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227. Chemical Selectivities Disguised by Mass Diffusion.
II. Mixing-Disguised Nitrations of Aromatic Compounds with Nitronium Salts[1,2])

2nd Communication on the Selectivity of Chemical Processes[1])

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(16. XI. 73)

Summary. The results of this study show that three parameters are sufficient to describe the selectivity behaviour of nitrations influenced by mixing as long as a fast combination of the reactant solutions takes place and fast agitation is employed. This is in full agreement with the prediction of the mixing-reaction model developed previously [1]. Furthermore, the results show clearly that in nitromethane the formation rate of nitronium ions from nitric acid is slower than the mixing rate and the rate of the electrophilic substitution proper. From the mixing-disguised selectivity curves for the nitrations of durene and prehnitene with nitronium hexafluorophosphate in nitromethane the ratio of the rate constants k_2 for the second nitrations can be estimated to be 1:2. For the two aromatic compounds the k_1/k_2 ratios are $\geqslant 10^4$. Finally it could also be shown that small impurities in the solvent (e.g. water) can influence strongly the selectivity curves, depending on the method used for mixing.

1. Introduction. – In the Part I of this series [1] a simple mixing-reaction model was developed which allowed a description and simulation of the coupling of

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[1]) Part I and 1st Communication cf. [1].
[2]) Results taken from the PhD. thesis of F. Pfister [2].

the mass diffusion with the chemical reaction during the mixing process of two reactant solutions. For competitive consecutive and competitive parallel reactions the general behaviour and the dependence of the product selectivity on diffusion effects was demonstrated.

In the present paper, the disguise of the selectivity of competitive consecutive reaction systems[3]) by the mixing process is demonstrated experimentally, using the fast nitrations with nitronium salts in aprotic solvents. Since 1961, these nitrations have been the subject of mechanistic investigations[4]). However, in some cases there still appears to be some doubt about the possible influence of diffusion effects on the nature and proportions of the products formed (selectivity) in these and other systems used for nitration.

In nitrations of aromatic compounds with an equimolar amount of nitronium salt in aprotic solvents, high yields of dinitro products were found [5] [6] which is a little surprising in view of the fact that the introduction of a nitro group into a benzene ring has a deactivating effect of about 10^8. Furthermore, in nitrations with nitronium salts reactivities of a number of aromatic hydrocarbons relative to benzene have been reported which are much lower than those obtained with nitric acid [4] [7]. The evidence suggests that the observed selectivities of these nitrations with nitronium salts depend on the rate of mixing of the reactants [4–6][9]. Yet, the fact that the difference in the relative reactivities is not accompanied by a marked change in the *ortho*: *meta*: *para* ratios (positional selectivity) is often used as an argument against the possibility that low relative reactivities of the aromatic substrates arise from imperfect mixing, *i.e.* from diffusion effects. However, these experimental facts are in agreement with what has been discussed in Part I [1], namely that the substrate selectivities do depend on mass diffusion, whereas the positional selectivities do not. In addition, it is often thought that the product distribution of competitive parallel reactions is not influenced by diffusion effects if the kinetics of the reactions are of the same order. This, however, is only true if the reactions are performed under *steady-state* conditions [8]; under *non steady-state* conditions the substrate selectivity can be markedly disguised by diffusion [1]. Such conditions are encountered, for example, if a reaction is carried out batch-wise.

In general, there are at least two situations which may lead to diffusion effects. The observed kinetics of a reaction can be:

a) influenced by the rate of mixing of the reactant solutions (mixing-disguised kinetics). Examples are the nitrations with nitronium salts[4]) [5–7] and some brominations and iodinations of aromatic compounds [10] [11];

b) determined by the rate of the formation of the encounter complex (encounter rate-determined kinetics). Examples are nitrations with nitric acid [12] [13] and some proton transfer reactions [14].

In Part I [1] it was demonstrated that the selectivity behaviour observed in second-order consecutive reactions influenced by the mixing rate is fully described by the three parameters $^*E, ^*\varphi^2_{B,1}$ and $^*\varphi^2_{B,2}$ if the method of mixing assures a quick addition of one reactant solution to the other[5]).

$$^*E = \frac{[A]_0\,\alpha}{[B]_0}\;;\quad ^*\varphi^2_{B,1} = \frac{\overline{R}^2 k_1 [B]_0}{D\,\alpha}\;;\quad ^*\varphi^2_{B,2} = \frac{\overline{R}^2 k_2 [B]_0}{D\,\alpha}$$

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[3]) Similar investigations of competitive parallel reaction systems are in progress.
[4]) For a summary see [3]; for a critical review see [4].
[5]) The influence of different mixing methods on the selectivity will be discussed in section 3.1. of this paper.

$[A]_0$ initial concentration of **A** in the reactant solution of **A** before mixing with the reactant solution of **B** [mol/l];

$[B]_0$ initial concentration of **B** in the reactant solution of **B** before mixing with the reactant solution of **A** [mol/l];

α volume ratio of the initial reactant solutions of **A** and **B**: $(V_A)_0/(V_B)_0$ [–]

$\overline{R}$ mean radius of the eddies of reactant solution **A** [cm]

D mean diffusion coefficient of the reactants [cm²/s]. For solvents of low viscosity: $10^{-5}\ldots\ldots 10^{-6}$ cm²/s

k_1 and k_2 intrinsic second-order rate constants of the first and second reaction step, respectively (cf. *Scheme 1*) [1] [l/(mol · s)].

To demonstrate the disguise of chemical selectivities by mass diffusion we chose the fast consecutive nitrations of prehnitene and durene (1,2,3,4- and 1,2,4,5-tetramethylbenzene) with nitronium salts in nitromethane:

Scheme 1

$$X^{\ominus} = PF_6^{\ominus}, \quad BF_4^{\ominus} \quad \text{etc.}$$
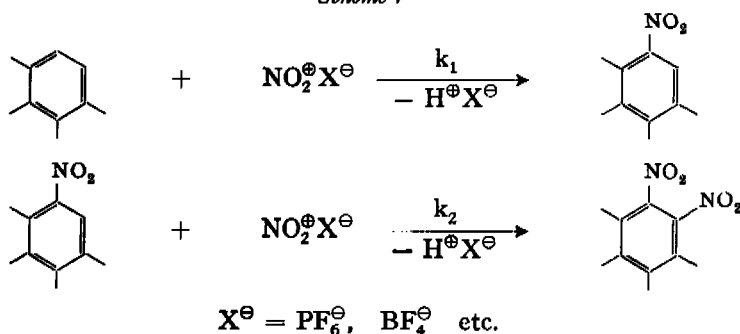
A similar scheme can be written for durene. Following the nomenclature in Part I [1]:

Reactant **A** Prehnitene or durene   Product **R** Mononitro product
Reactant **B** · Nitronium ion   Product **S** Dinitro product

Before discussing the product distribution as a function of the parameters *E, *$\varphi_{B,1}^2$ and *$\varphi_{B,2}^2$ (Section 3), we will consider some characteristics of the system used for nitration.

2. Some Characteristics of the System. – 2.1. *The Influence of Water on the Kinetics.* Since the relative yield[6]) X_S of the product **S** of mixing-disguised nitrations depends on the initial nitronium ion concentration $[B]_0$, reactant solutions with the same amount of nitronium salt but with different water contents and therefore with different $[B]_0$ (*Scheme 2*) are expected to give different X_S. This, however, is only true if the rate of formation of nitronium ions from nitric acid is slower than the mixing rate.

Scheme 2

$$NO_2^{\oplus} X^{\ominus} + H_2O \;\rightleftharpoons\; H_2O^{\oplus}NO_2 X^{\ominus} \;\rightleftharpoons\; HNO_3 + H^{\oplus}X^{\ominus}$$

It will be proved later (Section 2.2., Fig. 3) that this condition applies to our system. Fig. 1 shows examples representative of the kinetic behaviour of the nitration of durene in nitromethane in the absence and presence of water[7]).

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[6]) For definition of X_S, see Table 2.

[7]) Other examples at different water contents for both durene and prehnitene can be found in [2].

In the absence of water, the product **S** is always formed within less than 1 sec and no further reaction occurs after this time. However, when water is present the product **R** is formed at a rate much slower than the rate of formation of **S**. From this one might conclude that the dinitro product **S** is formed in a reaction which does not involve **R**, but a closer examination of the kinetic data suggests the following interpretation: *Before* mixing is completed, the nitronium ion, the effective concentration of which at the beginning of the reaction is determined by the nitronium ion/nitric acid equilibrium (*Scheme 2*), reacts in a fast step with **R** to give **S**. *After* mixing is completed, the rate of the nitration is then given by the rate of formation of nitronium ions from nitric acid; the nitronium ions react with durene to give **R**. Thus, no **S** is formed because the product distribution is not disguised by mixing anymore. These findings suggest that the rate of mixing is faster than the rate of formation of nitronium ions from nitric acid.
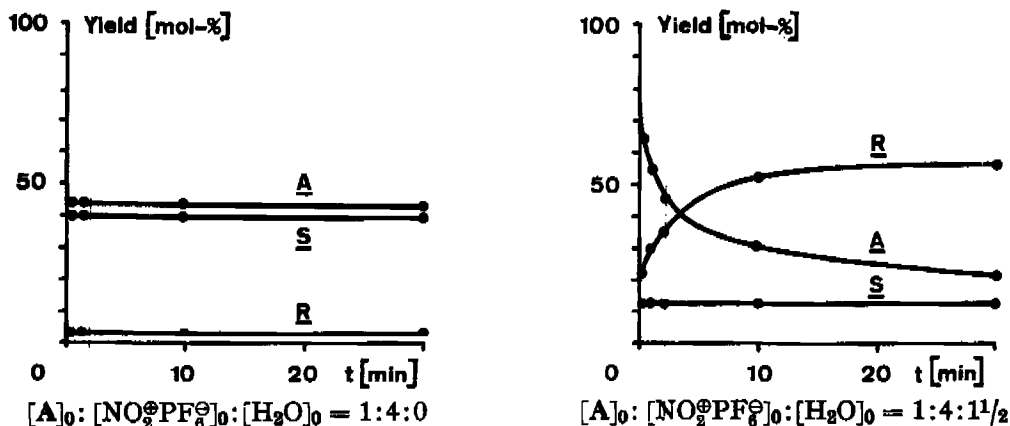

$[A]_0 : [NO_2^{\oplus}PF_6^{\ominus}]_0 : [H_2O]_0 = 1:4:0$ $[A]_0 : [NO_2^{\oplus}PF_6^{\ominus}]_0 : [H_2O]_0 = 1:4:1^1/_2$

Fig. 1. *Nitration of Durene with Nitronium Hexafluorophosphate in Nitromethane* (20.0°) *in the absence and presence of Water*[8]. $[A]_0 = 0.1M$; $(V_A)_0 = 20$ ml; $(V_B)_0 = 5$ ml; $\alpha = 4$; A: Durene; R: Mononitrodurene; S: Dinitrodurene; Mixing Method: I (see Section 3.1. of this paper)

2.2. *Determination of the Effective Nitronium Ion Concentration in Mixtures of Nitronium Hexafluorophosphate and Water in Nitromethane.* Since the relative yield X_S is a function of the nitronium ion concentration, it can, in turn, be used to determine kinetically the nitronium ion concentration at each water content. The dependence of X_S on the nitronium ion concentration under known constant mixing conditions can be determined from experiments carried out in the absence of water using different amounts of nitronium hexafluorophosphate. Whether the dependence of X_S on the *effective* or on the *apparent* nitronium ion concentration is obtained depends on whether the purity (82 ± 2%) of the nitronium salt is taken into account. All nitronium ion concentrations reported in this paper, such as $[NO_2^{\oplus}PF_6^{\ominus}]_0$, $[NO_2^{\oplus}]_{ex}$ or $[NO_2^{\oplus}]_{IR}$, are apparent concentrations. The apparent nitronium ion concentration in the presence of water can then be determined from the above $[NO_2^{\oplus}PF_6^{\ominus}]_0$-scale, see Fig. 2: For example, in the nitration of prehnitene with 0.08M nitronium salt and 0.04M water an X_S-value of 0.68 is found. From the $[NO_2^{\oplus}PF_6^{\ominus}]_0$-scale this value of

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[8]   The remaining products are by-products (compare [9]).

X_S corresponds to an equilibrium value of the apparent nitronium ion concentration $[NO_2^\oplus]_{ex}$ of 0.043M. An analogous experiment with durene gives an X_S-value of 0.30, and 0.042M for $[NO_2^\oplus]_{ex}$. In other words this simply means that a water-free experiment with a nitronium salt concentration of 0.043M would yield X_S values of 0.68 for prehnitene and 0.30 for durene, respectively.

The nitronium ion concentration of nitronium-salt solutions containing water was also determined independently by IR. measurements which gave $[NO_2^\oplus]_{IR}$. Fig. 3 shows that at various contents of water there is an excellent agreement between the
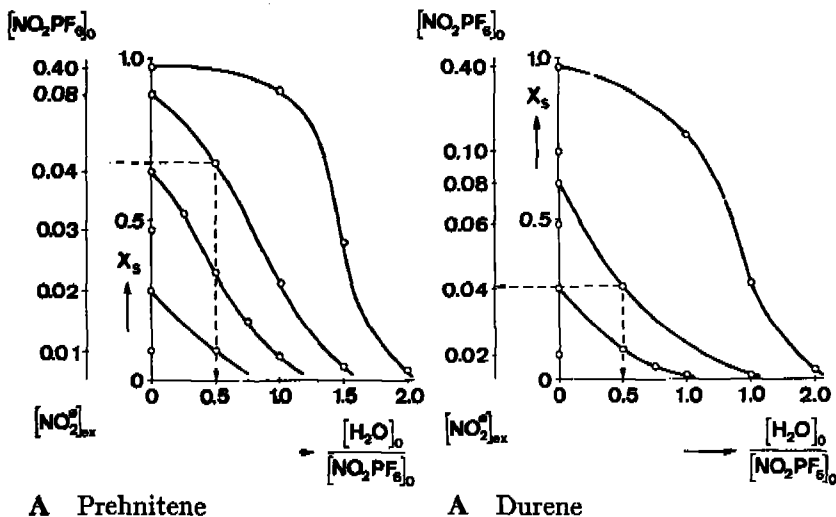

A   Prehnitene   A   Durene

Fig. 2. *Nitration of aromatic compound* **A** *with Nitronium Hexafluorophosphate in Nitromethane* (20.0°) *in the presence of Water* (Concentrations in M)
$[A]_0 = 0.1M$; $\alpha = 4$: $(V_A)_0 = 20$ ml and $(V_B)_0 = 5$ ml; Mixing Method: I

Determined kinetically   Determined by IR-measurement
                                  at 2380 cm^{-1}
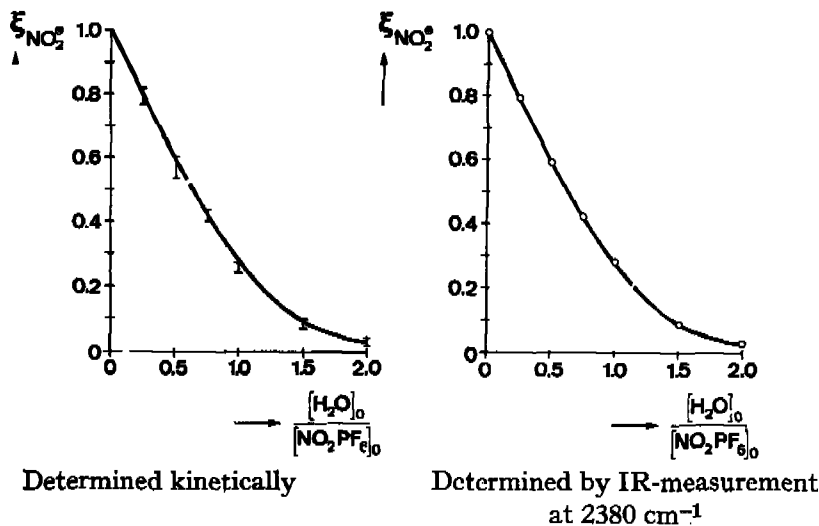
Fig. 3. *Relative Nitronium Ion Concentrations* $\xi_{NO_2^\oplus}$ *in Solutions of Nitronium Hexafluorophosphate containing Water* (Nitromethane, 20.0°C)

kinetically and the spectrophotometrically determined *relative* nitronium ion concentration $\xi_{NO_2^\oplus}$. $\xi_{NO_2^\oplus}$ is the ratio $[NO_2^\oplus]_{ex}/[NO_2^\oplus PF_6^\ominus]_0$ or $[NO_2^\oplus]_{IR}/[NO_2^\oplus PF_6^\ominus]_0$, respectively. This agreement provides further evidence that in the systems used in this study the rate of formation of nitronium ions from nitric acid is much slower than the mixing process and also slower than the rate of nitration with these nitronium ions.

2.3. *The Solvation of the Proton Released.* The question arises whether the proton released during the electrophilic substitution might increase the nitronium ion concentration by shifting the equilibrium in *Scheme 2* to the left. On addition of water to the nitrating system, the nitric acidium ion is first formed which loses a proton to give nitric acid. The protons released can be solvated by either the gegen-ion of the nitronium salt, by the aromatic compound, by another molecule of water (if added) or by the solvent nitromethane. It is unlikely that the gegen-ion or the aromatic compound solvate the proton to an appreciable extent as, in addition to their low basicity, their concentration is small compared to that of the solvent which has a comparable basicity. In the case where *no water* is added, nitromethane seems to be the most probable solvating agent for the protons. If water is added to our nitrating system the nitronium ions and the protons (from the nitric acidium ion or released in the electrophilic substitution) will compete for solvation by water or by the solvent. A comparison of the acidities of protonated nitromethane and protonated water in the presence of the hydrogensulfate anion shows that nitromethane is a weaker base than water by a factor of *ca.* 200.

$$K_{CH_3NO_2} = \frac{[CH_3NO_2H^\oplus][HSO_4^\ominus]}{[CH_3NO_2]} = 5.5 \times 10^{-3} \text{ mol/kg} \quad [15]$$

(in 100% H_2SO_4 at 10.0°C)

$$K_{H_2O} \quad \frac{[H_3O^\oplus][HSO_4^\ominus]}{[H_2O]} = 1.0 \ldots 1.2 \text{ mol/kg} \quad [16]$$

(in 100% H_2SO_4 at 10.0°C)

A nitromethane solution is about 18.5M, thus an effective water concentration of about 0.1M would be needed to make both substrates equally effective in the solvation of protons. In our experiments the effective water concentrations are always less than 0.1M. Therefore, we can assume that the protons are solvated by nitromethane.

3. **The Mixing-Disguised Selectivity.** – 3.1. *The Method of Mixing.* The model developed in Part I of this series [1] to describe the coupling of a chemical reaction with the process of mixing is based on the following assumptions:
a) the reactant solutions are brought together at once;
b) the macroscopic eddy-diffusion is fast compared to the molecular mass diffusion within the eddies.

In our nitration experiments vigorous stirring ensured that condition b) was fulfilled. Furthermore, the stirring rate was kept constant in all experiments, thus keeping the mean radius of the eddies constant. Consequently, the parameters $^*\varphi_{B,1}^2$ and $^*\varphi_{B,2}^2$ could only be varied by changing the concentration $[B]_0/\alpha$, as the values for L, D, k_1 or k_2 remain constant. However, condition a) was not fulfilled for

every method of mixing employed. In order to demonstrate the influence of the mixing *method* on the product distribution, the following three methods were investigated:

I: The nitronium salt solution was added *dropwise* to the solution of the aromatic compound;

II: The solution of the aromatic compound was added *dropwise* to the nitronium salt solution;

III: The solution of the aromatic compound was very quickly *poured* into the nitronium salt solution.

Fig. 4 and 5 show the dependence of the relative yield X_8 of dinitrodurene on the various methods I, II and III at different $[B]_0^*$ for $\alpha = 1$ and $\alpha = 4$, respectively. $[B]_0^*$ is the apparent nitronium ion concentration corrected, using Fig. 3, for the water which remains in the nitromethane even after careful drying[9]. The average water content of the nitromethane used was determined to be 5×10^{-3} M (*Karl-Fischer*-titration).
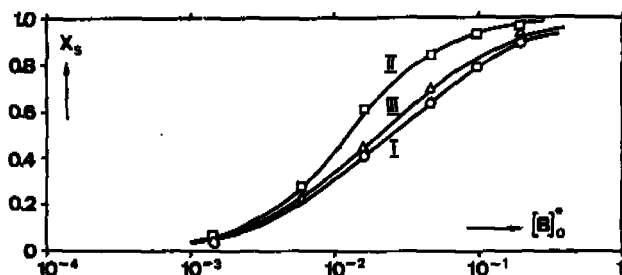

Fig. 4. *Nitration of Durene* (A) *with* $NO_2^{\oplus} PF_6^{\ominus}$ (B) *in Nitromethane* (20.0°C) *using the various mixing methods I, II and III*

$$*E = \frac{[A]_0 \alpha}{[B]_0} = 1 \quad \alpha = 1$$

Fig. 5. *Nitration of Durene* (A) *with* $NO_2^{\oplus} PF_6^{\ominus}$ (B) *in Nitromethane* (20.0°) *using the various mixing methods I, II and III*

$$*E = \frac{[A]_0 \alpha}{[B]_0} = 1 \quad \alpha = 4$$

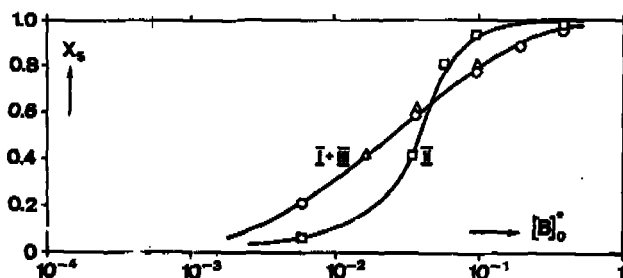[9] See the Exper. Part.

The dependence of X_S on $[B]_0^*$ is different for each method: In method I the aromatic compound is always in excess; this leads to X_S-values lower than those obtained with the other mixing methods. With method II the situation is reversed. If the addition of the aromatic compound is much slower than the rate of nitration, every molecule of the aromatic compound can be dinitrated before the next drop is added. Hence, relatively more S is formed (Fig. 4). The faster the aromatic compound is added (method III), the more the results resemble those obtained using method I.

The curves I in Fig. 4 and 5 are slightly steeper than the model calculations predict (cf. Fig. 4 in [1]) for $*\varphi_{B,1}^2/*\varphi_{B,2}^2 = k_1/k_2 > 10^4$. Two main reasons may account for this small difference:

(i) In contrast to the real system the mean radius $\bar{R}$ of the eddies is assumed for the calculations to be constant from 0 to 100% conversion.

(ii) In the determination of $[B]_0^*$ only the water in the nitronium ion solution can be considered and not that in the solution of the aromatic compound.

The small amount of water remaining in the solution of the aromatic compound might also account for the difference between the curves II for $\alpha = 1$ and $\alpha = 4$. The higher the α-value, the more water is added to the reaction mixture; the concentration of the nitronium ions is therefore lowered because more react to give nitric acid. This (deactivating) effect of water is more pronounced at lower $[B]_0^*$-values and can even lead to a situation where there is less product S formed with the mixing method II than with I.

3.2. *The Nitration of Various Aromatic Compounds under Constant Mixing Conditions.* The product distributions in the nitrations of prehnitene and durene have been determined under identical experimental conditions. In Fig. 6 the X_S-values are plotted against $[B]_0^*$ (prop. to $*\varphi_{B,2}^2$) to give the individual selectivity curves. From the relative positions of these curves the relative values of the rate constants k_2 for the second nitration step can be estimated according to model calculations [1] to be 1:2 for mononitrated durene: mononitrated prehnitene.
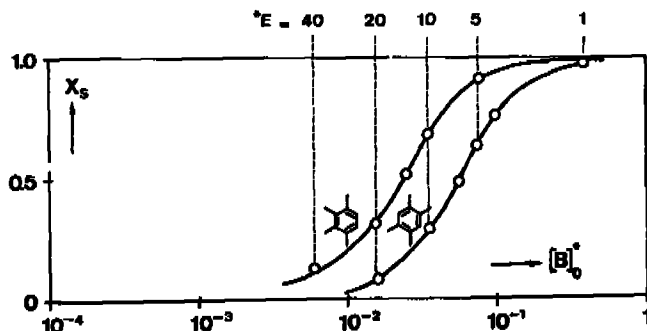

Fig. 6. *Nitrations of Various Aromatic Compounds* (A) *with* $NO_2^\oplus PF_6^\ominus$ (B) *in Nitromethane* (20.0°C). *Mixing Method I.*

$[A]_0 = 0.1 M$ $\alpha = 4$
$(V_B)_0 = 0.25 \times (V_A)_0;$ $(V_A)_0 = 20$ ml

From the results presented it is easy to see that a disguise of the substrate selectivity by mixing would be sufficient in itself to explain the high yield of dinitro products in fast nitrations. Therefore, from the experimental evidence there is no need to postulate a new mechanism as *Olah* [7] has done, to account for the increased dinitration. If the nitro group of monosubstituted aromatic nitro compounds (which is a polar n-donor group) can readily interact with excess nitronium ion and subsequently cause increased dinitration by transferring the nitro group to a favored *ortho* position, such an effect would evidently be too small to account for the high extent of disubstitution found experimentally. The experimental results in Fig. 2 suggest that even for the positional selectivity such an effect would be a moderate one: The nitration of mononitro prehnitene is only about 2 times faster than the nitration of mononitro durene.

4. Experimental. – *Purification of Materials.* Nitromethane was distilled twice under N_2 from P_2O_5. Aromatic compounds were recrystallized or distilled. Nitronium salts: commercial product (*Ozark Mahoning Co.*) was dried under vacuum over P_2O_5 and stored in a desiccator. Purity: $82 \pm 2\%$.

Preparation of the Reagent Solutions. All operations were carried out as described in [9].

Nitration Experiments. – In all experiments the same thermostated ($20.0° \pm 0.1°$) reaction vessel was used. It was a threenecked flask of 100 ml volume and 60 cm diameter. Before use the flask was dried under vacuum and purged with dry nitrogen gas to exclude moisture. The stirrer used had a symmetrical fourwing propeller of 23 mm diameter; the rate of stirring was 1000 rev./min.

One of the reagent solutions was transferred into the vessel, while the other solution was added by means of a pipette (always at the same drop rate). Samples were taken by syringe after the appropriate time interval and quenched with ammonia gas. In experiments carried out in the presence of water, the weighed amount of water was added to the nitronium salt solution two minutes before the reaction was started.

Analysis of the Product. – The product distribution was analysed by gas chromatography with naphthalene as internal standard. The column has been described [5].

Kinetic Results:

Table 1. *Nitration of Durene with Nitronium Hexafluorophosphate in Nitromethane* (20.0°)
A: Durene; R: Mononitrodurene; S: Dinitrodurene; Mixing Method: I

Reaction time in min	Yield in mol-% related to initial moles of $NO_2^{\oplus}PF_6^{\ominus}$ $[A]_0 = 0.1M$; $(V_A)_0 = 20$ ml; $(V_R)_0 = 5$ ml; $\alpha = 4$					
	$[A]_0 : [NO_2^{\oplus}PF_6^{\ominus}]_0 : [H_2O]_0 = 1:4:0$			$[A]_0 : [NO_2^{\oplus}PF_6^{\ominus}]_0 : [H_2O]_0 = 1:4:1^1/_2$		
	A	R	S	A	R	S
0.25	43.6	2.6	39.3	63.6	22.2	12.1
1	43.2	2.6	39.3	52.0	30.7	12.1
2	–	–	–	46.4	35.8	12.1
10	43.0	2.6	39.3	30.8	51.1	12.1
30	42.4	2.6	39.3	22.9	56.0	12.1

Influence of Water on the Product Distribution:

Table 2. *Nitration of the Aromatic Compound* **A** *with Nitronium Hexafluorophosphate* (**B**) *in Nitromethane* (20.0°) *in the presence of Water*

5 ml of reactant solution **B** was added to 20 ml of reactant solution **A** by the Mixing Method I ($\alpha = 4$)

$N = 2(\text{mol-\% } \mathbf{S}) + \text{mol-\% } \mathbf{R}$ at $[\mathbf{B}]_0 = 0.40\,\text{M}$ and $[H_2O]_0 = 0.0\,\text{M}$

$$X_S = \frac{2(\text{mol-\% } \mathbf{S})}{N} \qquad \xi_{NO_2^\oplus} = \frac{[NO_2^\oplus]_{ex}}{[NO_2^\oplus PF_6^\ominus]_0}$$

$[NO_2^\oplus]_{ex}$: extrapolated apparent nitronium ion concentration from Fig. 2. All mol-% are related to the initial moles of $NO_2^\oplus PF_6^\ominus$.

$[NO_2^\oplus PF_6^\ominus]_0$ M	$\dfrac{[H_2O]_0}{[NO_2^\oplus PF_6^\ominus]_0}$	mol-% $\mathbf{S}$	N mol-%	X_S	$[NO_2^\oplus]_{ex}$ M	$\xi_{NO_2^\ominus}$
Durene: $[\mathbf{A}]_0 = 0.1\,\text{M}$						
0.40	0	39.30 ± 0.40	81.2	0.97	0.400	1.00
	1	30.90 ± 0.80		0.76	0.110	0.28
	1.5	12.10 ± 0.40		0.29	0.040	0.10
	2	1.25 ± 0.10		0.03	0.016	0.04
0.08	0	24.90 ± 0.90		0.61	0.080	1.00
	0.5	11.70 ± 0.60		0.30	0.042	0.53
	1.5	0.08 ± 0.02		0.01	0.008	0.10
0.04	0	11.60 ± 0.60		0.29	0.040	1.00
	0.5	3.60 ± 0.30		0.09	0.023	0.58
	0.75	1.38 ± 0.05		0.04	0.017	0.42
	1	0.24 ± 0.03		0.01	0.011	0.28
Prehnitene: $[\mathbf{A}]_0 = 0.1\,\text{M}$						
0.40	0	39.60 ± 0.9	81.7	0.97	0.400	1.00
	1	36.90 ± 1.0		0.90	0.100	0.26
	1.5	17.60 ± 1.2		0.43	0.028	0.07
	2	1.35 ± 0.2		0.04	0.008	0.02
0.08	0	36.40 ± 0.8		0.89	0.080	1.00
	0.5	27.70 ± 0.7		0.68	0.043	0.54
0.04	0	26.60 ± 1.1		0.65	0.040	1.00
	0.25	21.20 ± 0.8		0.52	0.032	0.80
	0.5	13.90 ± 0.6		0.34	0.024	0.60
	0.75	7.40 ± 0.5		0.18	0.016	0.40
	1	2.80 ± 0.4		0.07	0.009	0.23
0.02	0	11.30 ± 0.7		0.28	0.020	1.00
	0.5	3.60 ± 0.9		0.09	0.010	0.50

Determination of the Nitronium Ion Concentration by IR.: The apparent nitronium ion concentration $[NO_2^{\oplus}]_{IR}$ was determined from the optical density of the $NO_2^{\oplus}$-band at 2380 cm^{-1} with the help of a calibration curve. This curve was constructed using water-free nitronium salt. The optical density measurements were made in an AgCl-cell.

Table 3. *Nitronium Ion Concentration in Solutions of Nitronium Hexafluorophosphate in the presence of Water in Nitromethane* (20.0°)

IR.-Measurements at 2380 cm^{-1}

$$\xi_{NO_2^{\oplus}} = \frac{[NO_2^{\oplus}]_{IR}}{[NO_2^{\oplus}PF_6^{\ominus}]_0}$$

$[NO_2^{\oplus}PF_6^{\ominus}]_0 = 0.1 M$

$\dfrac{[H_2O]_0}{[NO_2^{\oplus}PF_6^{\ominus}]_0}$	$[NO_2^{\oplus}]_{IR}$ M	$\xi_{NO_2^{\oplus}}$
0	0.100	1.00
0.25	0.079	0.79
0.5	0.059	0.59
0.75	0.042	0.42
1	0.028	0.28
1.5	0.009	0.09
2	0.003	0.03

Correction of the Nitronium Ion Concentration for the Water Content of Nitromethane:

Table 4. *Water Correction for* $[B]_0$

B: $NO_2^{\oplus}PF_6^{\ominus}$; $[B]_0^* = \xi_{NO_2^{\oplus}}[B]_0$

Mean Water: $[H_2O]_0 = 5 \times 10^{-3} M$ determined by *Karl-Fischer*-titration

For the definition of $\xi_{NO_2^{\oplus}}$, compare Table 2

$[B]_0$ M	$\dfrac{[H_2O]_0}{[NO_2^{\oplus}PF_6^{\ominus}]_0} = \dfrac{5 \times 10^{-3}}{[B]_0}$	$\xi_{NO_2^{\oplus}}$	$[B]_0^*$ M
6×10^{-1}	0.00833	1.00	6.00×10^{-1}
4×10^{-1}	0.0125	0.99	3.96×10^{-1}
2×10^{-1}	0.025	0.98	1.96×10^{-1}
1×10^{-1}	0.05	0.96	9.6×10^{-2}
8×10^{-2}	0.0625	0.95	7.6×10^{-2}
6×10^{-2}	0.0833	0.93	5.6×10^{-2}
5×10^{-2}	0.1	0.91	4.6×10^{-2}
4×10^{-2}	0.125	0.89	3.6×10^{-2}
3×10^{-2}	0.166	0.85	2.55×10^{-2}
2×10^{-2}	0.25	0.79	1.6×10^{-2}
1×10^{-2}	0.5	0.59	5.9×10^{-3}
5×10^{-3}	1	0.28	1.4×10^{-3}

Dependence of the Selectivity on the Mixing Method and the Parameter *E:

Table 5. *Nitration of Durene* (**A**) *with* $NO_2^{\oplus} PF_6^{\ominus}$ (**B**) *in Nitromethane* (20.0°). *E = 1; for the definitions of N, X_S and $[B]_0^*$ see Tables 2 and 4, respectively. For the different mixing methods, compare text

Mixing method	$[A]_0$ M	$[B]_0$ M	$[B]_0^*$ M	R mol-%	S mol-%	N mol-%	X_S
	Vol. of solution **A**: 10 ml; Vol. of solution **B**: 10 ml; $\alpha = 1$						
I	2×10^{-1}	2×10^{-1}	1.96×10^{-1}	9.2 ± 0.8	37.6 ± 0.8	84.4	0.89
	1×10^{-1}	1×10^{-1}	9.6×10^{-2}	12.2 ± 0.4	33.3 ± 0.9		0.79
	5×10^{-2}	5×10^{-2}	4.6×10^{-2}	14.4 ± 0.4	26.8 ± 1.1		0.64
	2×10^{-2}	2×10^{-2}	1.6×10^{-2}	21.1 ± 0.6	16.7 ± 0.7		0.40
	5×10^{-3}	5×10^{-3}	1.4×10^{-3}	8.9 ± 0.5	2.2 ± 0.5		0.05
II	2×10^{-1}	2×10^{-1}	1.96×10^{-1}	1.2 ± 0.1	41.8 ± 0.6	84.8	0.98
	1×10^{-1}	1×10^{-1}	9.6×10^{-2}	1.4 ± 0.1	39.6 ± 1.0		0.93
	5×10^{-2}	5×10^{-2}	4.6×10^{-2}	1.6 ± 0.1	36.0 ± 1.2		0.85
	2×10^{-2}	2×10^{-2}	1.6×10^{-2}	4.8 ± 1.2	25.9 ± 0.4		0.61
	1×10^{-2}	1×10^{-2}	5.9×10^{-3}	10.1 ± 0.8	11.4 ± 0.7		0.27
	5×10^{-3}	5×10^{-3}	1.4×10^{-3}	14.3 ± 0.4	2.6 ± 0.7		0.06
III	2×10^{-1}	2×10^{-1}	1.96×10^{-1}	5.4 ± 0.1	37.7 ± 0.4	80.8	0.93
	5×10^{-2}	5×10^{-2}	4.6×10^{-2}	5.7 ± 0.3	28.6 ± 0.9		0.70
	2×10^{-2}	2×10^{-2}	1.6×10^{-2}	6.4 ± 0.4	18.2 ± 0.9		0.45
	1×10^{-2}	1×10^{-2}	5.9×10^{-3}	12.3 ± 0.7	9.0 ± 0.8		0.22
	5×10^{-3}	5×10^{-3}	1.4×10^{-3}	8.7 ± 0.5	2.3 ± 0.4		0.05
	Vol. of solution **A**: 20 ml; Vol. of solution **B**: 5 ml; $\alpha = 4$						
I	1×10^{-1}	4×10^{-1}	3.96×10^{-1}	2.6 ± 0.2	39.3 ± 0.5	81.2	0.97
	5×10^{-2}	2×10^{-1}	1.96×10^{-1}	8.1 ± 0.2	36.1 ± 0.7		0.89
	2.5×10^{-2}	1×10^{-1}	9.6×10^{-2}	11.0 ± 0.2	31.5 ± 0.3		0.78
	1×10^{-2}	4×10^{-2}	3.6×10^{-2}	12.6 ± 0.4	23.8 ± 0.5		0.59
	2.5×10^{-3}	1×10^{-2}	5.9×10^{-3}	16.4 ± 0.6	8.2 ± 0.1		0.20
II	1×10^{-1}	4×10^{-1}	3.96×10^{-1}	1.1 ± 0.1	37.1 ± 0.4	75.3	0.98
	2.5×10^{-2}	1×10^{-1}	9.6×10^{-2}	1.5 ± 0.1	35.6 ± 0.6		0.94
	1.5×10^{-2}	6×10^{-2}	5.6×10^{-2}	2.2 ± 0.7	30.3 ± 1.3		0.80
	1×10^{-2}	4×10^{-2}	3.6×10^{-2}	25.4 ± 3	15.9 ± 0.7		0.42
	2.5×10^{-3}	1×10^{-2}	5.9×10^{-3}	6.3 ± 0.9	2.3 ± 0.6		0.06
III	1×10^{-1}	4×10^{-1}	3.96×10^{-1}	2.3 ± 0.1	38.7 ± 1.4	79.7	0.97
	2.5×10^{-2}	1×10^{-1}	9.6×10^{-2}	4.2 ± 0.1	31.8 ± 0.6		0.80
	1×10^{-2}	4×10^{-2}	3.6×10^{-2}	7.1 ± 0.5	24.0 ± 0.8		0.60
	5×10^{-3}	2×10^{-2}	1.6×10^{-2}	13.4 ± 0.6	16.2 ± 0.5		0.41

Table 6. *Nitrations of Aromatic Compounds (A) with* $NO_2^\oplus PF_6^\ominus$ *(B) in Nitromethane* (20.0°). Mixing Method I; $[A]_0 = 0.1\text{M}$; $a = 4$. For definitions of N, X_S and $[B]_0^*$, see Tables 2 and 4, respectively.

Aromatic Compound A	•E	$[B]_0$ M	$[B]_0^*$ M	R mol-%	S mol-%	A mol-%	X_S
Durene	1	4×10^{-1}	3.96×10^{-1}	2.6 ± 0.2	39.3 ± 0.4	81.2	0.97
	4	1×10^{-1}	9.6×10^{-2}	13.4 ± 0.3	30.3 ± 0.6		0.75
	5	8×10^{-2}	7.6×10^{-2}	20.8 ± 0.9	25.2 ± 0.7		0.62
	6.66	6×10^{-2}	5.6×10^{-2}	17.3 ± 0.5	19.1 ± 0.8		0.47
	10	4×10^{-2}	3.6×10^{-2}	25.6 ± 0.8	11.2 ± 0.6		0.28
	20	2×10^{-2}	1.6×10^{-2}	22.9 ± 0.4	2.9 ± 0.3		0.07
Prehnitene	1	4×10^{-1}	3.96×10^{-1}	2.5 ± 0.4	39.6 ± 0.7	81.7	0.97
	5	8×10^{-2}	7.6×10^{-2}	7.9 ± 0.6	36.7 ± 0.8		0.90
	10	4×10^{-2}	3.6×10^{-2}	26.7 ± 0.9	27.0 ± 0.7		0.66
	13.33	3×10^{-2}	2.55×10^{-2}	39.6 ± 0.6	20.3 ± 0.9		0.50
	20	2×10^{-2}	1.6×10^{-2}	40.1 ± 0.8	12.3 ± 0.8		0.30
	40	1×10^{-2}	5.9×10^{-3}	39.8 ± 0.9	5.0 ± 0.3		0.12

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