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Aromatic Nitration. III.[1] Competitive Nitration of Toluene and Benzene in Carbon Tetrachloride

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In the previous paper[2] we reported competitive nitration of toluene and benzene with nitric acid in several organic solvents, such as carbon tetrachloride, *n*-hexane, cyclohexane, methylene dichloride, and nitromethane. The rate ratios (k_T/k_B) were in the range of 2.0 to 3.2 in the first three solvents and in the range of 15.8 to 19.7 in the latter solvents. The reaction showed the high positional selectivities in all above solvents. In nitromethane at 30°C the ratio and the selectivity factor were 19.7 and 1.219, respectively. The results were similar to those obtained by Ingold *et al.*[3]

The results in the non-polar solvents (carbon tetrachloride, *n*-hexane, and cyclohexane) are contrary to the expectation that nitric acid in non-polar solvents is a weak electrophile. Therefore, in the present paper we have investigated the effects of concentrations of nitric acid, the polarity of mediums on the substrate (k_T/k_B) and positional selectivities (o/p) in the competitive nitration of toluene and benzene in carbon tetrachloride.

The results are shown in Table 1. With increasing amount of nitric acid, the positional selectivities (o/p) increased. The selectivity factors were comparatively low in comparing with those (about 1.2 to 1.3) obtained in the previous works.[4] The result, obtained when 0.12 mol of 75% nitric acid was used, is much similar to that of Olah *et al.*[3] This suggests that the system of nitric acid–carbon tetrachloride may become a strong electrophile.

Next, the results of the competitive nitration in a mixed solvent of carbon tetrachloride and nitromethane (1: 1 by volume) are shown in Table 2. These results are comparatively similar to that of Ingold *et al.*,[3]

TABLE 1. EFFECTS OF CONCENTRATIONS OF NITRIC ACID[a)]

HNO_3 Concn (%) (mol)	$\frac{k_T}{k_B}$	Isomer ratio (%)			Partial rate factor			S_f[b)]	$\frac{o}{p}$
		o-	*m*-	*p*-	o_f^T	m_f^T	p_f^T		
100 (0.02)	2.0	57.0	4.6	68.4	3.4	0.3	4.5	1.224	1.48
(0.06)	2.1	59.3	4.9	35.8	3.8	0.3	4.6	1.164	1.65
85 (0.03)	3.4	60.4	5.0	34.6	6.1	0.5	7.0	1.142	1.74
(0.06)	2.5	61.7	4.7	33.6	4.7	0.4	5.1	1.154	1.83
(0.12)	2.6	62.7	4.6	32.6	4.9	0.4	5.1	1.152	1.92
75 (0.03)	3.5	60.5	6.5	33.0	6.4	0.7	7.0	1.011	1.83
(0.06)	2.5	60.3	6.6	33.1	4.6	0.5	5.0	1.005	1.82
(0.12)	1.9	61.9	5.4	32.6	3.5	0.3	3.6	1.079	1.89

a) Toluene, 0.01 mol; benzene, 0.02 mol; CCl_4,40 m*l*; reaction temperature, 20°C; reaction time, 24 hr.
b) S_f; selectivity factor.

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Table 2. Competitive nitration of toluene and benzene with nitric acid in carbon tetrachloride–nitromethane (1:1 by volume)

Temperature (°C)	$\frac{k_T}{k_B}$	Isomer ratio (%)			Partial rate factor			S_f	$\frac{o}{p}$
		o-	m-	p-	o_f^T	m_f^T	p_f^T		
30	17.4	61.1	3.3	35.6	31.9	1.7	37.2	1.341	1.71
40	15.0	58.6	3.8	37.6	26.3	1.7	26.3	1.292	1.55
50	14.9	58.1	4.2	37.7	14.9	1.9	33.6	1.256	1.54

a) Toluene, 0.01 mol; benzene, 0.02 mol; mixed solvent,40 m*l*; nitric acid (99.67%), 0.03 mol; reaction time, 24 hr.

Table 3. Effect of nitromethane and acetic acid[a)]

Solvent (1 vol %)	$\frac{k_T}{k_B}$	Isomer ratio (%)			Partial rate factor			S_f	$\frac{o}{p}$
		o-	m-	p-	o_f^T	m_f^T	p_f^T		
CCl_4 (—)	2.0	57.0	4.6	38.4	3.4	0.3	4.5	1.224	1.48
CCl_4 (CH_3NO_2)	6.4	59.4	5.4	35.2	11.5	1.1	13.6	1.112	1.68
CCl_4 (CH_3COOH)	8.0	58.8	4.6	36.6	14.1	1.1	17.5	1.204	1.60

a) Toluene, 0.01 mol; benzene, 0.02 mol; mixed solvent, 40 m*l*; nitric acid (99.67%), 0.03 mol; reaction temperature, 20°C; reaction time, 24 hr.

indicating that the polarity of mediums has a large effect on the substrate selectivities.

Further, the results of the competitive nitration in carbon tetrachloride with one volume percentage of other solvent are shown in Table 3. The rate ratios are intermediate between those in Table 1 and 2, indicating that even the addition of a small amount of a polar solvent has a large effect on the rate ratios.

Experimental

Materials. Benzene, toluene, nitrobenzene, and *o*-, *m*-, and *p*-nitrotoluene were commercial materials of the highest available purity. Their purities were examined by vapor phase chromatography on a column containing 10% polypropylene glycol in Diasolid M at 170°C.

Competitive Nitration. The competitive nitration and product analysis were carried out by the method described in the previous paper.[1)]