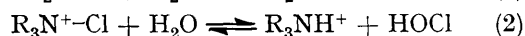
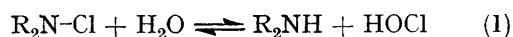


Mechanism and Thermodynamics of Chlorine Transfer among Organo-halogenating Agents. Part IV.¹ Chlorine Potentials and Rates of Exchange

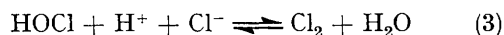
By T. Higuchi,*† A. Hussain, and Ian H. Pitman, School of Pharmacy, University of Wisconsin, Madison 53706, U.S.A.

The relative abilities of organohalogenating agents, *N*-chloroquinuclidinium ion, *N*-chlorosuccinimide, *N*-chloro- and *N*-methyl-benzenesulphonamide, chloramine-T, dichloramine-T, dimethylchloramine, diethylchloramine, di-isopropylchloramine, dibutylchloramine, dipropylchloramine, methylbutylchloramine, *N*-chloropiperidine, and *N*-chloromorpholine to transfer their active chlorine to a suitable acceptor have been determined from both thermodynamic and kinetic standpoints. The secondary chloramines, although extremely weak bases, appear to react only in their protonated form. Of the tertiary *N*-chloro-ions, only *N*-chloroquinuclidinium ion and related bridge-head-nitrogen compounds are sufficiently stable to permit evaluation of their thermodynamic properties. The tendency to donate positive chlorine changes at pH 7 by a factor of 10⁸ on going from diethylchloramine to *N*-chloroquinuclidinium ion. The work partly overlaps the classical studies of Soper and his co-workers although the experimental approaches and some of the results differ substantially.

NITROGEN-CONTAINING organic molecules can be oxidised to *N*-chloro-derivatives by a wide variety of chlorinating agents. Because the *N*-chloro-derivatives are themselves chlorinating agents an attempt has been made to classify them with regard to their chlorinating ability or chlorine potential. For this purpose, chlorine potential, pK_{cp} , of an *N*-chloro-compound is defined as $pK_{cp} = -\log_{10} K_{cp}$, where pK_{cp} is the equilibrium constant for the hydrolysis of the *N*-chloro-compound to yield hypochlorous acid. Typical reactions are (1) for uncharged *N*-chloro-compounds and (2) for charged *N*-chloro compounds. This method of referring



measurements directly to hypochlorous acid was used by Soper and his co-workers in earlier studies.²⁻⁸ Also, since hypochlorous acid can be related to elemental chlorine through the equation (3) its aqueous solutions were considered to be a convenient reference state.



Direct determination of K_{cp} values is possible in only

† Present address: Pharmaceutical Chemistry Laboratory, University of Kansas, Lawrence, Kansas 66044, U.S.A.

¹ Part III, T. Higuchi, K. Ikeda, and A. Hussain, *J. Chem. Soc. (B)*, 1968, 1031.

² F. G. Soper, *J. Chem. Soc.*, 1924, 125, 1899.

³ F. G. Soper, *J. Chem. Soc.*, 1925, 98.

a few cases since the equilibria are usually so far to the left that direct measurement becomes impracticable. In such cases it is more convenient to measure equilibrium constants, K_E , for chlorine exchange reactions of the type (4) and to relate the results directly to hypochlorous acid.



This paper gives preliminary results of (a) measurements in aqueous solution designed to establish the chlorine potential of a series of *N*-chloro-compounds and (b) determinations of the chemical kinetics and mechanism of chlorine exchange reactions.

N-Chloroquinuclidinium salts were useful for comparative studies because they have chlorine potentials intermediate between those of hypochlorous acid and common chlorinating agents. Also, their aqueous solutions are more stable, especially above pH 5, than those of compounds such as trimethylchlorammonium salts.⁹ Chloramine-T appeared to be a useful model compound but its chemistry is complicated by its tendency to disproportionate into the free sulphonamide

⁴ F. G. Soper and G. F. Smith, *J. Chem. Soc.*, 1928, 138.

⁵ D. R. Pryde and F. G. Soper, *J. Chem. Soc.*, 1931, 1510.

⁶ D. R. Pryde and F. G. Soper, *J. Chem. Soc.*, 1931, 1514.

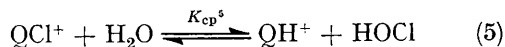
⁷ R. E. Corbett, W. S. Metcalf, and F. G. Soper, *J. Chem. Soc.*, 1953, 1927.

⁸ L. G. Brown and F. G. Soper, *J. Chem. Soc.*, 1953, 3576.

⁹ A. J. Ellis and F. G. Soper, *J. Chem. Soc.*, 1954, 1750.

and to dichloramine-T.¹⁰ Hence, the chlorine potential of *N*-chloroquinuclidinium ion was first determined accurately and the equilibrium constants for the chlorine exchange between this compound and other nitrogen-containing molecules were measured.

Chlorine Potential of N-Chloroquinuclidinium Ion at 25°.—*N*-Chloroquinuclidinium ion (QCl⁺) appeared to be



stable in aqueous acid at 25° and the equilibrium constant for reaction (5), K_{cp}^5 , could not be measured directly.

However, at higher pH, where hypochlorous acid (HOCl) and quinuclidinium ion (QH⁺) are dissociated appreciably, a more readily measured equilibrium was rapidly established. Experimentally, aqueous solutions of HOCl were added to alkaline solutions of the amine and equilibrium concentrations of hypochlorite ion (OCl⁻) and HOCl were calculated from the observed u.v. absorbance at 293 mμ and the pH of the solution. The molar extinction coefficients (ϵ) at this wavelength (HOCl 27 and OCl⁻ 356 l. mole⁻¹ cm.⁻¹) and dissociation constant of HOCl ($K_a = 2.83 \times 10^{-8}$) were previously measured under the experimental conditions. The observed equilibrium constant K_{obs} was calculated from

$$K_{\text{obs}} = \frac{[\text{QCl}^+][\text{OH}^-]}{([\text{Q}] + [\text{QH}^+])[\text{ClO}^-]}$$

these values by using the identities (6) and (7). Values

$$[\text{QCl}^+] = [\text{HOCl}]_{\text{added}} - ([\text{HOCl}] + [\text{OCl}^-]) \quad (6)$$

$$([\text{QH}^+] + [\text{Q}]) = ([\text{Q}]_{\text{added}} - [\text{QCl}^+]) \quad (7)$$

of K_{obs} which were calculated from experiments at two different amine concentrations and several pH values are in Table 1.

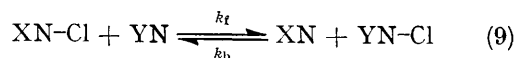
The value of the equilibrium constant for reaction (5), K_{cp}^5 , is related to K_{obs} by the identity (8) where K_b is

$$K_{\text{cp}}^5 = \frac{K_w K_b [\text{H}^+]}{K_{\text{obs}} K_a (K_b [\text{H}^+] + K_w)} \quad (8)$$

the basic dissociation constant of quinuclidine (5.13×10^{-4}), K_w is the dissociation constant of water (1.008×10^{-14}), and K_a is the dissociation constant of hypochlorous acid (2.83×10^{-8}). Values of K_{cp}^5 so calculated are in Table 1. The mean value of 13 determinations was $(7.049 \pm 0.352) \times 10^{-6}$ (95% confidence limit). Thus, the chlorine potential of *N*-chloroquinuclidinium ion was 5.15 ± 0.02 at 25°.

Equilibrium Constants for Chlorine Exchange Reactions.

—Rates and equilibrium constants for chlorine exchange reactions between a series of *N*-chloro-compounds and other nitrogen-containing molecules have been determined. The reactions studied were of the type (9)



where XN-Cl and YN-Cl are *N*-chlorinated derivatives of the nitrogen-containing molecules XN and YN, respectively. The equilibrium constant, K_E , for these reactions was defined by (10). Wherever possible K_E

$$K_E = \frac{k_f}{k_b} = \frac{[\text{XN}][\text{YN-Cl}]}{[\text{YN}][\text{XN-Cl}]} \quad (10)$$

values were calculated directly from spectrophotometry of equilibrium concentrations of reactants and products. In other cases, the rate constants, k_f and k_b , for the

TABLE 1

Observed equilibrium constants, K_{obs} , values for formation of *N*-chloroquinuclidinium ion in alkaline hypochlorite solution, and the hydrolytic constant, K_{cp}^5 , for *N*-chloroquinuclidinium ion at 25°

10 ³ [Added quinuclidine] ^a (M)	pH	10 ² K_{obs}	10 ⁶ K_{cp}^5
4.43	8.286	4.812	7.401
4.43	8.470	5.036	7.064
4.43	8.742	5.095	6.941
4.43	8.766	5.072	6.968
4.43	8.850	5.050	6.981
4.43	9.160	5.056	6.874
4.43	9.300	5.042	6.822
4.43	9.624	4.711	7.121
4.17	8.342	5.028	7.078
4.17	8.362	4.988	7.135
4.17	8.688	4.993	7.092
4.17	8.861	4.979	7.078
4.17	8.898	4.973	7.078

^a Added hypochlorous acid was 3.30×10^{-3} M in every instance.

TABLE 2

Abbreviated names used

<i>N</i> -Chloroquinuclidinium ion	QCl ⁺
Quinuclidinium ion	QH ⁺
<i>N</i> -Chlorosuccinimide	StCl
Succinimide	SI
<i>N</i> -Chloro- <i>N</i> -methylbenzene-sulphonamide	NMBSACl
<i>N</i> -methylbenzene-sulphonamide	NMBSA

forward and back reactions were determined from spectrophotometry and the equilibrium constant, K_E , calculated from k_f/k_b . This method was based on the assumption that the forward and back reactions proceeded *via* the same transition state under the different experimental conditions employed when the rate constants were measured. To test this assumption K_E was determined both directly and from measured rate constants where possible. The method by which each K_E value was determined is included in Tables 5 and 7.

The observed equilibrium constants for reactions of *N*-chloroquinuclidinium ion, *N*-chlorosuccinimide, and *N*-chloro-*N*-methylbenzenesulphonamide with secondary amines increased with increasing pH whereas the values for reactions not involving secondary amines were pH-independent. Thus, it is convenient to discuss the two types of systems separately.

Chlorine Exchange Reactions involving Secondary Amines.—Logarithmic plots against pH of observed

¹⁰ T. Higuchi, K. Ikeda, and A. Hussain, unpublished data.

second-order rate constants, $k_{f, \text{obs}}$ and $k_{b, \text{obs}}$, for reactions in the dimethylamine-*N*-chloroquinuclidinium ion system are shown in Figure 1. The rate constant for the forward reaction can be described by the identity, $\log k_{f, \text{obs}} = -3.5874 + 1.045 \text{ pH}$ while that for the back reaction is essentially independent of pH in the pH region studied and $k_{b, \text{obs}} = 0.00245 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. At pH 2.3 $k_{f, \text{obs}}/k_{b, \text{obs}}$ gave $K_{E, \text{obs}} = 27$.

$K_{E, \text{obs}}$ was also determined directly from spectrophotometry at 263 m μ following addition of quinuclidine to a mixture of dimethylamine and dimethylchloramine

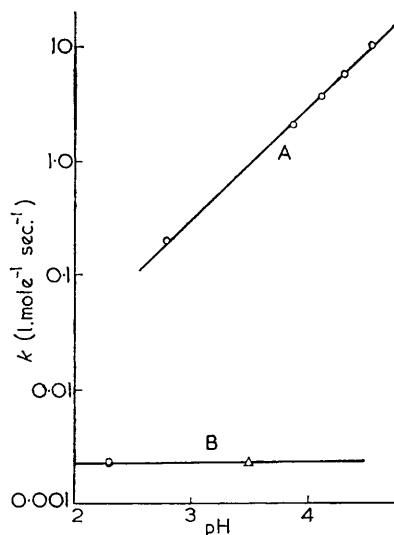


FIGURE 1 pH-Rate profiles of $\text{QCl}^+ + \text{Me}_2\text{NH} \xrightleftharpoons[k_b]{k_f} \text{QH} + (\text{Me})_2\text{NCl}$ at 25°. The reactions were followed spectrophotometrically at 263 m μ in both directions. The solid circle plot B was calculated from the equilibrium constant and k_f .

A, $k_{f, \text{obs}}$ and B, $k_{b, \text{obs}}$

(prepared previously by adding a known amount of hypochlorous acid to a known excess of dimethylamine at pH 7). Values of the equilibrium constant so calculated are in Table 3. Extrapolation of these data

TABLE 3

Observed equilibrium constant for chlorine exchange between *N*-chloroquinuclidinium ion and dimethylamine at 25°

pH	$10[\text{QH}^+]$ added (M)	$10^3[\text{HOCl}]$ added (M)	$10^4 \times$ Excess of $[\text{Me}_2\text{NH}]$ to $[\text{HOCl}]$ added (M)	Absorb. at Equim.	$K_{E, \text{obs}}$
3.54	1.04	0.367	0.630	0.410 ^a	418
4.12	1.00	1374.0	21,000.0	0.422 ^b	1410

^a Optical path = 5 cm.

^b Optical path = 10 cm.

to pH 2.3 gives $K_{E, \text{obs}} = 22.5$ which is close to the value calculated from $k_{f, \text{obs}}/k_{b, \text{obs}}$.

Similar pH-dependence was found for equilibrium reactions of other secondary amines with organohalogenating agents in acidic solution. Observed rate and equilibrium constants are included in Tables 4 and 5

respectively, together with pH values at which measurements were made and the analytical wavelength.

The close agreement between $K_{E, \text{obs}}$ values obtained from direct measurement and those calculated from kinetic data supports the assumption that the forward and back reactions proceed *via* identical transition states and that either kinetic or thermodynamic data can be used in the calculations.

Further, the pH-dependence of the rate constants strongly suggest that the significant reactions in these systems were between neutral molecules of the secondary amines and the non-protonated *N*-chloro-compound and

TABLE 4

Second-order rate constants (l. mole⁻¹ sec.⁻¹) for reactions of secondary amines with organohalogenating reagents at pH 3.91 and 25°

Reactants		pK _b of second- ary amine	Anal. λ (m μ)	$k_{f, \text{obs}}$	$10^{-7}k_f$	$10^4k_{b, \text{obs}}$ ^a
QCl ⁺	Me ₂ NH	3.28	263	3.152 ^b	2.019	0.0245
NMBSACl	Me ₂ NH	3.28	288	0.0382 ^c	0.0245	0.341
SICl ^d	Me ₂ NH	3.28	263	2.41	1.53	8.8
SICl	Et ₂ NH	3.02	263	1.15	1.35	3.7
SICl	Pr ₂ NH	2.95	263	1.1	1.52	4.8
SICl	Pr ₂ HN	2.95	263	0.2	0.27	23.0
SICl	Bu ₂ NH	2.8	263	1.05	2.0	4.4
SICl	MeBuNH	3.10	263	1.55	1.50	6.8
SICl	Piperidine	2.72	263	1.83	4.3	1.4
SICl	Morpholine	5.55	263	12.8	0.04	2.0

^a Values are essentially independent of pH in acid solution.

^b Five values at different pH values could be correlated by the equation $\log k_{f, \text{obs}} = -3.587 + 1.045 \text{ pH}$. ^c Five values at different pH values could be correlated by the equation $\log k_{f, \text{obs}} = -5.141 + 1.029 \text{ pH}$. ^d Method as described in ref. 12.

TABLE 5

Equilibrium constants for reactions of secondary amines with organohalogenating reagents at 25°

Reactants		Anal. λ (m μ)	pH	$K_{E, \text{obs}}$ ^a Direct	$K_{E, \text{obs}}$ ^b Kinetic	$10^{-9}K_E$ ^c
QCl ⁺	Me ₂ NH	263	3.54	418	—	6.00
			4.12	1410	—	5.57
			2.30	22.5 ^d	26.0	5.78
NMBSACl	Me ₂ NH	288	3.91	—	1.36	0.008709
SICl	Me ₂ NH	263	3.91	2.6	2.71	0.01665
	Et ₂ NH	263	3.91	3.04	3.1	0.03543
	Pr ₂ NH	263	3.91	—	2.3	0.0315
	Pr ₂ HN	263	3.91	0.092	0.091	0.00126
	Bu ₂ NH	263	3.91	—	2.44	0.0472
	MeBuNH	263	3.91	—	2.3	0.0223
	Piperidine	263	3.91	13.0	12.8	0.3022
Morpholine	263	3.91	64.5	64.0	0.00222	

^a Calculated directly from spectrophotometric measurements. ^b Calculated from $k_{f, \text{obs}}/k_{b, \text{obs}}$. ^c When the directly measured $K_{E, \text{obs}}$ value was available it was made pH-independent by correcting to allow for the concentration of amine cation. In other cases the kinetic value was corrected. ^d Interpolated value.

between the protonated forms of the secondary chloramines and non-protonated forms of the other nitrogen-containing acceptors. Thus, the appreciable concentration of protonated amine present in acid solutions could be taken into account, and pH-independent rate constants for the forward reaction calculated by multi-

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plying the observed constants by the factor $(1 + K_b[H^+]/K_w)$, where K_b is the basic dissociation constant of the secondary amine and K_w is the dissociation constant of water. Values of this pH-independent rate constant, k_t , are in Table 4. Similarly, the observed

TABLE 6

Rate constants^a for chlorine exchanges not involving secondary amines

Reactants	Anal. λ	$\log k_{f, \text{obs}}$	$\log k_{b, \text{obs}}$
$\overbrace{\text{XN-Cl}}^{\text{YN}}$ (m μ)			
QCl ⁺ NMBSA 250		$-2.224 \times 1.006\text{pH}$	$-4.930 + 0.966\text{pH}$
QCl ⁺ SI 223		$-1.364 \times 0.970\text{pH}$	$-3.875 + 0.956\text{pH}$
SI-Cl NMBSA 250		$-4.877 \times 0.975\text{pH}$	$-5.2014 + 0.997\text{pH}$

^a Rate constants were determined at, at least, 4 different pH values for each system.

TABLE 7

Equilibrium constants for chlorine exchanges not involving secondary amines

Reactants	Anal. λ	$K_{E, \text{obs}}$ Direct	$K_{E, \text{obs}}$ Kinetic
$\overbrace{\text{XN-Cl}}^{\text{YN}}$ (m μ)			
QCl ⁺ SI 223		—	360
QCl ⁺ NMBSA 250		708	—
SI-Cl NMBSA 250		—	1.63

equilibrium constants, $K_{E, \text{obs}}$, were made pH-independent by multiplying by the factor $(1 + K_b[H^+]/K_w)$ and values of the pH-independent equilibrium constant, K_E , are in Table 5.

Chlorine Exchanges not involving Secondary Amines.—Observed second-order rate constants are in Table 6 and observed equilibrium constants in Table 7 for chlorine exchanges between *N*-chloroquinuclidine, *N*-chlorosuccinimide, and *N*-chloro-*N*-methylbenzenesulphonamide, and their non-chlorinated analogues. For each reaction the plot of $\log k_{\text{obs}}$ against pH had a slope approaching unity, strongly suggesting that the favoured reactions occur between a non-protonated chlorine donor and an acceptor with a non-protonated nitrogen atom. K_E was pH-independent over the pH range studied.

Chlorine Potentials calculated from Equilibrium Constants for Chlorine Exchange Reactions.—Equation (11) follows from the definitions of pK_{cp} and K_E . Thus, if

$$pK_{\text{cp}}^{\text{YN-Cl}} = pK_{\text{cp}}^{\text{XN-Cl}} + \log K_E \quad (11)$$

K_E for a particular equilibrium system and pK_{cp} of one of the *N*-chloro-components are known, the chlorine potential of the other *N*-chloro-component can be calculated.

Values of chlorine potentials of the compounds studied were calculated from the measured K_E values and are in Table 8 together with the acceptor molecule in the system investigated. The values in column 3 are essentially pH-independent as required by the definition of a chlorine potential. However, because secondary amines actually exist mainly as cations in the pH regions studied a pH-dependent or 'practical' chlorine potential of secondary amines is included in Table 8 for

comparison with other systems. These values correspond to the relative availability of hypochlorous acid at pH 7. In more acid solution, chlorine potential will decrease directly with pH thus reflecting the increasing

TABLE 8

Chlorine potentials of a series of *N*-chloro-compounds

Donor XN-Cl	Acceptor YN	Chlorine potential pK_{cp}	Practical chlorine potential at pH 7
QCl ⁺ ^a	H ₂ O	5.15	
SI-Cl ^b	QH ⁺	7.71	
NMBSA-Cl ^a	QH ⁺	8.00	
NMBSA-Cl ^b	SI	7.92	
Chloramine-T	SI	7.77 ^c (7.31) ^d	
Dichloramine-T	SI	6.55 ^c (6.1) ^d	
Me ₂ NHCl ^{a, b}	QH ⁺	14.93	11.18
Me ₂ NHCl ^b	SI	14.93	
Me ₃ NHCl ^b	NMBSA	14.94	
Et ₂ NCl ^{a, b}	SI	15.23	11.26(7.7) ^e
Pr ₂ NCl ^{a, b}	SI	15.21	11.16
Pr ₁ ⁺ NCl ^{a, b}	SI	13.10	9.77
Bu ₂ NCl ^{a, b}	SI	15.38	11.18
MeBuNCl ^{a, b}	SI	15.06	11.16
<i>N</i> -Chloropiperidine ^{a, b}	SI	16.19	11.93
<i>N</i> -Chloromorpholine ^{a, b}	SI	14.06	12.62

^a Calculated from directly measured equilibrium constants.

^b Calculated from equilibrium constants which were obtained from the ratio of forward and reverse rate constants. ^c From ref. 1. ^d From ref. 2. ^e From ref. 8.

chlorination potential of the dialkylchloramines in acid. Hence, at pH 7 and dialkylchloramines are substantially weaker chlorinating agents than compounds such as *N*-chlorosuccinimide, but at pH 3 the differences are greatly reduced.

The constancy of pK_{cp} for a particular compound, regardless of the system chosen for its evaluation, supports the concept and usefulness of chlorine potentials.

While no serious attempt has been made to correlate values of chlorine potentials with chemical structure, it is apparent that the relative availability of positive chlorine depends on the competition between a proton and positive chlorine atoms for the same site. Mechanistic aspects of these reactions will be treated elsewhere.

The earlier values are shown in parentheses in Table 8. The constant for diethylchloramine as calculated by Brown and Soper⁸ appears to differ from the present value by several orders of magnitude. We cannot completely account for the differences except to state that the earlier value is based on a rather lengthy extrapolation of the rate of reaction of diethylchloramine with *p*-cresol from high concentrations of the latter to zero concentration. Anber and Yagil¹¹ have suggested that some data employed in the earlier calculation may be wrong. The only two remaining literature comparisons, *i.e.*, for chloramine-T and dichloramine-T, agree at least within an order of magnitude with our results. Since our values appear to be based on more reliable procedures we accept them.

¹¹ M. Anber and G. Yagil, *J. Amer. Chem. Soc.*, 1962, **84**, 1790.

EXPERIMENTAL

Procedures were as before.¹²

Reagents.—All reagents were of good commercial grade and were further purified before use. Dialkylamines were distilled and their concentration in water determined by potentiometric titration. 1 Equiv. of sulphuric acid was added to convert the amines into their sulphates. *N*-Chloro-*N*-methylbenzenesulphonamide was prepared as described by Chattaway and Orton,¹³ and recrystallized, m.p. 79–80° (lit., 81°).

Quinuclidine (Melpar Inc.) was converted into its perchlorate by dissolving 5 g. in 5 ml. of ether and precipitation with excess of perchloric acid. The perchlorate salt was recrystallized from 95% ethanol. This treatment was necessary to eliminate contaminants.

Determination of the Equilibrium Constants.—*Equilibrium formation of chloroquinuclidine species.* Exactly 5 ml. of quinuclidine solution (4.43×10^{-2} M) was transferred to a 50 ml. volumetric flask. To this exactly 5 ml. of hypochlorous acid solution (3.3×10^{-2} M) was added and the volume brought to the mark with 0.1M-acetate buffer (pH 5.5). After 30 min., several 5 ml. portions of the mixture were transferred to individual 50 ml. volumetric flasks and brought to the marks with buffer solutions of different pH values.

The flasks were allowed to equilibrate in a water-bath for 30 min. at 25° before the peak heights were determined spectrophotometrically at 293 m μ in a 5 cm. light-path silica cell. Appropriate blank solutions were used in each instance.

Equilibrium constant for transfer of positive chlorine between quinuclidine and N-methylbenzenesulphonamide. The equilibrium solutions were prepared by mixing exactly 5 ml. of 5.59×10^{-4} M-*N*-chloro-*N*-methylbenzenesulphonamide with an appropriate excess of quinuclidine in a 50 ml. volumetric flask. The volume was brought to mark with 0.10M acetate buffer (pH 3.8). The mixed solutions were permitted to equilibrate overnight at 25° before their absorbance at 250 m μ was determined in a 10 cm. light-path silica cell.

Equilibrium constant for chlorine exchange between quinuclidine and dimethylamine. Solutions of dimethylchloramine and quinuclidine were prepared with appropriate buffers and allowed to equilibrate in a water-bath at 25° for 60 min. The peak height at 263 m μ was measured in either a 5 or a 10 cm. light-path silica cell. The chloramine concentration was checked from its maximum absorbance at 263 m μ and the value of its molar absorptivity as given by Weil and Morris¹⁴ and as confirmed by our work. The molar absorptivity values were as follows, $\overset{+}{\text{QCl}}$, 15.6, and $\overset{+}{\text{QH}}$, 0.145 expressed in units of litre mole⁻¹ cm.⁻¹ in water.

Equilibrium constant for chlorine exchange between dialkylamine and succinimide. The procedure essentially as described by Higuchi and Hasegawa¹² was followed.

Determination of Rate Constants.—Reaction rates were determined on a Cary Model 15 spectrophotometer, the change in absorbance being followed in either a 1 or a 2 cm. light-path silica cell. Solutions were usually made up at double the concentration at which they were to be used and mixed within the spectrophotometric cell by syringe injection. The specific rate constants were calculated from spectrophotometric measurements of rates of change of

absorbance when one of the reactants (or products) was rapidly mixed with a large excess of the second component. Under such conditions the reaction went essentially to completion in one direction and exhibited first-order behaviour. Second-order rate constants were calculated from the measured first-order constants. When the forward rate constant in equation (10) was of the order of 600–800 times smaller than the back rate constant it was not possible to obtain experimental conditions which would permit essentially stoichiometric reaction of the *N*-chloroamine with an excess of the other reagent. It can readily be shown, however, that if the component YN is in very large excess over the *N*-chloro-component, XN-Cl, the

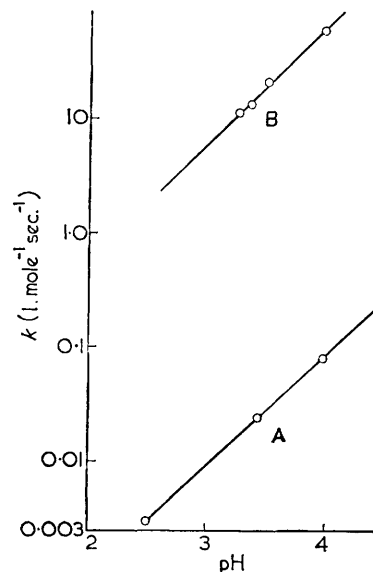


FIGURE 2 pH-Rate profile for the reaction $\text{NMBSA} + \text{QH}^+ \xrightleftharpoons[k_b]{k_f} \text{NMBSA} + \text{QCl}^+$ at 25°. The points were calculated as described in the Experimental section.

A, k_f , obs and B, k_b , obs

integrated equation (12) is valid provided equation (10) holds, where a_0 , a_e , and a_t are the concentrations of the

$$\ln \frac{a_0 - a_t \left(\frac{a_e}{a_0} \right)}{a_t - a_e} = t \sqrt{[4B_0 a_0 k_b k_f + (B_0 k_f)^2]} \quad (12)$$

N-chloro-component (XN-Cl) initially, at equilibrium, and at time t , respectively, and B_0 is the initial concentration of component YN. Under conditions where $a_e/a_0 \ll 1$, this equation reduces to (13) and a plot of $\ln(a_t - a_e)$ (or an

$$\ln a_0 - \ln(a_t - a_e) = t \sqrt{[4B_0 a_0 k_f k_b + (B_0 k_f)^2]} \quad (13)$$

equivalent term which allows for the change in absorbance) against time will yield a straight line with a slope of $B_0 k_f \sqrt{[(4a_0 k_b/B_0 k_f) + 1]}$. An example of a system for which this process was used was to calculate the forward rate constant for the reaction of quinuclidinium ion with *N*-chloro-*N*-methylbenzenesulphonamide. Initially the solution contained $[\text{QH}^+] = 1.06 \times 10^{-1}$ M, and $[\text{NMBSA}] = 5.59 \times 10^{-5}$ M and the pH was 3.5. The forward second-

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¹³ I. Weil and J. C. Morris, *J. Amer. Chem. Soc.*, 1949, **71**, 3132.

¹⁴ F. D. Chattaway and K. J. P. Orton, *J. Chem. Soc.*, 1901, **79**, 274.

order rate constants determined in this fashion at pH 3.45 and at pH 2.50 are shown on plot B in Figure 2. The straight line through these plots with a slope of unity falls directly on the third point at pH 4 which was calculated indirectly from the equilibrium constant for this reaction and the reverse rate constant. The agreement constitutes an approximate check on the equilibrium constant; the values of the forward rate constant determined at lower pH values contain, however, a term in which $k_{b, \text{obs}}/k_{f, \text{obs}}$ appears as a factor. For the concentration used the numerical values of the forward rate constants determined in this

manner are influenced by about a third of this ratio. Although the two methods are not altogether independent, it is evident on this basis that for practical purposes they may be considered so. This method was also used to compute the rate constant for the reaction of *N*-chlorosuccinimide and quinuclidinium ion.

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