The Hofmann Rearrangement. II. Kinetic Substituent Effects of *ortho-*, *meta-*, and *para*-Substituted *N*-Chlorobenzamides

Tsuneo IMAMOTO, Yuho TSUNO, and Yasuhide YUKAWA

The Institute of Scientific and Industrial Research, Osaka University, Yamadakami, Suita, Osaka

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The reaction rates of the Hofmann rearrangement of *ortho-*, *meta-*, and *para*-substituted *N*-chlorobenzamides were measured under the same reaction conditions as were used for the preceding *N*-bromo series. The rate constants of the *N*-chloroamides were found to be slightly larger than those of the *N*-bromoamides. The relative values of the activation entropy and the activation enthalpy of *N*-chloro- and *N*-bromo-derivatives were approximately −4 e.u. and −1.3 kcal/mol respectively. The LFER between the two series was excellent, indicating that the reaction mechanism was almost the same for both series. The effects of the leaving group on the reactivity of *ortho*-substituents were discussed in terms of the *ortho*/*para* rate ratios and the relative values of the activation parameters of *ortho-* and *para*-substituents.

As has been described in the preceding paper,[1] the kinetic substituent effects on the Hofmann rearrangement of substituted *N*-bromobenzamides were studied in order to elucidate the mechanism precisely. The results appeared to suggest that this rearrangement proceeded through a concerted-type transition state; the dissociation of the nitrogen-bromine bond and the migration of the phenyl group to nitrogen took place simultaneously. Furthermore, the results indicated that the contribution of the $d\pi$–$p\pi$ conjugation to the nitrogen-bromine bond in the initial state was also an important factor in depressing the reactivity.

It remained necessary to examine whether or not these qualities of the rearrangement are changed by the substitution of the leaving group, bromide, for chloride. In the present study, the substituent effects of substituted *N*-chlorobenzamides have thus been determined, and the results are discussed in terms of the effects of the leaving group on the reactivity.

Experimental

Materials. Various substituted *N*-chlorobenzamides, but not *m-* and *p*-methoxy and *p*-ethoxy derivatives, were prepared by a modification of Elliott's method.[2] Ten grams of pure amide was dissolved in 10% hydrochloric acid, and chlorine gas was passed into this solution for one hour. The *N*-chloroamide thus precipitated was collected, washed with water, and dried *in vacuo*. The yields of the crude products were generally 70—80% of the theoretical amounts.

In the cases of *m-* and *p*-methoxy and *p*-ethoxy benzamides, chlorination on the benzene ring was also present and the corresponding pure *N*-chloroamides could not be isolated by the above method. However, these *N*-chloroamides could be obtained by the application of the method of Altenkirk and Israelstam.[3] Ten grams of pure amide and 0.4 g of borax were dissolved in methanol, and into this solution an equimolar quantity of *t*-butyl hypochlorite was added at room temperature. After standing in the dark for *ca.* 15 hr, the reaction mixture was diluted with water to twice the original volume. The *N*-chloroamide thus precipitated was collected, washed with water, and dried *in vacuo* (yield 50—70%).

The crude *N*-chloroamides were recrystallized from dichloroethane or from a mixed solvent of methanol and dichloroethane. The analytical data and melting points for *N*-chlorobenzamides are listed in Table 1.

Kinetic Measurements. The rates of the rearrangement of the substituted *N*-chlorobenzamides except those of the *m*-methyl derivative were measured by the same method as was previously used for *N*-bromobenzamides.[1] The initial concentrations of *N*-chloroamide and sodium hydroxide were 0.025 mol/*l* and 0.5 N respectively.

In the case of *m*-methyl benzamide, from which the corresponding *N*-chloro derivative could not be isolated,[4] the kinetic measurements were carried out as follows. Finely-pulverized amide (0.0055 mol) was added at the reaction temperature to 200 m*l* of a hypochlorite solution (0.025 mol/*l*, $f=1.000$), freshly prepared by passing chlorine gas into an ice-cold 0.5 N ($f=1.000$) NaOH solution. The mixture was shaken vigorously for a few minutes, and then the reaction was followed by titrating the residual active chlorine with a 0.025 N $Na_2S_2O_3$ solution.

In order to compare the two rate constants, that obtained by the usual method and that obtained by the conventional modification applied to the *m*-methyl derivative, the rates of the *m*-chloro derivative were measured at 30°C by both the above methods. The rate constant obtained by the latter method was, at most, *ca.* 2% smaller than the constant obtained by the former method.

Results and Discussion

The rates of the release of the chloride ion from the conjugate bases of substituted *N*-chlorobenzamides were measured under the same reaction conditions as were used for the previous *N*-bromo series. All the runs strictly obeyed first-order kinetics, at least to 75% completion of the reaction, except for those of the *m*-methyl derivative. Some examples of first-order plots are shown in Fig. 1. In the case of the *m*-methyl derivative, the rates of which were measured by using a hypochlorite solution, a short induction period was observed when the reaction was about 15% complete (see Fig.1),[5] and the rate constants were calculated from the first-order plots, excluding the induction period. The reproducibility of the rate constant obtained from repeated runs was within 0.7%, and the plots of $\log k/T$ *vs.* $1/T$ gave an excellent straight line in every case. The ob-

1) T. Imamoto, Y. Tsuno, and Y. Yukawa, This Bulletin, **44**, 1632 (1971).

2) G. R. Elliott, *J. Chem. Soc.*, **121**, 203 (1922).

3) B. Altenkirk and S. S. Israelstam, *J. Org. Chem.*, **27**, 4532 (1962).

4) Chlorination with chlorine gas gave solely a pasty mass.

5) The induction period may be caused by the *N*-chlorination of the amide with hypochlorite at the initial stage of the reaction.

TABLE 1. SUBSTITUTED *N*-CHLOROBENZAMIDES

Subst.	Mp °C (lit[3])	Analysis (Calcd)				
		C%	H%	N%	Cl%	Active Cl%
p-CH_3O	142—143 (142—143)	51.77 (51.77)	4.40 (4.34)	7.47 (7.55)	18.94 (19.10)	19.00 (19.10)
p-C_2H_5O	128.0—129.0	54.04 (54.15)	5.08 (5.05)	6.88 (7.02)	17.91 (17.76)	17.69 (17.76)
p-CH_3	153.5—154.5 (147)	56.87 (56.65)	4.60 (4.75)	8.38 (8.26)	20.79 (20.90)	20.52 (20.90)
p-C_2H_5	106.5—107.0	58.49 (58.86)	5.41 (5.49)	7.69 (7.63)	19.18 (19.31)	19.23 (19.31)
Unsubst.	117.0—118.0 (117—118)	53.93 (54.04)	3.67 (3.89)	9.00 (9.00)	22.98 (22.79)	22.48 (22.79)
p-F	178—180	48.28 (48.44)	3.02 (2.90)			20.13 (20.43)
p-Cl	196—198 (194—195)	44.05 (44.24)	2.58 (2.65)	7.46 (7.37)	37.48 (37.31)	18.46 (18.66)
p-Br	198—199	35.86 (35.86)	2.01 (2.15)	5.99 (5.97)		15.00 (15.12)
p-NO_2	230—233 (200—202)	41.99 (41.92)	2.19 (2.51)	13.78 (13.97)	17.70 (17.68)	16.98 (17.68)
m-CH_3O	103.0—103.5 (165—166)	51.90 (51.77)	4.29 (4.34)	7.55 (7.55)	19.27 (19.10)	18.86 (19.10)
m-Cl	121—122 (119—120)	44.14 (44.24)	2.54 (2.65)	7.60 (7.37)	37.37 (37.31)	18.30 (18.66)
m-Br	127.0—127.5	35.81 (35.86)	2.08 (2.15)	6.00 (5.97)		14.85 (15.12)
m-NO_2	188—189 (184)	42.21 (41.92)	2.37 (2.51)	14.02 (13.97)	17.82 (17.68)	17.41 (17.68)
o-CH_3	87.0—88.5 (88—89)	56.28 (56.65)	4.63 (4.75)	8.14 (8.26)	20.80 (20.90)	20.54 (20.90)
o-Cl	107.0—107.5 (105—106)	44.10 (44.24)	2.46 (2.65)	7.55 (7.37)	37.20 (37.31)	18.44 (18.66)
o-Br	149.0—150.5 (151—152)	36.00 (35.86)	1.96 (2.15)	6.02 (5.97)		14.98 (15.12)
o-NO_2	172—173	41.89 (41.92)	2.22 (2.51)	14.30 (13.97)	17.82 (17.68)	17.45 (17.68)

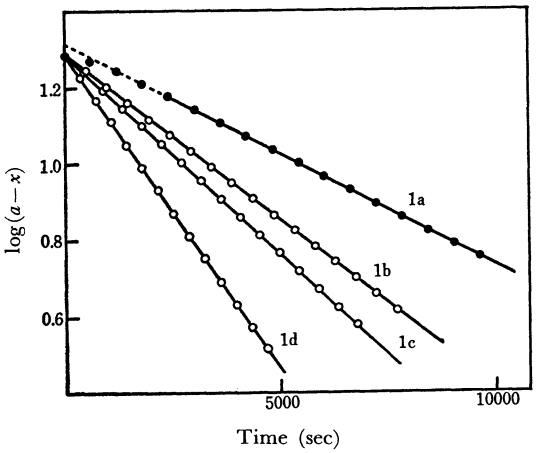


Fig. 1. Typical first-order plots.
1a: *m*-CH_3, at 15°C; 1b: *p*-F, at 25°C
1c: *p*-Cl, at 30°C; 1d: H, at 25°C.

served rate constants are listed in Table 2. The rate constants at 30°C and the derived activation parameters are summarized in Table 3.

The rate constant at 30°C is found to be slightly larger than that of the corresponding *N*-bromoamide, and the chloride/bromide rate-ratio is calculated to be *ca.* 1.2 in every substituent. It should be noted that the observed rate-ratio is considerably different from that of the usual alkyl halide reported hitherto in various nucleophilic substitution reactions and elimination reactions. That is, an alkyl chloride reacts 10—1000 times slower than the corresponding bromide,[6] whereas in the Hofmann rearrangement the *N*-chloroamide is slightly more reactive than the *N*-bromoamide. This result might possibly be referred to the fact that the bond-breaking of the nitrogen-halogen bond does not take place in the rate-determining step, but this possibility is entirely obviated by the kinetic results on the Lossen rearrangement. Hauser *et al.*[7] had studied the kinetic substituent effect on the Lossen rearrangement of dihydroxamates (I), and obtained a comparatively large positive ρ-value (+1.0). This result evidently indicates that the rate-determining step involves the bond-cleavage of the nitrogen-oxygen bond. From the similarity of the reaction mechanism of the Lossen

6) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Company, Inc., New York (1962), p. 29; C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca and London (1969), p. 453.

7) W. B. Renflow and C. R. Hauser, *J. Amer. Chem. Soc.*, **78**, 5002 (1937); R. D. Bright and C. R. Hauser, *ibid.*, **61**, 618 (1939).

Table 2. Rate constants of the Hofmann rearrangement of substituted *N*-chlorobenzamides

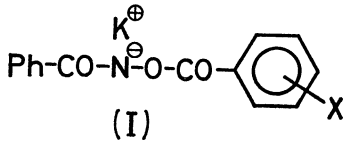
Subst.	Temp. °C	$k_1 \times 10^4$ (sec^{-1})	Subst.	Temp. °C	$k_1 \times 10^4$ (sec^{-1})
p-CH_3O	13.00	5.456 ± 0.001		40.00	0.5807 ± 0.0001
	10.00	3.414 ± 0.009		30.00	0.1218 ± 0.0002
	5.00	1.507 ± 0.003			
	0.00	0.6492 ± 0.0009	*m*-CH_3	15.00	1.341 ± 0.002[a]
				10.00	0.5852 ± 0.0005[a]
p-C_2H_5O	13.00	5.826 ± 0.007		5.00	0.2487 ± 0.0005[a]
	10.00	3.629 ± 0.008			
	5.00	1.619 ± 0.002	*m*-CH_3O	30.00	4.999 ± 0.008
	0.00	0.7000 ± 0.0019		25.00	2.355 ± 0.002
				20.00	1.085 ± 0.0008
p-CH_3	15.00	2.364 ± 0.004		15.00	0.4812 ± 0.0002
	10.00	1.041 ± 0.002			
	5.00	0.4448 ± 0.0007	*m*-Cl	38.00	3.500 ± 0.001
	0.00	0.1843 ± 0.0003		30.00	1.061 ± 0.0006
					1.043 ± 0.002[a]
p-C_2H_5	20.00	5.091 ± 0.006		20.00	0.2181 ± 0.0003
	15.00	2.302 ± 0.002			
	10.00	1.012 ± 0.001	*m*-Br	38.00	3.728 ± 0.001
	5.00	0.4333 ± 0.0004		30.00	1.139 ± 0.001
				20.00	0.2331 ± 0.0002
Unsubst.	30.00	8.045 ± 0.008			
	25.00	3.789 ± 0.004	*m*-NO_2	50.00	2.524 ± 0.002
	20.00	1.749 ± 0.001		45.00	1.258 ± 0.001
	15.00	0.7754 ± 0.0007		40.00	0.6026 ± 0.0005
				30.00	0.1272 ± 0.0002
p-F	30.00	4.297 ± 0.004			
	25.00	2.013 ± 0.001	*o*-CH_3	5.00	12.3 ± 0.07
	20.00	0.9200 ± 0.0008		0.00	5.23 ± 0.010
	15.00	0.4075 ± 0.0004			
			o-Cl	20.00	2.619 ± 0.003
p-Cl	35.00	5.083 ± 0.006		15.00	1.139 ± 0.001
	30.00	2.428 ± 0.002		10.00	0.4794 ± 0.003
	25.00	1.132 ± 0.001		5.00	0.1964 ± 0.0010
	20.00	0.5129 ± 0.0004			
			o-Br	20.00	3.096 ± 0.003
p-Br	35.00	4.633 ± 0.003		15.00	1.345 ± 0.001
	30.00	2.219 ± 0.002		10.00	0.5667 ± 0.0004
	25.00	1.021 ± 0.001		5.00	0.2313 ± 0.0006
	20.00	0.4654 ± 0.0005			
			o-NO_2	50.00	4.740 ± 0.001
p-NO_2	50.00	2.464 ± 0.003		45.00	2.309 ± 0.002
	45.00	1.217 ± 0.001		40.00	1.095 ± 0.001
				30.00	0.2258 ± 0.0002

a) Measured by using sodium hypochlorite solution.

Table 3. Kinetic results of the Hofmann rearrangement of substituted *N*-chlorobenzamides

Subst.	$k_1 \times 10^4$ (sec^{-1}) 30.00°C	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e. u.)
p-CH_3O	67.4[a]	24.89±0.03	13.61±0.10
p-C_2H_5O	70.9[a]	24.75±0.01	13.26±0.04
p-CH_3	23.64[a]	26.04±0.02	15.33±0.08
p-C_2H_5	23.00[a]	26.04±0.01	15.27±0.05
Unsubst.	8.045	26.45±0.05	14.55±0.15
p-F	4.297	26.65±0.02	13.97±0.06
p-Cl	2.428	26.83±0.02	13.43±0.05
p-Br	2.219	26.88±0.08	13.37±0.28
p-NO_2	0.1218	28.66±0.06	13.52±0.21
m-CH_3	13.67[a]	26.27±0.02	15.01±0.06
m-CH_3O	5.008	26.49±0.03	13.73±0.11
m-Cl	1.061	27.35±0.03	13.49±0.09
m-Br	1.139	27.31±0.10	13.51±0.33
m-NO_2	0.1272	28.48±0.08	13.00±0.28
o-CH_3	575.[a]	25.2 ±0.20	18.9 ±0.66
o-Cl	12.78[a]	27.41±0.02	18.64±0.05
o-Br	15.16[a]	27.45±0.01	19.09±0.04
o-NO_2	0.2258	29.01±0.04	15.89±0.14

a) Extrapolated from data at other temperatures.



(I)

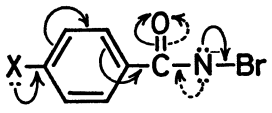
to that of the Hofmann rearrangement, it is also clear that the dissociation of the nitrogen-halogen bond in the Hofmann rearrangement takes place in the rate-determining step. The data on the relative reactivities of the *N*-chloro and *N*-bromo derivatives can be rather reasonably interpreted by considering the effect of solvation at the initial and the transition states. The reactant molecule, the conjugate base of *N*-haloamide, is strongly solvated by the hydrogen bond with the amide group, at which a large negative charge is acquired. Both *N*-chloro and *N*-bromo derivatives, however, will be subjected to almost the same degree of the solvation, since this solvation is controlled for the most part by the large acquired negative charge at the amide group, with a minor influence by the halogen atom. On the other hand, at the transition state the solvent water molecule is strongly hydrogen-bonded with a large negative charge on the halogen atom. Therefore, the degree of the solvation is proportional

to the ion potential of the halide ion itself; the *N*-chloro derivative is more solvated than the *N*-bromo derivative. The difference in the solvation effect in the transition state can be estimated to be one of the main factors in increasing the reactivity of *N*-chloroamide relative to that of *N*-bromoamide. This consideration is supported by the fact that the relative values of the activation entropy and the activation enthalpy have been found to be approximately −4 e.u. and −1.3 kcal/mol respectively.

In addition to the solvation effect, the effect of the $d\pi$–$p\pi$ conjugation on the relative rate effect can not be neglected. As has been described in the preceding paper, the $d\pi$–$p\pi$ conjugation on the nitrogen-halogen bond seems to be an important factor in depressing the reactivity. Therefore, if the $d\pi$–$p\pi$ conjugation on the N–Br bond is stronger than that of the N–Cl bond, the reactivity of the *N*-bromoamide will be relatively more depressed than that of the *N*-chloroamide. The above assumption regarding the relative strength of the $d\pi$–$p\pi$ conjugation on the nitrogen-halogen bond may be supported by the data on the $d\pi$–$p\pi$ conjugation of the carbon-halogen bond.[8] This might lead to a subsequent conclusion that, in the Hofmann rearrangement, the effects of the solvation and the $d\pi$–$p\pi$ conjugation on the relative reactivity are so important as to overcome the effects of the polarization and the σ-bond strength of the nitrogen-halogen bond.

The application of LFER to the present data will provide valuable information on the effect of the leaving group on the reactivity as well as on the more precise reaction mechanism of this rearrangement. In a preceding study of the substituent effect of the *N*-bromoamides, it has been inferred that the most important factors characterizing the Hofmann rearrangement are the $d\pi$–$p\pi$ conjugation on the N–Br bond in the initial state and the participation of the phenyl group migrating to electron-deficient nitrogen in the transition state.

These two factors can be influenced by the substituent on the migrating phenyl group, especially by the electron-releasing conjugative substituent at the para-position. In the initial state, such a substituent increases the $d\pi$–$p\pi$ conjugation on the nitrogen-bromine bond by the aid of the cross conjugation effect of the carbonyl group, as is indicated in Formula (II), and



(II)

makes it more difficult to release the bromide ion from the reactant molecule. On the other hand, in the transition state, the same electron-releasing conjugative substituent facilitates the additional conjugation of the phenyl group with electron-deficient nitrogen, with a considerable stabilization of the transition state, and promotes the rate acceleration.

It is one of the purposes of the present study to examine the effect of the leaving group on the conjugation effects mentioned above. The logarithms of the relative rate constants of *meta*- and *para*-substituted *N*-chlorobenzamides have been plotted against those of *N*-bromoamides. An excellent linear relation has been observed except for the nitro group,[9] as shown in Fig. 2. The slope of the correlation line and its correlation coefficient are calculated as 0.97 and 0.9999 respectively.

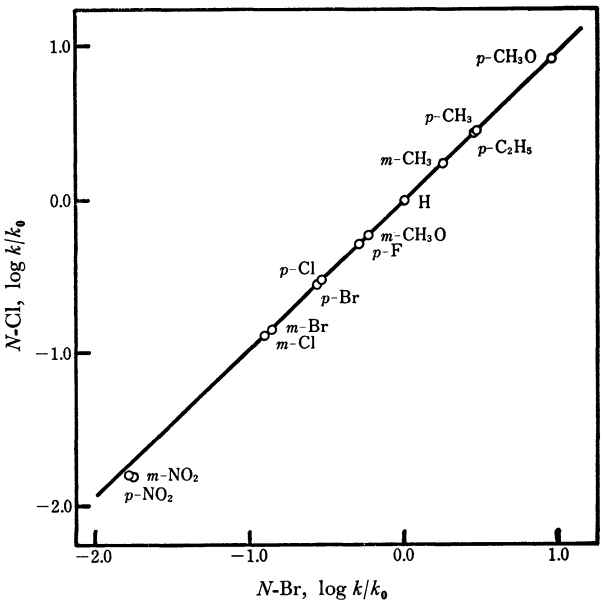


Fig. 2. Comparison of *N*-chloro with *N*-bromo derivatives.

Furthermore, as may be anticipated from the above results, the application of the Linear Aromatic Substituent-Reactivity relationship (LArSR relationship; $\log k/k_0=(\sigma^0+r\Delta\bar{\sigma}_R^+)$) to the present data gives almost the same values of the reaction constant, ρ, and of the resonance parameter, r, as those of the *N*-bromo series.

$$\log k/k_0 = -2.43(\sigma^0+0.41\Delta\bar{\sigma}_R^+) + 0.02$$

These results obviously indicate that the conjugation effects in both the initial and the transition states are also important factors for the reaction of *N*-chloroamides; furthermore, it may be concluded that the substituent effect for each conjugation effect is almost the same for both the *N*-chloro and *N*-bromo series. This conclusion does not conflict with the earlier estimation of the relative strength of the $d\pi$–$p\pi$ conjugation of N–Cl and N–Br bonds; such a small difference in the strength of the $d\pi$–$p\pi$ conjugation will not be so sensitively reflected in the substituent effect as to give a certain trend to the correlation plots.

It is also of interest to discuss the effect of the leaving group on the *ortho* effect. The *ortho*/*para* rate ratios for several substituents observed in Hofmann, Lossen and Curtius rearrangements are listed in Table 4. In

8) Although the data on the relative strength of the $d\pi$-$p\pi$ conjugation on the nitrogen-halogen bond have not yet been reported, its relative strength may be presumed to be the order, F$\ll$Cl$<$Br$<$I, from that of $d\pi$-$p\pi$ conjugation on the carbon-halogen bond; J. Hine and P. D. Langford, *J. Amer. Chem. Soc.*, **78**, 5002 (1956); J. Hine, N. W. Burske, M. Hine, and P. D. Langford, *ibid.*, **79**, 1406 (1957).

9) The deviations of the nitro groups are attributable to the uncertainty of the rate constants of the nitro-*N*-bromobenzamides.

Table 4. *ortho/para* rate ratios

$X\text{-}C_6H_4\text{-}CO\text{-}N^-\text{-}Y$

X/Y	Br	Cl	CO_2-	Cl CO_2-	NO_2 CO_2-	N_2
CH_3O	6.3		8.5			150.
CH_3	21.0	24.3				131.
Cl	4.2	5.3		5.9		208.
Br	5.5	6.8		8.0		277.
NO_2	1.5	1.9			2.2	70.

Table 5. Relative values of activation parameters of *ortho-* to *para*-derivatives

	N-Br		N-Cl		$N\text{-}N_2$	
	$\Delta\Delta H^{\neq}$ (kcal/mol)	$\Delta\Delta S^{\neq}$ (e. u.)	$\Delta\Delta H^{\neq}$ (kcal/mol)	$\Delta\Delta H^{\neq}$ (e. u.)	$\Delta\Delta H^{\neq}$ (kcal/mol)	$\Delta\Delta S^{\neq}$ (e. u.)
CH_3O	+0.7±0.5	+5.9±1.8				
CH_3	−0.2±0.2	+5.2±0.6	−0.8±0.2	+3.6±0.7	−5.0±0.3	−6.4±0.8
Cl	+1.0±0.2	+6.2±0.6	+0.6±0.0	+5.2±0.1	−5.4±0.6	−6.8±1.9
Br	+0.7±0.1	+5.5±0.3	+0.6±0.1	+5.7±0.3	−5.5±0.2	−4.1±0.7
NO_2	0.0±0.8	+0.8±2.5	+0.4±0.1	+2.4±0.4	−3.1±0.2	−1.7±0.5

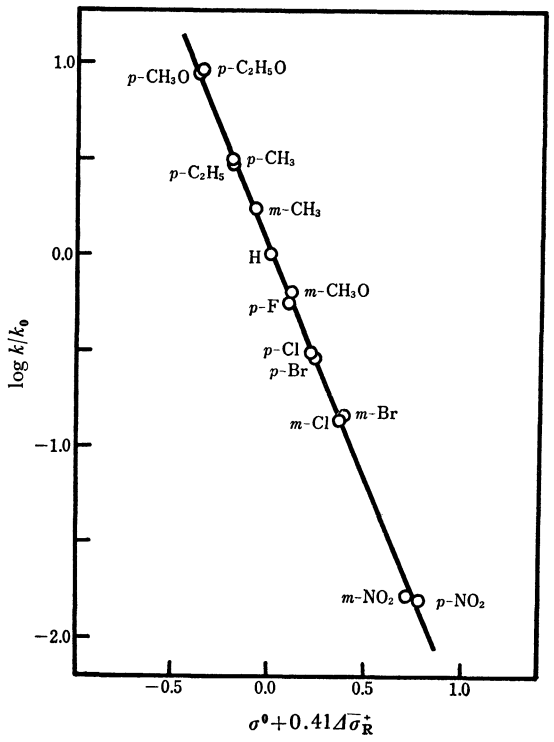


Fig. 3. Application of the LArSR relationship.

the case of the *N*-bromo series, the *ortho/para* rate ratio varies over a considerably wide range, depending on the substituent, but it tends to decrease with an increase of the electron-attracting character of the substituent except for the methoxy group. This tendency appears also in the present *N*-chloro series and in the Lossen rearrangement. Another noticeable fact is the relative value of the activation parameters of *ortho-* and *para*-substituents. In both the *N*-chloro and *N*-bromo series, similar values of $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ are observed in a given substituent except for nitro groups,[10] as is shown in Table 5. These facts apparently indicate that the *ortho* effects in the Hofmann and the Lossen rearrangements are almost the same in every leaving group.

On the other hand, the Curtius rearrangement, of which leaving group is a nitrogen molecule, is expected to be considerably different from the Hofmann and the Lossen rearrangements with respect to the reaction mechanism. The structure of the transition state of the Curtius rearrangement is considerably closer to that of the initial state, since, in this rearrangement, a stable nitrogen molecule is released in the rate-determining step. The reactivity, therefore, depends greatly on the strength of the $N\text{–}N_2$ bond.[11] In the case of an *ortho*-substituent, the bond-order of the $N\text{–}N_2$ bond is reduced by the steric restriction of the through conjugation of the phenyl group with the carbonyl group with an elevation in the reactivity. The exclusive significancy of this bond-energy effect on the Curtius rearrangement is evidently reflected in the *ortho* effects—the quite large *ortho/para* rate ratios and the enthalpy dependency of their rate ratios (see Tables 4 and 5). It is especially to be noted that the *ortho* effects on the Curtius rearrangement are in marked contrast to those on the Hofmann and the Lossen rearrangements, which are caused both by the bond-energy effect in the initial state and by the participation of the phenyl group migrating to nitrogen in the transition state.

10) The comparatively large disagreement of the nitro groups is caused by the uncertainty of the activation parameters of *N*-bromoamides. The *p*-nitro-*N*-bromobenzamide did not obey first-order kinetics at 30°C due to accompanying hydrolysis of the reactant molecule itself, and the reaction rates were measured at 45—55°C where satisfactory first-order plots were obtained. The narrow temperature range and the side reaction may afford considerable uncertainty to the derived values of activation parameters. In the case of *o*-nitro-*N*-bromobenzamide the reaction rate gradually increased as the reaction proceeded, and the rate constants were calculated from the initial stage of the reaction. Therefore, the activation parameters of this derivative may be also attended with large uncertainty.

11) Y. Yukawa and Y. Tsuno, *J. Amer. Chem. Soc.*, **79**, 5530 (1957); Y. Yukawa and Y. Tsuno, *ibid.*, **80**, 6346 (1958).