

The Kinetics of the Cannizzaro Reaction

The Free Energy, Heat Content, and Entropy of Activation

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In a previous paper¹ one of us (E. T.) reported the results of his investigation of the kinetics of the Cannizzaro reaction with benzaldehyde and several substituted benzaldehydes in aqueous methanol. The paper contains the parameters of the Arrhenius equation

$$k = Ae^{-E/RT} \quad (1)$$

obtained for solutions of constant solvent composition (E_C and A_C). As the second of the authors (A. M.) has stated², the parameters of the Arrhenius equation in isodielectric solutions (E_D and A_D) may be got by a graphical method from such results. The values for benzaldehyde thus obtained are now given in Table 1.

Plotting the values of E_D against $1/D$ and through extrapolation with regard to $1/D$ to zero (Fig. 1) one obtains for the bond-stretching energy³ (for the complex Y , see later) the value

$$E_{D\infty} = 15.1 \text{ kcal/mole}$$

Theoretically, in very dilute solutions $\log A_D$ should be constant²; we see that this condition is rather well fulfilled, although the k -values are not extrapolated to zero concentration. The influence of the concentration on k is in this case, of course, only very small owing to the fact that one of the reactants is a neutral molecule. From the values for E_D in Table 1 and from equation⁴

$$E_D = E_{D\infty} + \Delta G_D^\ddagger \quad (2)$$

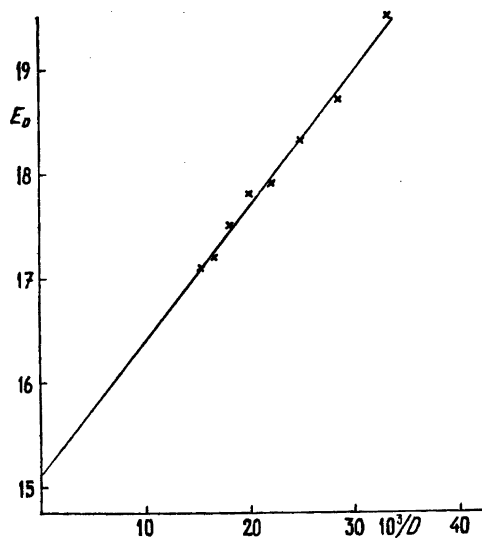


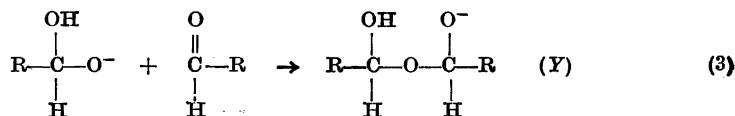
Fig. 1. Plotting of E_D against $1/D$.

where ΔG_D^\ddagger is the repulsion energy, we see that the latter energy is always only a rather small fraction of the total energy E_D of the reaction.

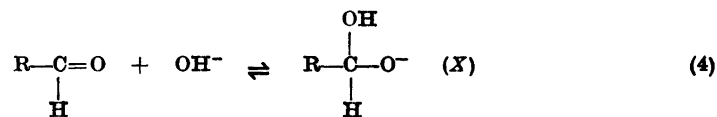
Table 1. The reaction between benzaldehyde and NaOH in isodielectric water-methanol mixtures. (k is the trimolecular rate constant in $\text{ml}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$, E_D kcal).

D	k_{40°	k_{60°	k_{80°	E_D	$\log A_D$
65	31.6	166	—	(17.1)	(13.44)
60	19.1	100	363	17.2	13.26
55	12.0	67.6	282	17.5	13.30
50	8.13	44.7	209	17.8	13.34
45	5.50	31.6	145	17.9	13.24
40	3.72	22.9	105	18.3	13.35
35	2.57	16.2	77.6	18.7	13.46
30	—	11.5	60.3	(19.5)	(13.85)
				Mean	13.32

It is now generally accepted^{1,5,6,7} that the rate-determining step of the reaction is



and that before this there exists the following equilibrium:



the corresponding equilibrium constant being

$$K = \frac{[\text{RHC(OH)O}^-]}{[\text{RCHO}][\text{OH}^-]} \quad (5)$$

The rate of the formation of the critical complex Y is thus proportional to the product $[\text{RHC(OH)O}^-] [\text{RCHO}]$ and as net result there follows a reaction formally of third order:

$$\frac{dY}{dt} = k'K[\text{RCHO}] [\text{RCHO}] [\text{OH}^-] = k[\text{RCHO}]^2[\text{OH}^-] \quad (6)$$

where k' is the rate constant of the bimolecular reaction (3), and k the experimentally found trimolecular constant. The values given in Tables 1 and 2 are obtained from k -values for different temperatures in different solvents. As k is the product of the real bimolecular rate constant k' and of the equilibrium constant K , $k = k'K$, the next task is to eliminate the effect of K and state the details of this bimolecular reaction (3). Because, however, nothing is known about the absolute values of K in conditions prevailing during the experiments, conclusions of only general nature can be drawn.

In connection with the experimental determination of the trimolecular rate constant k at different temperatures and in various solvents, the dependence of the equilibrium constant K on these factors was also measured. As

$$\log k = \log k' + \log K \quad (7)$$

we can generally write

$$2.303RT^2 \frac{\partial \log k}{\partial T} = 2.303RT^2 \frac{\partial \log k'}{\partial T} + 2.303RT^2 \frac{\partial \log K}{\partial T} \quad (8)$$

or consequently, taking Eq. (1) and the van't Hoff reaction isochore into consideration:

$$E_c = E'_c + W_{p,c} \quad (9)$$

which shows that the experimental activation energy, E_C , is the sum of the activation energy of the true bimolecular reaction (3), E'_C , and of the heat, $W_{p,C}$, of the equilibrium reaction (4). From Eqs. (1), (7) and (9) it follows directly:

$$\log A_C = \log A'_C + \log A_{p,C} \quad (10)$$

or, according to the theory of absolute reaction rates, that

$$\Delta S^\ddagger = \Delta S^{\ddagger'} + \Delta S_p^\ddagger \quad (11)$$

For isodielectric conditions the following equations, respectively, are obtained ⁴:

$$E_D = E'_D + W_{p,D} \quad (12)$$

$$\Delta S_0^\ddagger = \Delta S_0^{\ddagger'} + \Delta S_{p,0}^\ddagger \quad (13)$$

Thus the non-electrical contribution ΔS_0^\ddagger in the Table 2 is also the sum of the corresponding constants for the reactions (3) and (4).

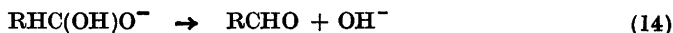
According to Meretoja ⁴, by means of the values of A_C , E_C , A_D , E_D , and the constant $E_{D\infty}$, the free energy, heat content, and entropy of activation, as well as their non-electrical and dielectric contributions can be calculated. These values for benzaldehyde in different methanol-water mixtures are given in Table 2. In so far as W_p and ΔS_p^\ddagger are negative, the activation energy E'_C and the frequency factor A'_C of the reaction (3) are greater than the experimental values, which would explain the unexpected low activation energy of

Table 2. The free energy, heat content, and entropy of activation and their non-electrical and dielectric contributions for the Cannizzaro reaction with benzaldehyde in different methanol-water mixtures. ΔG and ΔH in kcal, ΔS in E. U.:

Wt. % alcohol	D_{60°	ΔG_0^\ddagger	ΔH_0^\ddagger	ΔS_0^\ddagger	ΔG_D^\ddagger	ΔH_D^\ddagger	ΔS_D^\ddagger	ΔG^\ddagger	ΔH^\ddagger	ΔS^\ddagger
0	66.6	14.5	14.5	0	1.4	-5.0	-19.3	15.9	9.5	-19.3
8.5	62.9	14.5	14.5	0	1.7	-4.4	-18.4	16.2	10.1	-18.4
17.6	59.2	14.5	14.5	0	1.9	-3.9	-17.5	16.4	10.6	-17.5
26.9	55.2	14.5	14.5	0	2.2	-2.7	-14.7	16.7	11.8	-14.7
36.2	51.3	14.5	14.5	0	2.5	-2.2	-14.1	17.0	12.3	-14.1
45.9	47.2	14.5	14.5	0	2.7	-1.3	-12.0	17.2	13.2	-12.0
55.8	43.1	14.5	14.5	0	2.9	-0.4	-9.9	17.4	14.1	-9.9
71.2	36.5	14.5	14.5	0	3.2	+0.6	-7.8	17.7	15.1	-7.8
87.9	29.8	14.5	14.5	0	3.5	+2.2	-4.0	18.0	16.7	-4.0
100	26.0	14.5	14.5	0	3.9	+5.9	+5.9	18.4	20.4	+5.9

the Cannizzaro reaction for many aromatic aldehydes (*cf.* 1, pp. 50, 51), as well as the fact that the value of the nonelectrical entropy ΔS_p^\ddagger in Table 2 happens to be equal to zero.

The assumption that W_p and ΔS_p^\ddagger are negative is very reasonable, because it is quite natural to believe that the extent of the dissociation



increases with temperature, or that K decreases as the temperature rises.

As already mentioned, concerning the value of K nothing certain is known. However, taking into consideration that E'_C for reaction (3) must be equal to or greater than 10 200 cal,¹ we get

$$\log A'_C - \log k' \geq \frac{10\,200}{2.303RT} = 6.70$$

As furthermore, for bimolecular reactions, the steric factor⁸ $P \leq 1$ or $A (=PZ) \leq 2.6 \cdot 10^{14}$ (when the kinetic collision number Z is given in absolute system), we obtain at 60° C for benzaldehyde in aqueous solution:

$$\log k' = \log k - \log K = 2.30^1 - \log K \leq \log A'_C - 6.70 = \log 2.6 \cdot 10^{14} - 6.70 = 7.72,$$

and therefore

$$\log K \geq -5.42$$

or

$$K \geq 4 \cdot 10^{-6} \text{ ml.mole}^{-1}$$

The value obtained for K is so great that the complex X in Eq. (4) must be a true molecule in equilibrium with its parent substances, and not a simple collision pair with a short life time of the order of a collision duration.

If the second stage of the reaction is not much slower than the first, different kinetic velocity laws are possible. This is probably the case, *e. g.*, with nitrobenzaldehydes¹ and furfural⁹.

The values of ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger for the Cannizzaro reaction with a number of substituted benzaldehydes in 46 wt. per cent aqueous methanol and in

50 per cent dioxane are given in Table 3. It is interesting to note that although ΔH^\ddagger and ΔS^\ddagger for various aldehydes are very different, the values of ΔG^\ddagger show much smaller differences. Also in both the solvents the ΔG^\ddagger -values for the same aldehyde are about the same, but ΔH^\ddagger and ΔS^\ddagger are very different. Furthermore, a comparison of the values for benzaldehyde in water given in Table 2 with those in Table 3 shows that the values in 50 per cent dioxane are about the same as in water. The influence of methanol on the reaction is much more powerful.

Table 3. The energy and entropy quantities for several substituted benzaldehydes in 46 wt. % methanol and in 50 % dioxane (25—100° C).

Solvent	46 % Methanol			50 % Dioxane		
	ΔG^\ddagger	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger	ΔH^\ddagger	ΔS^\ddagger
Benzaldehyde	17.2	13.2	— 12.0	17.6	9.9	— 20.6
<i>m</i> -Bromobenzaldehyde	14.6	11.7	— 8.8			
<i>m</i> -Chlorobenzaldehyde	14.9	12.2	— 8.0	15.3	6.9	— 22.5
<i>p</i> - »	15.7	14.2	— 4.6	16.3	7.6	— 23.4
<i>o</i> - »	16.5	18.6	+ 6.3	16.7	8.1	— 23.1
<i>p</i> -Methyl benzaldehyde	18.2	14.0	— 12.7			
<i>p</i> - <i>iso</i> -Propyl »	18.1	15.7	— 7.2			
<i>p</i> -Methoxy »	18.8	15.8	— 9.1			
<i>m</i> -Nitrobenzaldehyde	13.4	17.1	+ 11.1			
<i>p</i> - »	13.4	20.1	+ 21.9			
<i>o</i> - »	14.4	26.5	+ 36.2			
<i>p</i> -Dimethylaminobenzaldehyde	23.5	23.0	— 1.4			

SUMMARY

The free energy, heat content, and entropy of activation for the Cannizzaro reaction with benzaldehyde and a number of substituted benzaldehydes in various solutions, calculated on the basis of the experimental values found by Tommila, and Eitel and Lock, are given, as well as the non-electrical and dielectric contributions to these quantities for benzaldehyde in different methanol-water mixtures. This new interpretation brings strong evidence for the previously proposed mechanism for the reaction.

REFERENCES

1. Tommila, E. *Ann. Acad. Scient. Fenn.* A LIX 8 (1942).
2. Meretoja, A. *Ibid.* A II 24 (1947).

3. Hinshelwood, C. N., Laidler, K. J., and Timm, E. W. *J. Chem. Soc.* (1938) 848; cf. also Meretoja, A. (*l. c.*).
4. Meretoja, A. *Acta Chem. Scand.* **2** (1948) 352.
5. Eitel, A., and Lock, G. *Monatsh.* **72** (1939) 410.
6. Alexander, E. R. *J. Am. Chem. Soc.* **69** (1947) 289.
7. Geissman, T. A. *Organic reactions* Vol. II, New York (1944) p. 94.
8. Hinshelwood, C. N., and Winkler, C. A. *J. Chem. Soc.* (1936) 371.
9. Eitel, A. *Monatsh.* **74** (1942) 124.

Received March 1, 1948.