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Aromatic Nitration. II.[1] Competitive Nitration of Toluene and Benzene in Organic Solvents

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Nitration is one of the most studied of electrophilic aromatic substitutions. Many papers and reviews have been published on the nitration of toluene,[2–7] some dealing with its nitration with nitric acid in organic solvents.[4b,5] The nitration of toluene and benzene with nitric acid in carbon tetrachloride has recently been studied by Coombes,[6] and Bonner *et al.*[7] However, their results differ and do not deal with isomer distribution.

In the present investigation the competitive nitration of toluene and benzene in various organic solvents has been carried out to obtain a closer insight into solvent effects on the nitration rate and isomer distribution.

Experimental

Material. Commercial benzene, toluene, nitrobenzene, *o*-, *m*-, and *p*-nitrotoluenes of the highest purity were used. Their putities were checked by vapor phase chromatography (vpc) on a column packed with 10% propylene glycol on Diasolid M at 170°C. Helium was used as a carrier gas. The solvents were purified prior to use.[8] The concentration of nitric acid was 99.67%.

Competitive Nitration. After 1.897 g of nitric acid (0.03 mol) had been added at a definite temperature to 40 ml of each solvent containing 1.562 g of benzene (0.02 mol) and 0.921 g of toluene (0.01 mol), the mixture was stirred for 24 hr and then was washed with three 100 ml portions of water and dried over calcium chloride. After the mixture had been filtered off, a certain amount of acetophenone was added as an internal standard. The mixture was concentrated and analyzed by vpc under the conditions described above. The values of $k_\mathrm{T}/k_\mathrm{B}$ were calculated by means of the equation:

$$\frac{k_\mathrm{T}}{k_\mathrm{B}} = \frac{\log T_0 - \log T_t}{\log B_0 - \log B_t} \tag{1}$$

where T_0 and B_0 are the initial amounts of toluene and benzene, respectively, and T_t and B_t the amounts of unreacted toluene and benzene, respectively, at time t when the reaction is stopped.[9,10]

The partial rate and selectivity factors were obtained from the following equations:[2a,11]

$$o_\mathrm{f}^\mathrm{T} = \frac{k_\mathrm{T}^\mathrm{o}}{k_\mathrm{B}} = \frac{k_\mathrm{T}}{(k_\mathrm{B}/6)} \times \frac{\%\ \mathrm{ortho}}{2 \times 100} \tag{2}$$

$$m_\mathrm{f}^\mathrm{T} = \frac{k_\mathrm{T}^\mathrm{m}}{k_\mathrm{B}} = \frac{k_\mathrm{T}}{(k_\mathrm{B}/6)} \times \frac{\%\ \mathrm{meta}}{2 \times 100} \tag{3}$$

$$p_\mathrm{f}^\mathrm{T} = \frac{k_\mathrm{T}^\mathrm{p}}{k_\mathrm{B}} = \frac{k_\mathrm{T}}{(k_\mathrm{B}/6)} \times \frac{\%\ \mathrm{para}}{100} \tag{4}$$

$$S_\mathrm{f} = \log \frac{p_\mathrm{f}^\mathrm{T}}{m_\mathrm{f}^\mathrm{T}} \tag{5}$$

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Table 1. Competitive nitration of toluene and benzene with nitric acid in various organic solvents

Solvent	Temp. °C	k_T/k_B	Isomer ratio			Partial rate factor			S_f	o/p
			o-	*m-*	*p-*	o_f^T	m_f^T	p_f^T		
CCl_4	30	2.31	58.9	4.4	36.7	4.08	0.30	5.08	1.228	1.60
	40	2.23	59.1	4.7	36.2	3.95	0.31	4.84	1.193	1.63
	50	2.15	58.2	4.9	36.9	3.75	0.31	4.76	1.186	1.57
n-C_6H_{14}	20	2.82	57.4	4.2	38.4	4.85	0.35	6.49	1.268	1.49
	30	2.50	56.7	4.7	38.6	4.25	0.35	5.79	1.218	1.46
	40	2.45	56.4	5.0	38.6	4.14	0.36	5.67	1.197	1.46
cyclo-C_6H_{12}	20	2.56	56.2	4.6	39.2	4.31	0.35	6.02	1.235	1.43
	30	2.44	57.3	4.6	38.1	4.19	0.33	5.57	1.227	1.50
	40	2.20	55.9	4.9	39.2	3.68	0.32	5.17	1.208	1.42
CH_2Cl_2	20	17.3	56.6	3.1	40.3	29.3	1.60	41.8	1.416	1.40
	30	15.8	56.3	3.8	39.9	26.6	1.80	37.8	1.322	1.41
CH_3NO_2	30	19.7	59.3	4.2	36.5	35.0	2.48	43.1	1.240	1.62
	40	17.7	58.3	4.8	36.9	30.9	2.54	39.2	1.188	1.57
	50	16.3	59.0	5.1	35.9	28.8	2.49	35.1	1.149	1.64
CH_3CN	50	13.8	59.1	5.0	35.9	24.4	2.07	29.7	1.156	1.64

Table 2. Summary of nitration of toluene and benzene

Reaction condition		k_T/k_B	Isomer ratio			Partial rate factor			S_f	o/p
			o-	*m-*	*p-*	o_f^T	m_f^T	p_f^F		
HNO_3[12] $HOAc-H_2O$	45°C	24.5	56.5	3.5	40.0	42	2.5	58	1.366	1.41
HNO_3[4b] CH_3NO_2	30°C	21	58.5	4.4	37.1	37	2.8	47	1.225	1.57
HNO_3[5] CH_3NO_2	25°C	21	61.7	1.9	36.4	38.9	1.3	45.8	1.547	1.69
$AcONO_2$[4b] Ac_2O	30°C	23	58.4	4.4	37.2	40	3.0	51	1.230	1.56
$AcONO_2$[5] Ac_2O	25°C	23	63.3	2.8	33.9	46.5	2.1	48.5	1.364	1.86
$AcONO_2$[12] Ac_2O	0°C	27	61.4	1.6	37.0	49.7	1.3	60.0	1.664	1.65
NO_2BF_4[3] $C_4H_8SO_2$	25°C	1.67	65.4	2.8	31.8	3.2	0.14	3.2	1.354	2.05
HNO_3[6] CCl_4	25°C	17.2	—	—	—	—	—	—	—	—
HNO_3[7] CCl_4	25°C	1.2	—	—	—	—	—	—	—	—

Results and Discussion

The results of the competitive nitration of toluene and benzene in non-polar or polar solvents are shown in Table 1. The results of previous works mainly related to the nitration in organic solvents are given in Table 2 for comparison. We see that the rate ratios (k_T/k_B) of nitration in the organic solvents studied have a value of about 20 in all cases except for the case of Olah *et al.*[3] and Bonner *et al.*[7] However, the result of the latter differs from that of Coombes,[6] although Coombes suggests that the discrepancy is due to heterogeneity. According to our results in carbon tetrachloride, *n*-hexane, and cyclohexane, the lower values of k_T/k_B were obtained. In the nitration of toluene involving an ideally strong electrophile, in which the π-complex formation is rate-determining, an *ortho* to *para* ratio of 2:1 and a lower value of k_T/k_B would be obtained.[3] The *ortho*/*para* ratios in the above three solvents are not so high as expected on the basis of the lower values of k_T/k_B in Table 1. All the partial rate factors of the *meta* position (m_f^T) in the above three solvents are below 1. The results are in line with those of Olah *et al.*[3]

Hughes *et al.*[4a] indicated by conductivity measurements that the self-dissociation of nitric acid is represented as follows:

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

They showed that according to Raman spectroscopic observations, anhydrous nitric acid contains approximately 1% of nitronium ion and solutions of nitric acid in organic solvents such as nitromethane contain no detectable amount of nitronium ion. On the other hand, in the nitration of aromatics with nitric acid in carbon tetrachloride, the rate dependence on nitric acid concentration was indicated by Coombes,[6] and Bonner *et al.*[7] to be an order of 5 or 6. Thus nitronium ion may not exist as free ion but as aggregate

Table 3. Relationship between dielectric constants and rate ratios

Solvent	ε (20°C)	k_T/k_B
Carbon tetrachloride	2.23	2.15— 2.31
n-Hexane	1.89	2.45— 2.82
Cyclohexane	2.02	1.75— 2.56
Methylene dichloride	9.08	15.8 —17.3
Nitromethane	35[a)]	16.3 —19.7
Acetonitrile	37.5	13.8

a) The value at 30°C.

such as $NO_2^+ \cdots NO_3^-$ or $NO_2^+ \cdots NO_3^- \cdot HNO_3$. This aggregation might partly correspond to the smaller value of the *ortho*/*para* ratios.

The relationships between dielectric constants and rate ratios are summarized in Table 3. This indicates that the more polar the solvent, the higher the substrate selectivity (k_T/k_B). The activation parameters are shown in Table 4. We see from Tables 1 and 4 that the values of k_T and ΔE_B are larger than those of k_B and ΔE_T, respectively. On the other hand, the values of $\Delta S_B^{\neq}$ are larger than those of $\Delta S_T^{\neq}$. Thus, toluene is nitrated faster with nitric acid than benzene ($k_T > k_B$), primarily depending upon the differences in activation energies with the compensating effects in the entropies of activation. It is concluded that in the competitive nitration of toluene and benzene with nitric acid in organic solvents, the polarity of solvents affects the relative rate constant (k_T/k_B) considerably.

Table 4. Activation parameter

Solvent	$\Delta E_B - \Delta E_T$ (kcal·mol^{-1})	$\Delta S_T^{\neq} - \Delta S_B^{\neq}$ (cal·mol^{-1}·deg^{-1})
Carbon tetrachloride	0.67	−0.56
n-Hexane	1.26	−2.3
Cyclohexane	1.35	−2.68
Nitromethane	1.83	−0.11