

**Chemistry.** — *Influence of temperature on the substitution type in the bromination and chlorination of aromatic compounds in the gas phase.* By F. L. J. SIXMA and J. P. WIBAUT.

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§ 1. The rules governing the introduction of substituents into the benzene nucleus during reactions in the liquid phase were determined by extensive investigations in the latter half of the nineteenth and the beginning of this century; in this respect the work of HOLLEMAN and his co-workers occupies a prominent place (1). Two cases can be distinguished:

- a. the new substituent preferably occupies the ortho and para positions (ortho-para substitution);
- b. the new substituent chiefly occupies the meta position (meta substitution).

To which of these two types the substitution reaction belongs was found to be in general independent of the nature of the new substituent and to be conditioned only by the substituent present already in the benzene nucleus. Investigations carried out by WIBAUT and co-workers, however, showed that when halogen atoms are introduced into aromatic compounds in the gas phase between 300° and 600°, the substitution type will in many cases be governed by the reaction temperature. Thus ortho and para dibromobenzene are the main products of the non-catalytic bromination of *monobromobenzene* (2,3) below 350° in the gas phase; in this case the reaction is therefore of the ortho-para type, which is also the case with the reaction in the liquid phase. Between 350° and 450°, however, a sudden change takes place; the quantity of *p*-dibromobenzene rapidly decreases, whereas the quantity of *m*-dibromobenzene rises; the relative quantity of *o*-dibromobenzene, on the contrary, remains almost unchanged. Upwards of 450° *m*-dibromobenzene is the main product of the reaction (fig. 1). According to HOLLEMAN's criterion the ortho-para substitution type therefore changes into the meta substitution type between 350° and 450°. A similar change was observed in the bromination of chlorobenzene (fig. 2) and of fluorobenzene <sup>1</sup>). In these experiments purified pumice and graphite were used as contact material.

If the bromination reaction is carried out by means of a ferric bromide (or ferric chloride) catalyst on a suitable carrier, the total reaction velocity is much greater. In the temperature range from 200—450° the substitution reaction develops according to the ortho-para type; the substitution type

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<sup>1</sup>) Owing to experimental difficulties the quantities of ortho and meta fluorobenzene in the reaction product of the bromination of fluorobenzene could not be determined.

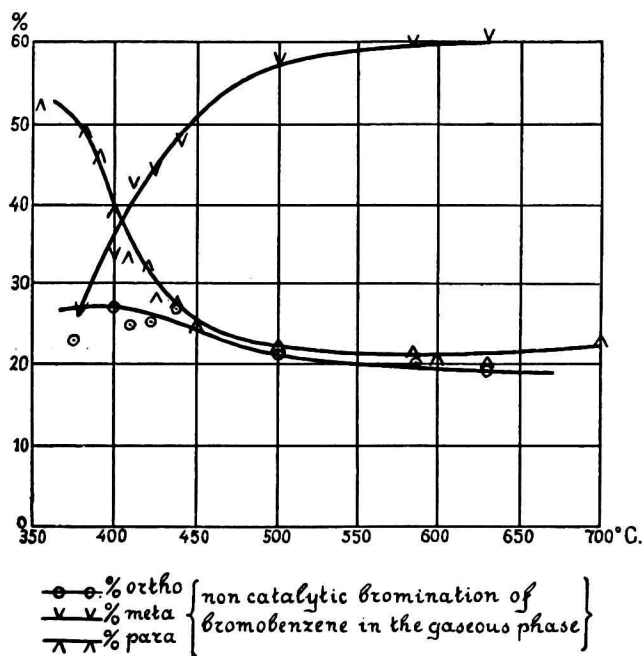


Fig. 1.

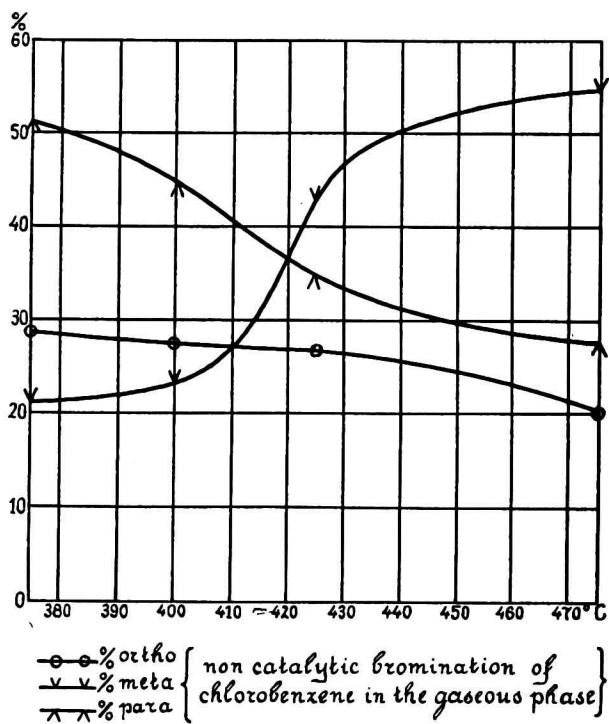


Fig. 2.

does not change. Experimental difficulties prevented the investigation of this heterogeneously catalytic reaction upwards of 450°.

The ratio of the isomeric dibromobenzenes formed in the catalytic bromination of bromobenzene is represented by the following formulae of SCHEFFER (4):

$$\ln \frac{2 \text{ conc.}_p}{\text{conc.}_m} = \frac{E_m - E_p}{RT} \dots \dots \dots (1)$$

and

$$\ln \frac{2 \text{ conc.}_p}{\text{conc.}_o} = \frac{E_o - E_p}{RT} \dots \dots \dots (2)$$

assuming that  $E_m - E_p = 2890$  cal/mol and  $E_o - E_p = 2036$  cal/mol;  $E_o$ ,  $E_m$  and  $E_p$  in these formulae represent the energies of activation of the substitution in the ortho, meta and para positions<sup>2)</sup>. Fig. 3 shows satisfactory agreement between the values calculated according to formulae

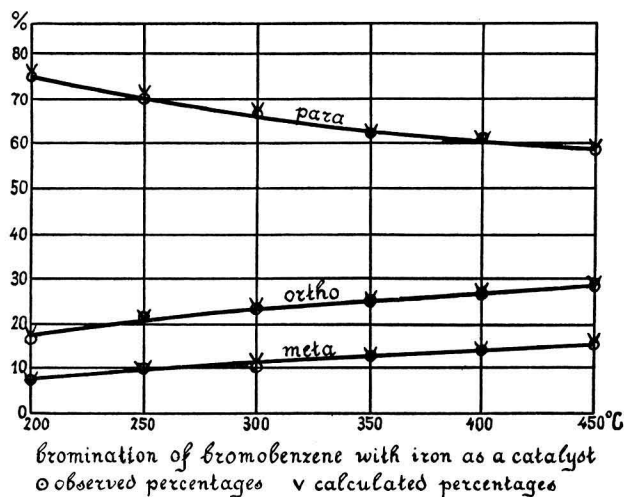


Fig. 3.

(1) and (2) and the experimental figures. This investigation carried out in 1937 by WIBAUT and VAN LOON (2) therefore showed that the formulae of SCHEFFER hold within a temperature range of 250°. Before that time these formulae had been tested for a narrow temperature range (−30° to ca + 30°) on a number of nitration reactions.

The results of the non-catalytic bromination of the halogenobenzenes (figs. 1 and 2) cannot be represented by formulae of the types (1) and (2). Neither can the more general formulae derived by SCHEFFER, which contain an energy term as well as an entropy term account for the change

<sup>2)</sup> In our former publication the energy of activation was represented by  $\epsilon$ ; for typographical reasons the symbol  $E$  is used in this paper.

in the para:meta ratio which takes place within a narrow temperature range. To gain a better insight into the influence of the temperature on substitution reactions in aromatic rings, the monobromination of naphthalene has been investigated extensively in our laboratory (6, 8, 9). Introduction of one substituent into the naphthalene molecule is theoretically simpler than into a mono-substituted benzene ( $C_6H_5A$ ), because in the former case only two isomers are formed. Moreover, the naphthalene molecule consists only of carbon and hydrogen atoms, whereas the substituent in a monosubstituted benzene has in most cases a polar character, which enables it to influence the charge distribution in the molecule.

In our former publication (9) we subjected the results obtained in the bromination of naphthalene to a theoretical discussion, special attention being paid to the reversible conversion  $\alpha$ -bromonaphthalene  $\rightleftharpoons$   $\beta$ -bromonaphthalene, which takes place under the influence of catalysts such as ferric chloride or ferric bromide. We shall now consider the *non-catalytic bromination* of naphthalene, which is not accompanied by conversion of the monobromonaphthalenes into each other — neither at elevated temperatures nor otherwise —, which has been proved experimentally.

The monobromination of gaseous naphthalene in the presence of a non specific contact material (pumice, glass wool) yields in the temperature range from  $250^\circ$ — $300^\circ$  chiefly  $\alpha$ -bromonaphthalene in addition to small quantities of  $\beta$ -bromonaphthalene. In this temperature range the  $\alpha$  :  $\beta$  ratio satisfies SCHEFFER's formula and is therefore determined by the difference in energies of activation required for the substitution in the  $\alpha$ - and  $\beta$ -positions. In the temperature range from  $500^\circ$ — $650^\circ$  equal quantities of  $\alpha$ - and  $\beta$ -bromonaphthalene are formed; the difference in energy of activation does no longer play a part and the  $\alpha$  :  $\beta$  ratio is only determined by the probability of the collision of a bromine particle with the naphthalene molecule in the  $\alpha$ - or  $\beta$ -position.

In the transition zone from  $350^\circ$ — $500^\circ$  the relative quantity of  $\beta$ -isomer rapidly increases, which is reflected in the S-shape of the curve (see fig. 4). The question is how to account for the experimental result that from a certain temperature the difference in energy of activation no longer plays a part and that within a narrow temperature range a rather sudden change in the substitution type develops.

In our first paper reference was made to a theoretical consideration by one of us (S.), on the strength of which the existence of a transition temperature was made plausible (9). It was found, however, that the formulae derived lead to a less sudden change in the substitution type than had been observed experimentally.

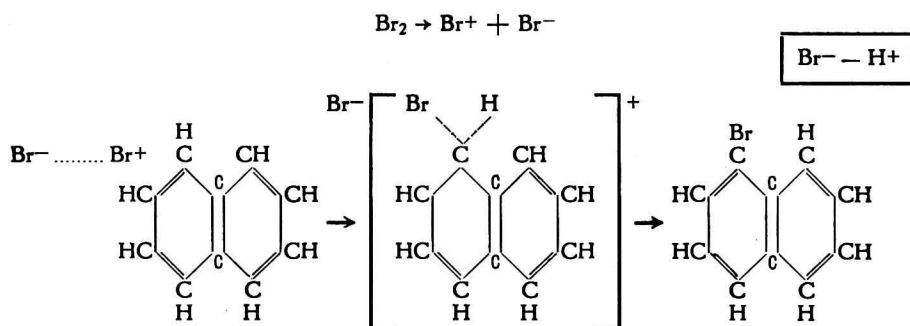
We shall now derive a formula by means of which the S-shaped curve found experimentally can be represented.

§ 2. In the bromination of gaseous naphthalene we must distinguish between a wall reaction and a real gas reaction. At a low temperature the

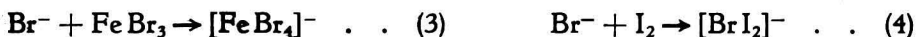
former will predominate (5). Our investigations into the isomerization of bromonaphthalene in the gas phase in the presence of a ferric bromide contact indicate that upwards of 400° the adsorption of the bromonaphthalene molecules to the catalyst surface is very slight. Obviously, we may assume that the adsorption of naphthalene on any solid surface at that temperature will also be negligible, so that we may put forward the hypothesis that the bromination of naphthalene vapour at about 300° and below will chiefly proceed as a wall reaction and from 400° upwards chiefly as a gas reaction.

We shall now explain how the change from wall reaction to gas reaction may lead to a pronounced change in the ratio of the isomeric substitution products. In our former publication we showed that the monobromination of liquid naphthalene, which takes place in the temperature range from 85—215°, can be described as an electrophilic substitution. By starting from this theory and using wave-mechanical calculations, one of us (S.) found an approximate value for the difference in energy of activation for substitution in the  $\alpha$ - and  $\beta$ -positions ( $E_\beta - E_\alpha$ ); this theoretical value was in fair agreement with the value calculated from the experimental data by means of SCHEFFER's formula (10).

We now assume that the bromination in the gas phase in the temperature range from 250—300° also takes place according to an electrophilic substitution type. For this it is necessary that a bromine particle is strongly polarized in the transition state of the reaction, which can be represented schematically by a splitting into a positive and a negative bromine ion:



As stated formerly, catalysts such as ferric bromide, aluminium chloride or iodine can stabilize the transition state by the formation of complexes with the negative bromine particle:



This increases the reaction velocity.

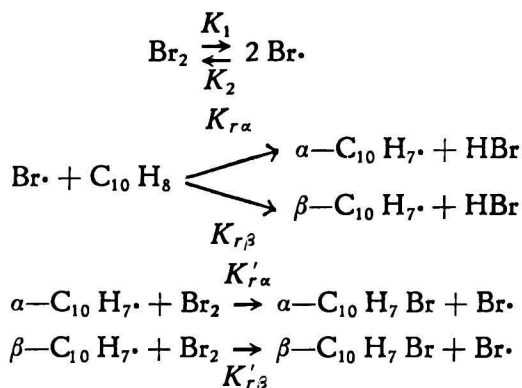
Such a stabilization of the transition state by a second bromine molecule is also conceivable:



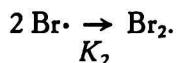
This is in agreement with the fact that some brominations in the liquid

phase proceed according to a second order reaction with respect to the bromine concentration (11).

In our experiments on the non-catalytic bromination in the absence of metal halides, the stabilization of the transition state may proceed according to equation (5). It should be borne in mind, however, that collisions between three molecules in a gas phase reaction are rare. In the temperature range from 250—300°, however, the reaction will chiefly proceed on the wall, so that in this range the electrophilic reaction is possible. According as the temperature rises, the adsorption of the reacting substances to the wall decreases; the normal rise in reaction velocity with the temperature is thus counteracted. The electrophilic substitution reaction on the wall is ultimately reduced to such an extent that the reaction in the gas phase predominates. For this reaction we assume a radical mechanism. As a result of the thermal dissociation of the bromine molecules bromine atoms are formed, which may introduce a chain reaction. This does not require adsorption to the wall. The chain reaction is represented by the following scheme:



By means of the values of bond energies mentioned by PAULING (12) the heat effect of these reactions can be computed. The reactions  $K_{r\alpha}$  and  $K_{r\beta}$  will show hardly any heat effect, while in the reactions  $K'_{r\alpha}$  and  $K'_{r\beta}$  about 8 kcal/mol of energy is liberated. It is therefore conceivable that the reactions should proceed according to this scheme. The chains can be broken by:



which reaction may proceed at the wall of the vessel.

At low temperatures the overall rate of this radical substitution will be low, because the dissociation of the bromine is then extremely slight. According as the temperature rises, the dissociation increases (at 800° 0.16 % of the bromine has been dissociated; at 900° 1.5 %); the rate of the atomic reaction rises, whereas the rate of the electrophilic reaction decreases. At a certain temperature the atomic substitution will therefore predominate.

§ 3. To obtain a quantitative formulation we assume that the dissociation equilibrium of the bromine is established so quickly that the concentration of the bromine atoms during the experiment may be considered constant. If the heat of dissociation of bromine is  $D$  cal/mol and  $C_D$  the corresponding entropy term, the concentration of the bromine atoms is:

$$[\text{Br}\cdot] = C_D^{1/2} \cdot e^{-D/2RT} \cdot [\text{Br}_2]^{1/2}.$$

The rate at which  $\alpha$ - and  $\beta$ -monobromonaphthalene are formed according to the radical reaction is then:

$$\left(\frac{da}{dt}\right)_r = C_D^{1/2} \cdot C_{r\alpha} \cdot e^{(-E_{r\alpha} - 1/2 D)/RT} \cdot [\text{C}_{10}\text{H}_8] \cdot [\text{Br}_2]^{1/2} \cdot \dots \quad (6)$$

$$\left(\frac{d\beta}{dt}\right)_r = C_D^{1/2} \cdot C_{r\beta} \cdot e^{(-E_{r\beta} - 1/2 D)/RT} \cdot [\text{C}_{10}\text{H}_8] \cdot [\text{Br}_2]^{1/2} \cdot \dots \quad (7)$$

In these equations  $E_{r\alpha}$  and  $E_{r\beta}$  are the energies of activation for the reactions  $K_{r\alpha}$  and  $K_{r\beta}$ ;  $C_{r\alpha}$  and  $C_{r\beta}$  are the corresponding collision factors, whose dependence on the temperature is relatively small. Since each naphthalene molecule has as many  $\alpha$ - as  $\beta$ -positions and both positions are sterically equally favoured, we put  $C_{r\alpha} = C_{r\beta}$ .

The electrophilic reaction, which develops exclusively on the wall, is based on adsorption. In the case of catalytically inactive adsorbents such as pumice or glass wool, we have adsorption by VAN DER WAALS forces; the number of adsorbed molecules is proportional to  $e^{E_{\text{ads}}/RT}$ , where  $E_{\text{ads}}$  is a function of the heat of adsorption of naphthalene, bromine and the reaction products. The rate at which  $\alpha$ - and  $\beta$ -monobromonaphthalene are formed according to the electrophilic reaction is then:

$$\left(\frac{da}{dt}\right)_e = C_{e\alpha} \cdot C_{\text{ads}} \cdot e^{(-E_{e\alpha} + E_{\text{ads}})/RT} \cdot [\text{C}_{10}\text{H}_8] \cdot [\text{Br}_2]^n \cdot \dots \quad (8)$$

$$\left(\frac{d\beta}{dt}\right)_e = C_{e\beta} \cdot C_{\text{ads}} \cdot e^{(-E_{e\beta} + E_{\text{ads}})/RT} \cdot [\text{C}_{10}\text{H}_8] \cdot [\text{Br}_2]^n \cdot \dots \quad (9)$$

In these equations the bromine concentration occurs to the power  $n$ ,  $n$  being 1 or 2 according as the reaction mainly proceeds with two or three collisions (cf. § 2). The collision factors  $C_{e\alpha}$  and  $C_{e\beta}$  are now equalized again; also  $E_{\text{ads}}$  has the same value in both equations, because of the simultaneous reactions between the adsorbed bromine and naphthalene molecules.  $E_{e\alpha}$  and  $E_{e\beta}$  are the energies of activation for the electrophilic substitution reactions in the  $\alpha$ - and  $\beta$ -positions in the naphthalene nucleus. The ratio in which  $\alpha$ - and  $\beta$ -monobromonaphthalene will occur in the reaction product is:

$$\frac{[\alpha]}{[\beta]} = \frac{\left(\frac{da}{dt}\right)_e + \left(\frac{da}{dt}\right)_r}{\left(\frac{d\beta}{dt}\right)_e + \left(\frac{d\beta}{dt}\right)_r} \cdot \dots \cdot \dots \quad (10)$$

After substitution of (6)—(9) in (10) and dividing numerator and denominator by  $\left(\frac{d\beta}{dt}\right)_e$  we find:

$$\frac{[\alpha]}{[\beta]} = \frac{e^{(E_{e\beta} - E_{e\alpha})/RT} + C \cdot e^{Q_\alpha/RT}}{1 + C \cdot e^{Q_\beta/RT}} \cdot \dots \cdot \dots \quad (11)$$

where

$$C = \frac{C_D^{1/2} \cdot C_{r\alpha} \cdot [\text{Br}_2]^{1-n}}{C_{e\beta} \cdot C_{\text{ads}}} = \frac{C_D^{1/2} \cdot C_{r\beta} \cdot [\text{Br}_2]^{1-n}}{C_{e\beta} \cdot C_{\text{ads}}}$$

and

$$Q_\alpha = + E_{e\beta} - \frac{1}{2} D - E_{\text{ads}} - E_{r\alpha};$$

$$Q_\beta = + E_{e\beta} - \frac{1}{2} D - E_{\text{ads}} - E_{r\beta}.$$

As the bromination of naphthalene below 100° in the liquid phase proceeds fairly rapidly,  $E_{e\alpha}$  and  $E_{e\beta}$  will be of the order of 10 to 20 kcal/mol. The dissociation heat ( $D$ ) of bromine is about 46 kcal/mol, so that  $Q_\alpha$  and  $Q_\beta$  are negative magnitudes. From theoretical considerations as well as from the experiment we know that the difference between  $E_{e\beta}$  and  $E_{e\alpha}$  is a positive magnitude (about 4 kcal/mol) (9, 10). At elevated temperatures the terms  $C \cdot e^{Q/RT}$  will therefore predominate in equation (11).

The experiment showed that at elevated temperatures  $\alpha$ - and  $\beta$ -bromonaphthalene are formed in equal quantities (§ 1), so that  $\frac{[\alpha]}{[\beta]} = 1$ . This holds if  $Q_\alpha = Q_\beta$ . The absolute values of  $E_{r\alpha}$  and  $E_{r\beta}$  will be much lower than those of  $E_{e\alpha}$  or  $E_{e\beta}$ . This renders it possible that even at moderate temperatures the average energy of the molecules is so great that any sterically favourable collision of a bromine atom with a naphthalene molecule may cause a reaction. The orienting effect is then eliminated and  $E_{r\alpha}$  and  $E_{r\beta}$  can be equalized, so that

$$\frac{[\alpha]}{[\beta]} = \frac{C \cdot e^{Q_\alpha/RT}}{C \cdot e^{Q_\beta/RT}} = 1.$$

On the other hand,  $C \cdot e^{Q/RT}$  will be very small at a low temperature in the gas phase, so that in this case

$$\frac{[\alpha]}{[\beta]} = e^{(E_{e\beta} - E_{e\alpha})/RT} \cdot \dots \cdot \dots \cdot \dots \quad (12)$$

The electrophilic reaction then predominates and SCHEFFER's relation is found again. For the bromination of naphthalene at a low temperature in the gas phase  $E_{e\beta} - E_{e\alpha} = 4215$  cal/mol.

§ 4. Unfortunately, there are no data available to calculate  $Q$  and  $C$  independently of the results of the bromination experiments. Therefore we can only calculate these magnitudes from the ratio in which the isomeric substitution products are formed at two different temperatures. The



difference in energy of activation for the electrophilic substitution ( $E_{e\beta} - E_{e\alpha}$ ) in the non-catalytic bromination of naphthalene can be calculated from the ratio in which  $\alpha$ - and  $\beta$ -isomers are formed at a temperature below the transition zone (6).

By means of the following values of the constants we find satisfactory agreement between the calculated and experimental values for the bromination and for the chlorination of naphthalene (see table I and II and fig. 4).

	Q cal/mol	$E_{e\beta} - E_{e\alpha}$ cal/mol	C
bromination of naphthalene	$-3.8 \times 10^4$	4215	$5 \times 10^{12}$
chlorination of naphthalene	$-2.8 \times 10^4$	(4215)	$3 \times 10^{12}$

For the chlorination of naphthalene ( $E_{e\beta} - E_{e\alpha}$ ) cannot be calculated according to the above method, because the measurements cannot be extended to temperatures sufficiently below the transition zone (cf. fig. 4);

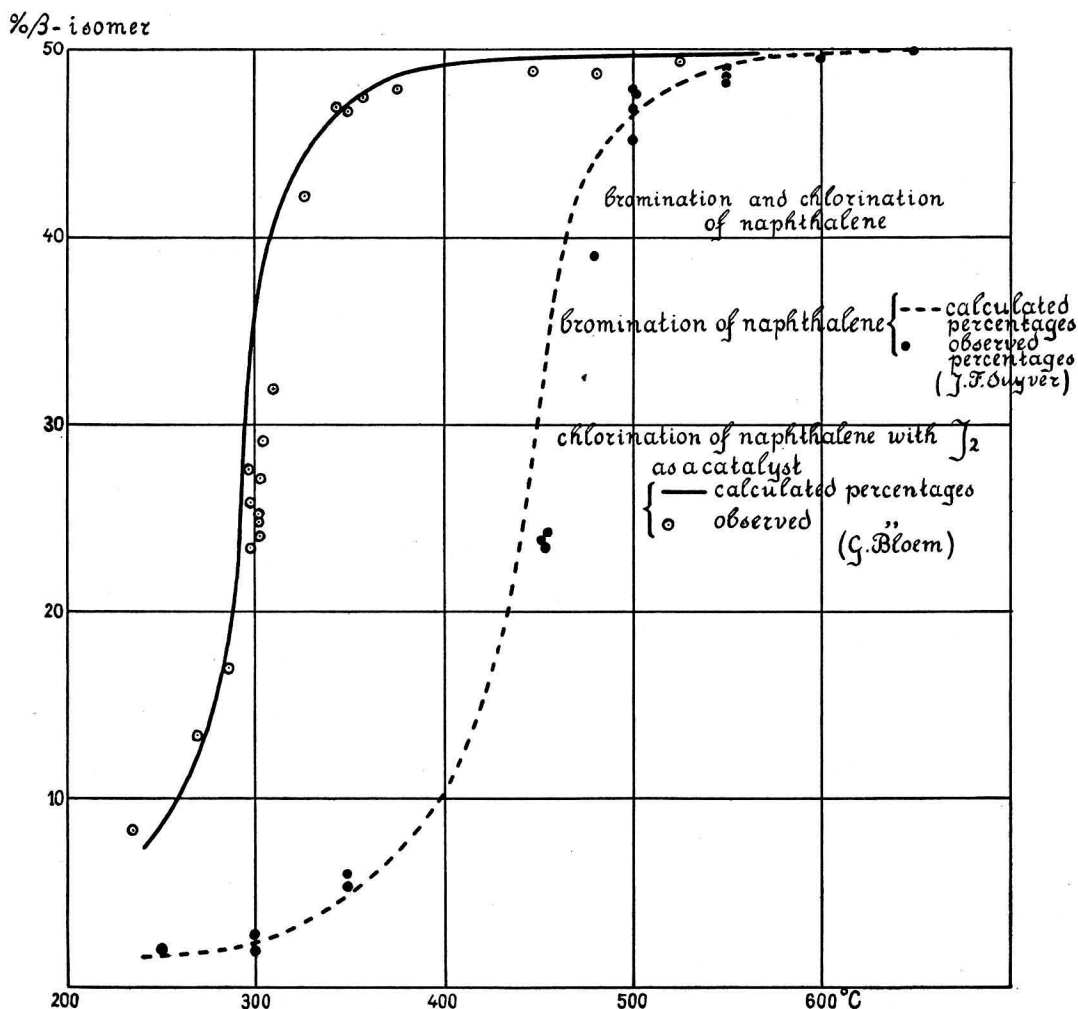


Fig. 4.

we assumed the same value as found for the bromination of naphthalene, i.e. 4215 cal/mol.

TABLE I.  
Non-catalytic bromination of naphthalene in the gas phase (6).

Temperature ° C	% $\beta$ -monobromonaphthalene	
	experimental (J. F. SUYVER)	calculated
250	1.7	1.7
300	2.4	2.4
350	5.5	4.9
450	23.9	32.4
500	46.7	46.5
550	49.0	49.7
650	50.0	50.0

TABLE II.  
Chlorination of naphthalene in the gas phase (under the influence of iodine) (7)

Temperature ° C	% $\beta$ -chloronaphthalene	
	experimental (G. BLOEM)	calculated
250	10.4	8.7
300	24—29	36.0
350	46.9	47.5
450	48.9	49.9
550	49.9	50.0

In the steepest part of the curve the deviation between the experimental and the calculated figures is fairly great. As the ratio of the isomers varies considerably with the temperature in this range, both the calculated and the experimental results are less accurate.

The ratio in which  $\alpha$ - and  $\beta$ -bromonaphthalene are formed in the bromination of naphthalene in the gas phase with iron compounds as catalysts cannot be represented either by our own formula or by SCHEFFER'S. As we showed in a previous publication, the two isomers are converted into each other under these conditions (9).

In the bromination of bromobenzene over iron compounds as catalyst such a conversion of the isomeric reaction products does not take place (2, 10), so that for this case formula (11) can be applied. These iron compounds, however, only catalyze the electrophilic reactions, the rate of the radical substitution reaction remaining unchanged. The result is that in the catalytic bromination of bromobenzene the electrophilic wall reaction will predominate up to 450°; the sudden change in the substitution type is thus completely suppressed (fig. 3). In formula (11) the terms  $C.e^{Q/RT}$

are therefore smaller than  $\exp(E_{e\text{ meta}} - E_{e\text{ para}})/RT$  so that this relation can be replaced by SCHEFFER's formula (form. 12; cf. § 1).

In the non-catalytic bromination of bromobenzene the substitution type changes. The ratio in which para and meta dibromobenzene are formed is then represented by formula (11). The ortho position is partly screened by steric influences, so that

$$C_{e\text{ ortho}} \neq C_{e\text{ para}} \quad \text{and} \\ C_{r\text{ ortho}} \neq C_{r\text{ para}}$$

As the magnitude of this effect is unknown we shall restrict the calculation to the ratio meta : para dibromobenzene. The difference in energy of activation for the electrophilic reaction ( $E_{e\text{ meta}} - E_{e\text{ para}}$ ) is derived from the values found for the catalytic bromination. In this calculation we assume therefore that the catalyst reduces the energies of activation for the meta and para substitution reaction by the same amount, which supposition may hold only approximately.

In table III the experimental values for the para : meta isomer ratio in the non-catalytic bromination of bromobenzene are compared with the values derived from formula (11) with

$$Q = -5.65 \times 10^4 \text{ cal/mol} \\ E_{e\text{ meta}} - E_{e\text{ para}} = 2890 \text{ cal/mol} \\ C = 9.6 \times 10^{18}$$

TABLE III.  
non-catalytic bromination of bromobenzene in the gas phase (2).

Temperature ° C	Ratio of the reaction velocities $\frac{K_{\text{para}}^1}{K_{\text{meta}}}$	
	experimental (V. LOON)	calculated
380	4.18	4.18
400	2.45	2.41
410	1.64	1.685
420	1.51	1.35
440	1.135	1.11

Experiments are in progress to test the hypothesis underlying this theory of the influence of the temperature on the substitution type, i.e. the development of a radical type of reaction at high temperatures.

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<sup>1)</sup> Calculation of percentages was impossible in this case, because the reaction mixture contains the ortho isomer as third component.

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