

## Mechanism of Ferrocenylmethyl Benzoate Formolysis and Acetolysis

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The formolysis and acetolysis of ferrocenylmethyl benzoate are proton catalyzed and accelerated by addition of perchloric acid. Our earlier experiments have shown that at a temperature of about 20 °C addition of a common benzoate ion in formolysis of  $3.2 \times 10^{-4}$  mol dm<sup>-3</sup> ferrocenylmethyl benzoate suppresses the formolysis rate only slightly but the formolysis is significantly slower at 40 °C. Such rate lowering is not observed in acetolysis of the same substrate. Decrease of the formolysis rate at increased temperatures (20–40 °C) is most probably caused by the decrease of the hydrogen ion concentration, because the stronger formic acid displaces the weaker benzoic acid from sodium benzoate, thus reducing the formic acid concentration in this acid-catalyzed system. This, however, does not occur in the weaker acetic acid. Besides, the acetolysis rates are equal in the presence of 0.1 and 0.2 mol dm<sup>-3</sup> sodium benzoate, while the formolysis rates decrease with the addition of benzoate. The strong temperature dependence of the formolysis rates is probably connected with the formation of formic acid dimers and the temperature dependent hydrogen bonding. Hydrogen bonding and the dimer formation in acetic acid are less pronounced than in formic acid.

### Keywords

ferrocenyl esters solvolyses  
acid catalyzed solvolyses  
formolysis and acetolysis  
ferrocenylmethyl benzoate  
solvent separated ion pairs

## INTRODUCTION

The mechanism of ester solvolyses is in principle well explained by the half-a-century old reaction scheme of S. Winstein, which involves contact ( $R^+X^-$ ) and solvent separated ( $R^+||X^-$ ) ion pairs.<sup>1</sup> These solvolyses are usually proton catalyzed because the uncharged molecule (HX), formed by proton addition, can be more easily separated from  $R^+$ . Since the ferrocene system is a strong electron donor, the positive charge of the ferrocenylmethyl cation ( $FcCH_2^+$ ) is not localized but rather dispersed over the whole cation. It is also well known that the addition of perchlorate prevents the reverse of the solvent

separated ion pair into a contact ion pair by displacing  $X^-$  from  $R^+||X^-$ .<sup>2</sup> It could be expected that the addition of a common ion would suppress the reaction according to the mass law retardation, but in the absence of lithium perchlorate.

Our earlier experiments have shown that at a temperature of about 20 °C the addition of benzoate hardly affects the rate of formolysis, but the formolysis is significantly slower at 40 °C.<sup>3,4</sup> On the other hand, the rate of acetolysis of ferrocenylmethyl benzoate ( $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>) does not change with addition of benzoate, as shown by our experiments.

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## EXPERIMENTAL

The ferrocenylmethyl benzoate was prepared from ferrocenylmethyl alcohol in a pure argon atmosphere according to literature.<sup>5</sup>

All kinetic measurements were also performed in argon in order to avoid the formation of ferricinium salts. The formolysis and acetolysis were followed in anhydrous formic acid and glacial acetic acid of analytical grade (Merck *p.a.*). A perchloric acid concentration of 70 % (vol. fraction) was used (Merck *p.a.*).

Kinetics of the solvolyses was followed spectrophotometrically at 322 and 436 nm, using an Agilent 8453 spectrophotometer with software support of the PC-HP 845x UV-Visible System (Hewlett-Packard).

## RESULTS AND DISCUSSION

Influence of the acid ( $\text{HClO}_4$ ) on the rate of the ferrocenylmethyl benzoate complex formolysis and acetolysis was examined at various temperatures. The complex concentration in formolysis amounted to  $3.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$  while perchloric acid concentrations were  $3.0 \times 10^{-6}$ ,  $1.5 \times 10^{-5}$ , and  $3.0 \times 10^{-5}$  mol  $\text{dm}^{-3}$ .

The complex concentration in acetolysis of  $1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$  was allowed by the increased complex solubility in acetic acid, compared to formic acid. Perchloric acid concentrations were  $1.0 \times 10^{-5}$ ,  $5.0 \times 10^{-5}$ , and  $1.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$  (see Tables I and II).

It can be seen that the rates of formolysis and acetolysis were almost equal at the zero perchloric acid con-

centration, and that the addition of perchloric acid increased the rates of formolysis and acetolysis in a similar manner.

Reduction of solvolysis rates upon addition of benzoate was observed only in formolysis but not in acetolysis, as shown in Table III.

It can be seen that the rates of acetolysis in 0.1 and 0.2 M Na-benzoate were practically equal and also equal to the rates of acetolysis without addition of benzoate ions.

The decrease of the rate of formolysis at higher temperatures (40 °C) was most probably caused by the decrease of hydrogen ion concentration, since the stronger formic acid displaced the weaker benzoic acid from sodium benzoate. It appears that the small decrease in the solution acidity, upon addition of sodium benzoate, causes a significant rate decrease in this acid catalyzed system. On the other hand, this did not occur in acetic acid, which was the weakest of all the three acids. The ionization constants of formic, benzoic, and acetic acids are  $1.8 \times 10^{-4}$ ,  $6.0 \times 10^{-5}$ , and  $1.8 \times 10^{-5}$  mol  $\text{dm}^{-3}$ , respectively.

The question arises why the common ion rate depression is so strongly temperature dependent, as shown by our earlier measurements,<sup>3,4</sup> now presented in a modified manner (see Figure 1).

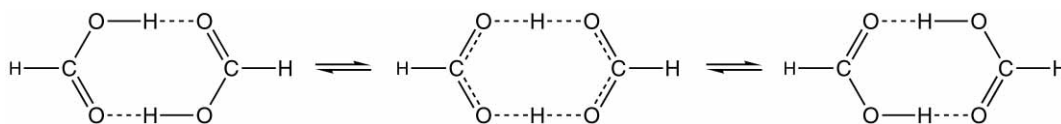
We believe that this temperature dependence is connected with the existence of a formic acid dimer at lower temperatures, *i.e.*, the equilibria (Scheme 1) as suggested in the literature.<sup>6,7</sup> The dimer formation in acetic acid is probably much less pronounced than in formic acid. As

TABLE I. Rates of formolysis of  $3 \times 10^{-4}$  mol  $\text{dm}^{-3}$  ferrocenylmethyl benzoate in anhydrous formic acid upon addition of perchloric acid

<i>T</i> /K	[HClO <sub>4</sub> ]/mol dm <sup>-3</sup> :			
	zero	$3.0 \times 10^{-6}$	$1.5 \times 10^{-5}$	$3.0 \times 10^{-5}$
	<i>k</i> <sub>form.</sub> /10 <sup>-4</sup> s <sup>-1</sup>			
293.16	2.3	2.6	9.6	24.0
298.16	6.0	5.9	18.1	40.1
303.16	8.1	7.5	28.1	too fast for
308.16	9.1	9.0	33.0	measurement
313.16	20.0	18.0	51.0	

TABLE II. Rates of acetolysis of  $1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$  ferrocenylmethyl benzoate in glacial acetic acid upon addition of perchloric acid

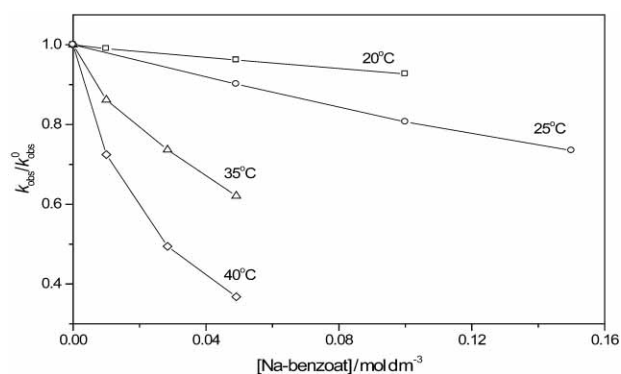
<i>T</i> /K	[HClO <sub>4</sub> ]/mol dm <sup>-3</sup> :			
	zero	$1.0 \times 10^{-5}$	$5.0 \times 10^{-5}$	$1.0 \times 10^{-4}$
	<i>k</i> <sub>acet.</sub> /10 <sup>-4</sup> s <sup>-1</sup>			
293.16	2.5	3.5	11.0	25.7
298.16	5.0	5.1	12.5	44.2
303.16	7.9	6.9	28.5	93.6
308.16	11.0	10.0	31.0	too fast for
313.16	19.1	16.4	49.5	measurement



Scheme 1.

TABLE III. Rates of acetolysis of  $1.0 \times 10^{-3}$  mol dm $^{-3}$  ferrocenylmethyl benzoate in glacial acetic acid upon addition of Na-benzoate as a common ion

T/K	[Na-benzoate]/mol dm $^{-3}$ :	
	0.1	0.2
	$k_{\text{acet.}}/10^{-4} \text{ s}^{-1}$	
293.16	2.9	3.3
298.16	4.8	5.4
303.16	6.5	7.2
308.16	11.0	11.0
313.16	15.0	14.9

Figure 1. Decrease of the rate of formolysis of  $3.2 \times 10^{-4}$  mol dm $^{-3}$  ferrocenylmethyl benzoate upon addition of sodium benzoate (modified from Ref. 4);  $k_{\text{obs}}^0$  is the rate in the absence of a common ion.

long as formic acid is in the dimer form, the displacement of benzoic acid from sodium benzoate might be prevented, which is being investigated.

It appears very strange that a relatively small amount of hydrogen ions, introduced by addition of  $10^{-5}$  to  $10^{-4}$  M perchloric acid into anhydrous formic acid, or glacial acetic acid, can acid-catalyze the ferrocenylmethyl benzoate complex formolysis or acetolysis. One would expect no observable kinetic effect whatsoever. The conclusion can be drawn that the protons of anhydrous formic acid, or glacial acetic acid, are, under the reaction conditions, not able to exhibit acid-catalysis, probably

because of the protons association to their counter-ions, formate and acetate, respectively. Further investigation is being planned.

#### Added in Proof:

In the meantime, we have calculated the Arrhenius parameters for the formolysis of  $3 \times 10^{-4}$  mol dm $^{-3}$  ferrocenylmethyl benzoate in anhydrous formic acid (temperature interval: 20–40 °C) upon addition of perchloric acid. It was found that the rate acceleration is accompanied by a decrease in the energy of activation of about 10 kJ mol $^{-1}$  K $^{-1}$ . In general, the rate increase might be due to the decrease of the energy of activation, or the increase of the entropy of activation. Since we found that the entropy of activation is negative, and varies between  $-82 \text{ J K}^{-1} \text{ mol}^{-1}$  (at zero perchloric acid concentration) and  $-104 \text{ J K}^{-1} \text{ mol}^{-1}$  (at  $1.5 \times 10^{-5}$  mol dm $^{-3}$  HClO $_4$ ), the rate acceleration upon addition of perchloric acid must be a consequence of the lowering of the energy of activation.

In acetolysis, the decrease of the energy of activation upon addition of perchloric acid is similar to that in formolysis. The entropy of activation is also negative and depends on the perchloric acid concentration, as it does in formolysis.

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## SAŽETAK

### Mehanizam formolize i acetolize ferocenilmetil benzoata

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Formoliza i acetoliza ferocenilmetil benzoata katalizirane su protonima, a ubrzava ih dodatak perklorne kiseline. Naši raniji pokusi pokazali su da na temperaturi od približno 20 °C dodatak zajedničkog iona benzoata u formolizi  $3,2 \times 10^{-4}$  mol dm<sup>-3</sup> ferocenilmetil benzoata neznatno smanjuje brzinu formolize, dok je na 40 °C formoliza bitno sporija. Takovo smanjenje brzine ne zamjećujemo u acetolizi istog kompleksa. Smanjenje brzine formolize na povišenoj temperaturi (20–40 °C) vrlo je vjerojatno posljedica smanjenja koncentracije vodikovih iona, jer jača mravlja kiselina istiskuje slabiju benzojevu kiselinu iz natrijeva benzoata, što dovodi do smanjenja koncentracije mravlje kiseline u tom kiselinom kataliziranom sustavu. To se međutim ne događa u slabijoj octenoj kiselini. Nadalje, brzine acetolize jednake su u prisutnosti 0,1 i 0,2 mol dm<sup>-3</sup> benzoata, dok se brzine formolize smanjuju dodatkom benzoata. Izgleda da je jaka temperaturna ovisnost brzine formolize povezana sa stvaranjem dimera mravlje kiseline pri čemu je dimerizacija jako ovisna o temperaturi. Vodikove veze i stvaranje dimera u octenoj kiselini od manjeg su značaja nego u mravljoj kiselini.