under various pressures are given in Table 3.

Table 3   Effect of pressures on the migratory aptitude of the o-anisyl group of [V] in acetic acid[a]

P (kg/cm^2)	1	1000	2000	3000
meso	3.73	3.39	3.19	3.09
racemic	3.24	2.95	2.74	2.65

a)   temperature 77.4°C, p-toluenesulfonic acid 0.055~0.088 N

The above results indicate that the application of pressure gives rise to increased phenyl migration. As it is reasonable to assume that the migratory aptitudes are the relative migration rates of the o-anisyl group to the phenyl group, from the results in Table 3, Fig. 2 is obtained, in which k_{Ph} is the rate of migration of the phenyl group and k_{An} is that of the o-anisyl group. A difference of the activation volumes of the migration steps (product determining steps) at zero pressure, $\delta \Delta V_0^{\ddagger} = \Delta V_0^{\ddagger}{}_{Ph} - \Delta V_0^{\ddagger}{}_{An}$[*3], can be calculated from the slope of Fig. 2 at zero pressure.
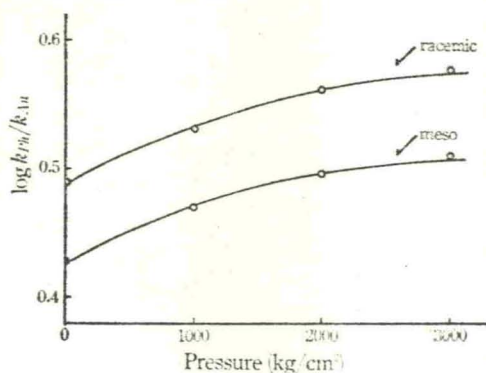

Fig. 2   Plot of log (k_{Ph}/k_{An}) vs. pressure obtained from the results in Table 3

The curves give $\delta \Delta V_0^{\ddagger} = -3.4 \pm \sim 0.5$ ml/mole in both isomers. Apparently, these results show that there should be some effects retarding the migration of the o-anisyl group besides the purely sterical repulsion between the o-methoxyl group and the nonparticipating aryl groups.

The effect of pressures on the migratory aptitudes in acetonitrile is shown in Table 4 and Fig. 3.

Table 4   Effect of pressures on the migratory aptitude of the o-anisyl group of [V] in acetonitrile[a]

P (kg/cm^2)	1	1000	2000	3000
meso	5.47	4.96	4.60	4.40
racemic	4.70	4.17	3.90	3.77

a)   temperature 77.4°C, p-toluenesulfonic acid 0.023 N

* 3 $\left(\dfrac{\partial \ln k_{Ph}/k_{An}}{\partial P}\right)_T = \left(\dfrac{\partial \ln k_{Ph}}{\partial P}\right)_T - \left(\dfrac{\partial \ln k_{An}}{\partial P}\right)_T = -\dfrac{1}{RT}(\Delta V^{\ddagger}{}_{Ph} - \Delta V^{\ddagger}{}_{An})$