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OSCILLATING REACTIONS - A PHENOMENON STUDIABLE BY DTA?

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INTRODUCTION

The fascinating phenomenon of chemical oscillations is caused by a very sophisticated interchange of numerous reactions; in the case of the BELOUSOV-ZHABOTINSKII reaction there are 14 or even more particular steps (1-3).

The aim of our first studies in this field was rather to find non-isothermal characteristics of this reaction than to study particular reactions with respect to their effects on the oscillatory behaviour. Körös (4) has tried to represent the system - due to temperature - as a series of autocatalytic bursts showing unimolecular rates corresponding to activation parameters $E = 67.2$ kJ/mol and $\lg A = 10.56$ (time=min), the A value showing a dependence of catalyst and reactant concentration. Using reactant amounts for $KBrO_3$, KBr, malonic acid and Ferroine as proposed by Field (5), we studied the u.v. absorption of Ferroine during the oscillation at $\lambda = 550$ nm in an isothermal and non-isothermal way (Fig. 1) resulting in a net activation energy of $\simeq 100$ kJ/mol.

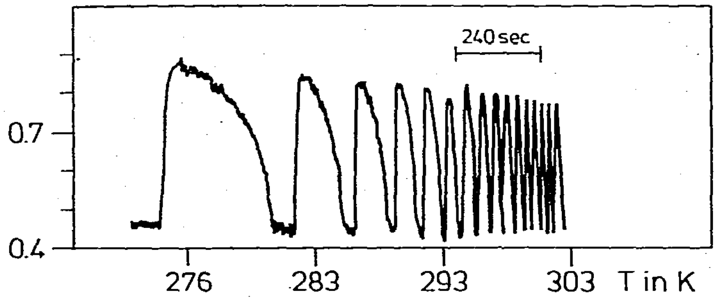


Fig. 1 u.v. extinction at 550 nm for heating rate 2.0 K/min; KBr = 0.053; $KBrO_3$ = 0.1; Ferroine = 5×10^{-4}; malonic acid = 0.375 M; 1 M sulfuric acid

DTA studies.

Using DTA equipment spezialized for reactions in stirred solution (6), we recorded ca. 100 DTA curves with features depending on the parameters varied such as concentrations of bromate, bromide, catalyst and heating rate. Although part of the solutions was oscillating, and the enthalpies measured were partially high, there were no direct calorimetric indications to the oscillations since the lag of our equipment must smooth the fluctuations in rate (kinetic cell constant $\simeq$ 0.18 min^{-1}).

The influence of the bromate concentration on the overall reaction enthalpy shows a step increase from small values beginning at an equimolecular ratio of bromide and bromate (0.05 M; Fig. 2). After passing through a maximum of $\simeq$ 500 kJ/mol for a composition which is appropriate for the demonstration of the oscillations (0.1 bromate), there is a subsequent decrease. The reason is that the autocatalytic step, the formation of bromous acid via the $BrO_2^{\bullet}$ radicals (B process; ref. (1)) is stronly exothermic while the concurrent A-reaction between bromate and bromide is not. For even higher BrO_3^- concentrations, the less exothermic bimolecular termination reaction of $HBrO_2$ may prevail which reduces the overall heat.

Before considering activation data of particular steps, we tried a mechanistic peak analysis based on the corrected shape indices S and the reaction type indices M(7-8; cf. Fig. 3). For Ferroine, increasing bromate concentration causes a tendency of the mechanistic coordinates from the region of cooperative processes (process A preferred; small S, M $\simeq$ $M_{2.order}$) to move to the first-order zone (equimolarity of KBr and $KBrO_3$; M $\simeq$ M_1, S $\simeq$ S_1), then passing through the AB zone (formal reaction A + B = C; periodical change of processes A and B) and ending in the region of mixed-order consecutive reactions (S $\simeq$ S_1, M $\simeq$ M_2).

On the other hand, we have found that an increase of the catalyst concentration for $CeCl_3 \cdot 6H_2O$ (1.25 x 10^{-4}) leads to a continuous decrease of S and M due to a movement from the autocatalytic to the second-order zone and even to the zone of higher-order consecutive reactions when cat = 1.25 x 10^{-3} M (Fig. 3).

Increasing the heating rate from 0.3 to 4.3 K/min partially leads to confusing plots in the mechanistic diagram (Fig. 4). Obviously, the change of the bromate concentration from 0.1 M (standard) to 0.12 M (catalyst: Ferroine) causes the line of increasing heating rate to show a reversing course. For the moment, the question remains of how many steps have to be set up to give such a phenomenon. Considering possible two-reaction mechanisms, it is obvious that concurrent reactions, the prior of which being first-order, the later of second-order type, would lead to decreasing M values if the heating rate is increased.

From the trend of the overall activation energy, E_B, with catalyst concentration, it was confirmed that there is a range (10^{-3} to 10^{-4} M) wherein E_B is minimum and nearly independent of this concentration. (E_B = 68 kJ/mol for the ceric salt, 80 kJ/mol for Ferroine). Under these conditions, oscillations may be favourably performed.

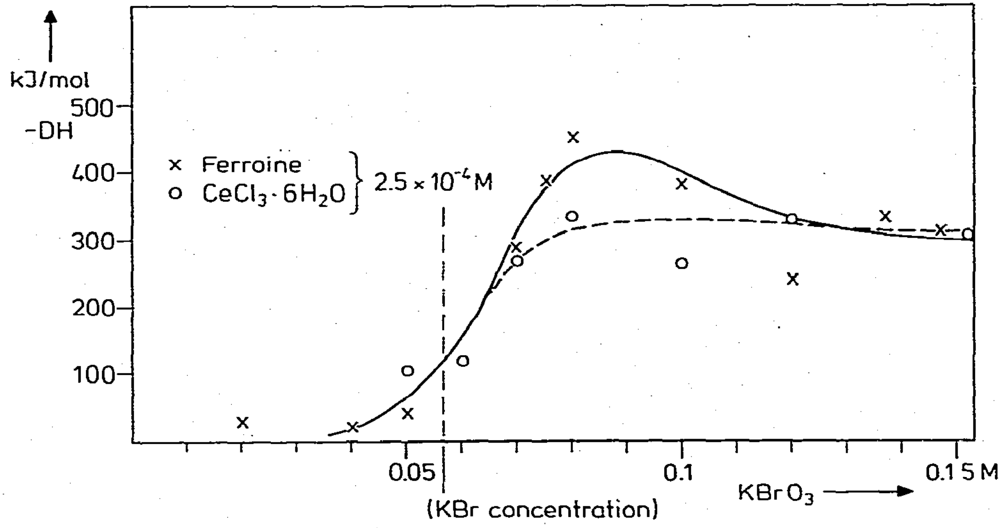


Fig. 2 Overall reaction enthalpy for different $KBrO_3$ concentrations

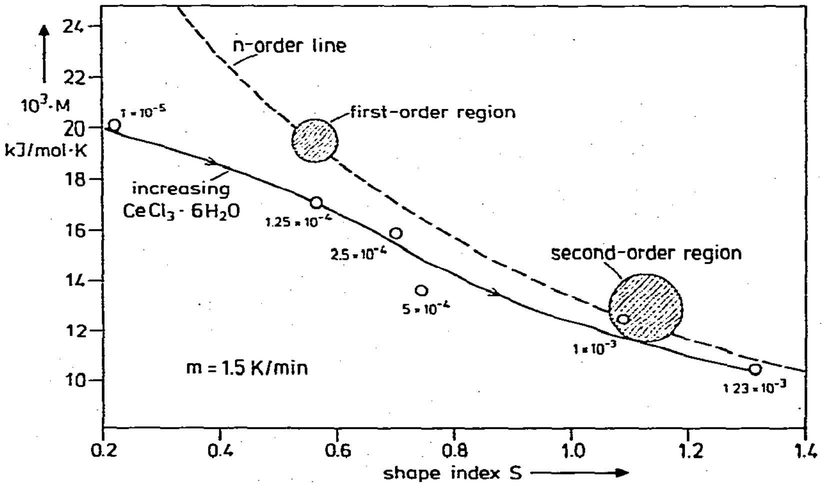


Fig. 3 Mechanistic points vs. catalyst concentration

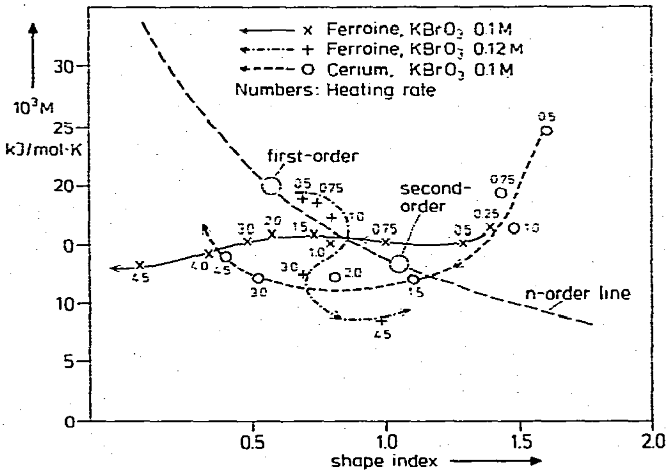
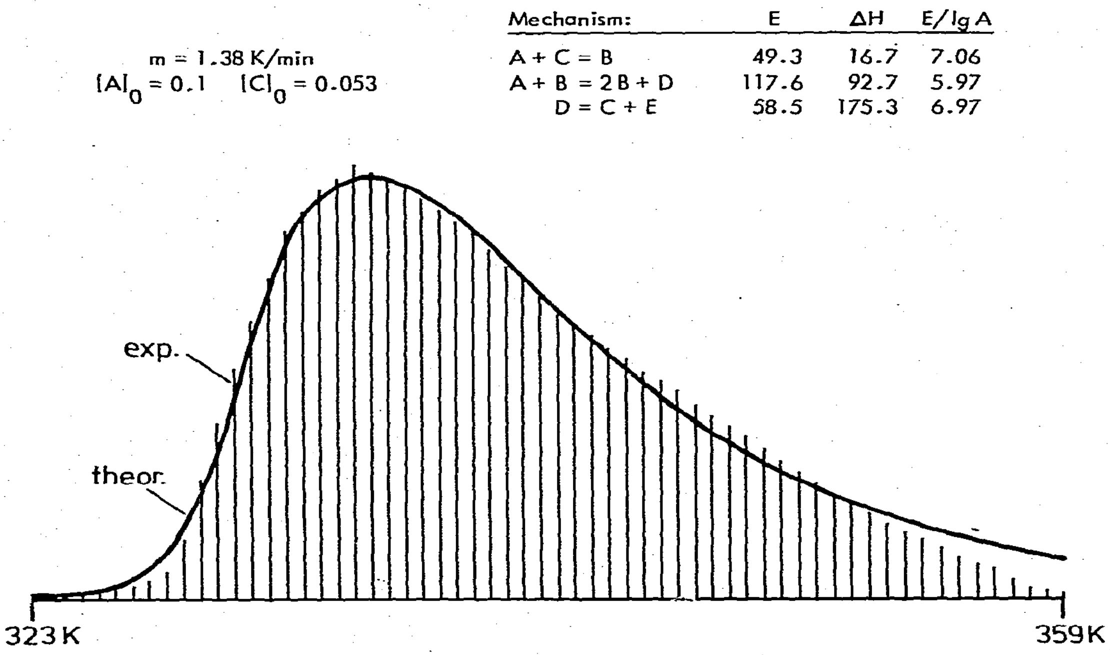


Fig. 4 Mechanistic points vs. heating rate



Mechanism:	E	ΔH	E/lg A
A + C = B	49.3	16.7	7.06
A + B = 2B + D	117.6	92.7	5.97
D = C + E	58.5	175.3	6.97

Fig. 5. Computer reconstruction of an individual DTA curve by the use of a three-step mechanism

TABLE:

Activation data and other quantities for the particular reactions of the three-step mechanism (cf. Fig. 5)

Time unit: min $[KBr]_o = 0.053$ M
Activation energies used:° $E_1 = 49.3$ $E_2 = 79.7$ $E_3 = 41.8$ kJ/mol

11 experiments with cat = Ferroine; $[KBrO_3]_o$ = 0.04, 0.06, 0.075 or 0.10 M (0.10 in 5 cases)
Heating rates: 0.6-1.6 K/min Correlation: R = 0.970 ± 0.036

step	lg A	k_{298}	-ΔH kJ/mol
1	7.59 ± 0.34	0.097	8 - 130
2	13.43 ± 0.61	0.33	6 - 80
3	5.17 ± 0.38	0.008	15 - 197

7 experiments with cat = $CeCl_3 \cdot 6H_2O$; $[KBrO_3]_o$ = 0.06, 0.10, 0.12 or 0.14
Heating rates: 0.5 - 1.5 K/min Correlation: R = 0.964 ± 0.044

step	lg A	k_{298}	-ΔH kJ/mol
1	7.57 ± 0.43	0.092	4 - 15
2	12.93 ± 0.39	0.105	42 - 133
3	5.18 ± 0.32	0.008	72 - 238

Reproduction of the DTA curves by computer.

All curves were both evaluated by the method of BORCHARDT and DANIELS (9) and compared with a computer-generated curve (10). We found that about 50% of all curves obtained may be reproduced by the assumption of a simple bimolecular rate law since correlation coefficients, then, were better than 0.99 including the total measuring range from about 275 to 340 K. The remainder of the curves which mostly involved special conditions due to catalyst concentration, heating rate or bromate concentration, could be reproduced by the following three-step mechanism in many cases (Fig. 5 and Table),

1. Bimolecular initiating step $A + C = B$ (= process A)
2. Autocatalytic (initiating) step $A + B = 2B + D$ (= process B)
3. Bromide-regenerating step $D = C + E$

$A = BrO_3^-$; $B = HBrO_2$; D = oxidized catalyst; $C = Br^-$; E = final product(s). As the table shows, there will often be a good fit when using for E_1 the value of SKRABAL and WEBERITSCH (cf. (12)) and for E_2 the E_B mean value of our AB-simulations, while for step 3 we found no material for comparison. The enthalpies used for the individual steps, however, show enormous variations when the best fit is required. This and a certain dependence of our fitted data on the heating rate indicates that the true mechanism is much more complicated and that the three reactions assumed are approximately rate-determing steps of three groups of reactions. It seems even to be a too simple concept to take the five-step OREGONATOR mechanism (12) as a true non-isothermal model since the catalyst effects cannot be explained by it.

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