UDC 547.831.4-31.07

147. Toshihiko Okamoto, Hikoya Hayatsu, and Yoshihiko Baba*2 : Reaction Mechanism in Aromatic Heterocyclic Compounds. III.[1] Kinetics of the Reaction of 4-Haloquinoline 1-Oxides and Related Compounds with Piperidine.

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It is well known that a substituent at 4-position in quinoline 1-oxide is quite reactive to nucleophilic reagents. Thus, the 4-nitro or 4-chloro group in quinoline 1-oxides is easily replaced by alkoxide, phenoxide, or amines.[2] 4-Substituent in quinoline is also reactive toward nucleophilic reagents and some kinetic studies on the reactions have been made,[3~5] but kinetic studies on the reaction of quinoline 1-oxide have not appeared in any literature. Comparative data for the reactivities of 4-substituted quinoline 1-oxide, quinoline, and related compounds are needed. For this purpose, 4-haloquinoline 1-oxides, 4-haloquinolines, 4-halo-1-nitronaphthalenes, and 4-halo-1-acetonaphthone were employed and these compounds were reacted with piperidine.

In the aromatic nucleophilic substitutions, the reaction of activated halo compounds with piperidine was proved to follow bimolecular reaction mechanism.[6] In the present series of experiments, a large excess of piperidine was mainly used to avoid undesirable effect of acid catalysis reported by Banks[7] and Chapman.[5] The rate coefficients were determined in three kinds of solvent; 70% and 95% ethanol, and benzene.

Experimental

Reactants and Products

4-Chloroquinoline 1-Oxide—4-Nitroquinoline 1-oxide[8] and AcCl were reacted[9] and resultant 4-chloroquinoline 1-oxide was recrystallized from Me_2CO to light yellow needles, m.p. 133~135°. *Anal.* Calcd. for C_9H_6ONCl : C, 60.01; H, 3.34; N, 7.80. Found : C, 60.33; H, 3.44; N, 8.13.

4-Bromoquinoline 1-Oxide—This compound was obtained by reacting 4-nitroquinoline 1-oxide with 30% HBr.[10] The product was crystallized from Me_2CO to light yellow needles, m.p. 126.5~127° (decomp.). *Anal.* Calcd. for C_9H_6ONBr : C, 48.20; H, 2.68; N, 6.25. Found : C, 47.84; H, 2.74; N, 5.99.

4-Iodoquinoline 1-Oxide—Diazonium compound obtained from 4-aminoquinoline 1-oxide[11] was converted to the corresponding iodo derivative[12] and was recrystallized from Me_2CO to light brown

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prisms, m.p. 163~163.5° (decomp.). *Anal.* Calcd. for C_9H_6ONI : C, 39.88; H, 2.23; N, 5.17. Found: C, 39.99; H, 2.33; N, 5.03.

4-Chloroquinoline—4-Nitroquinoline 1-oxide was reacted with PCl_3.[13] The product was purified by vacuum distillation and alumina chromatography. $b.p_3$ 110~115°; m.p. 29~29.5°. *Anal.* Calcd. for C_9H_6NCl : C, 66.06; H, 3.67; N, 8.57. Found : C, 65.84; H, 3.60; N, 8.23.

4-Bromoquinoline—4-Nitroquinoline 1-oxide was treated with PBr_3.[14] $b.p_2$ 105~110°; m.p. 29.5~30.5°. *Anal.* Calcd. for C_9H_6NBr : C, 51.95; H, 2.88; N, 6.73. Found : C, 52.16; H, 3.06; N, 6.78.

4-Iodoquinoline—4-Iodoquinoline 1-oxide was reacted with PI_3 in $CHCl_3$ at room temperature. The product was recrystallized from MeOH-H_2O mixture to needles, m.p. 94.5~95.5°.[15] *Anal.* Calcd. for C_9H_6NI : C, 42.38; H, 2.37; N, 5.49. Found : C, 42.80; H, 2.43; N, 5.04.

4-Chloro-1-nitronaphthalene—4-Amino-1-nitronaphthalene[16] was converted to this compound as described by Bassilios[17] and the product was recrystallized from EtOH to light yellow needles, m.p. 85~86°. *Anal.* Calcd. for $C_{10}H_6O_2NCl$: C, 57.85; H, 2.91; N, 6.75. Found : C, 58.04; H, 2.69; N, 6.45.

4-Bromo-1-nitronaphthalene—Diazonium compound of 4-amino-1-nitronaphthalene was converted to the corresponding bromo compound and recrystallized from EtOH to light yellow needles, m.p. 87~88°.[18a] *Anal.* Calcd. for $C_{10}H_6O_2NBr$: C, 47.61; H, 2.37; N, 5.56. Found : C, 47.96; H, 2.77; N, 5.21.

4-Chloro-1-acetonaphthone—This compound was obtained as described by Jacobs[18b] and purified by vacuum distillation, $b.p_{3.5}$ 153~155° (oil). Semicarbazone : m.p. 224~224.5°. *Anal.* Calcd. for $C_{13}H_{12}ON_3Cl$: C, 59.66; H, 4.58; N, 16.07. Found : C, 60.00; H, 4.17; N, 16.03.

Piperidine—Commercial piperidine (98%) was dehydrated with KOH and the dehydrated piperidine was refluxed with Na for several hr. Piperidine was then distilled, the distillate of b.p. 105~107° was collected, refluxed again with Na, and redistilled. The purified piperidine was further distilled (using Podbielniak rectifier) twice and the fraction of b.p. 106.8~107.4° was collected.[19]

4-Piperidinoquinoline 1-Oxide—4-Haloquinoline 1-oxide and an excess of piperidine was refluxed in EtOH. Piperidino compound thus obtained was recrystallized from Et_2O (containing some H_2O) to light yellow prisms, m.p. 69°. *Anal.* Calcd. for $C_{14}H_{16}ON_2 \cdot \frac{1}{2}H_2O$: C, 70.86; H, 7.22; N, 11.81. Found: C, 70.91; H, 7.32; N, 11.98.

Hydrobromide : Yellow prisms (from Me_2CO-AcOEt mixture), m.p. 112~113°. *Anal.* Calcd. for $C_{14}H_{16}ON_2 \cdot HBr \cdot H_2O$: C, 51.39; H, 5.82; N, 8.56. Found : C, 51.30; H, 6.14; N,8.79. IR (in Nujol): 1222 cm^{-1} (N-O).

The reaction of 4-haloquinoline 1-oxides and piperidine was repeated on a large scale under the conditions used in the kinetic studies. Even by careful analyses of the product, no detectable amount of a by-product was found. Further, 4-piperidinoquinoline 1-oxide showed no change on prolonged heating at these conditions.*3

4-Piperidinoquinoline—4-Haloquinoline was heated with an excess of piperidine in a sealed tube at 150~170° for 5~8 hr. and the resulting product was recrystallized from petr. ether to colorless prisms, m.p. 86~86.5°. *Anal.* Calcd. for $C_{14}H_{16}N_2$: C, 79.24; H, 7.92; N, 13.21. Found : C, 79.08; H, 7.71; N, 13.47.

Hydrobromide : Light yellow needles (from Me_2CO-AcOEt mixture), m.p. 209~210°. *Anal.* Calcd. for $C_{14}H_{16}N_2 \cdot HBr$: C, 57.35; H, 5.84; N, 9.56. Found : C, 57.03; H, 6.30; N, 9.17.

Picrate : Yellow needles (from EtOH), m.p. 210~211°. *Anal.* Calcd. for $C_{14}H_{16}N_2 \cdot C_6H_3O_7N_3$: C, 54.42; H, 4.34; N, 15.87. Found : C, 54.35; H, 4.47; N, 15.48.

4-Haloquinoline was reacted with piperidine on a large scale under the conditions used for kinetic studies and only one product, 4-piperidinoquinoline, was obtained.

4-Piperidino-1-nitronaphthalene—4-Halo-1-nitronaphthalene was reacted with piperidine by refluxing in 95% EtOH. The product was recrystallized from hexane to yellow prisms, m.p. 76°.[20] *Anal.* Calcd. for $C_{15}H_{16}O_2N_2$: C, 70.31; H, 6.29; N, 10.93. Found : C, 70.97; H, 6.24; N, 10.53. No detectable by-product was obtained in this reaction.

4-Piperidino-1-acetonaphthone—A mixture of 4-chloro-1-acetonaphthone and an excess of piperidine was heated in a sealed tube at 150° for 8 hr. and the product was recrystallized from hexane

*3 4-Piperidinoquinoline 1-oxide was deoxygenated to 4-piperidinoquinoline on vacuum distillation (20 mm. Hg, bath temperature, 190~200°).

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to colorless prisms, m.p. 70.5~71.5°. *Anal.* Calcd. for $C_{17}H_{19}ON$: C, 80.63; H, 7.51; N, 5.54. Found: C, 80.48; H, 7.50; N, 5.63. No by-product was produced in this reaction.

Solvents—95% and 75% EtOH were prepared from redistilled EtOH by dilution with distilled water. 95% EtOH, d_{20} 0.8042. 75% EtOH, d_{22} 0.8660. Benzene was redistilled and dried as usual.

UV-Spectra of the Reactants and Products—In Fig. 1, UV spectra of these reactants and products in 5% H_2SO_4 (95% EtOH-H_2O) are shown.

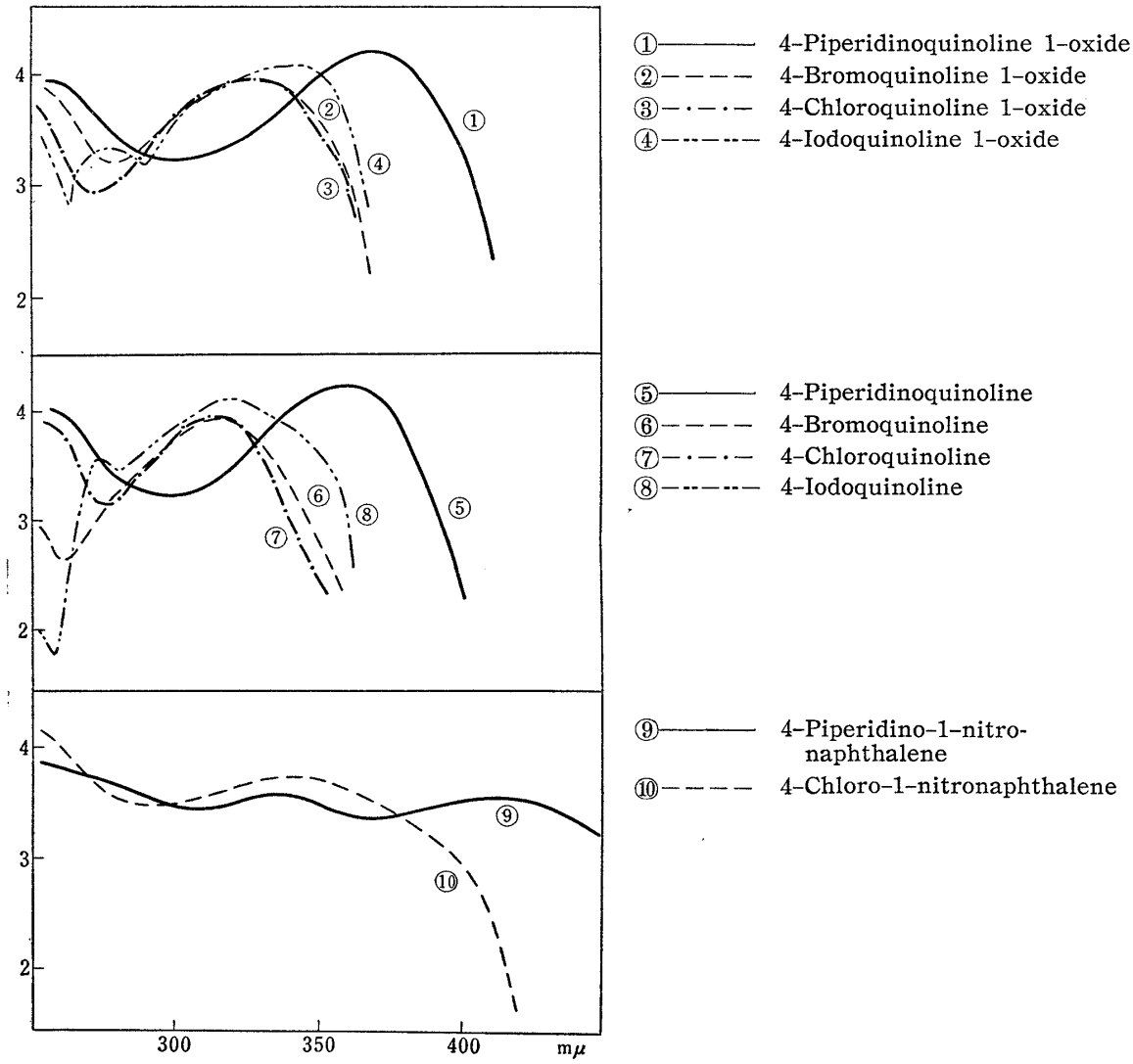


Fig. 1. Ultraviolet Spectra of the Reactants and Products in 5% H_2SO_4 (95% EtOH-H_2O)

Typical Rate Measurement by the Spectroscopic Method—A solution of 4-bromoquinoline 1-oxide (15.983 mg.) and piperidine (305 mg.) dissolved in 70% EtOH was diluted with the same solvent to 50 cc. in a volumetric flask. (Concentration of the bromo compound, $1.427\times10^{-3}M$; piperidine, $7.18\times10^{-2}M$). The solution was shaken thoroughly and each 5 cc. aliquot was pipetted from this solution into 8 ampules. The ampules were sealed and immersed, all at once, in a thermostat adjusted to 80°±0.3°. After the thermostat had returned to this temperature, one ampule was removed and chilled. Subsequently, other samples were removed at definite intervals, all times being recorded. The time when the first sample was removed was recorded as 0 (zero) time. After being removed from thermostat, each ampule was immersed in an ice bucket and then opened. One cc. of the sample was pipetted and 1.0 cc. of 10% H_2SO_4 was added to this sample. This was diluted accurately with 5% H_2SO_4 (prepared by mixing equal volumes of 10% H_2SO_4 and 70% EtOH) to make its optical density at 380 mμ between 0.1 and 0.4.

4-Piperidinoquinoline 1-oxide absorbs strongly between 330 and 400 mμ (λ_{max} 368 mμ), whereas piperidine and haloquinoline 1-oxides have negligible absorption over 370 mμ. Therefore, the reaction

was conveniently followed by determining the absorption at 380 mμ.*4

Rate coefficients were calculated from the expression $\log a - \log(a-x) = 0.4343\, k_1 t$, $k_2 = k_1/b$ (where a and b are the initial concentrations of the halo compound and piperidine, respectively, and x is the concentration of the product at time t). Fig. 2 shows the plots of $\log(a-x)$ vs. t and the plots were linear. The slope of the line was determined by the mothod of least squares and the first-order rate coefficient k_1 was obtained as 0.406×10^{-4}/sec. This first-order rate coefficient was divided by the concentration of piperidine to give the second-order rate coefficient k_2, as 0.564×10^{-3} L./mole/sec. (in this experiment, the reaction proceeded to 50% at 210 min.).

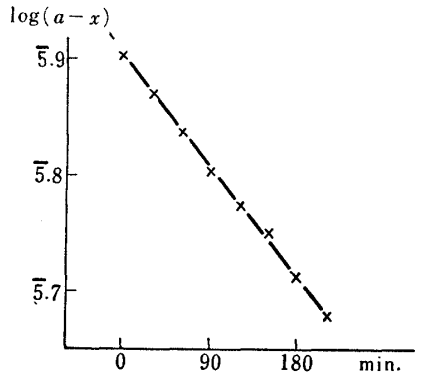


Fig. 2.

An Example of the Rate Measurement by Spectroscopic Method

Table I shows the rate coefficients of the reaction at 60°, 70°, and 80°.

Table I. Reactions of 4-Bromoquinoline 1-Oxide with Piperidine in 70% EtOH

Temp. (°C)	k_2 (L./mole/sec.) $\times 10^3$		Mean value
60±0.3	0.193	0.172	0.183
70±0.3	0.354	0.352	0.353
80±0.3	0.564	0.550	0.557

Arrhenius activation energy, $\Delta E\ddagger$, was calculated from the expression : $\log k = \log A - 1/2.303R \cdot \Delta E\ddagger \cdot 1/T$. In Fig. 3, the plots of $\log k$ vs. $1/T$ are shown. The slope of this line ($1/2.303R \cdot \Delta E\ddagger$) was calculated by the method of least squares and $\Delta E\ddagger$ was obtained.

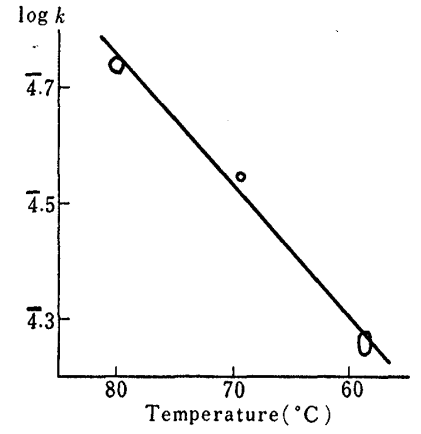


Fig. 3.

Reaction of 4-Bromoquinoline 1-Oxide with Piperidine

The entropy of activation, $\Delta S\ddagger$, was calculated from the standard expression : $k = \kappa T/h \cdot \exp(\Delta S\ddagger/R) \cdot \exp(-\Delta H\ddagger/RT)$, $(\Delta H\ddagger = \Delta E\ddagger - RT)$. From the above obtained value of $\Delta E\ddagger$, $\Delta H\ddagger$ and $\Delta S\ddagger$ were calculated, $\Delta H\ddagger = 12.36$ Kcal./mole, $\Delta S\ddagger = -36$ cal./mole/deg. Rate coefficient at 100° was calculated from these values : $k_2^{100°} = 1.62 \times 10^{-3}$ L./mole/sec.

The reactions of the other 4-haloquinoline 1-oxides, 4-haloquinolines, and 4-halo-1-nitronaphthalenes with piperidine were treated by the same technique. The absorptions at 370 and 430 mμ were used as the key band for 4-piperidinoquinoline and 4-piperidino-1-nitronaphthalene, respectively.

*4 Unicam spectrophotometer, Model 500, was used for the determination of the UV spectra.

TABLE IV. Summary of Kinetic Data

	Reaction No.	Solvent	Temp. (°C)	$k_2 \times 10^3$ L./mole/sec.		
4-Chloroquinoline 1-oxide						
	1	70% EtOH	90	0.637	0.685	
			80	0.421		
			70	0.264	0.268	
	2	95% EtOH	110	0.830	0.776	
			100	0.548	0.559	0.588
			90	0.428	0.427	
4-Bromoquinoline 1-oxide						
	3	70% EtOH	80	0.550	0.564	
			70	0.354	0.352	
			60	0.193	0.172	
			30.4	0.0323		
	4	95% EtOH	110	1.30	1.38	
			100	0.910	0.821	
			90	0.610	0.560	
	5	Benzene	120	0.0726		
			110	0.0495		
4-Iodoquinoline 1-oxide						
	6	70% EtOH	100	0.350		
			90	0.229		
			80	0.139	0.152	
	7	95% EtOH	110	0.390		
			100	0.251		
			90	0.171		
4-Chloroquinoline						
	8	70% EtOH	150	0.769		
			140	0.458		
			130	0.355	0.314	
			120	0.142	0.166	
			110	0.0873		
	9	95% EtOH	150	0.320		
			140	0.190	0.188	
			130	0.126	0.124	0.158
			120	0.0646		
4-Bromoquinoline						
	10	70% EtOH	130	0.477	0.423	
			120	0.249		
			110	0.137	0.142	
	11	95% EtOH	140	0.425	0.470	0.435
			130	0.257	0.275	0.292
			120	0.179	0.161	
	12	Benzene	120	0.00493		
4-Iodoquinoline						
	13	70% EtOH	150	0.604		
			140	0.354		
			130	0.214		
	14	95% EtOH	140	0.195		
			130	0.146		
			120	0.0900		
4-Chloro-1-nitronaphthalene						
	15	95% EtOH	90	0.264		
			75	0.127		
			65	0.0763		
4-Bromo-1-nitronaphthalene						
	16	95% EtOH	90	0.379	0.329	
4-Chloro-1-acetonaphthone						
	17	95% EtOH	150	0.0156		
			140	0.0102		

Typical Rate Measurement by the Titration Technique (A Slight Modification of Rheinlander's Method[21])—4-Chloro-1-acetonaphthone (1.054 g.) and piperidine (1.758 g.) were dissolved in 95% EtOH and the solution was diluted to 50 cc. in a volumetric flask (concentration of the chloro compound, 0.1031*M*; piperidine, 0.4129*M*). The solution was shaken thoroughly and 5-cc. aliquot was pipetted into ampules, then sealed as usual. The ampules were immersed in a thermostat (140°±3°). When the thermostat had returned to the temperature (requring about 5 min.), the time was recorded as 0 (zero). After being removed from the thermostat, each ampule was kept in an ice bucket. The reaction solution in the ampule was poured into a separatory funnel which contained 0.05*N* $AgNO_3$ (20 cc.), H_2O (20 cc.), 25% HNO_3 (7 cc.), and benzene (30 cc.). The ampule was washed with 10 cc. of EtOH and the washings were also added to the funnel. The funnel was shaken thoroughly. The water layer was separated and the benzene layer was washed with 20 cc. of H_2O. The precipitated AgCl remained in the benzene layer or between benzene and H_2O layers. The H_2O layer and H_2O washings were combined and, after adding $NH_4Fe(SO_4)_2$ reagent, the solution was titrated with 0.05*N* NH_4CNS (Volhard method). Thus the amount of liberated chloride ion was determined.

Tables II and III show the results obtained by this method. Rate coefficient was calculated from the expression : $k_2=\frac{2.303}{2t(0.5b-a)}\cdot\log\frac{0.5b(a-x)}{a(0.5b-x)}$ [*5] (where a and b are initial concentrations of the chloro compound and piperidine, respectively, and x is the cencentration of the product at time t).

Table II. Reaction of 4-Chloro-1-acetonaphthone with Piperidine in 95% EtOH, at 140°

Time (hr.)	5.0	20.5	26.0	45.5	68.0	75.0	94.0
Decomposition rate (%)	6.6	25.4	29.5	46.3	59.6	60.7	69.0
k_2 (L./mole/sec. $\times 10^5$)	0.936	1.020	0.985	1.046	1.073	1.006	1.046

mean $k_2=(1.016\pm0.046)\times10^{-5}$ L./mole/sec.

Table III. 4-Chloro-1-acetonaphthone with Piperidine in 95% EtOH at 150°

Time (hr.)	5.5	25.0	31.0	48.0	72.0
Decomposition rate (%)	8.0	28.8	33.3	42.9	56.0
$k_2\times10^5$	1.58	1.62	1.60	1.51	1.47

mean $k_2=(1.56\pm0.06)\times10^{-5}$ L./mole/sec.
4-Chloro-1-acetonaphthone, 1.066×10^{-1} mole/L., piperidine, 2.889×10^{-1} mole/L.

Results and Discussion

Rate measurements are summarized in Table IV. From these data, $\Delta H\ddagger$, $\Delta S\ddagger$, and rate coefficients (k_2) at 100° were calculated, and the reaction of 4-haloquinoline 1-oxides and 4-haloquinolines with piperidine was compared. Table V shows the results.

Table V.

	In 70% EtOH			In 95% EtOH			In benzene
	$k_2^{100°}\times10^3$	$\Delta H\ddagger$ kcal./mole	$\Delta S\ddagger$ cal./deg./mole	$k_2^{100°}\times10^3$	$\Delta H\ddagger$	$\Delta S\ddagger$	
4-Chloroquinoline 1-oxide	1.01	10.8	−42	0.582	7.96	−52	
4-Bromoquinoline 1-oxide	1.56	12.4	−36	0.887	10.7	−44	$k_2^{120°}=0.0726\times10^{-3}$ $\Delta H\ddagger=10.7$ $\Delta S\ddagger=-51$
4-Iodoquinoline 1-oxide	0.351	10.6	−46	0.261	10.6	−47	
4-Chloroquinoline	0.039	20.6	−24	0.021	16.3	−37	
4-Bromoquinoline	0.075	17.0	−32	0.059	14.5	−39	$k_2^{120°}=0.00493\times10^{-3}$
4-Iodoquinoline	0.037	16.6	−35	0.032	13.2	−44	

The errors of k, $\Delta H\ddagger$, and $\Delta S\ddagger$ are within ±5%, ±1 kcal., and ±3 cal./deg./mole, respectively.

Tables VI and VII show the relative reactivities of haloquinoline 1-oxides, haloquinolines, and halonaphthalenes.

[*5] The chloro compound consumed 2 moles of piperidine. See Reference (5a).

21) A. H. Rheinlander : J. Chem. Soc., **123**, 3099(1923).

Table VI. Reaction with Piperidine in 95% EtOH

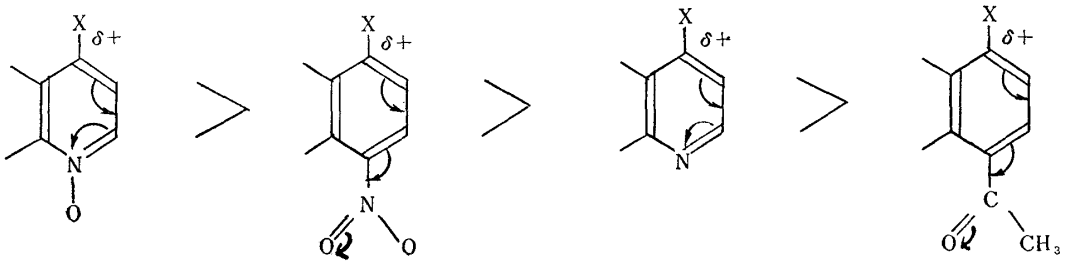
	$k_2^{90°} \times 10^3$	$\Delta H‡$	$\Delta S‡$
4-Chloroquinoline 1-oxide	0.424	7.96	−52
4-Chloro-1-nitronaphthalene	0.264	11.4	−44
4-Chloroquinoline	0.0112	16.3	−37
4-Chloro-1-acetonaphthone	0.000876	13.9	−48
p-Chloronitrobenzene*	0.0108	16.4	−37

Table VII. Reaction with Piperidine in 95% EtOH

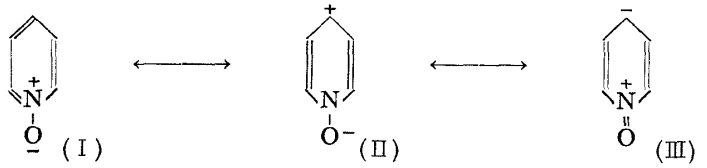
	4-Bromoquinline 1-oxide	4-Bromo-1-nitronaphthalene	4-Bromo-quinoline	*p*-Bromonitro-benzene*
$k_2^{90°} \times 10^3$	0.583	0.354	0.0335	0.0139

* N.B. Chapman, ref. (5d). solvent : 99.8% EtOH

As shown in Tables V, VI, and VII, 4-haloquinoline 1-oxides react more than ten times faster than 4-haloquinolines. Further, 4-haloquinoline 1-oxides react faster than 4-halo-1-nitronaphthalenes. Thus, the N-oxide group is considered as the strongest accelerating group for nucleophlic substitution. The order of the accelerating power found from the present experiments was as follows :



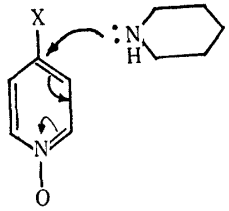
Linton[22] pointed out from the dipole moment studies that the canonical formulae of types II and III contribute to the electronic state of pyridine 1-oxide. Ochiai[2] experimentally supported this conception, especially by studies on the nitration of aromatic N-oxides.



Further, Shindo[23] gave +0.25 for σ(p) value of the N-oxide group from the data of infrared spectra of pyridine 1-oxides and this small value again supports the above-mentioned data.

However, Jaffé[24] gave 1.36 for σ(p) of the N-oxide group from the pK values of pyridine 1-oxides. The present data also showed that the N-oxide group is more negative than the nitro group. Thus, σ^*(p) of the N-oxide group should have larger value than +1.27 which is σ^*(p) value of the nitro group. As already shown by Bunnett,[25] σ^* value should be used for aromatic nucleophlic substitution. In the present case, approach of piperidine, which bears electron pair, should accelerate the -T effect of the N-oxide group as follows :

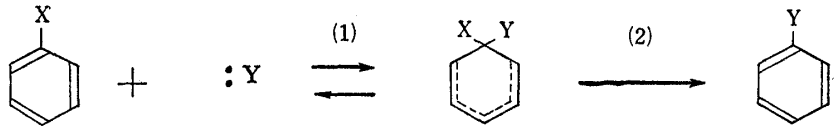
22) E.P. Linton : J. Am. Chem. Soc., **62**, 1945(1940).
23) H. Shindo : This Bulletin, **6**, 117(1958).
24) H.H. Jaffé : J. Am. Chem. Soc., **76**, 3527(1954); *ibid.*, **77**, 4441(1955).
25) J.F. Bunnett, F. Draper, Jr., P.R. Ryason, P. Noble, Jr., R.G. Tonkyn, R.E. Zahler : *Ibid.*, **75**, 642(1953).



Consequently the present estimation of σ^* value is larger than plain σ value. Even so, it should be emphasized that the N-oxide group seems to have the most negative character.

Considering the ease of nitration at 4-position of pyridine 1-oxide and the above-described results, it may be said that 4-position of the aromatic N-oxides is reactive to both electrophilic and nucleophilic substitutions. An explanation for these phenomena is that the polar effect of the N-oxide group may be greatly varied by the reaction conditions.

From Table V, decrease in the order of the reactivity of halogen atoms is shown to be Br, Cl, and I, in both haloquinoline 1-oxides and haloquinolines. This order can be explained well by the mechanism of intermediate formation. The reaction rate depends



on two factors; the first is the rate of the formation of an intermediate and the second is the rate of the breaking of carbon-halogen bond. The first step should be accelerated in the order of the negativity of each halogen atom, i.e. F>Cl>Br>I. The second step should be accelerated in the order of I>Br>Cl>F, which is the reverse order of the strength of the carbon-halogen bond. Consequently, if the rates in both steps are responsible for this reaction, the order of Br>Cl>I is not incompatible. These examples have been shown in many papers.[6]

The polarity of a solvent also greatly affects the reaction rate. The order of the rate coefficients are parallel to that of the polarity of a solvent (Table V). It is known that the rate of a reaction involving the formation of an ionic transition state from uncharged molecule is dependent on a solvent. In these cases, as the solvent becomes more polar, the energy of activation (or heat constant of activation) increases slightly, the entropy of activation greatly increases from a large negative value to a smaller negative value, and the rate increases. These phenomena were well analysed by Pearson[26] and other examples have been shown by Bunnett.[27]

Comparing 4-haloquinoline 1-oxides and 4-haloquinolines, $\Delta H\ddagger$ of the N-oxide series are 5~10 kcal. and 3~8 kcal. smaller in 70% EtOH and 95% EtOH, respectively, and $\Delta S\ddagger$s of the N-oxides are also lower (larger negative) than those of the corresponding haloquinolines. These data show that transition states of haloquinoline 1-oxides are much solvated than those of haloquinolines.

The authors express their deep appreciation to Dr. E. Ochiai for his encouragement and also thank the members of the Central Analysis Room of this Faculy for microanalyses.

Summary

Reaction rates of 4-haloquinoline 1-oxides, 4-haloquinolines, 4-halo-1-nitronaphthalenes, and 4-halo-1-acetonaphthone with piperidine were compared. Rate coefficients, heat constants of activation, and entropies of activation were calculated. 4-Haloquinoline 1-oxides were most reactive and activating power of the N-oxide group was greater than that of the nitro group. (Received February 6, 1960)

26) R. G. Pearson : J. Chem. Phys., **20**, 1478(1952). cf. A. A. Frost, R. G. Pearson : "Kinetics and Mechanism," 122(1953).
27) J. F. Bunnett, R. J. Morath : J. Am. Chem. Soc., **77**, 5051(1955).