

**Chemistry.** — *Influence of temperature and catalysts on the bromination of naphthalene; the  $\alpha$ -bromonaphthalene  $\rightleftharpoons$   $\beta$ -bromonaphthalene equilibrium.* By J. P. WIBAUT and F. L. J. SIXMA (partly in collaboration with J. F. SUYVER and L. M. NIJLAND).

(Communicated at the meeting of June 26, 1948.)

§ 1. Since in 1835 LAURENT (1) described the bromination of naphthalene, this reaction has been repeatedly investigated in the liquid phase at temperatures below 100° C. According to the literature only one monobromonaphthalene is thus formed, namely  $\alpha$ -bromonaphthalene, and in addition, dibromonaphthalene in proportion to the quantity of bromine used. In continuation of the investigations carried out in our laboratory into the substitution in the benzene nucleus at high temperatures, one of us (W.) and SUYVER (2) investigated the bromination of liquid naphthalene in the temperature range from 85—215° C. It was found that from the lowest temperature  $\beta$ -bromonaphthalene is formed in addition to  $\alpha$ -bromonaphthalene. We determined the  $\alpha$ : $\beta$  ratio in the monobromonaphthalene mixture formed as a function of the reaction temperature and also found that this ratio is considerably influenced by the use of ferric chloride (or ferric bromide) as catalyst.

We shall first discuss these results, because the experiments on the reversible conversion  $\alpha$ -bromonaphthalene  $\rightleftharpoons$   $\beta$ -bromonaphthalene described in the present article links up with the work of WIBAUT and SUYVER.

Curve 1 in fig. I shows the  $\beta$ -bromonaphthalene content in the monobromonaphthalene mixture formed in the non-catalytic bromination of liquid naphthalene with less than the theoretical quantity of bromine ( $\frac{1}{2}$  mol of bromine : 1 mol of naphthalene).

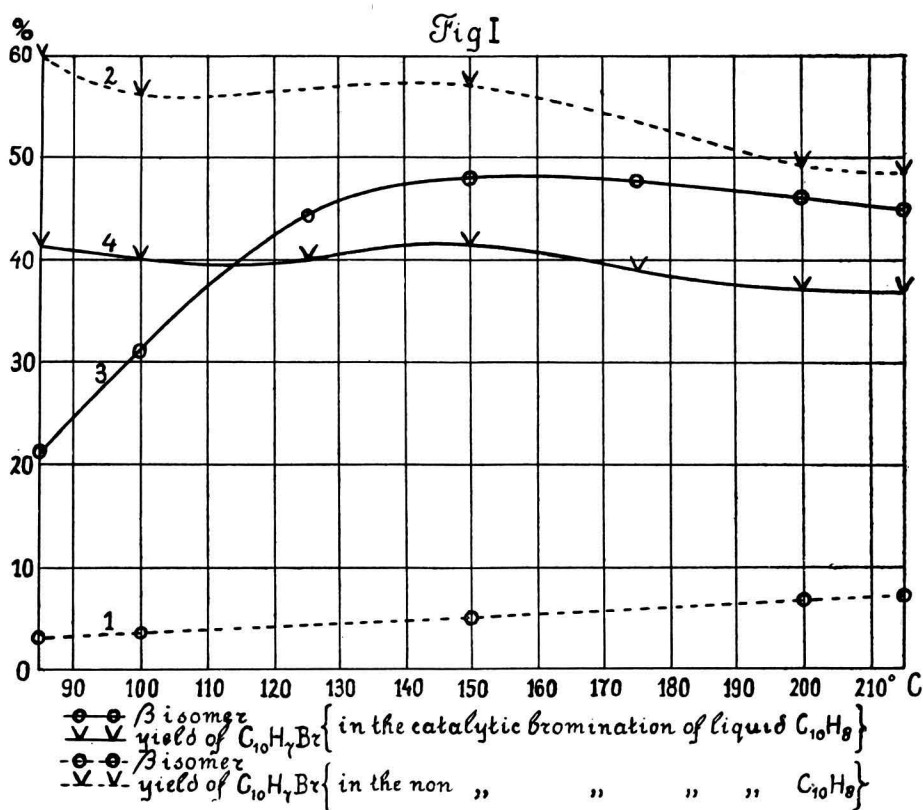
Curve 2 represents the total yield of monobromonaphthalene calculated on bromine used. The decline in this curve at rising temperature is caused by the increasing dibromonaphthalene formation.

Curve 1 shows that the  $\beta$ -isomer content in the monobromonaphthalene mixture rises slowly with the temperature. The  $\alpha$ : $\beta$  ratio as a function of the absolute temperature can be represented by:

$$\ln \frac{C_{\alpha}}{C_{\beta}} = \frac{\varepsilon_{\beta} - \varepsilon_{\alpha}}{RT}$$

In this formula, which has been derived from a theory on reaction velocities developed by SCHEFFER (4),  $\varepsilon_{\alpha}$  and  $\varepsilon_{\beta}$  represent the values of the energy of activation for bromination in the  $\alpha$ - or  $\beta$ -position. The figures calculated with  $\varepsilon_{\beta} - \varepsilon_{\alpha} = 2498$  cal/mol are in good agreement with the values found experimentally (3). The ratio in which the two isomeric

bromonaphthalenes are formed in the temperature range from 85—215° C and in the absence of a catalyst is therefore determined by the difference in energy of activation required for substitution in the  $\alpha$ - or  $\beta$ -position in the naphthalene molecule.



§ 2. Completely different results are obtained in the catalytic bromination of liquid naphthalene; 0.3 mol of bromine was added dropwise in these experiments to a mixture of 0.6 mol of molten naphthalene and 0.025 mol of pure ferric chloride. Curve 3 (fig. I) shows that under the catalytic influence of ferric chloride the quantity of  $\beta$ -bromonaphthalene formed is relatively far larger than in the non-catalyzed reaction. That the total yields of monobromonaphthalene calculated on bromine (curve 4) are lower than those of curve 2 is due to the fact that in catalytic bromination more di- and tribromonaphthalenes are formed.

A large number of experiments carried out by SUYVER (5) showed that the figures given in fig. 3 for the  $\beta$ -bromonaphthalene content are reproducible under accurately defined conditions, such as for instance the quality of the ferric chloride used. Nevertheless, we found afterwards that the figures of curve 3 have no absolute value, because they are determined by the duration of the experiment, the rate at which the bromine is added

and particularly by the activity of the catalyst. In the bromination of naphthalene at 150° C with ferric chloride as catalyst we even obtained 60 % of  $\beta$ -isomer in the monobromonaphthalene mixture. The maximum in curve 3 has no theoretical value. Curve 3 cannot be represented by a formula of SCHEFFER; the ratio of the isomers is not determined by the difference in energy of activation  $\epsilon_{\beta} - \epsilon_{\alpha}$ .

In SCHEFFER's theory it is assumed that the isomeric substitution products formed by simultaneous reactions are *not* converted into each other during these reactions. If, however, primarily formed  $\alpha$ -bromonaphthalene should be converted into  $\beta$ -bromonaphthalene under the influence of ferric chloride, the results represented by curve 3 would become comprehensible.

From experiments carried out in conjunction with NIJLAND the following facts became clear. When a mixture consisting of 96 % of  $\alpha$ -bromonaphthalene and 4 % of ferric chloride is heated for some hours at 150° C, various reactions develop, owing to which a little naphthalene and dibromonaphthalene is formed, 9—11 % of the  $\alpha$ -bromonaphthalene originally present being converted into  $\beta$ -bromonaphthalene. This conversion  $\alpha \rightleftharpoons \beta$ , however, proceeds too slowly and too incompletely to cause formation of 50—60 % of  $\beta$ -bromonaphthalene in the catalytic bromination of naphthalene at 150°.

Starting from the assumption that the action of ferric chloride towards  $\alpha$ -bromonaphthalene cannot be compared with what takes place in the catalytic bromination of naphthalene, i.e. action of bromine in the presence of ferric chloride, the following experiments were made.

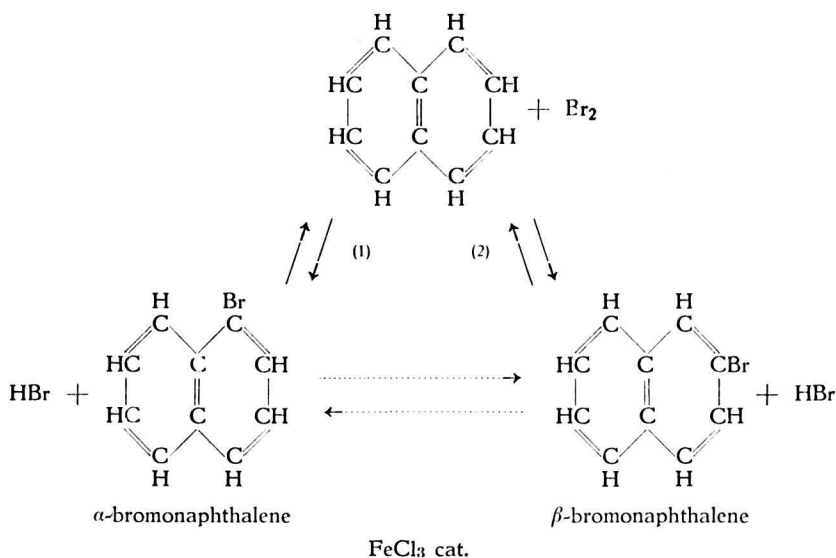
A mixture of 0.12 mol of  $\alpha$ - or  $\beta$ -bromonaphthalene and 0.007 mol of ferric chloride was treated at 150° with less than the theoretical quantity of bromine; the quantity of bromine used varied from 0.04—0.06 mol. Only part of the monobromonaphthalene can therefore be further brominated. The reaction product contained a small quantity of naphthalene, monobromonaphthalene and dibromonaphthalene. The monobromonaphthalene mixture separated from it contained 40 % of  $\alpha$ - and 60 % of  $\beta$ -isomer, it being immaterial whether  $\alpha$ - or  $\beta$ -bromonaphthalene had been used as starting material.

When monobromonaphthalene is therefore brominated catalytically with less than the theoretical quantity of bromine reactions develop, as a result of which a 40 %  $\alpha$ -bromonaphthalene  $\rightleftharpoons$  60 %  $\beta$ -bromonaphthalene equilibrium is established. It was found that the equilibrium ratio is only slightly dependent on the temperature, because about the same values were found when the experiments were carried out at 150°, 200° or 250°. It is important that this conversion  $\alpha \rightleftharpoons \beta$  does not take place when the further bromination of  $\alpha$ -bromonaphthalene is carried out without the addition of ferric chloride. During the *non-catalytic* bromination of liquid  $\alpha$ -bromonaphthalene at 150°, 50 % of the starting product was converted into di- and tribromonaphthalenes; the monobromonaphthalene recovered consisted of the pure  $\alpha$ -isomer.

§ 3. Then we carried out a systematic investigation into the reversible reactions which play a part in the catalytic bromination of naphthalene (6).

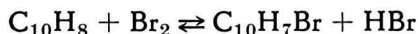
The fact that in catalytic bromination of bromonaphthalene a small quantity of naphthalene is formed, points towards the reversibility of the bromination reactions, since the naphthalene can only have been formed by debromination of bromonaphthalene. This reversibility was proved as follows: A current of gaseous hydrogen bromide was passed for 50 minutes through a mixture of 0.062 mol of monobromonaphthalene ( $\alpha$  or  $\beta$ ) and 0.002 mol of ferric chloride heated at  $150^\circ$ . During the experiment the reaction mixture was stirred vigorously, its temperature being kept constant within 1—2 degrees. After being worked up the monobromonaphthalene mixture contained about 60 % of  $\beta$ - and about 40 % of  $\alpha$ -isomers, it being immaterial whether the starting product had been  $\alpha$ - or  $\beta$ -bromonaphthalene. In addition, about 0.01 mol of naphthalene and about 0.004 mol of dibromonaphthalene had been formed. For checking purposes  $\alpha$ -bromonaphthalene was heated with gaseous hydrogen bromide under pressure at  $150^\circ$  without adding ferric chloride. No reaction took place.

These experiments show that both the formation of  $\alpha$ -bromonaphthalene and that of  $\beta$ -bromonaphthalene from naphthalene and bromine are reversible reactions, at least under the influence of ferric chloride:



If an equilibrium is established in the reactions 1 and 2, the catalytic debromination of  $\alpha$ -bromonaphthalene or of  $\beta$ -bromonaphthalene will yield an  $\alpha$ - and  $\beta$ -bromonaphthalene mixture, the  $\alpha$  :  $\beta$  ratio in which is determined by the equilibrium constants of these reactions. If the equilibria of 1 and 2 are established rapidly enough we shall find that also in the *catalytic bromination of naphthalene* a mixture of  $\alpha$ - and  $\beta$ -isomers is formed; the duration of the experiment, the temperature and the activity of the catalyst will determine whether the equilibrium belonging to a certain temperature will actually be established.

The experiments show that the equilibrium



is strongly in favour of bromonaphthalene. In spite of this one-sided equilibrium an  $\alpha$ -bromonaphthalene  $\rightleftharpoons$   $\beta$ -bromonaphthalene equilibrium is established via the reversible reactions 1 and 2; under the influence of ferric chloride the direct conversion  $\alpha \rightleftharpoons \beta$  develops so slowly that the  $\alpha \rightleftharpoons \beta$  equilibrium is not established in this way.

These debromination experiments were carried out at various temperatures. The  $\alpha : \beta$  equilibrium ratio (table I) was determined at various temperatures from these results and from the experimental results on the bromination of monobromonaphthalene with less than the theoretical quantity of bromine (§ 2).

TABLE I.  $\alpha : \beta$ -bromonaphthalene equilibrium

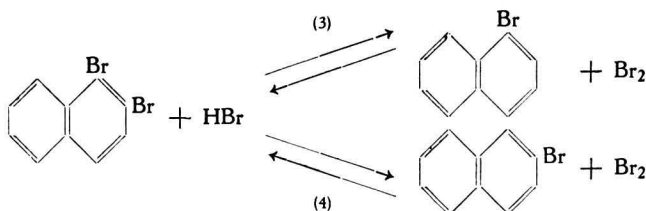
Temperature °C	100	150	200	250
% of $\beta$ in equilibrium mixture of the monobromonaphthalenes	63.1	62.3	60.4	58.8

From the formula 
$$\ln \frac{C_\alpha}{C_\beta} = \frac{\Delta Q}{RT} - \frac{\sum S_0}{R}$$

we calculate the heat of conversion  $\alpha \rightleftharpoons \beta : \Delta Q = -500$  calories/mol. In this calculation the variation of the entropy difference  $S_\alpha - S_\beta$  with the temperature is ignored, which is permissible because the specific heats of  $\alpha$ - and  $\beta$ -bromonaphthalene will not differ much. The error in the measurements of the equilibrium concentrations is  $\pm 0.5\%$ , so that the error in  $\Delta Q$  may be  $\pm 130$  calories/mol. The heat of conversion  $\alpha$ -bromonaphthalene  $\rightarrow$   $\beta$ -bromonaphthalene is small as compared with the difference in energy of activation for  $\alpha$ - and  $\beta$ -bromination in the liquid phase, because this ( $\varepsilon_\beta - \varepsilon_\alpha$ ) is about 2498 cal/mol. In comparing the figures of table I it appears that in the experiments on catalytic bromination of naphthalene, represented in curve 3 (fig. I), the  $\alpha \rightleftharpoons \beta$  equilibrium is not established. As mentioned above, however, it is possible to obtain the maximum  $\beta$ -isomer content (about 60%) by catalytic bromination. The formation of large quantities of  $\beta$ -bromonaphthalene in the bromination of naphthalene with ferric chloride (or ferric bromide) as catalyst<sup>1)</sup> is therefore a result of the fact that the reactions 1 and 2 are reversible under the influence of the catalyst. It is useless to assume a "directing effect" of the catalyst, for small quantities of  $\beta$ -isomer are also formed in the non-catalytic bromination of naphthalene (§ 1). Similar debromination reactions take place when dibromonaphthalenes are heated at 150° with hydrogen bromide and ferric chloride as catalyst.

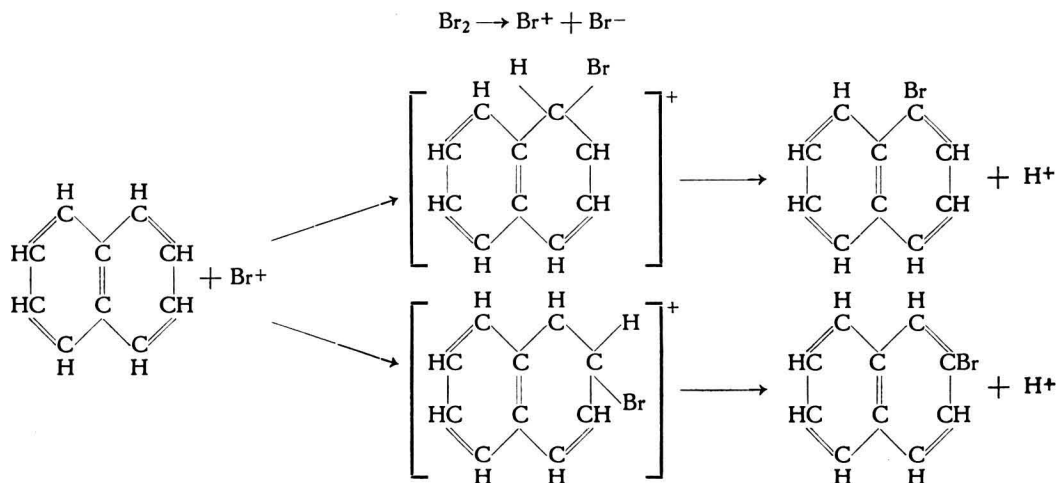
<sup>1)</sup> When using ferric bromide or ferrous bromide as catalysts, the results are quantitatively and qualitatively the same as those obtained with ferric chloride. For experimental reasons we used ferric chloride in the final experiments, because it is easier to obtain this substance in an anhydrous state.

Apart from very little naphthalene, a mixture consisting of 56 % of  $\beta$ - and 44 % of  $\alpha$ -bromonaphthalene is formed from 1 : 2-dibromonaphthalene under these conditions, which approach the equilibrium values  $\alpha \rightleftharpoons \beta$ .



With 1 : 3- and 1 : 6-dibromonaphthalene a similar qualitative result was obtained. These observations afford an explanation for the experimentally established fact that in the further catalytic bromination of monobromonaphthalene with less than the theoretical quantity of bromine, the remaining monobromonaphthalene consists of a mixture of  $\alpha$ - and  $\beta$ -bromonaphthalene, the equilibrium ratio  $\alpha : \beta = 2 : 3$  being established under favourable conditions.

§ 4. Various investigations into the nuclear substitution of aromatic compounds at relatively low temperatures (liquid phase) have made it very likely that these reactions develop according to an ionogenic mechanism. For a bromination reaction it is therefore assumed that the bromine molecule is split into a positively and a negatively charged part, or what amounts to the same for the theory, that the bromine molecule is polarized. The positive part of the bromine molecule then forms a covalent bond with a carbon atom of the aromatic ring to be substituted. This requires two electrons to be available at this carbon atom. Under the influence of the positively charged bromine particle the naphthalene nucleus is polarized in such a way that two  $\pi$ -electrons are restricted to the reacting carbon atom ( $\alpha$  or  $\beta$ ). The above assumptions are expressed in the following scheme for naphthalene bromination:



The localization<sup>2)</sup> of two  $\pi$ -electrons to an  $\alpha$ - or  $\beta$ -carbon atom of the naphthalene nucleus, in which the ground state of the aromatic nucleus is disturbed, requires energy. It may be expected that this energy will be different for the localization to an  $\alpha$ - or to a  $\beta$ -carbon atom. If we assume that the energy required for the splitting of the bromine molecule is the same for the reaction with an  $\alpha$ - or with a  $\beta$ -carbon atom, then the difference in energy of activation required for  $\alpha$ - and  $\beta$ -substitution will be chiefly caused by the difference in energy required to restrict two  $\pi$ -electrons to the  $\alpha$ - or  $\beta$ -carbon atom.

One of us (SIXMA) (6) has calculated the difference in energy of localization for the  $\alpha$ - and the  $\beta$ -position by means of approximate methods elaborated in wave mechanics, i.e. by application of the "molecular orbital method". In this article only the result will be mentioned.

For the difference between the energy of a naphthalene nucleus, in which two  $\pi$ -electrons are restricted to an  $\alpha$ -carbon atom and that of a naphthalene nucleus in which two  $\pi$ -electrons are restricted to a  $\beta$ -carbon atom we find:

$$\Delta E = E_{\beta} - E_{\alpha} = 3180 \text{ calories/mol.}$$

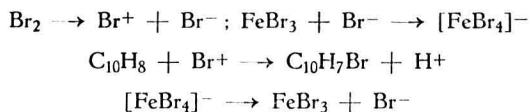
SUYVER and WIBAUT in their experiments calculated the difference in energy of activation for bromination in the  $\beta$ - and  $\alpha$ -position as 2498 calories/mol for the reaction in the liquid phase and as 4215 calories/mol for the reaction in the gas phase. The agreement with the value found by application of the molecular orbital method is therefore satisfactory, considering that a number of approximations have been introduced into the theoretical derivation.

So far it has been assumed that the bromination of naphthalene proceeds as an electrophilic substitution. From the calculation it follows, however, that the same value is obtained for  $\Delta E$ , if one assumes substitution by bromine atoms (radical substitution) or by negatively charged bromine particles (nucleophilic substitution). The directing effect in the substitution in the naphthalene nucleus is therefore independent of the substitution mechanism when the temperature is not too high. In GOMBERG's reaction between naphthalene and the diazonium compound of methyl anthranilate, which reaction proceeds as a radical substitution, the substituent occupies the  $\alpha$ -position, which is in agreement with the above conclusion. Also from a qualitative study by means of resonance structures, on the assumption that the molecule with the highest possible number of resonance structures has the greatest stability, it follows that substitution in the  $\alpha$ -position requires least energy of activation.

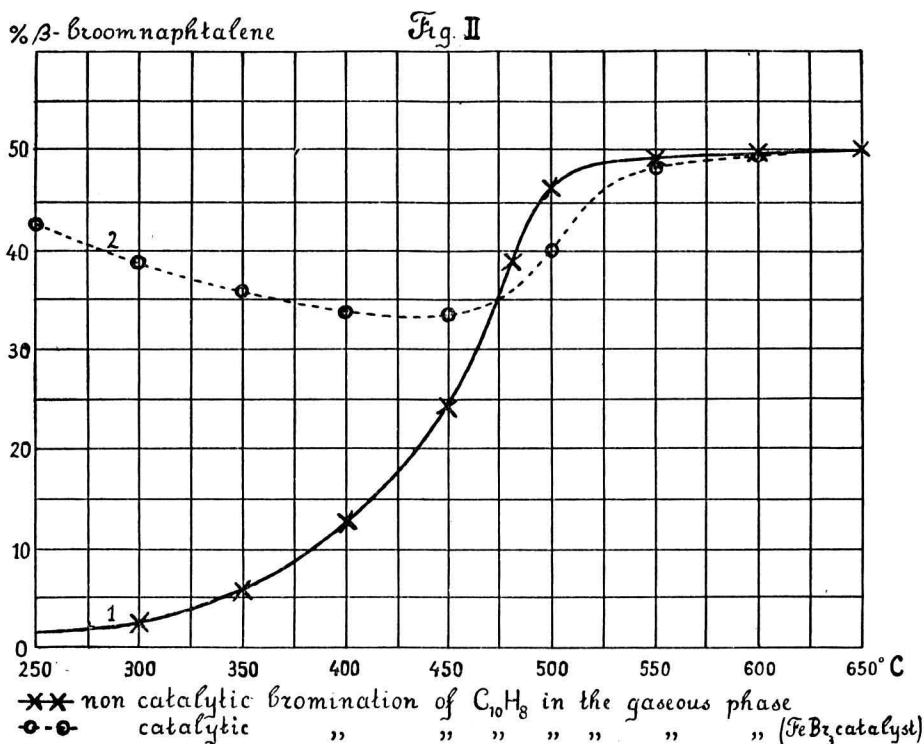
The above therefore accounts for the fact that in the non-catalytic

<sup>2)</sup> E. C. KOOYMAN and J. A. A. KETELAAR [Rec. trav. chim. **65**, 859 (1946)] have defined the concept localization of two  $\pi$ -electrons as the disturbance of the resonance by restriction of two of the  $\pi$ -electrons of the resonance system to two adjacent C-atoms reacting with ozone. In this case we extend the concept to restriction of two  $\pi$ -electrons to one carbon atom.

bromination of naphthalene below 300° chiefly  $\alpha$ -substitution takes place. A catalyst such as ferric bromide (or ferric chloride) reduces the energy of the transition state of the reaction in such a way that the reaction becomes reversible. If the bromination develops according to an electrophilic mechanism it is easy to see that ferric bromide may promote the formation of positively and negatively charged bromine particles by the formation of a complex ion:



§ 5. Let us now consider the formation of monobromonaphthalenes by direct bromination of naphthalene in the gas phase.



The results obtained by one of us (WIBAUT) in collaboration with SUYVER (2, 3) are represented in figure II.

Curve 1 shows the  $\alpha$  :  $\beta$  ratio in the monobromonaphthalene mixture obtained by *non-catalytic bromination of naphthalene vapour*. In these experiments naphthalene vapour and bromine vapour were passed in the ratio of 1 mol of  $\text{C}_{10}\text{H}_8$  to  $\frac{1}{2}$  mol of  $\text{Br}_2$  at a constant rate through a glass tube filled with glass wool or purified pumice and kept at constant temperature. The yields of monobromonaphthalene vary from 55 — 35 % (calculated on bromine) in the temperature range from 250 — 500°, but



rapidly decrease above  $550^{\circ}$ , because the primarily formed bromonaphthalenes decompose at the elevated temperature. The lower part of curve 1 to approximately  $300^{\circ}$  is in agreement with a formula of SCHEFFER with  $\varepsilon_{\beta} - \varepsilon_{\alpha} = 4215$  calories/mol. In this temperature range the  $\alpha : \beta$  ratio is determined by the difference in energies of activation for  $\alpha$ - and  $\beta$ -substitution, just as is the case in the non-catalytic bromination in the liquid phase.

According to an article published by SPEEKMAN (7) two cases must be distinguished in the bromination of gaseous bromobenzene, naphthalene, pyridine, etc. in the temperature range from  $300 - 500^{\circ}$ . At temperatures below  $350^{\circ}$  the reaction chiefly proceeds on the wall of the reaction vessel or at the surface of the pumice, glass wool or graphite with which the tube is filled (wall reaction); at  $500^{\circ}$  and higher the reaction proceeds between free molecules in the gas phase (gas reaction). In the transition zone from  $350 - 400^{\circ}$  the adsorption of the bromine and naphthalene molecules decreases, so that when the temperature rises the gas reaction will predominate over the wall reaction. Fact is that many qualitative observations on the bromination of gaseous aromatic compounds are in agreement with the assumption that the bromination at  $300^{\circ}$  chiefly develops as a wall reaction. From the experimentally established fact that at  $500^{\circ}$  and higher equal quantities of  $\alpha$ - and  $\beta$ -bromonaphthalenes are formed SPEEKMAN concludes that in this temperature range the  $\alpha : \beta$  ratio is not determined by the difference in energy of activation for  $\alpha$ - and  $\beta$ -substitution, but is exclusively dependent on the probability of collision between the bromine molecule (or bromine atom, if one wants to assume atomic substitution) and an  $\alpha$ - or  $\beta$ -position of the naphthalene molecule. As this probability is the same for both positions, equal quantities of  $\alpha$ - and  $\beta$ -bromonaphthalene are formed. The question is now why from a certain temperature — in the case of naphthalene bromination from about  $500^{\circ}$  — the difference in energy of activation is no longer of importance. One of us (SIXMA) has treated this problem theoretically. Only the results of his studies are mentioned below. As the reaction temperature rises the energy of the molecule will increase. When the temperature is sufficiently high the average energy of the molecules may become of the same order of magnitude as the energy of activation of the reaction. Then the energy barrier is exceeded at each collision and the ratio of the substitution products is exclusively determined by *steric factors*.

The average energy of a system with three degrees of freedom is of the order of  $RT$ , the energy of activation of a halogenation reaction in the aromatic nucleus being of the order of 10,000 — 20,000 calories.

On the strength of these figures the monobromination of naphthalene would only yield equal quantities of  $\alpha$ - and  $\beta$ -isomers at a temperature which might be roughly estimated at some thousands of KELVIN degrees. In SIXMA's (6) theory it is assumed that in naphthalene bromination the energy of the system is built up from  $2n$  quadratic terms; the calculation

shows that the transition temperature, i.e. the temperature at which equal quantities of  $\alpha$ - and  $\beta$ -isomers begin to be formed is lower as  $n$  is larger.

This accounts in principal for the fact, that the transition temperature found experimentally, is much lower than might be expected according to the formula:

$$\ln \frac{C_\alpha}{C_\beta} = \frac{\varepsilon_\beta - \varepsilon_\alpha}{RT};$$

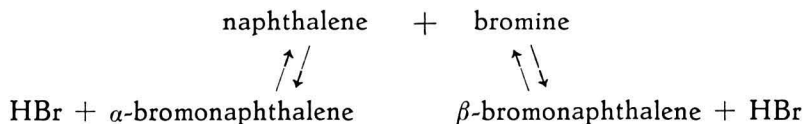
it has not yet been possible to calculate this transition temperature. From the calculation it also follows that at a low temperature the reaction between bromine and naphthalene satisfies SCHEFFER'S formula, also when the energy of the system must be described by  $2n$  quadratic terms.

The catalytic bromination of naphthalene vapour shows quite a different development (curve 2 in fig. II). In these experiments carried out by SUYVER the reaction tube was filled with a catalyst consisting of *pumice impregnated with ferric bromide*. The presence of this catalyst not only increases the total rate of reaction at which monobromonaphthalene is formed, but it also highly promotes the  $\beta$ -substitution. The peculiar shape of this curve suggested that partial conversion  $\alpha \rightleftharpoons \beta$  takes place under the influence of ferric bromide. If, however,  $\alpha$ - or  $\beta$ -bromonaphthalene vapour is passed slowly over the ferric bromide contact at  $350^\circ$  or at  $500^\circ$  no  $\alpha \rightleftharpoons \beta$  conversion takes place. In continuation of our experiments on the reversibility of the catalytic bromination of naphthalene in the liquid phase described in § 3, we have investigated the debromination reaction in the vapour phase.

We passed a mixture of gaseous  $\alpha$ -bromonaphthalene and gaseous hydrogen bromide in the molecular ratio 1 : 15 over a ferric bromide pumice contact at  $300^\circ$  (0.06 mol of  $\alpha$ -bromonaphthalene, 0.92 mol of hydrogen bromide in 300 minutes). The reaction product consisted of some naphthalene (about 0.001 mol) and the two monobromonaphthalenes in the ratio of 53.1 % of  $\beta$ - to 46.9 % of  $\alpha$ -isomer. When the same experiment was made with  $\beta$ -bromonaphthalene as starting material, the monobromonaphthalene mixture obtained consisted of 60 % of  $\beta$  and 40 % of  $\alpha$ .

As the ferric bromide is markedly volatile in the investigated temperature range and precipitates in cold parts of the apparatus, it is impossible to measure the heterogeneous gas equilibrium  $\alpha \rightleftharpoons \beta$  at various temperatures with accuracy. However, the experiments allow of the following conclusions. In the gas phase the bromination of naphthalene is reversible; also in case of a great excess of hydrogen bromide the equilibrium in the temperature range from  $300 - 500^\circ$  is still strongly in favour of the bromonaphthalenes.

As a result of the reversible reactions:



a monobromonaphthalene mixture is formed, in which the  $\alpha : \beta$  ratio may approach an equilibrium ratio. When we started in our experiments from the  $\alpha$ - and  $\beta$ -bromonaphthalenes the same final condition was only roughly approached at 300° C. At 400° and 460° the rate of conversion  $\alpha \rightleftharpoons \beta$  is considerably lower than at 300°. This apparently paradoxal result must be accounted for as follows.

As the temperature rises the adsorption of bromonaphthalene and hydrogen bromide to the catalyst surface decreases, so that the ratio (adsorbed molecules) : (molecules in the gas phase) decreases. As we use flowing gases and the  $\alpha \rightleftharpoons \beta$  conversion only takes place at the catalyst surface, the number of  $\alpha$ -molecules converted per unit of time into  $\beta$ -molecules (or conversely) will be smaller as the temperature is higher. Though the rate of reaction in the catalyst layer will be considerably increased when the temperature is raised, the above-mentioned decrease in adsorption, which has an opposite effect, apparently predominates. The curve 2 in fig. II does not represent equilibria, because they have not been established. At about 500° the curve of the catalytic bromination begins to approach that of the non-catalytic bromination and almost coincides with it at higher temperatures, because in this range the reaction proceeds almost exclusively in the gas phase and because the adsorption of the molecules to the catalyst layer has dropped to a very low value.

June, 1948.

*Laboratory of Organic Chemistry of the  
University of Amsterdam.*

#### BIBLIOGRAPHY.

1. A. LAURENT, *Ann. chim.* (2) **59**, 216 (1835).
2. J. F. SUYVER, Thesis, Amsterdam (1941).
3. See J. F. SUYVER and J. P. WIBAUT, *Rec. trav. chim.*, **64**, 65 (1945).
4. F. E. C. SCHEFFER, *Proc. Kon. Akad. v. Wetensch.*, Amsterdam, **15**, 1109, 1118 (1913).  
F. E. C. SCHEFFER and W. F. BRANDSMA, *Rec. trav. chim.*, **45**, 522 (1926).
5. These experiments on the catalytic bromination have so far only been published in J. F. SUYVER's thesis.
6. F. L. J. SIXMA, Thesis, Amsterdam (1948).
7. B. W. SPEEKMAN, Thesis, Amsterdam (1941).