Table 3. Reaction constant ρ and correlation coefficient r for the nitration by mixed acid in acetic acid at 45°C

P (kg/cm^2)	1	1000	2000
ρ	-7.22	-7.05	-6.92
r	0.988	0.989	0.986

On the contrary, chlorobenzene and bromobenzene show an increasing relative reactivity with an increase in the pressure. The results are shown in Table 2. In all three cases in Table 2, the increase in f_m is striking; bromobenzene and chlorobenzene reveal an apparent increase in the *ortho* : *para* ratio with the pressure, as is also observed in alkylbenzenes.

The partial rate factors in Tables 1 and 2 are plotted against Brown-Okamoto's σ^+ value to give a straight line. The ρ values calculated by the method of least squares and the correlation coefficients, r, are listed in Table 3. (The values of biphenyl were not included in the calculations. This will be discussed below.) The correlation of these plots is not excellent, but it may be concluded that the ρ value increases appreciably with an increase in the pressure.

Fischer *et al.*[5] have pointed out that the magnitude of $\Delta V^{\ddagger}$ values could be an indication of anticipating whether or not ρ depends on the pressure. This can be interpreted as follows. Assuming that σ^+ is not a function of the pressure, one can obtain Eq. (9) from Eqs. (7) and (8):

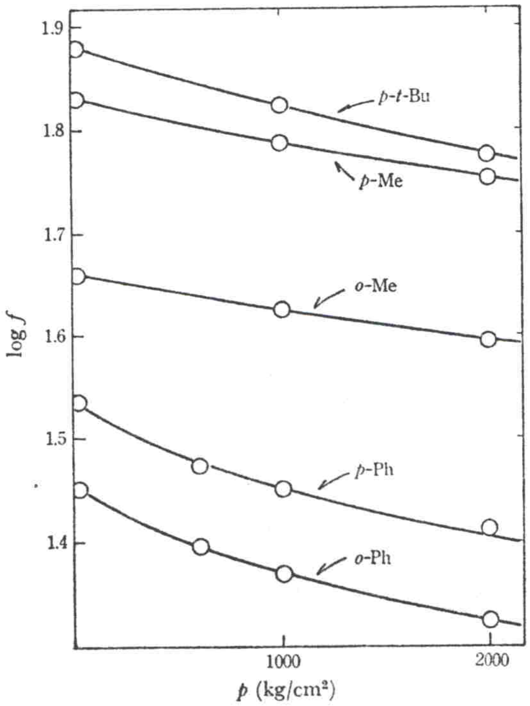

Fig. 1. log f-p curves for the nitration of activated monosubstituted benzenes.

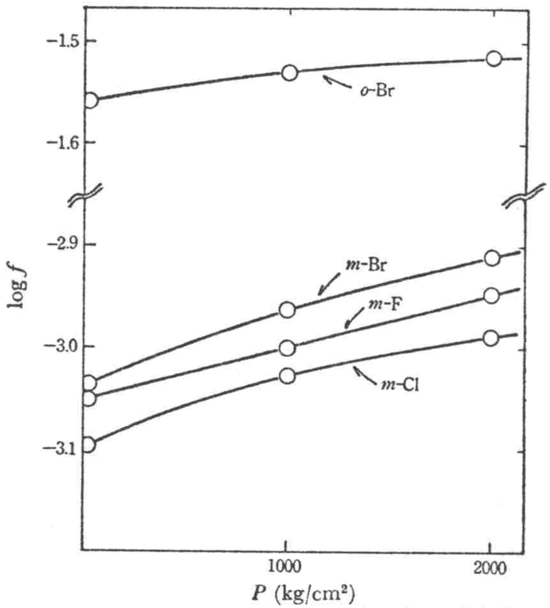

Fig. 2. log f-p curves for the nitration of halobenzenes.

Table 4. $\delta\Delta V^{\ddagger}_1$ or $\delta\Delta \bar{V}^{\ddagger}_{1000}$ values for the nitration by mixed acid in acetic acid at 45°C (ml/mol)[a]

Substituent	o-	m-	p-
Methyl	2.1	1.2*	3.2
t-Butyl	0.6*	1.6*	3.5
Fluoro	0.1*	-3.1	0.4*
Chloro	-1.2*	-5.0	-0.5*
Bromo	-2.0	-5.2	-1.1*
Phenyl	6.2		6.6

*: $\delta\Delta \bar{V}^{\ddagger}_{1000}$ values

a) The error is estimated at most 0.5 ml/mol.

$$\Delta V^{\ddagger} = -RT(\partial \ln k/\partial P)_T \tag{7}$$

$$\log f = \rho\sigma^+ \tag{8}$$

$$\begin{aligned}\delta\Delta V^{\ddagger} &= -RT(\partial \ln f/\partial P)_T \\ &= -2.3RT\sigma^+(\partial\rho/\partial P)_T\end{aligned} \tag{9}$$

Thus, if σ^+ is independent of the pressure and if ρ varies with the pressure, then the plot of $\delta\Delta V^{\ddagger}$ at a constant pressure and temperature against σ^+ should give a linear line, including the point of origin. Figures 1 and 2 show the dependence of log f on the pressure. From the slopes of the curves at zero pressure, the $\delta\Delta V^{\ddagger}{}_1$[*5] values were calculated; they are listed in Table 4, together with the values of $\delta\Delta \bar{V}^{\ddagger}_{1000}$[*6] for the other positions.[*7]

[*5] $\delta\Delta V^{\ddagger}$ values at 1 atm.

[*6] $\delta\Delta \bar{V}^{\ddagger}_{1000} = -RT(\ln f_{1000} - \ln f_1)1/1000$. The numerals indicate the pressure.

[*7] The values of $\delta\Delta \bar{V}^{\ddagger}_{1000}$ are adopted instead of $\delta\Delta V^{\ddagger}{}_1$ for the *meta* positions of alkylbenzenes and the *para* positions of halobenzenes because the changes in the reactivity of these positions with the pressure are relatively small; hence, $\delta\Delta V^{\ddagger}$ should change little with the pressure.