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288. Chemical Selectivities Disguised by Mass Diffusion. IV. Mixing-Disguised Nitrations of Aromatic Compounds with Nitronium Salts1)2)

4th Communication on the Selectivity of Chemical Processes1)

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Summary

The disguise of the intrinsic selectivity of competitive, consecutive reaction systems by the mixing process is demonstrated experimentally using the fast nitration of a number of aromatic compounds with nitronium salts in nitromethane. The measured product distributions were compared with the distributions predicted from our mixing-reaction model developed previously [2] [4]. This comparison enabled the relative intrinsic rate constants for the second nitration step of the aromatic compounds investigated to be determined.

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1) Part III and 3rd Communication *cf.* [4].

2) Results taken from the PhD. thesis of *F. Nabholz* [1].

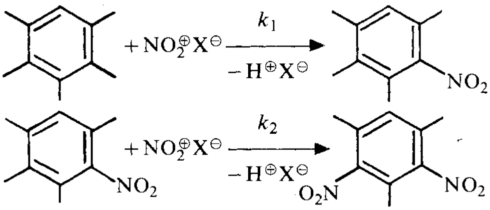
1. Introduction. - The observed kinetics and the product distribution of a chemical reaction can depend on the ratio of the diffusion rate and the rate of the chemical events. This is the case if this ratio is small, for example in mixing-disguised or encounter rate-limited fast reactions. The disguising effect of diffusion on the substrate and on the positional selectivity has been discussed elsewhere [2].

In Parts I and III of this series [2] [4] the general behaviour and the dependence of the product distribution on the coupling of the mass diffusion with the chemical reaction during the mixing process have been simulated and discussed in detail. In Part II of this series [3] this dependence has been demonstrated experimentally using the fast nitration of prehnitene and durene with nitronium salts in nitromethane.

In the present paper further experimental evidence for mixing-dependent product distributions in nitration with nitronium salts of a number of aromatic hydrocarbons is presented and discussed.

The reaction systems investigated are represented by *Scheme 1:*

Scheme 1



$X^{\ominus} = PF_6^{\ominus}, BF_4^{\ominus}$ *etc.*

A similar scheme can be written for the other compounds investigated, namely prehnitene, isodurene and durene (1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetramethylbenzene) and *m*- and *p*-xylene. Following the nomenclature in Part I [2] and Part III [4]:

Reactant *A*: Aromatic compound; Product *R*: Mononitro product
Reactant *B*: Nitronium ion; Product *S*: Dinitro product

2. The Nitrating System. - In the present investigation the nitration was performed with nitronium hexafluorophosphate in nitromethane. The general characteristics of this nitrating system have been reported elsewhere [3]. Nitrosonium salt impurity in the nitronium salt was determined by a modification of *Shinn*'s method [5]. The water which remains in nitromethane even after careful drying was determined by the *Karl-Fischer*-method. Since the rate of formation of nitronium ions from nitric acid in nitromethane is slower than the mixing rate [3] only the *effective* nitronium ion concentration is important for appraising the mixing-dependent product distribution. This initial, effective concentration of the nitronium ions has been calculated either from the content of the nitro groups in the products formed immediately after mixing or from the weighed amount of the commercially available nitronium salt corrected for the nitrosonium salt impurity and the water content of the reaction medium. Both determinations agreed within experimental error.

3. The Mixing-Disguised Selectivity. - The product distributions in the nitration of several aromatic compounds have been determined under identical experimental conditions. Of the various methods of mixing available[3]) the method in which the nitronium salt solution was quickly poured into the solution of the aromatic compound was employed. Vigorous stirring ensured that the macroscopic eddy-diffusion (dispersion) was fast compared to the molecular mass diffusion within the eddies. Furthermore, the stirring rate was kept constant in all experiments, thus ensuring that the eddies formed had the same mean radius.

In Parts I and III [2] [4] of this series it was demonstrated that the selectivity behaviour observed in second-order consecutive reactions influenced by the mixing rate is fully described by the four parameters $\boldsymbol{E}$, $\boldsymbol{\alpha}$, $\varphi^2_{\mathrm{B},1}$, $\varphi^2_{\mathrm{B},2}$ and the initial and boundary conditions.

$$\boldsymbol{E}=\frac{[A]_0}{[B]_0}; \qquad \varphi^2_{\mathrm{B},1}=\frac{\bar{\mathrm{R}}^2 k_1 [B]_0}{\mathrm{D}}; \qquad \varphi^2_{\mathrm{B},2}=\frac{\bar{\mathrm{R}}^2 k_2 [B]_0}{\mathrm{D}}; \qquad \boldsymbol{\alpha}=\frac{\mathrm{V_A}}{\mathrm{V_B}}.$$

$[A]_0$	initial concentration of A before mixing $[M]$;
$[B]_0$	initial concentration of B before mixing $[M]$;
$\bar{\mathrm{R}}$	mean radius of the eddies [cm];
D	mean diffusion coefficient of the reactants [$\mathrm{cm^2/s}$];
k_1, k_2	intrinsic second-order rate constants of the first and second reaction step, respectively (cf. *Scheme 1*) [$\mathrm{M^{-1}s^{-1}}$];
$\mathrm{V_A}$, $\mathrm{V_B}$	volume of the solution of reactant A and B respectively [1].

Figure 1 shows the experimental selectivity curves for the consecutive nitration of several aromatic compounds[4]). They are compared with the predicted curves calculated according to version I (*Fig. 1* (I)) and to version II (*Fig. 1* (II)) of the mixing-reaction model presented earlier [4]. The relative yields $\mathrm{X_S}$ of the dinitro products S are plotted against $\boldsymbol{E}$. $\mathrm{X_S}$ is defined as the fraction of reagent B which has reacted after 100% conversion to product S.

The selectivity curves all lie on S-shape curves whose positions along the $\boldsymbol{E}$-axis depend, for a given $\boldsymbol{\alpha}$, only on the values of $\boldsymbol{E}\,\varphi^2_{\mathrm{B},2}$ and $\varphi^2_{\mathrm{B},1}/\varphi^2_{\mathrm{B},2}$ (i.e. k_1/k_2). For $\varphi^2_{\mathrm{B},1}/\varphi^2_{\mathrm{B},2} \geqslant 100$ and a given $\boldsymbol{\alpha}$, these positions are essentially determined only by the values of $\boldsymbol{E}\,\varphi^2_{\mathrm{B},2}$. This can be concluded from the calculations discussed previously (*Fig. 1* in [4]). Since it can be assumed that $k_1/k_2 > 100$, in the nitration of aromatic compounds the experimental curves *(Fig. 1)* can be fitted to the corresponding curves calculated for $\varphi^2_{\mathrm{B},1}/\varphi^2_{\mathrm{B},2} = 100$. A comparison of the calculated data with the experimental results demonstrates the usefulness of version II of the mixing-reaction model to predict the product distribution in mixing-disguised consecutive nitration steps. The relative k_2-values for different aromatic substrates can be found from the relative positions of the respective selectivity curves. They are summarized in *Table 1*. If one of the intrinsic k_2-values can be measured experimentally, *e.g.* in a rapid mixing chamber, the others can be calculated from

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[3]) The influence of different mixing methods on the selectivity has been discussed in [3].

[4]) The experimental values are listed in *Table 2*.

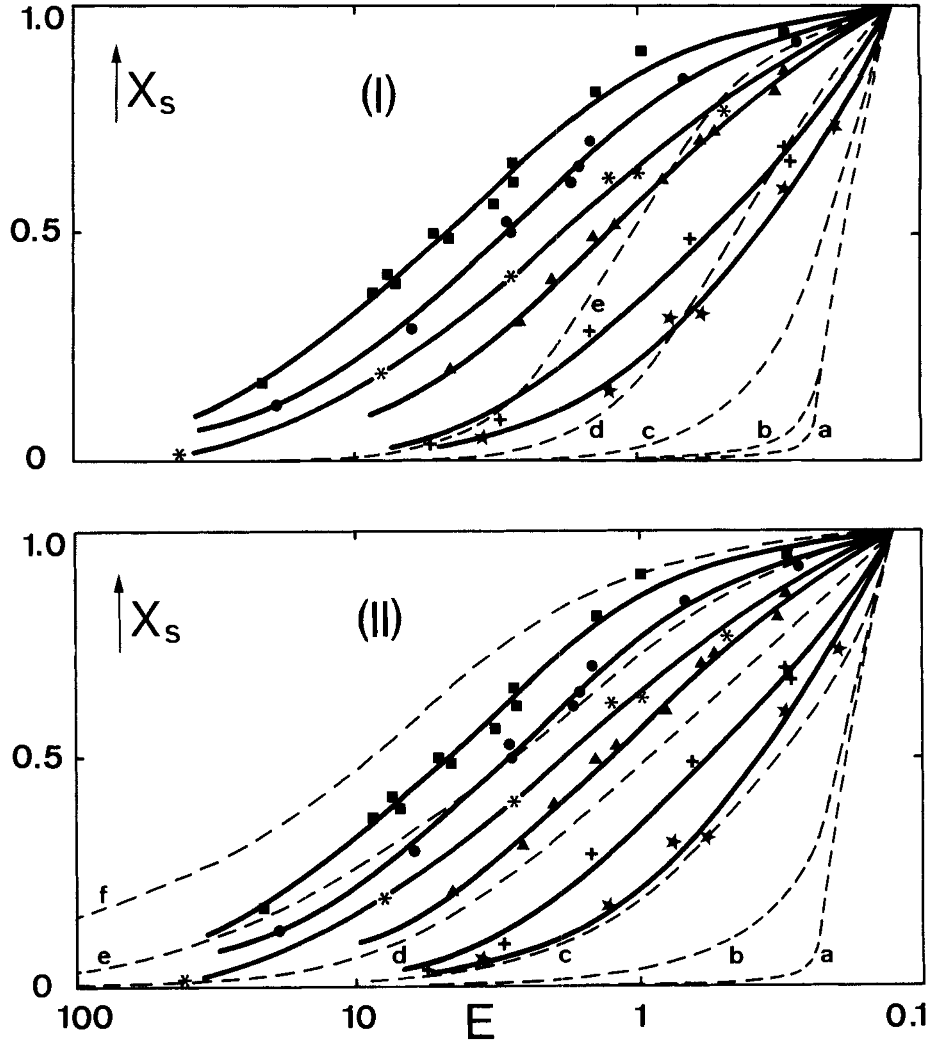

Fig. 1. *Experimental and calculated relative yields X_S as a function of E for the consecutive mixing-disguised nitration of several aromatic compounds.* Experimental values [1] [3]: ★ (*p*-xylene); + (*m*-xylene); ▲ (mesitylene); ∗ (isodurene); ● (durene); ■ (prehnitene)

Calculated curves (---): (I) Version I; (II) Version II

$\varphi^2_{B,1}/\varphi^2_{B,2} = 100$; $\alpha = 4$

Parameter values ($E\,\varphi^2_{B,2}$): a ($\ll 1$, reaction controlled); b(1); c(10); d(100); e(1000); f(10000)

the relative k_2-values *(Table 1)*. Furthermore, with the help of a measured k_2-value and the corresponding $E\,\varphi^2_{B,2}$-value the mean eddy size $\bar{R}$ can be calculated:

$$\bar{R} = \left(\frac{D\,E\,\varphi^2_{B,2}}{[A]_0\,k_2}\right)^{1/2}.$$

For mesitylene:

$[A]_0 = 0.1\,\text{M}$; $E\varphi^2_{B,2} = 200$; $k_2 = 6.6 \times 10^3\,\text{M}^{-1}\,\text{s}^{-1}$ (Ref. [6]); $D \approx 10^{-5}\,\text{cm}^2/\text{s}$;
$\bar{R} \approx 1.7 \times 10^{-3}$ cm.

The value of $\bar{R}$ can also be estimated from the theory of turbulence [7] using the impeller *Reynolds* number, Re_G, and the propeller diameter, l_G, of the stirrer.
The appropriate values for the experimental set up used are:

$Re_G = 20000$; $l_G = 2.4$ cm; $\bar{R} \approx l_G(Re_G)^{-3/4} \approx 1.4 \times 10^{-3}$ cm.

The $\bar{R}$-values are in reasonable agreement.

Table 1. *Estimated relative and intrinsic rate constants* k_2 *of the second step of the nitration of various aromatic compounds*

Aromatic compound	$E\varphi^2_{B,2}$	k_2 (rel.)	k_2 (cal.)[5] $[\text{M}^{-1}\text{s}^{-1}]$
Prehnitene	3000	300	99000
Durene	1000	100	33000
Isodurene	400	40	13200
Mesitylene	200	20	6600
m-Xylene	30	3	990
p-Xylene	10	1	330

In the case of *m*-xylene the interpretation of the experimental data is complicated by the fact that in the primary step two mononitro compounds are formed, namely 2-nitro- and 4-nitro-*m*-xylene in a ratio of 1:5. Therefore, the secondary nitration step has to be treated as a parallel reaction and as such is also dependent on mixing effects [2] [4]. However, since the reactivity of both mononitro isomers for the second nitration step is similar (3.5:1), in a first approximation, this additional mixing effect can be neglected [1] [8].

No conclusions from the selectivity curves presented can be drawn about the intrinsic rate constant of the primary nitration step. However, it is expected that this nitration step occurs at, or close to, the encounter rate.

4. Conclusion.

From the results presented above it can be concluded that the product distributions of mixing-disguised consecutive nitration steps can adequately be described by version II of our mixing-reaction model discussed elsewhere [4]. This model explains why, in second-order consecutive reactions in which the intrinsic rate constants follow the sequence $k_1 > k_2 > etc.$, the subsequent products are preferentially formed. Therefore, there is no need to postulate a new mechanistic route for the nitration to explain the high yield of dinitro products.

The present method of analysing the experimental results has proved very useful in the determination of the relative *intrinsic* reactivities of highly reactive substrates.

Partial financial support of this investigation by the *Swiss National Science Foundation* (Project Nr. 2.620.72) and by *Ciba-Geigy AG., Basel* is gratefully acknowledged.

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[5] Calculated, using the measured k_2-value for mesitylene [6] as reference.

Table 2. *Nitration of Aromatic Compounds* (A) *with Nitronium Hexafluorophosphate* (B) *in Nitromethane* (20.0°). $V_A = 20$ ml; $V_B = 5$ ml; $[A]_0 = 0.1$ M; stirring rate: 1000 rev./min.

Aromatic Compound *A*	$[B]_0$ *M*	*A* mol-%	*R* mol-%	*S* mol-%	$[B]_{0,\mathrm{eff}}$ *M*	*E*	X_S
Prehnitene[6]	4.0×10^{-1}	39.0	5.40	39.4	3.37×10^{-1}	0.297	0.936
	1.0×10^{-1}	81.5	2.19	11.9	1.04×10^{-1}	0.962	0.916
	8.0×10^{-2}	79.5	3.36	7.30	7.18×10^{-2}	1.39	0.813
	6.0×10^{-2}	85.5	3.12	3.00	3.65×10^{-2}	2.74	0.657
	4.0×10^{-2}	91.0	3.40	2.80	3.64×10^{-2}	2.75	0.616
	4.0×10^{-2}	93.7	3.57	2.73	3.61×10^{-2}	2.77	0.605
	4.0×10^{-2}	80.5	3.24	2.17	3.03×10^{-2}	3.30	0.574
	4.0×10^{-2}	89.1	2.36	1.22	1.92×10^{-2}	5.21	0.509
	3.0×10^{-2}	91.3	3.00	1.46	2.37×10^{-2}	4.22	0.493
	2.0×10^{-2}	91.7	1.92	0.68	1.31×10^{-2}	7.63	0.415
	2.0×10^{-2}	92.8	2.12	0.69	1.40×10^{-2}	7.14	0.395
	2.0×10^{-2}	95.9	1.80	0.53	1.14×10^{-2}	8.77	0.370
	1.0×10^{-2}	98.9	0.97	0.10	4.70×10^{-3}	21.3	0.176
Durene[6]	4.0×10^{-1}	50.4	6.64	42.3	3.65×10^{-1}	0.274	0.927
	2.0×10^{-1}	72.9	5.75	15.5	1.47×10^{-1}	0.680	0.843
	1.0×10^{-1}	83.8	4.82	5.84	6.60×10^{-2}	1.52	0.708
	8.0×10^{-2}	82.3	5.42	4.90	6.09×10^{-2}	1.64	0.644
	8.0×10^{-2}	88.5	5.58	4.48	5.82×10^{-2}	1.72	0.616
	6.0×10^{-2}	91.1	4.04	2.29	3.45×10^{-2}	2.90	0.531
	4.0×10^{-2}	93.8	4.37	2.24	3.54×10^{-2}	2.82	0.506
	2.0×10^{-2}	96.9	2.75	0.57	1.56×10^{-2}	6.43	0.292
	1.0×10^{-2}	97.4	1.13	0.08	5.20×10^{-2}	19.2	0.128
Isodurene	3.22×10^{-1}	56.3	12.9	20.2	2.13×10^{-1}	0.469	0.758
	1.61×10^{-1}	71.6	9.61	8.01	1.03×10^{-1}	0.975	0.625
	1.29×10^{-1}	74.6	7.79	6.16	8.05×10^{-2}	1.24	0.613
	6.44×10^{-2}	82.8	5.52	1.80	3.65×10^{-2}	2.74	0.395
	3.22×10^{-2}	89.4	2.56	0.29	1.26×10^{-2}	7.97	0.185
	1.61×10^{-2}	95.6	0.64	0	0.25×10^{-2}	39.3	0
Mesitylene	4.0×10^{-1}	43.9	12.5	34.7	3.28×10^{-1}	0.305	0.847
	4.0×10^{-1}	44.9	14.4	31.1	3.06×10^{-1}	0.327	0.812
	2.4×10^{-1}	61.3	12.6	16.8	1.85×10^{-1}	0.541	0.727
	2.0×10^{-1}	66.0	12.3	14.9	1.68×10^{-1}	0.594	0.708
	1.6×10^{-1}	71.1	11.8	9.30	1.22×10^{-1}	0.822	0.612
	1.0×10^{-1}	75.3	9.78	5.48	8.30×10^{-2}	1.21	0.520
	1.0×10^{-1}	81.4	8.88	4.28	6.98×10^{-2}	1.43	0.491
	6.0×10^{-2}	85.5	7.59	2.49	5.03×10^{-2}	1.99	0.396
	6.0×10^{-2}	84.6	6.56	1.47	3.80×10^{-2}	2.63	0.309
	4.0×10^{-2}	87.7	4.65	0.60	2.34×10^{-2}	4.27	0.205
m-Xylene[7]	4.0×10^{-1}	47.5	26.1	29.0	3.36×10^{-1}	0.298	0.690
	4.0×10^{-1}	50.5	27.5	28.9	3.41×10^{-1}	0.293	0.678
	2.0×10^{-1}	67.0	18.6	9.05	1.47×10^{-1}	0.680	0.493
	1.0×10^{-1}	83.0	11.8	2.40	8.03×10^{-2}	1.25	0.290
	6.0×10^{-2}	85.2	7.20	0.41	3.20×10^{-2}	3.13	0.101
	4.0×10^{-2}	97.5	4.44	0.10	1.86×10^{-2}	5.38	0.043
p-Xylene[7]	6.0×10^{-1}	23.0	30.6	45.8	4.88×10^{-1}	0.205	0.749
	4.0×10^{-1}	41.5	33.1	24.8	3.31×10^{-1}	0.302	0.600
	2.0×10^{-1}	66.1	27.4	6.70	1.63×10^{-1}	0.613	0.328
	1.6×10^{-1}	71.6	22.4	5.08	1.30×10^{-1}	0.769	0.312
	1.0×10^{-1}	86.3	16.2	1.60	7.77×10^{-2}	1.29	0.165
	4.0×10^{-2}	96.3	6.43	0.19	2.72×10^{-2}	3.68	0.056

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[6] Results taken in part from [3], recalculated according to the definition of X_S used in this paper.

[7] Results taken in part from [6].

5. Experimental Part. - *Materials: Nitromethane* (*Fluka,* puriss.) was distilled three times in N_2 from P_2O_5. The water content was determined using the method of *Karl-Fischer.*

Aromatic Compounds were distilled or recrystallized.

Nitronium Hexafluorophosphate (*Cationics Inc.,* Cleveland, Ohio) was dried for at least 15 h under high vacuum over P_2O_5 and stored in a desiccator. The salt contained 17% impurity of nitrosonium salt which was determined by a modification of *Shinn*'s method [5].

Nitration Experiments. - In all experiments the same thermostated ($20.0° \pm 0.1°$) reaction vessel was used. It was a three-necked flask of 100 ml volume and 6.5 cm diameter. Before use the flask was washed with acetone/ether, dried under vacuum and purged with dry nitrogen gas to exclude moisture. The stirrer used had a symmetrical three-wing propeller of 2.4 cm diameter and 1.5 cm height. The blades were arranged at an angle of 20° with respect to the rotational axis. The rate of stirring was always 1000 rev. min^{-1}.

All reagent solutions were prepared in a dry box (Typ HE-63-P *Pedatrol,* Vacuum/Atmospheres Corp.) as by the method described in [9].

The solution of the aromatic compound was transferred into the reaction vessel which at the same time was purged with dry nitrogen gas. The solution of the nitronium salt was added to the stirred solution by means of a pipette in such a way that the feed stream entered directly at the tip of the wings of the stirrer (*i.e.* the place of heighest turbulence) and the total addition time was 1 s. Samples were taken by syringe after the appropriate time interval and quenched with ammonia gas.

Analysis of the Product. The product distribution was analysed by gas chromatography (*Varian Aerograph* 1440-1, FID) with naphthalene as internal standard. The column was a 1/8" steel tube of 4 m length filled with Silicon Gum Rubber SE 52 (5% Phenyl) on 50-80 mesh Chromosorb G. The operating temperature was 180-220°. The analysis gave the amounts of the products, (*R*) and (*S*), in mol-% of the initial amount of *A*. The effective, initial concentration of the nitronium ions, $[B]_{0,\text{eff}}$, was calculated as follows:

$$[B]_{0,\text{eff}} = \boldsymbol{\alpha}[A]_0\{(R) + 2(S)\}/100.$$

Only minor amounts of by-products were observed. The values for $[B]_{0,\text{eff}}$ agreed with the weighed amounts of the nitronium salt corrected for the nitrosonium salt impurity (17%) and the water content of the solvent.

The relative yield X_S was calculated as the fraction of the reagent *B* which has reacted after 100% conversion to the product *S*. An estimation of the experimental error gives $\Delta X_S = \pm 0.05$.

Experimental Results are listed in *Table 2.*

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