

## Concentrated water solutions of salts as solvents for reaction of carbohydrates.

### Part 2<sup>1</sup>. Influence of some magnesium salts and some ruthenium species on catalysis of dehydration of glucose

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#### Abstract

Saturated water solutions of  $\text{MgCl}_2$  and  $\text{MgSO}_4$  were applied as solvents/matrices for dehydration of glucose. The product of reaction between  $\text{RuCl}_3(\text{aq.})$  and  $\text{Ag}_2\text{SO}_4$  abbreviated as ' $\text{RuSO}_4$ ' was used as catalyst. As the most selective systems are:  $\text{MgSO}_4/\text{benzene(ethanol)}/\text{RuSO}_4$  the mechanistic hypothesis was designed for these cases. Interaction of glucose with  $\text{MgSO}_4/\text{RuSO}_4$  consists of:  $\text{Mg}^{2+}$  complexation of glucose oxygens; hydrogen bonds between the glucose OH groups and the  $\text{SO}_4^{2-}$  groups; between the glucose OH groups and water, hydroxy ligands in the Ru complex and  $\text{SO}_4^{2-}$  donation to the glucose carbons.

**Keywords:** Glucose; Dehydration; Ruthenium; Magnesium

#### 1. Introduction

Dehydration of hexoses to hydroxymethylfurfural (HMF) catalyzed by  $\text{H}^+$  was thoroughly studied in the case of fructose [1]. For glucose the mechanism is much less founded. There are two principal hypotheses:

1. Glucose isomerises to an acyclic form, then to a 1,2 enediol; from this intermediate three

consecutive eliminations of water afford HMF [2].

2. Glucose isomerises directly to fructose [2], which is dehydrated to HMF according to a well founded mechanism [1].

The selective, high yield and fast process of producing HMF from glucose does not exist. Many undesired substances are formed: reversion products, levulinic acid, formic acid, hydroxyacetyl furan, soluble brown polymers and insoluble black polymers.

Catalysis by metal salts and a few transition metal complexes with or without  $\text{H}^+$  was de-

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<sup>1</sup> For Part 1 see Ref. [7].

scribed in a series of Krupenskii papers. In essence, his findings were:

1. Cooperative effect between  $\text{Cr}^{3+}$  and  $\text{H}^+$  resulting in a 4.4-fold increase of rate of dehydration of glucose or xylose [3]. By this mechanism hemiacetal oxygen is complexed by a metal cation but  $-\text{OH}$  located at C-3 is protonated.
2. Besides the cooperative effect of metal cations and  $\text{H}^+$ , special roles by  $\text{VO}^{2+}$ ,  $\text{TiO}^{2+}$  and  $\text{ZrO}^{2+}$  were observed. It was interpreted in terms of formation of an intermediate, in which hemiacetal oxygen donates electrons to the metal, the hydrogen located at C-2 interacts with  $\text{M}=\text{O}$  and hydroxyl located at C-3 is also protonated [4].

Reactions using this catalytic systems were performed at  $150^\circ\text{C}$  during 30 min. For 30% conversion of glucose HMF was formed in  $\sim 30\%$  yield using  $\text{VOSO}_4$  but 34% with  $\text{ZrOSO}_4$ . Besides, several acids were detected:

Acid	Amount of acid (%) in presence of:	
	$\text{VOSO}_4$	$\text{ZrOSO}_4$
levulinic	8	3
formic	3	1
glycerinic	8	2
succinic	9	22

The reaction is far from selective.

If  $\text{TiOSO}_4$  is used, HMF is formed from glucose in 26% yield, but furfural from xylose in 34% yield. Many acids also accompany HMF [5]. When sawdust [5] is used as a source of carbohydrate furfural is synthesized in 62% (with 5% of  $\text{H}_2\text{SO}_4$ ) but in 86% if one uses 3%  $\text{H}_2\text{SO}_4$  with  $\text{TiO}_2$ . A disadvantage of the system using Ti is that insoluble compounds are formed from  $\text{TiOSO}_4$  and the catalyst is eliminated from the reaction solution. Application of polymer-anchored metal complexes improves selectivity, only 10–15% of formic acid is formed [6]; the lifetime of such a catalyst is unfortunately short.

All these attempts indicate that the objective of high yield, selective and experimentally simple process of producing HMF from glucose is far from being achieved; similarly, the mechanism of its formation with participation of inorganic compound is not clarified.

A systematic study of the influence of salts, i.e. cations and anions, on the dehydration of glucose does not exist. Van Dam [2] studied the influence of  $\text{NaCl}$ ,  $\text{AlCl}_3$ ,  $\text{CrCl}_3$  and  $\text{LaCl}_3$  in the presence of  $\text{H}^+$  and found only minor effects of these salts on dehydration. We observed that neither HMF nor levulinic acid are formed from glucose when  $\text{NO}_3^-$  ions (also  $\text{HNO}_3$ ) are present in the reaction mixture [7]. This observation questions the validity of all the mechanisms of HMF formation which regard  $\text{H}^+$  as the only catalyst for HMF formation, neglecting the role of the anions.

Our objective was to find a catalyst for selective, fast synthesis in high yield of HMF from glucose, and to elucidate the mechanism of its formation without  $\text{H}^+$  but with transition metal complexes as catalysts.

## 2. Experimental

Glucose and magnesium salts (analytical grade) were manufactured by POCh (Polskie Odczynniki Chemiczne, Gliwice, Poland);  $\text{RuCl}_3(\text{aq.})$  was supplied by Aldrich; all reactants were used as received; water was distilled.

Reactions were performed under gentle reflux; compositions of the relevant reaction systems are given in Tables 1–5. After the required time lapse, the crude reaction product was extracted with  $\text{CHCl}_3$  in a Soxhlet extractor during 6 h. Chloroform was then evaporated by rotary evaporator and the remaining product dried to constant weight. An amount of  $\sim 0.02$  g of crude product was dissolved in  $2 \text{ cm}^3$  of acetone and analyzed by a Hewlett Packard 5890 Series II gas chromatograph combined with a Model 5972 mass selective detector us-

Table 1  
Systems for dehydration of glucose by saturated solutions of MgCl<sub>2</sub> and MgSO<sub>4</sub> without organic solvents

System number	Mg salt mmol	Ru compound mmol	Molar ratio		
			Mg <sup>2+</sup> / glu	Mg <sup>2+</sup> / Ru	glu/ Ru
1	MgCl <sub>2</sub> 49.42	—	5.93	—	—
2	MgCl <sub>2</sub> 26.26	RuCl <sub>3</sub> (aq.) 0.147	5.93	336.8	56.8
3	MgSO <sub>4</sub> 26.26	—	3.15	—	—
4	MgSO <sub>4</sub> 26.26	RuCl <sub>3</sub> (aq.) 0.147	3.15	178.6	56.8

Conditions: 10 cm<sup>3</sup> of salt solution; reaction time 3 h; 8.33 mmol of glucose.

ing HP-1 and Innovax columns. Column programs: for HP-1: 70°C 10 min, 5°C/min up to 150°C, 150°C/2 min, 5°C/min up to 300°C, 300°C 5 min. For Innovax: 35°C/30 min, 5°C/min up to 250°C, 250°C 5 min.

Chromatographic peaks were identified using the Wiley Library with a PBM search algo-

rithm; integration was by ChemStation Integrator contained in the HP ChemStation software.

'RuSO<sub>4</sub>' was synthesized as follows: to 0.8 g of RuCl<sub>3</sub>(aq.) in powder form was quickly added a solution of a 1.54 g (4.93 mmol) of Ag<sub>2</sub>SO<sub>4</sub> in 140 cm<sup>3</sup> of water, with strong agitation by a magnetic stirrer. Agitation was continued for two hours. The precipitated AgCl was filtered off with a cellulose filter, and the filtrate was evaporated at 80°C. The dried black residue was considered to be 'RuSO<sub>4</sub>'.

Proton noise decoupled <sup>13</sup>C NMR spectra were obtained with a Bruker AM-500 spectrometer operating at 500.13 MHz with deuterium lock, C<sub>6</sub>D<sub>6</sub> being placed in a capillary in a center of the probe. A probehead of 5 mm diameter sample tubes maintained at 303 K was used. A 3 μs pulse (45°, PW 3.0) was used. A sweep of 31.25 kHz with 64K data points, with acquisition time 1.049 s and repetition delay of 2 s was used. Glucose was dissolved 2.5 h prior to measurement. Longer times of interaction of the salt with carbohydrate does not influence the spectra.

UV-Vis spectra were obtained at room temperature on a Beckman DU-68 spectrophotome-

Table 2  
Composition and molar ratios of components of systems 5, 6 and 7 for dehydration of glucose

System number	Reaction time h	Mg salt mmol	Ru compound mmol	Molar ratio		
				Mg <sup>2+</sup> / glu	Mg <sup>2+</sup> / Ru	glu/ Ru
5A	12	MgCl <sub>2</sub> 49.42	—	not studied		
5B	24	"	—	not studied		
5C	48	"	1	5.93	—	—
6A	12	MgCl <sub>2</sub> 49.42	RuCl <sub>3</sub> (aq.) 0.147	5.93	336.8	56.8
6B	24	"	"	"	"	"
6C	48	"	"	"	"	"
7A	12	MgCl <sub>2</sub> 49.2	'RuSO <sub>4</sub> ' 0.147	5.93	336.8	56.8
7B	24	"	"	"	"	"
7C	48	"	"	"	"	"

Conditions: volume of saturated solution of magnesium chloride 10 cm<sup>3</sup>; volume of benzene 20 cm<sup>3</sup>; amount of glucose 8.33 mmol.

Table 3  
Composition and molar ratios of components of systems 8, 9 and 10 for dehydration of glucose

System number	Reaction time h	Mg salt mmol	Ru compound mmol	Molar ratio		
				Mg <sup>2+</sup> /glu	Mg <sup>2+</sup> /Ru	glu/Ru
8A	12	MgSO <sub>4</sub> 26.26	—	3.15	—	—
8B	24	"	—	"	—	—
8C	48	"	—	"	—	—
9A	12	"	RuCl <sub>3</sub> (aq.) 0.147	3.15	178.6	56.8
9B	24	"	"	"	"	"
9C	48	"	"	"	"	"
10A	12	"	'RuSO <sub>4</sub> '	"	"	"
10B	24	"	"	"	"	"
10C	48	"	"	"	"	"

Conditions: volume of saturated solution of magnesium sulphate 10 cm<sup>3</sup>; volume of benzene 20 cm<sup>3</sup>; amount of glucose 8.33 mmol.

ter with basic software. Basic data processing consisting of (1) transferring the data from spectrophotometer through a standard bidirectional RS-232 communication port, (2) storage in a memory of an IBM PC, (3) converting the data

to an ASCII code for further processing were done with Beckman PC software library [8]. The spectra were fitted with Gaussian bands using a CFP program [9], based on the Slavic algorithm [10].

Table 4  
Composition and molar ratios of components of systems 11, 12 and 13 for dehydration of glucose

System number	Reaction time h	Mg salt mmol	Ru compound mmol	Molar ratio		
				Mg <sup>2+</sup> /glu	Mg <sup>2+</sup> /Ru	glu/Ru
11A	12	MgCl <sub>2</sub> 49.42	—	not studied		
11B	24	"	—	not studied		
11C	48	"	—	5.93	—	—
12A	12	MgCl <sub>2</sub> 49.42	RuCl <sub>3</sub> (aq.) 0.147	5.93	336.8	56.8
12B	24	"	"	"	"	"
12C	48	"	"	"	"	"
13A	12	MgCl <sub>2</sub> 49.2	'RuSO <sub>4</sub> ' 0.147	5.93	336.8	56.8
13B	24	"	"	"	"	"
13C	48	"	"	"	"	"

Conditions: volume of saturated solution of magnesium chloride 10 cm<sup>3</sup>; volume of ethanol 3 cm<sup>3</sup>; amount of glucose 8.33 mmol.

Table 5  
Composition and molar ratios of components of systems 14, 15 and 16 for dehydration of glucose

System number	Reaction time h	Mg salt mmol	Ru compound mmol	Molar ratio		
				Mg <sup>2+</sup> /glu	Mg <sup>2+</sup> /Ru	glu/Ru
14A	12	MgSO <sub>4</sub> 26.26	—	3.15	—	—
14B	24	"	—	"	—	—
14C	48	"	—	"	—	—
15A	12	"	RuCl <sub>3</sub> (aq.) 0.147	3.15	178.6	56.8
15B	24	"	"	"	"	"
15C	48	"	"	"	"	"
16A	12	"	'RuSO <sub>4</sub> ' 0.147	"	"	"
16B	24	"	"	"	"	"
16C	48	"	"	"	"	"

Conditions: volume of saturated solution of magnesium sulphate 10 cm<sup>3</sup>; volume of ethanol 3 cm<sup>3</sup>; amount of glucose 8.33 mmol.

Table 6  
Yields in systems 1–4

System number	Product		Yield %	Humins %
1	2-furancarboxaldehyde	I	0.09	26.3
	1-(2-Furanyl)ethanone	II	0.05	
	5-methyl-2(5 <i>H</i> )-furanone 2-methoxyfuran	III	0.15	
	1-(2)-Furyl-2-Hydroxyethanone 2-furancarboxylic acid methyl ester	IV	0.75	
	levulinic acid	V	5.22	
	HMF	VI	8.85	
2	I		0.27	26.7
	II		0.09	
	III		0.32	
	5-methyl-2-furancarboxyaldehyde	VII	0.03	
	IV		1.15	
	V		10.54	
3	VI		7.40	no humins
	no products			
4	IV		0.04	2.0
	VI		2.80	
	5,5'-oxydimethylenebis(2-furaldehyde)			
	VIII		0.02	

### 3. Results and discussion

#### 3.1. Dehydration of glucose in saturated solutions of $MgCl_2$ and $MgSO_4$ without organic solvents

The systems studied are listed in Table 1.

Yields obtained in these systems are presented by Table 6.

Yields in this Table and in all others were calculated from the following equations:

glucose  $\rightarrow$  HMF

glucose  $\rightarrow$  all other one cycle heterocyclic products

glucose  $\rightarrow$  levulinic acid

glucose  $\rightarrow$  '154'

'154' is assumed to be a carbocyclic product (see Discussion below).

glucose  $\rightarrow$  0.5[5,5'-oxodimethylenebis (2-furaldehyde)]

Conversion to humins was calculated in weight % of humins of the weight of starting glucose.

The striking comparison of results from Table 6 and from other Tables showing yields is that in  $MgCl_2$  without benzene or ethanol the main reaction is the formation of humins. As humins do not contain chlorine, their formation is a catalyzed process. The absence of humins with  $MgSO_4$  suggests that  $Cl^-$  (or the chlorine end of an aggregate of the type  $Cl[MgCl_2MgCl_2Mg]_xCl$ ) [11] plays an essential role in humin formation. Interaction of  $Cl^-$  or a chlorine end with some classes of carbohydrates was postulated and interpreted in  $^{13}C$  NMR chemical shift studies of glucose carbons in saturated solutions of  $MgCl_2$  [11].

#### 3.2. Dehydration of glucose in saturated solutions of $MgCl_2$ and $MgSO_2$ in the presence of benzene

Tables 2 and 3 show composition of two phase system: water solution of magnesium

Table 7  
Yields in systems 5–7

System number	Product	Yield	Humins
		%	%
5C	II	0.05	no humins
	IV	0.41	
	V	0.95	
	VI	2.1	
	VIII	0.09	
6A	III	0.04	no humins
	IV	0.67	
	V	0.70	
	'146' (containing chlorine)	1.50	
	'154'	0.02	
	VI	2.6	
	VII	0.02	
	VIII	1.5	
6B	III	0.02	no humins
	VI	0.50	
	V	1.60	
	VI	2.70	
	VII	0.03	
	VIII	0.01	
6C	III	0.11	no humins
	IV	0.52	
	V	2.03	
	'154'	0.02	
	VI	1.31	
	VII	0.10	
	VIII	0.06	
	dihydro-5-methyl-2(3H)-furanone	X 0.03	
7A	III	0.5	7.2
	IV	1.7	
	V	13.0	
	VI	6.5	
	VII	0.2	
7B	III	1.0	21.33
	IV	2.73	
	V	14.3	
	'154'	0.64	
	VI	3.65	
	VII	0.33	
	X	0.17	
7C	III	0.77	26.13
	IV	2.6	
	V	28.9	
	VI	2.1	
	VII	0.3	
	VIII	1.1	

salts + glucose (with or without ruthenium compound) and a layer of benzene.

Yields of the products are shown in Tables 7 and 8.

Formation of humins is restricted here. Reaction is rather nonselective for all of the combinations of  $MgCl_2$ , but quite selective for  $MgSO_4$ . The benzene was added to create conditions for transferring products from an aqueous phase, which contains catalyst and substrate, to an organic phase. This should ameliorate selectivity. This expectation was fulfilled by decrease of humin formation but it was unsuccessful for monomolecular species.

### 3.3. Dehydration of glucose in saturated solutions of $MgCl_2$ and $MgSO_4$ in the presence of ethanol

The compositions of the systems studied are shown in Tables 4 and 5.

In all of the cases described in these Tables are one phase systems. Ethanol was added for the following reasons:

Table 8  
Yields in systems 8–10

System number	Product	Yields %	Humins %
8A	VI	1.41	no humins
8B	VI	1.60	no humins
8C	VI	1.90	no humins
9A	VI	2.62	no humins
9B	IV	0.06	no humins
	VI	2.40	
9C	IV	0.06	no humins
	VI	2.90	
10A	IV	0.43	no humins
	VI	2.31	
	VIII	0.06	
10B	IV	0.02	no humins
	'154'	0.02	
	VI	2.31	
	VIII	0.06	
10C	IV	0.09	no humins
	VI	3.60	
	VIII	0.01	

Table 9  
Yields in systems 11–13

System number	Product	Yields %	Humins %
11C	III	0.17	53.6
	IV	1.03	
	V	13.0	
	'154'	1.5	
	VI	2.0	
	levulinic acid ethyl ester	X	
12A	IV	0.9	no humins
	'154'	0.07	
	VI	4.13	
12B	IV	0.8	no humins
	VI	1.7	
12C	V	0.40	no humins
	'154'	1.81	
	VI	3.70	
	X	0.15	
13A	II	0.04	no humins
	V	0.12	
	'154'	0.44	
	VI	1.33	
	X	0.05	
13B	IV	0.03	no humins
	'154'	0.03	
	VI	1.50	
	VIII	0.03	
13C	V	2.72	0.3
	'154'	0.87	
	'99'	0.28	
	VI	4.30	
	VII	0.34	
	dihydro-5-methyl-2(3H)-furanone	IX	0.18
	X	1.45	
	2-furanmethanol	XI	0.28

1. to provide another oxygen ligand to occupy some coordination sites and to improve selectivity.
2. to dilute and to esterify any acids that are formed.

Yields of the products are shown by Tables 9 and 10:

In the presence of ethanol humin formation is considerably diminished. The reaction remains rather nonselective for  $MgCl_2$ , and again quite selective if performed in  $MgSO_4$ . Besides identified compounds an unknown substance abbre-

Table 10  
Yields in systems 14–16

System number	Product	Yield %	Humins %
14A		negligible	no humins
14B		negligible	no humins
14C	VI	0.8	no humins
	VIII	0.01	
	IX	0.01	
15A	IV	0.02	no humins
	VI	0.82	
15B	IV	0.04	no humins
	VI	1.2	
15C	VI	4.00	no humins
16A		negligible	no humins
16B	VI	2.00	no humins
16C	IV	0.09	no humins
	VI	4.84	
	VIII	0.1	

viated as '154' is formed in greater quantities than for reactions performed with benzene. Gas chromatography and mass spectra for '154' are shown in Fig. 1.

We believe that it is a carbocyclic product. The final structure elucidation and mechanism of formation of '154' will be presented in the forthcoming paper. We are also doing efforts to

elaborate conditions for high yield and selective synthesis of '154'. Besides two other unidentified products were observed: '146' (containing chlorine) and '99'. They appear only in two reactions and we do not intend to study them in the present work.

### 3.4. Final conclusions concerning selectivity

The most selective systems in terms of formation of HMF without humins and with only minor amount of other products are  $MgSO_4$ /' $RuSO_4$ '/benzene and  $MgSO_4$ /' $RuSO_4$ '/ethanol.

The highest yield of levulinic acid ~ 29% was observed in the much less selective reaction, where levulinic acid was accompanied by ~ 26% of humins and ~ 7.2% of other individual compounds. Such a system is based on the  $MgCl_2$  solution. We therefore conclude that for selective synthesis of HMF  $Cl^-$  should be either completely avoided or used in minor quantities.

### 3.5. Preparation and UV-Vis spectra of ' $RuSO_4$ '

' $RuSO_4$ ' was prepared by addition of a solution of  $Ag_2SO_4$  in water to solid  $RuCl_3(aq)$

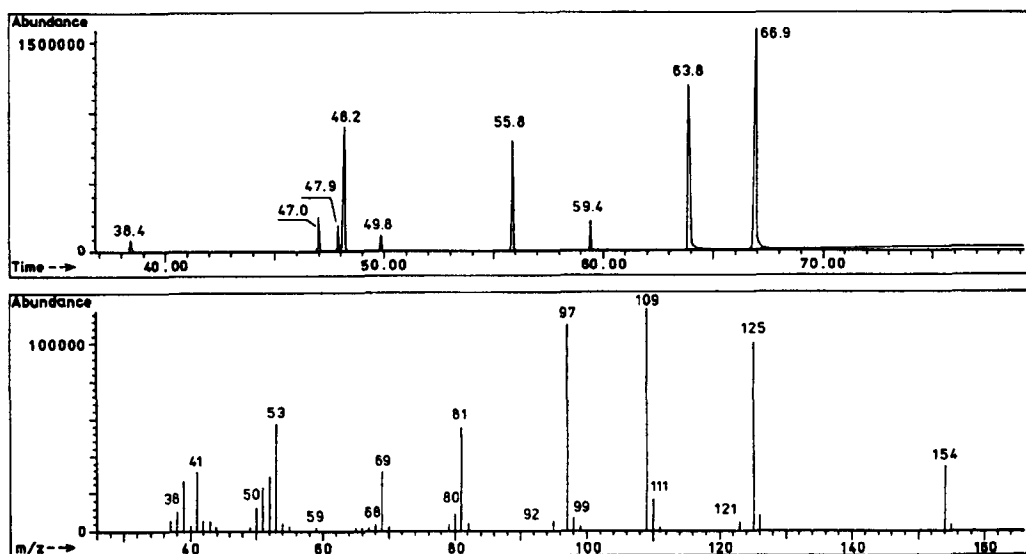


Fig. 1. Capillary gas chromatogram of one of a crude reaction products and mass spectrum of the product '154' (retention time 55.8 min.) supposed to be a carbocyclic substance.



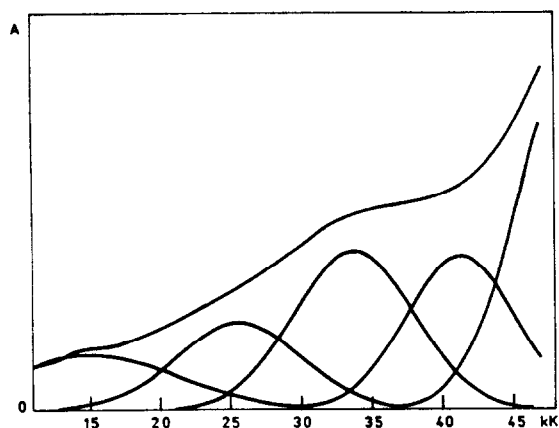


Fig. 2. The UV-Vis spectrum of solution of 'RuSO<sub>4</sub>' in a saturated solution of MgSO<sub>4</sub> in water. Also shown are the deconvolution curves.

accompanied by strong agitation. The solution of Ag<sub>2</sub>SO<sub>4</sub> was added to the solid, but not to a solution of commercial ruthenium chloride in water because water reacts instantaneously with RuCl<sub>3</sub>(aq.) and the composition of the solution changes rapidly [12]. Details of the preparation of 'RuSO<sub>4</sub>' are given in the Experimental. Obviously, there could be several methods of to prepare 'RuSO<sub>4</sub>'; the influence of the different procedures to synthesize 'RuSO<sub>4</sub>' on the catalytic activity will be described in a forthcoming paper.

The UV-Vis spectrum of a solution of 'RuSO<sub>4</sub>' prepared in a saturated solution of MgSO<sub>4</sub> in water, together with the curves – products of deconvolution – is shown in Fig. 2. The synthesis used in here gives AgCl in quantities indicating that all chlorine introduced with RuCl<sub>3</sub>(aq.) reacts to give silver chloride.

The shape of the absorption curve indicates the necessity to apply a deconvolution procedure in order to detect components of the observed curve. The deconvolution procedure results in four absorption bands around: 15262, 25594, 33748 and 41260 cm<sup>-1</sup>. In the range of the last two bands, ~33748 and ~41260 cm<sup>-1</sup>, one can expect the absorptions of [Ru(H<sub>2</sub>O)<sub>5</sub>OH]<sup>2+</sup> and [Ru(H<sub>2</sub>O)<sub>4</sub>(OH)<sub>2</sub>]<sup>+</sup> [12], so these compounds will also be considered in the discussion of the reaction mechanism. De-

convolutions applied to the spectra of 'RuSO<sub>4</sub>' obtained by alternative synthetic procedures will be described in a forthcoming paper.

### 3.6. Comparison of interaction of glucose with saturated solutions of MgSO<sub>4</sub> and MgCl<sub>2</sub> studied by <sup>13</sup>C NMR

We performed <sup>13</sup>C NMR study of displacements of glucose carbon signals when glucose is dissolved in saturated solutions of MgCl<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> in water [11]. We evoke here the two most important results for MgCl<sub>2</sub>:

1. greater shift to higher fields of the C-1, C-3 and C-5 signals in the β anomer of glucose in the MgCl<sub>2</sub> solution compared with the shifts of other carbons.
2. considerable shift to lower fields of the C-6 signals for both anomers.

For glucose dissolved in a saturated solution of MgSO<sub>4</sub> in water, the <sup>13</sup>C NMR spectrum is characterized by a rather equalized shift of all carbon signals (including that of C-6) to higher fields – for both anomers. Table 11 gives the susceptibility-corrected <sup>13</sup>C NMR chemical shift displacements of the glucose signals in a magnesium sulfate solution.

There is an essential difference in the situation of glucose when it is brought into contact with a saturated solution of MgCl<sub>2</sub> compared with that in one of MgSO<sub>4</sub>. We interpret the shifts to higher fields as a donation of electrons by SO<sub>4</sub><sup>2-</sup> oxygens to all the carbons in the situation when glucose oxygens are complexed by Mg<sup>2+</sup> and all –OH groups are hydrogen bonded to SO<sub>4</sub><sup>2-</sup>. This is illustrated by Fig. 3

Table 11  
Magnetic susceptibility corrected <sup>13</sup>C NMR chemical shift displacements δ<sup>a</sup> of glucose carbons in a saturated solution of magnesium sulfate in water

	δ					
	C-1	C-2	C-3	C-4	C-5	C-6
α	-0.78	-0.84	-0.79	-1.05	-0.70	-0.62
β	-0.84	-0.75	-0.84	-0.71	-0.86	-0.65

<sup>a</sup> δ(glucose solution in saturated salt solution) – δ(solution in water). Upper part α anomer, lower part β anomer.

As all of the carbons of glucose are 'treated' approximately equally by  $\text{MgSO}_4$ , reactions responsible for nonselectivity are diminished. Nonselectivity has its origins in C–C and C–H bond cleavages as can be seen from the results of Tables 6, 7 and 11 and Table 13.

### 3.7. Mechanism of the [Ru] catalyzed dehydration

The mechanism of the ruthenium catalyzed dehydration of glucose to HMF will be proposed for 'RuSO<sub>4</sub>' in  $\text{MgSO}_4$  matrix because this system affords a selective reaction.

The preparation of 'RuSO<sub>4</sub>' consists of the reaction of a solution of  $\text{Ag}_2\text{SO}_4$  in water with  $\text{RuCl}_3(\text{aq.})$ . A crude multicomponent product abbreviated as 'RuSO<sub>4</sub>' probably contains such compounds as  $[\text{Ru}(\text{H}_2\text{O})_5\text{OH}]^{2+} \text{SO}_4^{2-}$  and  $[\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+} \text{SO}_4^{2-}$ . Mechanistic hypotheses therefore should consider these two ruthenium complexes as likely candidates for catalyst precursors.

The reaction is only possible by hydrogen bond interactions. The proposed mechanism consists of the following steps:

1. Predissociation of water from  $[\text{Ru}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  or  $[\text{Ru}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}$ .
2. Coordination of predissociation products to glu, or ligand exchange reactions of starting complexes with glu, which gives I (Fig. 4).
3. Slow reaction within the coordination sphere of Ru in I (as shown by flashes in II) first forms a water molecule and a –CHO in the intermediate III (we did not attempt to detect this intermediate). The key member of

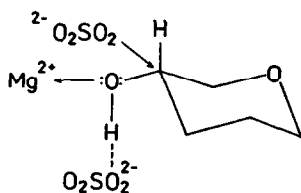


Fig. 3. Hypothesized interaction of glucose with  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  in saturated water solution of magnesium sulfate; for clarity only interaction of H–C–4–OH is shown; we suggest that the remaining –CH–OH groups interact similarly.

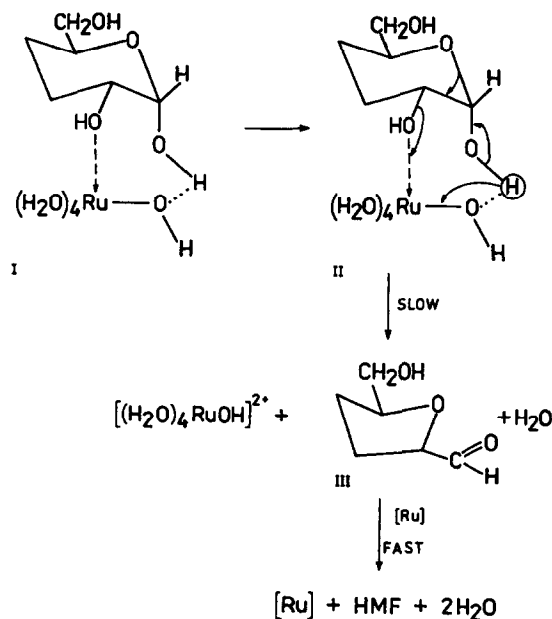


Fig. 4. Mechanistic hypothesis of glucose dehydration by 'RuSO<sub>4</sub>' in  $\text{MgSO}_4$ /water matrix.

the catalytic cycle  $[\text{Ru}(\text{H}_2\text{O})_4\text{OH}]^{2+}$  or  $[\text{Ru}(\text{H}_2\text{O})_3(\text{OH})_2]^{2+}$  is simultaneously regenerated.

4. Rapid reaction of III to HMF also catalyzed by ruthenium aquo/hydroxo species.

An important conclusion can be drawn from this research: to design a catalyst for the reaction of carbohydrates and other polyhydroxy compounds requires that an aquo/hydroxy metal complex must be used. This paper should stimulate research in this rather new field of catalysis.

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### References

- [1] M.J. Antal Jr., W.S.L. Mok and G.N. Richards, *Carbohydrate Res.*, 199 (1990) 91.

- [2] H.E. van Dam, A.P.G. Kieboom and H. van Bekkum, *Starch/Stärke*, 38 (1986) 95.
- [3] W.I. Krupenskii, *Chim. Drieviesiny*, 1 (1978) 72 (in Russian).
- [4] W.I. Krupenskii, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 24 (1981) 38 (in Russian).
- [5] W.I. Krupenskii, *Chim. Drieviesiny*, 5 (1983) 90 (in Russian).
- [6] G.A. Potapov, W.I. Krupenskii and M.I. Alieva, *React. Kinet. Catal. Lett.*, 2 (1985) 331.
- [7] S.K. Tyrlik, D. Szerszen, B. Kurzak and K. Bal Starch/Stärke, 47 (1995) 171.
- [8] Beckman Data Capture Software Manual, Beckman Instruments Inc., 1987.
- [9] K. Kurzak, PhD Thesis, Technical University Wrocław, Wrocław (1983).
- [10] I.A. Slavic, *Nucl. Instr. Methods*, 34 (1976) 2855.
- [11] S.K. Tyrlik, D. Szerszen and S. Szymanski, *New J. Chem.*, (1995) submitted.
- [12] S.K. Tyrlik, K. Kurzak and L. Randzio, *Trans. Met. Chem.*, (1994) accepted.