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RESEARCH ARTICLE

A study on the equilibrium reaction of benzaldehyde and sodium bisulphite by in situ Fourier transform IR spectroscopy

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Abstract

The addition of sodium bisulphite to benzaldehyde was monitored at different conditions by in situ Fourier transform IR spectroscopy and the equilibrium constant was determined.

Keywords

in situ Fourier transform IR spectroscopy · monitoring · equilibrium · benzaldehyde – sodium bisulphite adduct

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1 Introduction

In situ Fourier transform IR spectroscopy is a suitable method for monitoring a variety of organic chemical reactions [1]–[8]. The time-dependent IR spectra reveal the concentration profile of the components, which allows formal kinetic measurements, determination of equilibrium constants [2], and optimization of the reaction studied. This latter is important from the point of view of environmentally friendly chemistry. It is also possible to identify intermediates [7, 8] in the mixture and hence evaluate reaction mechanisms. *In situ* Fourier transform IR spectroscopy is a suitable tool to study organic chemical reactions over a wide range of temperatures, and even under pressure. The spectrometer is supplied with an attenuated total reflection (ATR) probe that is in contact with the reaction mixture. *In situ* Fourier transform IR has become a routine method in the fine chemical, pharmaceutical, and even plastics industries. Heterogeneous phase reactions can also be monitored by *in situ* Fourier transform IR spectroscopy [8].

2 Experimental part

2.1 Materials and methodology

The ReactIR apparatus used in the experiments was of Labmax, Mettler Toledo Internat. Inc. type.

The compounds used were of commercial quality ($Na_2S_2O_5$, Reanal, benzaldehyde, Sigma Aldrich).

The easily decomposable benzaldehyde–sodium bisulphite adduct was freshly prepared for IR examination according to the following:

At room temperature, 14.6 g of pyrosulphite ($Na_2S_2O_5$) (equal to 0.153 mol of $NaHSO_3$) was dissolved in 75 ml of water, and 10.5 ml (0.104 mol) of benzaldehyde was added. The immediately separated whitish precipitate was filtered, dried in a desiccator, and its IR spectrum was taken in KBr pellet.

The ReactIR experiments were carried out according to the following:

We dissolved 4.9 g of sodium pyrosulphite (equivalent to 0.051 mol of $NaHSO_3$) in 35 ml of distilled water, and then we added in three steps the benzaldehyde, in the quantities given in Table 1 at pH 5, and at the temperature values given in the

Table 1. Until the third addition of the benzaldehyde, the reaction mixture remained homogeneous. We have continuously monitored the reactions through the ReactIR equipment.

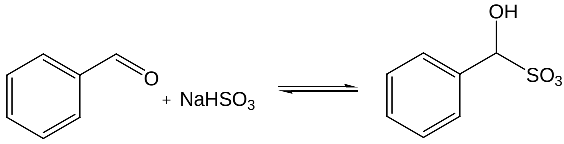
Tab. 1. Experimental data

Reaction	Bisulphite: benzaldehyde molar ratio	Quantity of benzaldehyde (ml)	Temperature (˚C)
Exp. 1/1. step	3.5	1.5	26
Exp. 1/2. step	2.1	1.0	26
Exp. 1/3. step	1.5	1.0	26
Exp. 2	1.5	3.5	60

3 Results and discussion

The reaction examined is the addition of $NaHSO_3$ to benzaldehyde. The bisulphite has been prepared *in situ*, through the reaction of pyrosulphite and water (reactions 1 and 2):

$$Na_2S_2O_5 + H_2O \rightleftharpoons 2\ NaHSO_3 \qquad (1)$$



(2)

At first, we have taken the IR spectra of the starting materials, as well as that of the bisulphite–benzaldehyde adduct. Some characteristic absorptions of the components are shown in Table 2.

Tab. 2. Characteristic IR absorptions of the reaction components in the range of 900–1300 cm^{-1}

Benzaldehyde[a]	$NaHSO_3$[a]	$Na_2S_2O_5$[b]	Bisulphite–benzaldehyde adduct	
			a	b
	965	978		
	1022		**1034**	1035
	1053[c]	1057		
1070		1066	1069[d]	1070
			1089[d]	1088
1165	1165[e]			
		1184	**1182**	1190
1204[f]	1204[e]		**1204**	1215

[a] ReactIR, solution in water; [b] Bruker Tensor 37 in KBr pellet; [c] SO_3 symmetric stretching vibration; [d] C-O stretching vibration; [e] SO_3 asymmetric stretching vibration; [f] ring C-CHO stretching vibration.

From the data in Table 2 one can see that, the ReactIR is suitable for the separate detection of the reaction components. This can be seen on the 3D spectrum shown in Fig. 1, which represents the steps of Experiment 1. In the figure one can see the rapid adduct formation, as well as the reduction of the quantity of sodium bisulphite.

Deconvolution diagrams of the reactions give only relative concentration values (Fig. 2).

Determination of the equilibrium constants requires the conversion of the relative concentration values to real concentrations. To this aim we had to check the validity of the Lambert–Beer law. The relative concentrations can be treated as pseudo-absorbances in the calculations. Fig. 2 shows that, the relative concentrations of both the bisulphite and the bisulphite–benzaldehyde adduct are proportional to the quantity of the corresponding substance (the corresponding value of absorbance and the amount of benzaldehyde added are constant), so the Lambert–Beer law is valid even in the rather concentrated solution used by us. We have checked the validity of this law also in the case of the solution of sodium pyrosulphite. The correlation was approximately linear (R^2 = 0.9723), but found a better, polynomial (R^2 = 0.999976) form.

The equilibrium concentration of bisulphite can be calculated by means of the Eq. 3.a, but we used a more accurate, empirical Eq. 3.b.

$$C^{\infty}_{NaHSO_3} = \frac{C^{0}_{NaHSO_3} \cdot A^{\infty}_{NaHSO_3}}{A^{0}_{NaHSO_3}} \qquad (3.a)$$

$$C^{\infty}_{NaHSO_3} = 0.03463 \cdot (A^{\infty}_{NaHSO_3})^3 + 0.07565 \cdot (A^{\infty}_{NaHSO_3})^2 + 0.4430 \cdot (A^{\infty}_{NaHSO_3}) \qquad (3.b)$$

where: C = bisulphite concentration (mol/l)
A = pseudo-absorbance
0 = initial status
∞ = state of equilibrium

The concentration of the adduct is equal to the difference between the initial and equilibrium bisulphite – concentration (Eq. 4):

$$C^{\infty}_{adduct} = C^{0}_{NaHSO_3} - C^{\infty}_{NaHSO_3} \qquad (4)$$

In the calculation of the initial bisulphite concentration, we have also taken into account equilibrium between pyrosulphite and bisulphite. The equilibrium constant at 26 and 60˚C (K_{26} = 22.8 l/mol, K_{60} =46.9 l/mol) was taken from the literature [9].

The equilibrium constant for the reaction studied was calculated by means of Eq. 5:

$$K_C = \frac{C^{\infty}_{adduct}}{C^{\infty}_{NaHSO_3} \cdot (C^{0}_{benzaldehyde} - C^{\infty}_{adduct})} \qquad (5)$$

After substituting the respective values in the formula, the following equilibrium constants were obtained for the case of different initial molar ratios and temperatures (Table 3):

The values of the equilibrium constants measured by us are smaller than those reported in the literature ($0.44 - 11.3 \cdot 10^3$ [10]). However, it is known that [10], the ionic strength exerts significant influence on the value of the equilibrium constant: when the ionic strength increases ten times (from 0.1 mol/l to 1.0), the value of the equilibrium constant will decrease from 4.81 l/mol to 0.98 l/mol. As we have performed our measuring

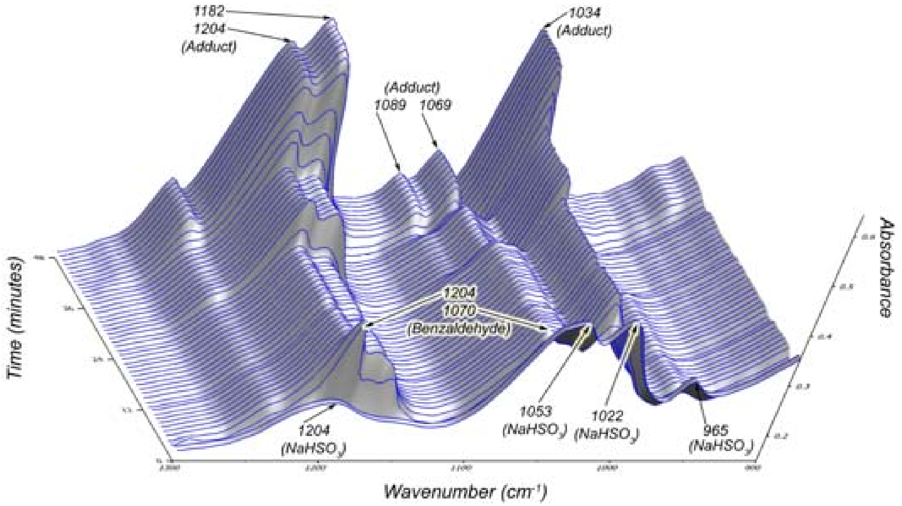


Fig. 1. Reaction of benzaldehyde and sodium bisulphite (Table 1, reaction 1/steps 1 and 2).

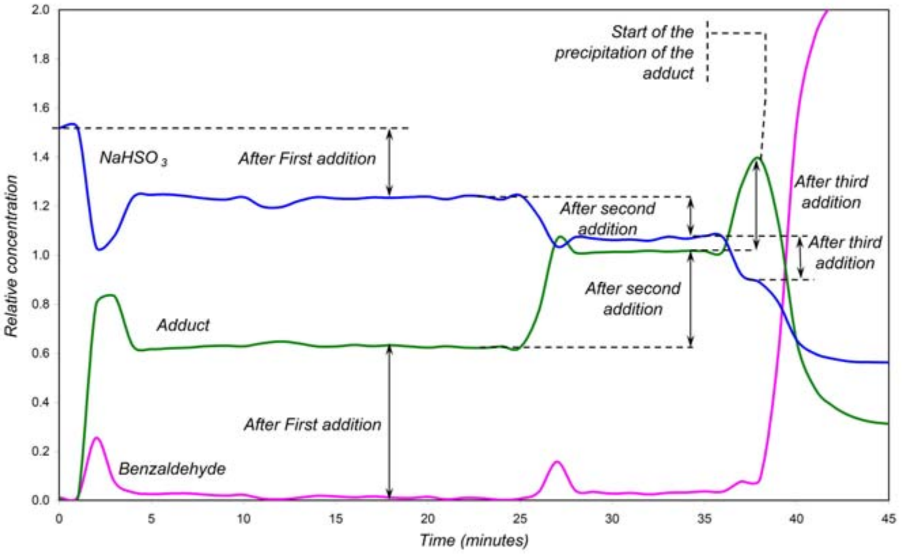


Fig. 2. Changes in the relative concentrations of bisulphite, benzaldehyde and the bisulphite–benzaldehyde adduct depending on time after addition of benzaldehyde portions.

Tab. 3. Equilibrium constants for the reaction of benzaldehyde and sodium bisulphite

Bisulphite:benzaldehyde molar ratio	Temperature (˚C)	Equilibrium constant (l/mol)
3.5	26	5.215
2.1	26	5.235
1.5	26	5.502
1.5	60	8.484

at higher concentrations than usual, we have calculated also the ionic strength (I) applied during our experiments:

$$I = \frac{1}{2}\sum_{B=1}^{n} c_B z_B^2$$

where: c_B is the concentration (mol/l) of ion B and z_B is the charge-number of ion B.

In our case the ion-intensity was 1.48 mol/l, so presumably the smaller equilibrium constants measured by us was a consequence of the higher concentrations, that is of the higher ionic strength.

We have disregarded the dependence of the equilibrium constant between pyrosulphite from the ionic strength, as the equilibrium is entirely shifted to the right side of the equation.

By means of the van t'Hoff equation, one can also calculate the reaction heat from the various equilibrium constants (Table 3) measured at different temperatures (26 and 60 ˚C). Applying a 1.5:1 bisulphite–benzaldehyde ratio this is −2.52 kJ/mol, that is, the temperature of the reaction does not exert any significant influence on equilibrium of the reaction.

Therefore we came to the conclusion that, the ReactIR apparatus can successfully be applied for the monitoring of the equilibrium reactions and for the determination of the equilibrium constant.

4 Summary

In our work we have studied a well-known reaction, the equilibrium addition reaction between benzaldehyde and sodium bisulphite. The reaction was followed by *in situ* Fourier transform IR spectroscopy. We have determined the equilibrium constant of the rapidly achieved equilibrium at different initial molar ratios and different temperatures. The values of the equilibrium constant proved to be smaller than those given by the literature. We demonstrated that, this was a consequence of the higher concentrations, that is, higher ionic strength, as we have performed our measurements at higher concentrations than usual.

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