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REACTION KINETICS AT LINEARLY INCREASED TEMPERATURE. II. DTA STUDY OF UNCATALYZED BROMATE OSCILLATORS

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ABSTRACT

Uncatalyzed bromate oscillators, composed of sodium bromate and some phenol and aniline derivatives in dilute sulphuric acid, are studied by means of DTA. Up to five non-oscillatory DTA peaks are obtained, apart from oscillatory structures observed under certain conditions.

Systematic changes of the initial concentrations of bromate, bromide or the aromatic compounds reveal different onset temperatures and heights of the peaks. It is concluded that 1,2-diquinones, brominated aromatic compounds, their dimers and/or di- or tribrominated aromatic molecules are formed as transients which carry information regarding the kinetic prehistory of the reaction from one peak to the next one which appears at higher temperature.

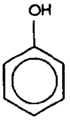
INTRODUCTION

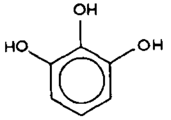
The non-isothermal DTA technique was shown to be particularly valuable for the study of solution systems exhibiting complicated reaction mechanisms. In such systems, DTA signals offer the advantage that kinetic information about the individual elementary steps is dissected along the temperature axis. Signal heights and onset temperatures of a separated (or even an overlapped) peak in an experimental concentration series [1,2] reflect the interplay of elementary reactions of different orders involved. The "mechanistic indices" (shape index S and reaction type index M) of an overlapped peak [3] yield information which exceeds the concept of reaction order allowing a forthcoming kinetic classification of the underlying processes. They are based on the deviations in behaviour from that of the comparable elementary reactions.

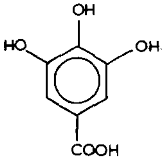
After some preliminary results on the catalyzed oscillatory BZ system [4,5] which have initiated further experiments [6], this communication presents the first results of an application of DTA to the uncatalyzed bromate oscillators, i.e., to reacting systems composed of acidic bromate and an aromatic compound [7,8]. However, before giving a detailed discussion of the various phenomena associated with the mechanistic indices (a general discussion was given in the first paper of this series [3]), we shall focus our attention on the onset temperature and signal height phenomena. The reason is that in the case of partially isolated peaks, which we shall encounter in the present work, the concentration effects on these easily studied quantities already indicate the occurrence of intermediates. This was confirmed by recent experiments using organic reaction systems in solution at low temperatures (down to 130 K; refs. 9–13).

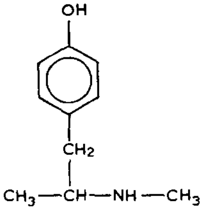
METHOD AND RESULTS

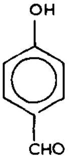
Our "all-liquid" apparatus for thermokinetic DTA experiments [14] as well as the computer programs and computer application modes have been described earlier [2,3,9,13,15,16]. The aromatic compounds studied were

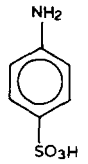












Hydroxy-benzene	1,2,3-tri-hydroxy-benzene	3,4,5-tri-hydroxy-benzoic acid	1-(4-hydroxy)-phenyl-2-methylamine propane	4-hydroxy-benzalde-hyde	4-amino-benzene sulphonic acid
(Phenol)	(Pyrogallol)	(Gallic acid)			(Sulphanilic acid)
PH	PY	GA	PS	HB	SA

These compounds are oxidized by bromate to dimeric and polymeric quinones or are brominated. Potentiometric studies have shown that up to 50 damped oscillations may occur during this process [7]. DTA curves of such systems consist of up to four peaks (α, β, γ, δ) in the range 265–390 K (heating rate 0.2–4 K min^{-1}); in special cases (ArOH=HB, PS), of even five when the β peak is split into two signals. Furthermore, during or after the α peak one or two sharp signals (="needles") and/or oscillatory periods with smaller, but sharp peaks were often observed (Fig. 1). The positions of the peaks on the time/temperature axis as well as their heights depend on the starting concentrations of bromate, aromatic substrate and additional bromide. These signal features led us to the study of some series of

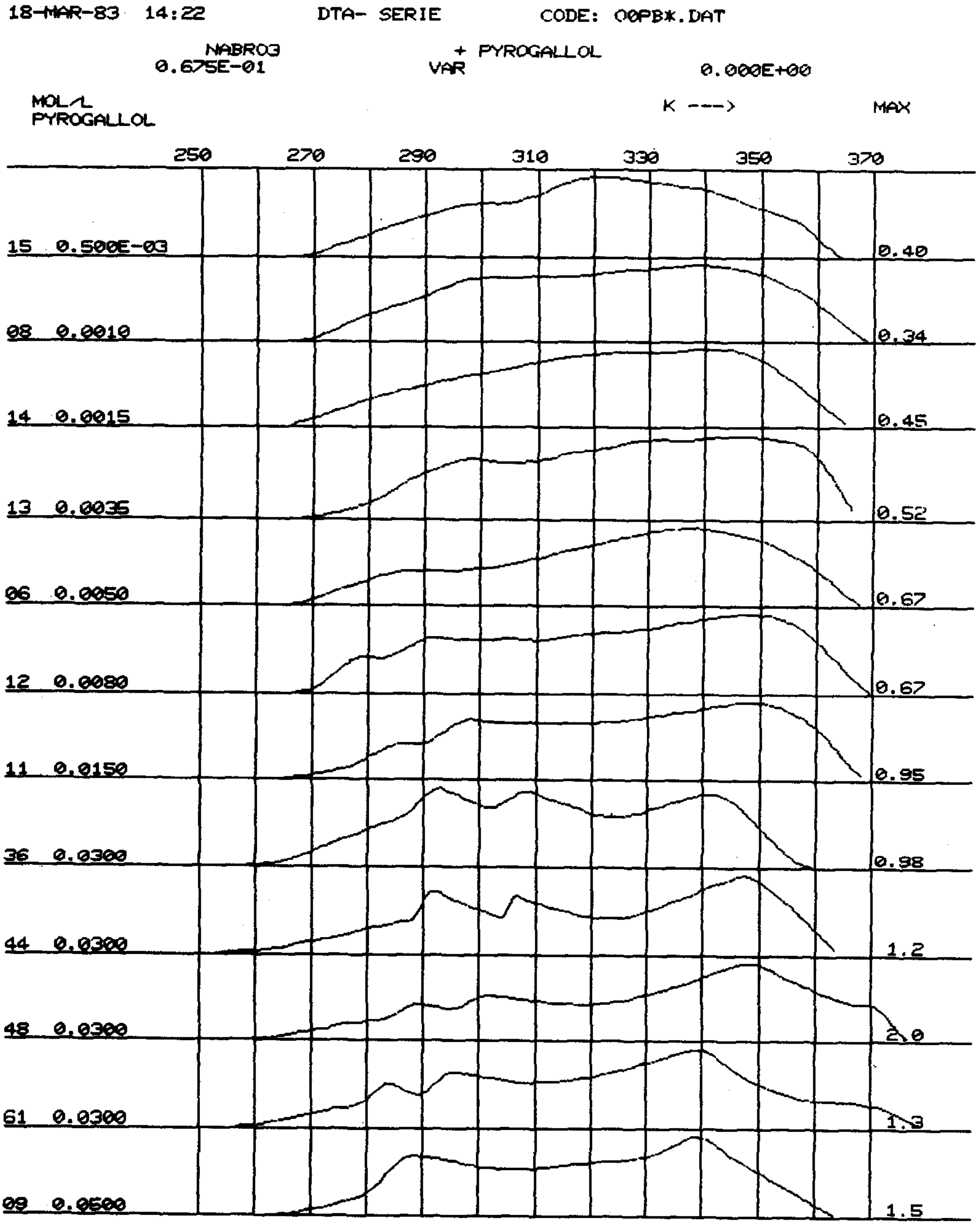


Fig. 1. DTA curves of a concentration series with $NaBrO_3$/Pyrogallol (PY was varied).

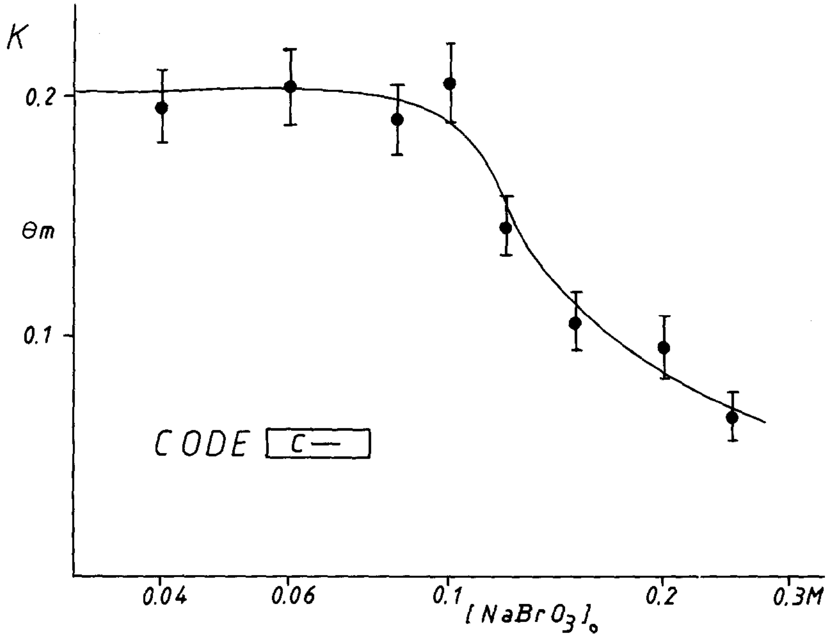


Fig. 2. Example of a correlation plot: series $NaBrO_3$ (varied)/0.025 M PS in 0.5 M H_2SO_4/β peak. Concentration axis: logarithmic; code: c – ; $m = 1.5$ K min^{-1}.

experiments in which only one of these three components was systematically varied.

A principal disadvantage of the application of DTA to an aqueous sulphuric acid system is that the initiating reaction proceeds too rapidly even at the lowest temperature possible, somewhat above the melting point of the system (263–268 K), especially when bromide has been added. Consequently, it is often not possible to record the first part of the α peak during the required standard heating rate (1.5 K min^{-1}); rather a change of isothermal to non-isothermal conditions had to be considered in this period. Hence, a careful kinetic evaluation of the α peak which is especially important for the initiating reaction(s) of the whole kinetic formalism was not possible (cf. Fig. 3). On the other hand, results of our detailed non-isothermal study of the bromide/bromate system [6] may fill information gaps.

Figure 2 shows, as an example, how a correlation diagram, stemming from one series of eight experiments, is evaluated in order to obtain a correlation code (in this case "c – "; cf. Table 1). The error limits [17] for the temperatures T_0 and T_m are ±1 K; for the α peak even up to ±2 K. The signal heights show an accuracy of ±8%, which may be increased to the noise level of ±0.007 K in the case of rather small Θ_m values ($\ll 0.1$ K). This presents some problems with the interpretation of the height phenomena especially of the very small β peaks which are below 0.3 K. Therefore, experiments with striking deviations of data were repeated once or several times.

TABLE 1

Shifts of temperatures and signal height

Components		H_2SO_4 (M)	Temp. shift						Signal-height shift		
Increased	Constant		α Peak		β Peak		γ Peak		α Peak	β Peak	γ Peak
			T_0	T_m	T_0	T_m	T_0	T_m			
PS	$NaBrO_3$[c]	0.5	c	+	c	+	−	−	+	+	−
	0.076 $NaBrO_3$	0.5	c	+	c	c	−	−	+	+	−
HB	$NaBrO_3$	1.5	c	c	c or +	~c	c−	~c	+	~c(+)	+c−
GA	$NaBrO_3$	1.25	c−	c+	−+c	−+?	c+	c	+	c or +	+−c
PY	$NaBrO_3$	1.25	c	c	c+?[a]	c+−	c−?[b]	+c	c	~c+	−+ or c
PH	$NaBrO_3$	1.0	~c	+	+	+	−+?w	−+?w	+c	−c?	−0
$NaBrO_3$	0.025 PS	0.5	(+)c?	−	(+)c	c−	+c−	+c	+c	+c−	+c
$NaBrO_3$	0.020 HB	0.02	−	−	~c	c?	0	0	m	m	0
$NaBrO_3$	0.030 GA	1.25	−	−	−	−	c	c?w	−	c?	c?
$NaBrO_3$	0.030 PY	1.25	−	−[a]	−?	−?w[b]	c	+−c	~c+	?[b]	c?
$NaBrO_3$	0.050 PH	1.00	+−	−	c	−+	0	0	+	+	0
NaBr	0.025 PS+BrO_3^-	0.50	−	−	?	?	+	+	+	−	+−
NaBr	0.02 HB+0.1 BrO_3^-	1.5	−	−	$\left\{\begin{matrix}\beta_1^-\\ \beta_2^+\end{matrix}\right.$	$\left.\begin{matrix}-\\ +\end{matrix}\right\}$	c+	+	~c?	$\left\{\begin{matrix}-\\ \sim c\end{matrix}\right\}$	+
NaBr	0.03 PY+BrO_3^-	1.0	+(c)	c[a]	c−	c?[b]	−+	~c	+	−	+−

[a] First needle.

[b] Second needle.

[c] Standard concentration = 0.0675 M.

w = Weak or indistinct; 0 = missing; m = merging; + = increasing; − = decreasing; c = constant. Two or more codes: behaviour in the order of increasing reactant concentration, e.g., c+− means constant for low, increasing for medium and decreasing for large starting concentration of reactant.

TABLE 2

Observable oscillations and "needles" (amplitude > 0.03 K) in series

Molarity of reactants		H_2SO_4 (M)	Heating rate (K min^{-1})	Oscillations		"Needles"		Remarks
				No.	Temp. range (K)	No.	Temp. range (K)	
0.05–0.68 BrO_3^-	0.02–0.03 GA	1.25	[a]	5–8	294–322	—		
BrO_3^- [b]	0.01 GA			—		2	315–325	
BrO_3^-	0.005 GA			—		3	281–300	
0.085–0.35 BrO_3^-	0.025 PS	0.5		4–7	270–320	—		Maximum number for 0.1 bromate
0.05–0.07 BrO_3^-	0.03 PY	1.25		—		2	260–320	
BrO_3^-	0.001–0.03 PY			5–9 [c]	283–330	1–2	283–305	
BrO_3^-	0.03 PY		0.27–3.1	5–12 [c]	274–345	2–3	275–315	Shift to higher temperatures

[a] Standard 1.5 K min^{-1}.

[b] Standard 0.0675 M.

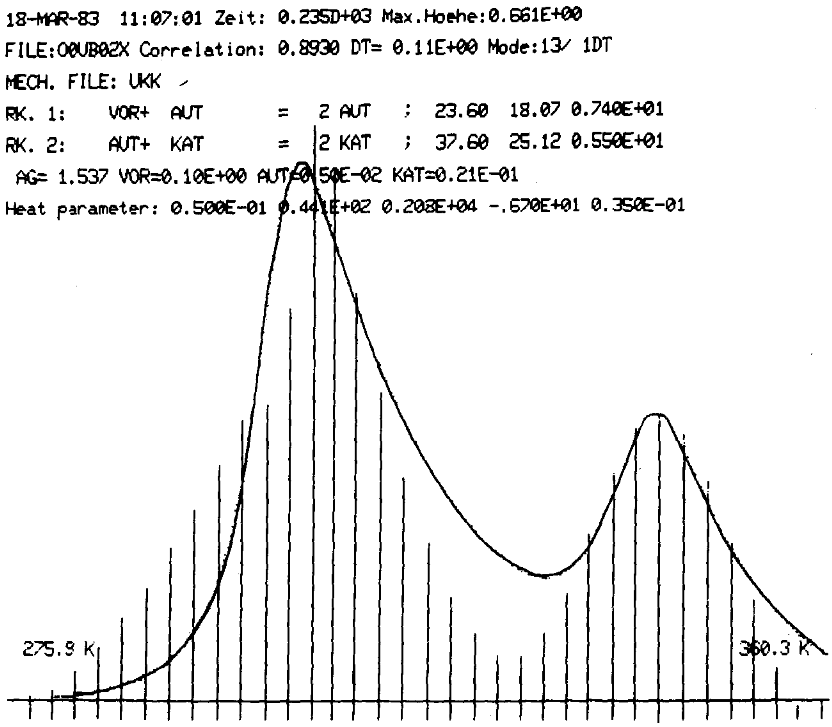
[c] Indistinct.

GA = Gallic acid; PY = Pyrogallol; PS = "pulsotylsulphate".

In Table 1, the concentrations of the reactants and the observed shifts for the onset temperatures T_0, maximum temperatures T_m and peak heights are listed for a heating rate of 1.5 K min^{-1}. All of our total 174 experiments were stored as data files including the signal data (original file: 3000 points per curve, extracted file for library: 100–150 points per curve) and the input and result parameters (cf. refs. 2 and 9). Hence, it was possible alternatively to either evaluate any isolated peaks or the whole signals. Figure 1 shows the total signals of a concentration series with PY/bromate as an example of an overlapped type; simultaneous occurrence of very sharp, sawtooth-like peaks (= "needles") and normal, smooth peaks (here the γ peaks), exhibiting typical temperature and peak-height shifts (last columns), are evident.

"Needles" were only found in systems also revealing oscillatory periods (Table 2); for HB and PH, no oscillations could be seen when the same conditions as for the other compounds (Table 1) had been selected.

An example of a partially separated signal with two isolated peaks is given in Fig. 3 (vertical bars) for 0.1 M $NaBrO_3$ and 0.024 M SA in 1.5 M aqueous H_2SO_4. Further, the (unsatisfactory) theoretical reproduction by assuming an oversimplified autocatalytic mechanism is demonstrated. Figure 4 may



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FILE:O0UB02X Correlation: 0.8930 DT= 0.11E+00 Mode:13/ 1DT
MECH. FILE: UKK /
RK. 1:    VOR+  AUT        =  2 AUT   ;  23.60  18.07 0.740E+01
RK. 2:    AUT+  KAT        =  2 KAT   ;  37.60  25.12 0.550E+01
 AG= 1.537 VOR=0.10E+00 AUT=0.50E-02 KAT=0.21E-01
Heat parameter: 0.500E-01 0.441E+02 0.208E+04 -.670E+01 0.350E-01
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Fig. 3. Example of an overlapping α, β peak and a separated γ peak (vertical bars) and simulation test (continuous line) for sulphanilic acid as a substrate. Activation energy, kcal $mole^{-1}$; A factor, referred to min; reaction enthalpy, kcal $mole^{-1}$.

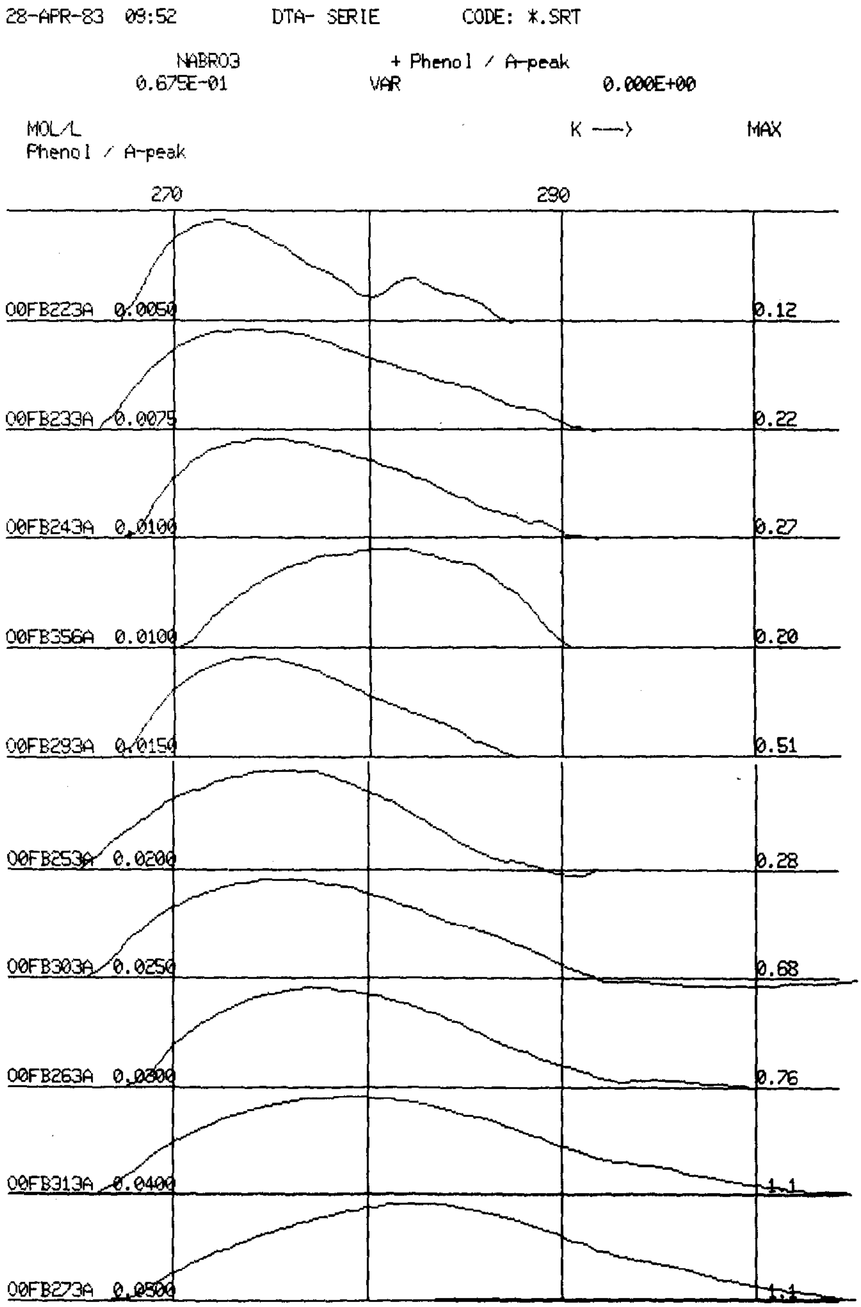


Fig. 4. Separated α peaks in a concentration series with $NaBrO_3$/phenol (varied).

serve as an example for the modifications of an isolated peak in a series, in this case the α peak for the system $NaBrO_3$/PH.

We have also checked the dependence of the peak features upon the heating rate where an unusual independence of the initial temperature and of the peak temperature (at peak maximum) was observed. A similar result was obtained at the onset of the signal of the catalyzed BZ oscillatory reaction using ceric sulphate or Ferroin [5]. In addition to general non-isothermal evaluation procedures, we also took advantage of integration programs based on a Gear/Hindemarsh subroutine [18,19], modified also for non-isothermal mode of operation and applicable to models with up to 20 reactions [2,4]; the results of such simulations will be presented in more detail in a subsequent publication.

DISCUSSION

Our results indicate that the aromatic substrates reveal some differences in their kinetic behaviour [20].

α Peak (265–310 K)

For ArOH = PS or GA, the "normal" cases, the onset temperature T_0 is independent of ArOH, but decreases with bromate and bromide concentration which is consistent with the assumption of the rate-determining reaction

$$BrO_3^- + Br^- + 2\,H^+ \rightleftarrows HBrO_2 + HOBr \qquad (1)$$

and the subsequent (generally faster) reactions (2), (3), (5) and (K8) (below) of the reaction mechanism proposed by Orbán et al. [21] and extended by Herbine and Field [22] (the numbers with preceding K refer to ref. 21). Activation data for this initiating reaction, using simulation tests, were found to be $E = 50$ kJ mole^{-1}, and $\log A = 11.9$ (referred to 1 mole^{-1} s^{-1}). Experiments without bromide added and with small PS concentrations confirm that the underlying reaction is fast so that enough Br^- must have been formed for an immediate start of reaction (1).

However, in the subsequent maximum region an increasing influence of $[ArOH]_0$ on the characteristic temperatures and a parallel increase of the maximum height of the α signal begins, as may be interpreted by a rising contribution of the reactions

$$HBrO_2 + Br^- + H^+ \rightleftarrows 2\,HOBr \qquad (2)$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftarrows 2\,BrO_2^{\cdot} + H_2O \qquad (3)$$

$$BrO_2^{\cdot} + ArOH \rightarrow HBrO_2 + OHArO^{\cdot} \qquad (4)$$

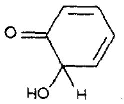
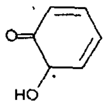
$$2\,HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \tag{5}$$

$$HOBr + OHArO^{\cdot} \rightleftarrows Br^{\cdot} + OHArO + H_2O \tag{6}$$

$$Br^{\cdot} + OHArO^{\cdot} \rightarrow Br^- + OHArO \tag{7}$$

$$HOBr + Br^- + H^+ \rightleftarrows Br_2 + H_2O \tag{K8}$$

$$HOBr + ArOH \rightarrow BrArOH + H_2O \tag{12}$$

for ArOH = *o*-diphenol: OHArO ≡  ; $OHArO^{\cdot}$ ≡ 

all of which may be exothermal. Ar denotes the remainder connected with the hydroxyl group. The remarkable reverse temperature shift with the ArOH concentration implies an inhibition effect which must be caused by the decrease in concentration of a long-lived intermediate, presumably a 1,2-quinone or semi-quinone. It is also worth mentioning that for ArOH=PY [23], the reverse temperature shift is missing over the full α-peak period, and an increase of the signal maximum requires higher ArOH concentrations than for the other compounds, whereas for higher amounts of ArOH=PH the reverse temperature shift is valid even at the onset, and, together with the analogous shift of the final temperature, causes the α peak to become isolated especially for low or medium PH concentration (Fig. 3). Hence, PY does not show such distinct recoupling effects on concentrations of long-lived intermediates although it readily undergoes faster consecutive steps. Conversely, for PH the recoupling effects are even stronger than for the "normal" cases, combined with a considerable suppression of the β and γ peaks by PH (Table 1).

Concerning the first part of the α peak, a rough numerical reproduction by a bimolecular process with data of reaction (1) is possible, but for the subsequent part a broadening, compared to the simple bimolecular signal, is stated [6].

Oscillations and needles

The calorimetric indication of oscillations depends both on the energy gap in the limit cycle and on the sensitivity of the equipment [4,5]. For sufficiently large concentrations of bromate and aromatic substrate, a series of normal oscillations were observed during or immediately after the α peak period (Table 2). For Pyrogallol (= PY), there were only some (two or three) very sharp, steep peaks (= "needles"; Fig. 1) which must also be identified with (perhaps incomplete) oscillations. Since the oscillations always ceased after the first period of the β signal, the reactions giving rise to the phenomenon must have occurred already within the α period [24], such as the autocatalytic step composed of reactions (3) and 2X(4) (for stochiometric reasons) generating bromous acid, and the bromide-ion reforming steps

$$Br^{\cdot} + HOArO^{\cdot} \rightarrow Br^- + OHArO + H_2O \tag{7}$$

$$Br^{\cdot} + ArOH \rightarrow HOArO^{\cdot} + Br^- + H^+ \tag{K12}$$

$$Br_2 + ArOH \rightarrow BrArOH + Br^- + H^+ \tag{11}$$

In the case of PY, the oscillations intrude more into the β-peak range.

β Peak (310–340 K)

The kinetics occurring during the β-peak period are governed by the concentration of any long-lived intermediates formed during the α period as well as by the original reactants ArOH, BrO_3^- and Br^- used. For HB and PS, even two β peaks were partially observed.

The concentration influence of the aromatic substrate on the characteristic temperatures is different for the compounds used: whereas PS shows no influence, PH shifts the β peak to higher temperatures, but GA to lower temperatures. For PY, no usual β peak can be identified or it is superposed by oscillation peaks (Fig. 1). On the other hand, the (positive) signal height is generally lifted by the aromatic component. This, in every case, indicates that the corresponding reactions strongly involve the aromatic reactants and are exothermic; however, whilst PS obviously pretends a first-order reactant, PH acts as an inhibitor for the long-lived intermediate(s) from above [24], and GA behaves as a "normal" bimolecular reactant.

The bromate starting concentration reveals a similarly varying influence on the initial temperature: GA has the normal "bimolecular" feature, whereas PH and HB do not show such a shift. This agrees with the preparative observation that in isothermal experiments at room temperature, PH and HB are completely consumed some minutes after the start [24,25]. The signal height reveals no remarkable dependence indicating that no bromate reactions can play an important role during the later β period. If we try to approximate the β signal by a simple bimolecular reaction, taking BrO_3^- (varied) and PS = 0.025 mole l^{-1} as reaction components, the correlation coefficients after fitting the activation data and reaction enthalpy are rather bad (Table 3); although the signal height shows a proportionality to the bromate feed, the reverse temperature shift, indicated by the need to take an even higher pre-exponential factor for increased BrO_3^-, reveals that BrO_3^- is not a rate-determining reactant at the onset. On the other hand, the molar reaction enthalpy is nearly constant if it is twice referred to the bromate used; therefore, two sequential steps with bromate—probably reactions (1) and (3)—must have occurred previously. Furthermore, the resulting activation data are unrealistic because they are too high. An assumption of an autocatalytic bimolecular reaction leads to more reliable A factors, but even then the very fast final decay of the signal could only be explained by an additional endothermic process.

The events during the β peak reflect both newly arising reactions and the kinetic prehistory, which had begun at the onset of the α peak. For the peak position referred to bromate, GA shows a negative shift, which means that this compound (or intermediates previously formed at an ArOH-proportional amount) acts clearly as quasi-bimolecular reactant. For PY and PH, this cannot be confirmed.

The β peak is suppressed by bromide ion (GA not tested). This implies that bromide had scavenged an intermediate required for generation of the β peak. From the reactions cited in the literature, the following species may only obey the necessary conditions for such an intermediate (= "type 1 information carrier") which has a sufficient lifetime to transfer the kinetic information from the first peak to the next one: BrO_3^-; Br_2; (HOBr); BrArOH; $OHArO^{\cdot}$ (semiquinone; too unstable); ArO_2(1,2-quinone); $Ar_2(OH)_2$ (dimer; less reactive).

Variation of the bromate concentration, however, did not cause a distinct change or shift of the β peak if GA and PY are excepted. Bromine-formation is accomplished, not inhibited by Br^-; therefore, the brominated aromatic compounds and the semiquinone or 1,2-quinone remain as the most probable candidates. However, it has indeed been stated that the brominated aromatic compounds may also react with the $BrO_2^{\cdot}$ radical [22], but the question then remains whether their reactivities are so strongly diminished compared to the unbrominated compounds that the reactions need a 20 or 30 K higher temperature. It seems more likely that the 1,2-quinones as were periodically formed via reactions (K11), (1), (2) and (6) and consumed in reactions (K13) and (8)

$$BrO_2^{\cdot} + OHArO^{\cdot} \rightarrow HBrO_2 + ArO_2 \qquad (K11)$$

$$ArO_2 + ArOH \rightleftarrows 2\ OHArO^{\cdot} \qquad (K13)$$

$$BrO_3^- + OHArO + 2\ H^+ \rightarrow BrO_2^{\cdot} + OHArO^{\cdot} + H_2O \qquad (8)$$

TABLE 3

Re-simulation of experimental β peaks by assuming a simple bimolecular process $A + B \rightarrow C$

$NaBrO_3$ (M)	Fitted data				Correlation coefficient	
	E_A (kJ mole^{-1})	A factor (l mole^{-1} s^{-1})	$-\Delta H$ (kJ mole^{-1} $NaBrO_3$)	$\frac{\Delta H}{[BrO_3^-]_0}$	Total	Section before maximum
0.04	180.7	1.26E+30	43.84	1096	0.6656	0.9898
0.08	180.7	1.32E+29	49.22	615	0.7813	0.9850
0.085	180.7	9.37E+28	43.84	516	0.7777	0.9997
0.1	180.7	8.35E+28	50.87	509	0.8820	0.9905
0.25	180.7	5.27E+28	135.66	542	0.8724	0.9902

PS = 0.02 M; H_2SO_4 = 0.5 M; cf. Fig. 3.

were accumulated; such compounds could be the desired information carriers. On the other hand, the "flow-through" intermediates $HBrO_2$, HOBr, $BrO_2^{\cdot}$, Br_2 and $Br^{\cdot}$ may act as second bimolecular components over the full temperature range whenever enough Br^- and BrO_3^- are present.

γ *Peak (320–370 K)*

In the γ-temperature region, oscillations or "needles" are absent, but for PS, PY or GA an often large peak with analyzable features appears, occasionally followed by a further, sometimes endothermic peak. However, the interpretation of the heat evolution rate towards 380 K is strongly handicapped by the nearly exponentially increasing or decreasing evaporation effects. On the other hand, it is certainly useful to discuss these signals because the physical evaporation processes are functions of the temporary chemical compositions of the solutions, too. Furthermore, it is well established that the dominant kinetic information about a DTA peak is obtained from the section before the peak maximum [14].

The γ peak shows a normal, negative temperature shift with the concentration of the aromatic compound (indistinct for PY) which suggests a direct bimolecular involvement of ArOH or of "information carriers" based on an amount monotonously coupled with the ArOH feed (= type 2). In addition, the different signal-height characteristics imply different reaction enthalpies or, alternatively, different rates of several competitive "ArOH-coupled" reactions.

The influence of bromate is similarly obvious: the position of the peak is independent of the bromate feed (HB, PS, PY) [24,25]. Changes in the signal height are variable.

The discussion of these effects has to be similar as for the β peak, but the double prehistory during the α and β peaks makes explanations rather difficult. The chemistry must involve quite stable "information carriers", probably of higher molecular weight, such as oxidatively coupled and polybrominated products (cf. refs. 21, 22, 24).

The role of added bromide is opposite to that in the previous period. The γ peak is not scavenged, it is strengthened by bromide, but the signal position reveals a positive instead of a negative temperature shift. Therefore, the γ-peak initiating process does not directly involve Br^-, but information carriers which were diminished by Br^- in the preceding periods (= type 1). Subsequent γ processes, however, must include both type 2 carriers and another type of carrier(s) (= type 3) which had been generated proportional to the bromide input. The latter are necessary to cause the observed increase of the bromide-coupled γ-signal height.

A test to reproduce the total γ peak by a simple bimolecular substitution reaction must fail since, in most cases, a subsequent endothermic signal (= δ peak) or, at least, a very steep decay of the γ signal after the maximum is observed. If the first half of the signal is only considered and Br^- has been absent, the activation data for GA, PH and PY are in the order of $E = 170$ kJ mole^{-1}, $\log A = 30.8$, which means apparent, not realistic data.

However, for the PS and PY series with added bromide, the simple autocatalytic model

$A + B \rightarrow 2\ B +$ product(s) (exothermic)

$B \rightarrow$ product(s) (endothermic)

is more capable of roughly reproducing the γ peak and part of the δ peak (Fig. 3). For the first step, the rather reliable activation data $E = 70$ kJ mole^{-1} and $\log A = 18.3$ would have to be assumed for the reactant concentrations $[A]_0 = 0.0675$, $[B]_0 = 0.02$ mole l^{-1}. These values are close to the initial concentrations of bromate and bromide ion, but these assignments are formal and are not the identities of the species A and B as was shown before.

CONCLUSIONS

Our results indicate that the entire reaction can be broken down into three stages, each corresponding to one separated DTA peak (peaks α, β and γ in the order of increased temperature). Each stage must involve one (or several) initiating reactions which are rate-determining at the onset of the respective peak. Whilst for the α peak such a step (exceptions PH and PY) may be identified with the reaction (1) of bromide with bromate, for the next peaks it becomes necessary to consider three types of long-lived intermediates X_1, X_2, and X_3 which are formed in periods α and/or β and represent components for the initiating steps of the β and γ peaks:

X_1 = formation is suppressed by bromide ion
X_2 = formation is accelerated by ArOH (or even =ArOH!)
X_3 = formation is accelerated by bromide ion (or even $=Br^-$).

Table 4 shows that the species to be discussed are somewhat different depending on the aromatic compound used. Obviously, PH and PY partially reveal features different from the other, "normal" compounds.

Based on the scheme of Herbine and Field [22], we have some reasons to assume that X_1 stands for a 1,2-diquinone [or even for $Ar_2(OH)_2$ for the γ peak], and X_2 for BrArOH or $Ar_2(OH)_2$ (γ peak). For X_3, it is difficult to see an identification from the 16 reactions hitherto discussed, but it seems that HOBr and Br^- represent transients on the kinetic path to this species, which must show a relatively high thermal stability and, hence, might be di- or tribrominated aromatic compounds.

Therefore, we conclude that for the β signal the initiating step is reaction

TABLE 4

Assumed reaction-initiating and subsequently involved reactants

Aromatic compounds	α Peak		β Peak		γ Peak	
	At onset	Later	At onset	Later	At onset	Later
GA, PS, HB	BrO_3^- Br^- No ArOH (except. large conc. of GA)	BrO_3^- Br^- ArOH	BrO_3^- (GA) X_1 or X_2 (HB)	Br^- X_1 X_2 (PS excepted) No BrO_3^-	X_1 X_2 No X_3	X_2, X_3 BrO_3^- if small conc.
PH, PY	BrO_3^-	BrO_3^-	BrO_3^-	BrO_3^- (PH)	X_1	X_3
	No Br^-	ArOH (PH)	X_1	X_1	X_2?	X_2 (variable)
	ArOH is inhibitor for large PH or small PY!		X_3(PY)	X_2	No BrO_3^-	No BrO_3^-

Intermediates:

X_1 = scavenged by bromide ion;

X_2 = increased by ArOH; X_2 may also be ArOH itself;

X_3 = increased by bromide ion; X_3 may also be Br^- itself.

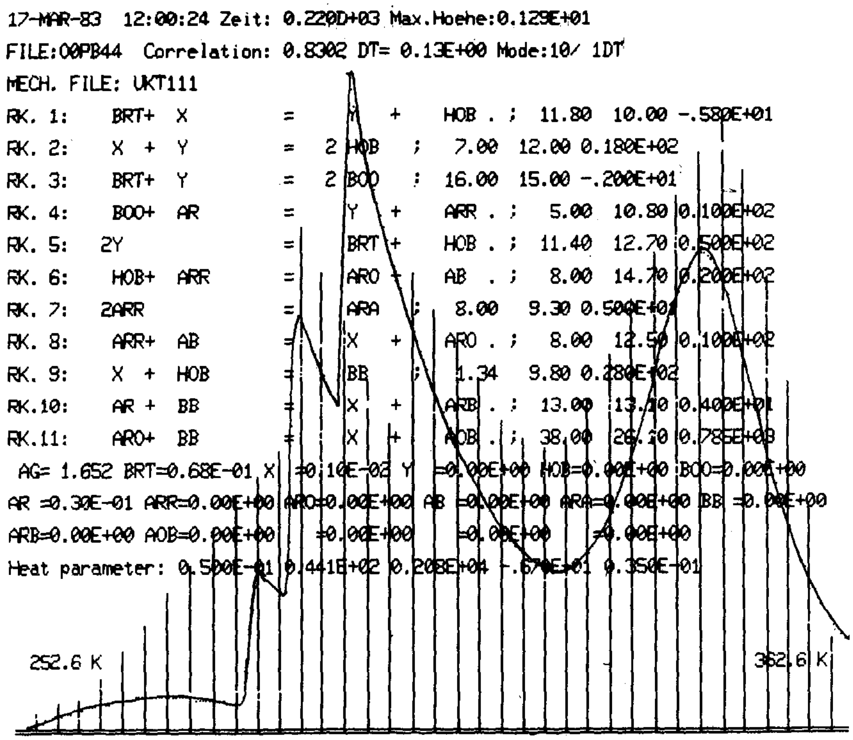
(K13) (ArOH + 1,2-quinone) for HB, but a reaction of bromate with quinone for GA. For all compounds, any further pseudo-unimolecular reactions of ArO_2 may also be taken into consideration.

In general, these initiating reactions are not rate-determining over the whole even isolated peaks. However, if we consider the results of our Borchardt–Daniels evaluations [12–14,17] of the complete isolated peaks of the various concentration series, based on the assumption of elementary bimolecular processes, then the tendencies of the mechanistic overall coordinates S and M [3] reveal that several ranges of constant M or S values with respect to the initial concentration of BrO_3^- or ArOH are found. These ranges, which are also observed for other parameters, reflect hitherto unidentified rate-determining steps [2,3,9]; one can distinguish two to three of such steps for the α signal, two for the β signal and one to two for the γ signal (the appended δ peak is excluded), dependent on the conditions. Looking at the rather slow reactions of the scheme, additional rate-determining processes inside the α period may be (K8) [= formation of bromine from bromide ion and HOBr, yielded by the fast reactions (2), (3) and (5)], further reaction (12) (= bromination of ArOH by HOBr) and, for PH, reaction (10) (= one-electron transfer reaction between 1,2-quinone and bromate). Apart from reaction (3), the latter process is also involved in the oscillations, because the autocatalytic character of the reaction sequence (3)–(4) is amplified.

All remaining reactions of the scheme are too fast to be identified with the observed rate-determining processes occurring during the β period, at the onset of the γ period or later (> 330 K). These hitherto unidentified processes must be very slow at room temperature and are not directly involved in the phenomenon of oscillation.

OUTLOOK

The fact that the oscillative region extends from the α to the β period suggests the use of the new technique for identifying particular signal-modifying or even rate-determining steps of the general scheme valid for the uncatalyzed oscillations, extended over the whole temperature range, in more detail. In addition, Fig. 5 shows that accompanying computer simulations



```
17-MAR-83  12:00:24 Zeit: 0.220D+03 Max.Hoehe:0.129E+01
FILE:00PB44  Correlation: 0.8302 DT= 0.13E+00 Mode:10/ 1DT
MECH. FILE: UKT111
RK. 1:    BRT+  X      =     Y   +   HOB . ;  11.80  10.00 -.580E+01
RK. 2:     X  +  Y     =   2 HOB   ;   7.00  12.00 0.180E+02
RK. 3:    BRT+  Y      =   2 BOO   ;  16.00  15.00 -.200E+01
RK. 4:    BOO+  AR     =     Y   +   ARR . ;   5.00  10.80 0.100E+02
RK. 5:   2Y            =     BRT +   HOB . ;  11.40  12.70 0.500E+02
RK. 6:    HOB+  ARR    =     ARO +   AB  . ;   8.00  14.70 0.200E+02
RK. 7:   2ARR          =     ARA   ;   8.00   9.30 0.500E+01
RK. 8:    ARR+  AB     =     X   +   ARO . ;   8.00  12.50 0.100E+02
RK. 9:    X  +  HOB    =     BB    ;   1.34   9.80 0.280E+02
RK.10:    AR +  BB     =     X   +   ARB . ;  13.00  13.10 0.400E+01
RK.11:    ARO+  BB     =     X   +   AOB . ;  38.00  26.10 0.785E+03
 AG= 1.652 BRT=0.68E-01 X  =0.10E-02 Y  =0.00E+00 HOB=0.00E+00 BOO=0.00E+00
AR =0.30E-01 ARR=0.00E+00 ARO=0.00E+00 AB =0.00E+00 ARA=0.00E+00 BB =0.00E+00
ARB=0.00E+00 AOB=0.00E+00    =0.00E+00    =0.00E+00    =0.00E+00
Heat parameter: 0.500E-01 0.441E+02 0.208E+04 -.670E+01 0.350E-01
```

Fig. 5. Preliminary attempt to reproduce a whole DTA signal (bars) for 0.0675 M $NaBrO_3$; 0.01 M Pyrogallol; 0.001 M NaBr using an 11-step mechanism (H_2SO_4 1.25 M in H_2O; cf. ref. 22); BRT = $NaBrO_3$; X = Br^-; Y = $HBrO_2$; HOB = HOBr; BOO = $BrO_2^{\cdot}$; Ar = Pyrogallol; ARR = $Ar^{\cdot}$; ARO = $HOArO^{\cdot}$; ARA = Ar_2O_4; BB = Br_2; ARB = BrArOH; AOB = BrOHArO or another brominated compound. Continuous curve: generated by numerical integration. Maximum signal height: 1.28 K. Activation energy, kcal $mole^{-1}$; *A* factor, referred to min; reaction enthalpy, kcal $mole^{-1}$.

may become a useful tool also from the non-isothermal view of this system [4]. But it is also important to adapt the DTA technique, which was originally developed for low-temperature research using organic solvents, to the conditions in aqueous systems in order to study the isolated signals more intensively. Furthermore, the exact determination of the identities of X_1, X_2 and X_3, each of which may consist of several species, requires the study of additional series, accompanied by analytical work.

In a forthcoming paper of this series, the general applicability of the temperature–height phenomena will be shown and discussed for a number of catalyzed or uncatalyzed oscillating and for simpler reacting systems.

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