water molecules when the water concentration is raised, producing a stabilization of the reactants compared to the transition state. A similar explanation may apply to the series of four acid catalysts. Both experiment and theory suggest (Ref. 4 and references therein) that there is a relation between the strength of an acid in aqueous solution and its degree

Table 2. Collected activation parameters, c_w and c_{cat} in mol dm^{-3}, E_a in kJ mol^{-1}, $\Delta S^{\ddagger}$ in JK^{-1} mol^{-1}. Each Arrhenius plot is based on rate measurements at five different temperatures in the range 285 to 315 K.

Catalyst	c_w	c_{cat}	E_a	$n=0$	$n=1$	$\Delta S^{\ddagger} - nR \ln c_w$ $n=2$	$n=3$	$n=4$	$n=5$
Water	2.72	2.72	7.8 ± 0.6	-243 ± 2	-251	-259	-267	-275	-283
	4.56	4.56	7.7 ± 0.8	-232 ± 3	-240	-253	-265	-278	-290
	6.75	6.75	7 ± 1	-227 ± 3	-243	-259	-275	-291	-307
	9.73	9.73	11.2 ± 0.7	-206 ± 2	-225	-244	-263	-282	-301
					A[a]	B[a]			
Hydrochloric acid	2.72	0.010	21.2 ± 0.4	-192 ± 1	-146	-97			
Trichloroacetic acid	2.72	0.048	18 ± 2	-211 ± 6	-178	-65			
Dichloroacetic acid	2.71	0.111	15 ± 4	-219 ± 12	-193	-50			
Acetic acid	2.74	0.068	6 ± 1	-255 ± 4	-224	-19			
Triethyl amine	6.74	9.40×10^{-3}	9 ± 2	-221 ± 8	-166	-61			
Diethyl amine	6.74	2.28×10^{-3}	9 ± 1	-221 ± 4	-154	-73			

[a] $A = \Delta S^{\ddagger} (n=0) - R \ln (c_{cat}/c_w)$; $B = \Delta S^{\ddagger} (n=0)$ for water catalysed reaction minus A.

of hydration, *i.e.* the strongest acids are most hydrated. This is in accord with the observation that E_a increases with increasing acid strength throughout the series, although it is worth pointing out that here a stabilization of the reactants will probably partly be cancelled by a stabilization also of the transition state. It is interesting to see that the activation energy is actually higher for the catalysed reactions — except for acetic acid — than for the uncatalysed ones, but this behaviour is overcompensated by a more favorable activation entropy for the catalysed reactions. For catalysis by triethylamine and diethylamine the activation energies are seen to be indistinguishable within experimental error.

Turning now to activation entropies, this parameter (Table 2) exhibits large negative values as was observed for the hydration of 1,3-dichloracetone[3] and this is good evidence for a transition state of highly ordered struc-

ture. Considering first the uncatalysed hydration, it is evident that correcting the obtained activation entropy values to a standard state of $c_w = 1$ M by adding $-R \ln c_w$ does not give a common value for $\Delta S^{\ddagger}$ at the four water concentrations investigated. Table 2 shows that a correction involving addition of $-3R \ln c_w$ or $-4R \ln c_w$ is optimal for this purpose, in particular if the value at $c_w = 6.75$, which seems less reliable, is omitted, and this agrees with the conclusion from reaction orders with respect to water that three or four water molecules take part in the transition state ($c_w = 2 - 10$ M). It has been pointed out[3] that it is probably a good approximation to attribute most of the observed activation entropies in the present type of reaction to freezing of translational degrees of freedom, rotations and internal rotations beeing effectively frozen in the solvents used. Calculation of ΔS (translational) for the reaction, chloral + nH$_2$O → chloral,

$n\mathrm{H_2O}$ in the gas phase at 298 K and corrected to a standard state of 1 M gives -430 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ and -574 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}*}$ for $n=3$ and 4, respectively. These figures are much more negative than the experimental values: -268 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ and -283 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ (mean values from Table 2, $n=3$ and 4, respectively). This is not surprising because the calculated values of $\Delta S^{\ddagger}$ are valid only for ideal solution (gas phase) while the experimental ones apply to a condensed phase, where considerable interaction takes place between the solvent molecules. From Dorsey's thermodynamic data for water [14] it is clear that the entropy loss corresponding to "freezing" of three or four water molecules in an "ice-like" transition state as suggested here cannot be larger than approximately 110 and 140 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$, respectively. Thus these figures are too small to explain satisfactorily the observed values for $\Delta S^{\ddagger}$.

However, it is not surprising that the use of a comparatively simple model for the reaction, which neglects, e.g., important effects such as solvent reorganization and low frequency bending and stretching modes of the transition state, does not lead to any exact prediction of the activation entropies and it confirms once more that water is an extremely difficult material to treat theoretically.

Table 2 also contains values for the activation entropies of some catalysed reactions. The figures in the column corresponding to $n=1$ are obtained by adding $-R \ln (c_{\mathrm{cat}}/c_{\mathrm{w}})$ to the column corresponding to $n=0$. This corrects the observed entropy values to a catalyst concentration equal to that for water in each case and makes possible a comparison with the uncatalysed reaction. Both acidic and basic catalysts make $\Delta S^{\ddagger}$ less negative (last column). As pointed out by Bell and Sørensen [3] such behaviour can readily be explained as reflecting the ability of the catalysts to bring with them one or more of the water molecules required for the transition state. A detailed discussion of the individual $\Delta S^{\ddagger}$ values is not possible but it is clear from the series of activation entropies for the acid catalysts that the stronger acids bring more water molecules with them.

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15. Note added in proof: Four uncatalysed, kinetic experiments in this solvent mixture at $c_{\mathrm{w}}=1.60, 2.11, 2.90$ and 4.54 M (298.2 K) were carried out recently by the present author and $k_{\mathrm{obs}} \times 10^2$ was found to 2.0, 2.5, 8.1 and 17.0 $\mathrm{s^{-1}}$, respectively. These results give a value of $n(c_{\mathrm{w}})$ only slightly smaller than the one observed for the water-dioxane mixture.

* There is a mistake in the calculation of ΔS (translational) for the reaction, $\mathrm{K.H_2O} + 2\mathrm{H_2O} \rightarrow \mathrm{K.3H_2O}$ (K is 1,3-dichloroacetone) in Ref. 3, p. 1743. The value reported as being -206 $\mathrm{JK^{-1}}$ $\mathrm{mol^{-1}}$ should be -232 $\mathrm{JK^{-1}}$ $\mathrm{mol^{-1}}$.