THE KINETICS OF REACTIONS OF CYANOGEN HALIDES WITH BASES IN AQUEOUS SOLUTION.

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Very few quantitative measurements of rates of reactions in which a cyanogen halide is a reactant are recorded in the literature. Mooney and Reid¹ have determined the rates of reaction of CNI, CNBr and CNCl with HI in CCl₄ solution. Angelescu and Popescu² gave the results of one experiment in which the reaction measured was effectively that between CNI and NaOH but did not state the concentration of alkali employed. Finally, Møller³ measured the rate of the analogous

¹ Mooney and Reid, J.C.S., 1933, 1318.

² Angelescu and Popescu, Z. physikal. Chem., A, 1931, 156, 258. ³ Møller, Det. Kgl. Danske Vid. Selsk., Math. fys. Medd., 1934, 12, No. 17.

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hydrolysis of CNBr by NaOH at o° C. and found the reaction to be unimolecular with respect to each reactant. He found that k_{bi} has the value 5.58 l./(moles-min.) at o°. As these appear to be the only kinetic measurements carried out with CNBr and CNI, it seemed of interest to extend them. Accordingly we have studied the reactions of these halides with alkalis (NaOH and KOH) at temperatures between 0° and 30°. Further work showed that the CO_3^{--} ion, NH₃, and amines also react with CNBr and CNI at conveniently measurable speeds, and we have studied the kinetics of several of these reactions and obtained their critical increments. In all, fifteen reactions have been investigated, nine with CNI as a reactant and six with CNBr. The amines used were mono-, di-, and tri-methylamines, mono-, di-, and tri-ethylamines, and triethanolamine.

Stoichiometrically the measured processes are the following :

$$\begin{array}{l} (\text{CNX} = \text{CNBr or CNI}) \\ & \text{CNX} + 2\text{OH}^- \rightarrow \text{CNO}^- + \text{X}^- + \text{H}_2\text{O}^{-4} \\ \text{CNX} + 2\text{CO}_3^{--} + \text{H}_2\text{O} \rightarrow \text{CNO}^- + 2\text{HCO}_3^- + \text{X}^- \\ & \text{CNX} + 2\text{NH}_3 \rightarrow \text{NH}_2\text{CN} + \text{NH}_4^+ + \text{X}^{--5} \\ & \text{CNX} + 2\text{R} \cdot \text{NH}_2 \rightarrow \text{RNHCN} + \text{RNH}_3^+ + \text{X}^{--6} \\ & \text{CNX} + 2\text{R}'\text{R''NH} \rightarrow \text{R'R''NCN} + \text{R'R''NH}_2^+ + \text{X}^{--6} \end{array}$$

For tertiary amines the resultants of the reactions with CNBr and CNI are not known with certainty. In organic solvents the reaction with CNBr yields a disubstituted cyanamide and an organic bromide,⁷ *i.e.*,

$$CNBr + R'R''R'''N \rightarrow R'R''NCN + R'''Br$$

In aqueous solution, however, we have found that the reaction between a tertiary base and cyanogen bromide produces bromide ion quantitatively. Possibly the reaction is

 $CNBr + 2R'R''R'''N + H_2O \rightarrow R'R''R'''N + R'R''R'''NH^+ + Br^$ with subsequent decomposition of R'R''R'''N into

$$R'R''NCN + R'''OH.$$

It is also possible that the cyano-compounds formed in the reactions of primary and secondary amines may polymerise, but this will not affect the reaction kinetics. It seems plausible to assume that each of the amine reactions (including those of ammonia) is in its first (and measured) stage a simple addition process, e.g.,

$$CNX + RNH_2 \rightarrow H_2N \xrightarrow{R} X$$

⁴ Nef, Annalen, 1895, 287, 316; Chattaway and Wadmore, J.C.S., 1902, 81, ⁵ Oberhauser and Schormuller, Ber., [B], 1929, **62**, 1436.

⁶ McKee, Amer. Chem. J., 1906, **36**, 208.

⁷ von Braun, Ber., 1900, **33,** 1438.

forming the halide of a very weak base or ampholyte which then rapidly reacts with a second molecule of a stronger base (the original amine):

$$\begin{array}{c} \underset{R}{\text{H}_{2}\text{N}} \xrightarrow{R} \\ \text{H}_{2} \xrightarrow{R} \\ \xrightarrow{R} \\ \text{CN} \end{array} \rightarrow \text{RHNCN} + \text{RNH}_{3} \text{X}.$$

Experimental.

Cyanogen iodide was prepared by the method of Grignard and Crouzier.⁸ It was recrystallised twice from alcohol or aqueous alcohol and preserved in the dark. Cyanogen bromide was prepared by Slotta's method ⁹ and purified by distillation. Stored in the dark it remained unchanged for over a year. Fresh stock aqueous solutions of CNBr and CNI were prepared for each experiment and their strengths determined iodometrically.

Ammonia was prepared from A.R. ammonium chloride, and an aqueous solution formed which was redistilled. The amines in most cases were purified by fractional distillation; in all cases they were converted into their hydrochlorides which were recrystallised two or three times from alcohol or water. For purposes of comparison with the commercial sample purified in this way a specimen of dimethylamine was prepared from A.R. dimethyl aniline, via p-nitroso-dimethylaniline. The methylamine hydrochloride obtained commercially contained about 10 per cent. of ammonium chloride and was too impure for satisfactory treatment by recrystallisation only. It was therefore subjected to preliminary purification by a method based on the fact that the methylamine is the stronger base, and hence on partial neutralisation of the impure base with HCl the ammonia is preferentially left free. The other chemicals employed (NaOH, KOH, Na₂CO₃, NaHCO₃, NH₄Cl, neutral salts, etc.) were of A.R. quality, and were employed without further purification.

Kinetic experiments have been carried out at temperatures between o° and $3o^{\circ}$, with the exception that the reaction between CNI and NH₃, which is too slow for convenient measurement at these temperatures, was studied between $4o^{\circ}$ and $6o^{\circ}$. Except for the reactions of CNI and CNBr with OH⁻, the measurements were carried out in buffered solutions, NaHCO₃ and Na₂CO₃ being present for the CO₃⁻⁻ reaction and mixtures of the base and its hydrochloride for the reactions of ammonia and the amines. Each experiment was started by pipetting the required volume of an aqueous solution of the cyanogen halide into the remainder of the reaction mixture contained in a glass-stoppered flask maintained in a thermostat. Samples withdrawn from time to time were run into acidified KI solution and the liberated iodine titrated with standard thiosulphate. The reaction :

$$CNX + 2HI \rightarrow HCN + HX + I_2$$

takes place quantitatively, very rapidly for CNI, but more slowly for CNBr. For the latter about half-an-hour was allowed for completion of this reaction before titrating the iodine liberated.

Each reaction was found to be of second order, and values of k_{bl} were calculated by means of the equation :—

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{bi}} (a - x)(b - 2x)$$

$$k_{\mathrm{bi}} = \frac{2 \cdot 303}{(t_2 - t_1)(b - 2a)} \log_{10} \frac{(a - x_1)(b - 2x_2)}{(a - x_2)(b - 2x_1)},$$

or

where a = initial concentration (moles/l.) of the cyanogen halide, $b = \text{initial concentration of the base (OH⁻, CO₃⁻⁻ or amine), and <math>x = \text{moles}$

⁸ Grignard and Crouzier, Bull. Soc. chim., 1921, 29, 214.

⁹ Slotta, Ber., 1934, **67,** 1029.

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per litre of cyanogen halide which has reacted at the time t (minutes). The initial concentration of cyanogen halide was usually between o oor and 0.005, and the other reactant was present in excess.

Reactions of CNI and CNBr with OH⁻.

In the reaction of CNI with NaOH good bimolecular constants were obtained in each experiment; as shown in Table I, however, the values of k_{bi} depend on the initial concentration of NaOH.

TABLE I.

$[CNI]_{init} = 0.005$; temp. = 20°.

[NaOH] _{init}	•		0.0103	0.0206	0.0412	0.0824	0.1648
k _{bi}	•	•	0.445	0.432	0.411	0.370	0.309

Similar experiments with KOH as reactant gave the same k_{bl} values at corresponding concentrations. Table II shows the effect of addition of various salts (at concentrations of $o \cdot I M$).

TABLE II.

$$[NaOH]_{init} = 0.0824$$
; $[CNI]_{init} = 0.005$; $[Salt] = 0.01$; temp. = 20°.

Salt			_	$NaNO_3$	KCl	KI	KCN
k _{bi} .	•	•	0.320	o·3 64	0.360	o•345	0.296

Sodium nitrate and potassium chloride have but a small depressing effect on $k_{\rm bl}$, much less than the effect of an equivalent amount of NaOH. KI and KCN have greater effects than NaNO₃ and KCl, but this is due to complex formation of these salts with CNI. Yost and Stone ¹⁰ obtained at 25° the values

$$K' = \frac{[I_2 CN^-]}{[ICN][I^-]} = I \cdot I7 \quad \text{and} \quad K'' = \frac{[I(CN)_2^-]}{[ICN][CN^-]} = 2 \cdot 50;$$

application of these values together with the assumption that only free CNI reacts accounts quantitatively for the retarding effects of KI and KCN.

Experiments have also been carried out at temperatures other than 20° ; the results of these are summarised in Table III, which gives also values of E_{obs} , the critical increment calculated from the Arrhenius formula.

TABLE III.

$[CNI]_{init} = 0.005.$

(NaOH)1-14		^k bi.	E _{obs} .				
	Temp.=0'2°.	10°.	20°.	30°.	$0.2^{\circ} - 10^{\circ}$.	$10^{\circ} - 20^{\circ}$.	20° – 30°.
0.0412	0.0355	0.1242	0.411	1.230	19600	19720	19370
0.0824	0.0325	0.1128	0.320	—	19490	19570	

Mean $E_{\rm obs} = 19550$ cal.

¹⁰ Yost and Stone, J. Amer. Chem. Soc., 1933, 55, 1889.

The reaction of CNBr with OH^- is about a hundred times faster than the analogous reaction of CNI; to obtain conveniently measurable rates the concentration of NaOH has therefore been considerably reduced. Constant values of k_{bi} in each experiment were obtained when precautions were taken to keep out CO₂. Table IV gives the mean values of k_{bi} found at 0.2°, 10° and 20°.

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Temp,	[CNBr] _{init} .	[NaOH] _{init} .	k _{bi} .	E _{obs} .
	0·22° 10° 20°	0.0006 0.006 0.0006 0.0018 0.0008 - 0.0016	0.0033 — 0.012 0.003 — 0.006 0.002 — 0.006	5.83 16.2 41.8	<pre>} 15030 } 15620</pre>

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Mean $E_{\rm obs} = 15820$ cal.

Reaction between CNBr and CO_3^{--} .

This reaction was studied at 10° and 20° in carbonate-bicarbonate buffers, the ionic strength (μ) of the medium being kept constant at $\mu = 0.5$ by addition of NaNO₃. The reaction of CNBr with CO₃⁻⁻ is accompanied under these conditions by the simultaneous reaction with OH⁻. The experimental data were therefore treated as follows. Separate experiments having shown that each of the simultaneous reactions is unimolecular with respect to CNBr, values of

$$k_{\text{uni}} = \frac{\mathbf{I}}{t_2 - t_1} \log_{\epsilon} \frac{[\text{CNBr}]_{t_1}}{[\text{CNBr}]_{t_2}}$$

were calculated for each experiment. These fell only slightly with time, since $[OH^-]$ and $[CO_3^{--}]$ were practically constant during each run. They were, however, extrapolated to zero time. The kinetic behaviour should then be expressible by an equation of the type :

$$k_{\text{uni}} = k_{\text{CO}_3^{--}}[\text{CO}_3^{--}] + k_{\text{OH}^{-}}[\text{OH}^{-}]$$

= $k_{\text{CO}_3^{--}}[\text{CO}_3^{--}] + k_{\text{OH}^{-}}\frac{K_{\omega}[\text{CO}_3^{--}]}{K_2[\text{HCO}_3^{--}]},$

where k_{CO_3} -- and k_{OH} - are the bimolecular velocity constants for the reaction of CNBr with CO_3^{--} and OH⁻ respectively, K_w is the ionic product of water and K_3 the second ionisation constant of carbonic acid. Table V shows that an equation of the above type holds at both 10° and 20°.

TABLE V.

[CNBr]init	===	0.001	;	μ	===	0.2.
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	1	1	1	1	1	1	1	1
[Na ₂ CO ₃]	0.10	0.10	0.10	0.02	0.02	0.02	0.025	0.025
[NaHCO ₂]	0.50	0.10	0.02	0.10	0.02	0.025	0.025	0.0125
toma and f kuni (o	bs.) 0.02702	0.02790	0.0303	0.01324	0.01474	0.01201	0.00838	0.01028
temp. = 20 k_{uni} (c	alc.) 0.02679	0.02779	0.0298	0.01390	0.01490	0.01601	0.00845	0.01046
kuni (o	bs.) —	0.00827	0.00840	1 —	0.00420	0.00420	0.00228	
temp. = 10 k_{uni} (c	alc.) —	0.00808	0.00841	- 1	0.00420	0.00423	0.00227	-
		1		1		1		

Values of k_{uni} (calc.) in the above table were obtained from the equations :—

temp. = 20°; k_{uni} (calc.) = 0.2578[CO₃⁻⁻] + 0.00201[CO₃⁻⁻]/[HCO₃⁻], temp. = 10°; k_{uni} (calc.) = 0.0775[CO₃⁻⁻] + 0.00033[CO₃⁻⁻]/[HCO₃⁻].

From the values $k_{\rm CO_3^{--}} = 0.2578$ at 20° and 0.0775 at 10°, $E_{\rm obs}$ for the reaction between CNBr and $\rm CO_3^{--}$ is found to be 19810 cal. The critical increment of $k_{\rm OH} - \frac{K_w}{K_2}$ is 29760 cal. Taking the heat of ionisation of water to be -13890 cal.¹¹ and the heat of the reaction $\rm HCO_3^- \rightarrow \rm CO_3^{--} + \rm H^+$ to be -1530 cal.¹² one obtains for the critical increment of $k_{\rm OH^-}$ the value 29760 -13890 + 1530 = 17400 cal., which is in fair agreement with the more directly obtained value of 15820 cal. The absolute value obtained for $k_{\rm OH^-} - \frac{K_w}{K_2}$ is also not inconsistent with the value previously found for $k_{\rm OH^-}$. Thus at 20° and $\mu = 0.5$ $k_{\rm OH} - \frac{K_w}{K_2} = 0.00201$; K_w under the same conditions ¹¹ is 1.27×10^{-14} , while from the data of MacInnes and Belcher ¹² we estimate K_2 to be 1.005×10^{-10} . Hence $k_{\rm OH^-}$ at 20° and $\mu = 0.5$ is 15.9, while the experimental value for $k_{\rm OH^-}$

Reactions of CNBr and CNI with NH₃.

at 20° and $\mu = 0.01$ is 41.8.

The CNBr reaction was studied at 10° and 20° in ammonia-ammonium chloride buffers, the ionic strength being maintained constant at $\mu = 0.2$ by addition of KCl. The accompanying hydroxyl ion reaction could not be neglected; hence in each experiment values of $k_{\rm unl}$ extrapolated to zero time were obtained as described above. Values of $[OH^-]$ in each buffer were calculated using for the ionisation constant of ammonia the value 4.0×10^{-5} found by Harned and Robinson ¹³ at 25° and $\mu = 0.2$. The results are given in Table VI.

TABLE VI.

[CNBr]init	=	0.005	;	μ		0.2.
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$[NH_4OH]$ $[NH_4CI]$ $[OH^-] \cdot ro^5$ temp. { kuni (obs.)} = zo^{\circ} { kuni (calc.)} temp. { kuni (obs.)} = ro^{\circ} { kuni (calc.)}	0-09342 0-200 1-87 0-0517 0-0533 	0-09342 0-100 3-74 0-0539 0-0540 0-01854 0-01860	0.09342 0.020 18.5 0.0602 0.0590 0.01995 0.02007	0.00342 0.010 36.0 0.0661 0.0648 	0.09342 0.005 65.5 0.0759 0.0747 	0.09342 0.002 116.6 0.0912 0.0917 	0.04671 0.050 3.74 0.0278 0.0276 0.00960 0.00949	0.04671 0.005 34.8 0.0381 0.0380 0.01100 0.01100
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In Table VI, values of k_{uni} (calc.) were obtained from the equations :----

temp. = 20° : k_{uni} (calc.) = $0.565[NH_4OH] + 34.0[OH^{-}]$ temp. = 10° : k_{uni} (calc.) = 0.195 [NH₄OH] + 10.6 [OH⁻].

Thus 0.565 and 0.195 are the bimolecular velocity constants at 20° and 10° respectively for the reaction between CNBr and NH₄OH; these yield an $E_{\rm obs}$ of 17530 cal. The values 34.0 and 10° (relating to $\mu = 0.2$ and 20° and 10° respectively) for the CNBr — OH⁻ reaction cannot be very accurate, but they are consistent with the data given above for this reaction.

The CNI – NH₄OH was found to be much slower than the corresponding reaction of CNBr. Kinetic experiments were carried out at 40° , 50° and 60° in ammonia-ammonium chloride buffers with the ionic strength maintained at 3° by the addition of NaCl. The data were dealt with in an analogous manner to those for the CNBr reaction. The value of

11 Harned and Hamer, J. Amer. Chem. Soc., 1933, 55, 2194.

¹² MacInnes and Belcher, *ibid.*, 2630; 1935, **57**, 1683.

13 Harned and Robinson, *ibid.*, 1928, **50**, 3172.

 $K_{\rm NH_4OH}$ used to calculate the concentrations of hydroxyl ion was that obtained by Harned and Robinson ¹³ at 50° and $\mu = 3.0$, viz., $K_{\rm NH_4OH} = 6.65 \cdot 10^{-5}$. Table VII reproduces some of the results obtained.

TABLE VII.

temp.	=	50°	';	[CNI] _{init}	=	0.004	ι;	μ	=	3.0	١.
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$\begin{bmatrix} NH_4OH \\ [NH_4Cl] \\ [OH^-] . 10^5 \\ k_{uni} (obs.) \\ k_{uni} (calc.) \end{bmatrix} $	0·1092 0·1092 0·02 0·05 0·0 14·5 0·00575 0·002 0·00574 0·002	02 0.1092 0.10 7.26 454 0.000420 456 0.000417	0·1092 0·20 3·63 0·00395 0·00396	0·1092 0·40 1·82 0·00374 0·00386
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The values of k_{uni} (calc.) were calculated from :—

 k_{uni} (calc.) = 0.0344 [NH₄OH] + 5.5 [OH⁻].

Thus 0.0344 is the bimolecular velocity constant (at 50° and $\mu = 3.0$) for the reaction between CNI and ammonia. From similar experiments carried out at 40° and 60°, temperature coefficients of k_{uni} between 50° and 60° were found to be 2.51, 2.47, 2.49, giving $E_{obs} = 19490$ cal.; and similarly between 40° and 50° we obtained 2.69, 2.66, 2.68 yielding $E_{obs} = 19790$. The mean value $E_{obs} = 19640$ cal. may be taken without any correction as the critical increment of the CNI – NH₄OH reaction, since the critical increment of the hydroxyl ion reaction with CNI is practically the same (19550 cal.), and since, moreover, the experimental conditions were such that the hydroxyl ion reaction contributed but little to the total change.

Reactions of CNBr and CNI with the Methylamines, Ethylamines and Triethanolamine.

The rates of reaction of the cyanogen halides with the above amines (with the exception of triethanolamine) are about a thousand times greater than the respective rates with ammonia. The concentrations of the amines had, therefore, to be considerably reduced. To minimise the extent of the accompanying hydroxyl ion reaction all the kinetic experiments were carried out in buffered solutions of the amine and its hydrochloride, the ionic strength of the medium being kept constant at 1 o by addition of NaCl. For the buffer ratios [Amine]/[Amine hydrochloride] of unity or less usually employed the hydroxyl ion reaction was in most cases less than 2 per cent. of the total. Suitable corrections were applied A more significant correction was necessitated by the fact that for this. certain of the amines are sufficiently strong bases to give appreciable ionisation (even in the presence of their salts) so that the true value of the concentration of unionised amine is less than its stoichiometric concentration. It was found, therefore, that for the reactions of the stronger amines using constant initial concentration of amine the value of k_{bi} (obs.) decreased with increasing alkalinity of the buffer. Values of k_{bi} (corrected) were obtained by multiplying the values of k_{bi} (obs.) by the ratios of the initial stoichiometric concentrations of amine to the true concentrations of free amine corrected for ionisation. In calculating the latter concentrations the value of $K_{\rm B}$ (ionisation constant of the amine) employed were obtained from the experiments themselves by the method of trial and error. The method was to choose a value of $K_{\rm B}$ such that when the three or more different values of k_{bl} (obs.) found for different buffer ratios were corrected for ionisation of the amine (and for the occurrence of the OH- reaction), these corrected values neither rose nor fell as the buffer ratio was varied.

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Table VIII summarises the results. To save space, the final corrected values of kbi only are given; similar data for the reactions of CNI and CNBr with OH-, NH_3 and CO_3^{--} are included for comparison. In this table the second column shows the temperatures at which kinetic measurements were made, while the fourth column gives the corrected values of k_{bi} at a common temperature (10° C.). The latter values were all experimentally determined except those for the reactions of CNI with NH₃ and $C_2H_5NH_2$, in which cases they were calculated from the k_{bi} values at another temperature and the critical increments. The column headed $K_{\rm B}$ gives the values of the ionisation constants employed to correct the experimental data, those for the amines (referring to $\mu = 1.0$) being obtained from the kinetic measurements in the manner already described. That these latter values are reasonable ones may be seen by comparison of this column with the column headed $K_{\rm B}(\mu = 0)$, which gives the ionisation constants determined by Britton and Williams ¹⁴ at 25° and $\mu = 0$.

Amine (or Base).	Temp.	μ.	$k_{\rm bi}$ (temp.=10°).	10 ⁴ K _B .	$10^4 K_{\rm B} (\mu = 0).$	E _{obs} .	Р.				
CNI with NH ₃ and Amines.											
NH ₈	40°; 50°; 60°	3.0	0.000456	0.62	0.181	19640	0.023				
CH ₃ NH ₂	10°; 20°	1.0	0.2022	7.0	3.62	17080	0.32				
(CH ₃) ₂ NH	0°; 10°; 20°	1.0	12.99	17.0	8.92	17040	9.8				
(CH ₃) ₃ N	0°; 10°	1.0	15.22		0.612	17630	36				
C ₂ H ₅ NH ₂	0°; 20°; 30°	1.0	0.2277	6.0	3.97	17190	0.52				
(C ₂ H ₅) ₂ NH	0°; 10°; 20°	1.0	3.83	37.0	14.5	16450	1.3				
$(C_{2}H_{5})_{3}N$	10°; 20°	1.0	2.70	17.0	6.23	16700	1.2				
(C ₂ H ₄ OH) ₃ N	10°; 20°; 30°	1.0	0.00261		<u> </u>	18480	0.037				
CNBr with NH ₃ and Amines.											
NH,	10°; 20°	0.5	0.192	0.40	0.181	17530	0.23				
CH,NH,	0°; 10°	1.0	133.0	7.0	3.62	14530	0.92				
C.H.NH.	0°; 10°	1.0	64.6	6.0	3.97	14330	0.37				
(C2H4OH)3N	0°; 10°; 20°	1.0	2.36	- 1		14880	0.021				
	CN	I with	h OH⁻.								
OH-	0°; 10°; 20°; 30°	0.04	0.124	- 1		19550	5.4				
CNBr with OH^- and $CO_3^{}$.											
OH-	0°; 10°; 20°	10.01	16.2	-	-	15820	0.19				
CO3	10°; 20°	0.20	0.0775		-	19810	8.4				
-							<u> </u>				

TABL	Æ	VI	II.
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Discussion.

Examination of Table VIII shows that with either CNBr or CNI as reactant the specific rate of reaction varies over a fairly wide range depending on the choice of base. The CNBr reactions are all faster than the corresponding CNI reactions, the ratio of the rates (at 10°) ranging from about 100 to 900. At the same time the critical increments of the cyanogen bromide reactions are less by 2000-4000 cal. than those of the corresponding cyanogen iodide reactions. The velocity constants of reaction of CNI (or CNBr) with the various bases bear no simple relation to the strength of the base. For the CNI reactions the specific rate as we ascend the series NH₃, CH₃NH₂, (CH₃)₂NH, (CH₃)₃N progressively

14 Britton and Williams, J.C.S., 1935, 3172.

increases, the increase being especially great between NH_3 and CH_3NH_2 but almost negligible between $(CH_3)_2NH$ and $(CH_3)_3N$. The same general behaviour is shown for the reactions of cyanogen iodide with the ethylamines, except that here there is a slight fall in rate in passing from $(C_2H_5)_2NH$ to $(C_2H_5)_3N$. The critical increments of all the reactions lie between 14300 cal. and 19800 cal.; roughly a low value of E_{obs} corresponds with a high k_{bi} and vice versa.

The last column of Table VIII gives values of P, the ratios of k_{bl} (observed) to those calculated from the equation :

$$k_{\rm bi} = Z \cdot e^{-E/RT}$$

Here

$$E = E_{\text{obs.}} - \frac{1}{2} \mathbf{R} T$$

and the collision number

$$Z = 1.663 \cdot 10^{27} \sigma_{12}^2 \left(\frac{T}{M}\right)^{\frac{1}{2}},$$

where M is $\frac{M_1M_2}{M_1 + M_2}$ and M_1 and M_2 are the molecular weights of the

two reactants. We have taken σ_{12}^2 to be $2 \cdot 5 \times 10^{-15}$ cm.² for each reaction. Some slight gain in accuracy might possibly have been attained by employing an estimated value of σ_{12} for each reaction specifically; however, the approximate values of P obtained by use of this average square of a molecular diameter are sufficiently accurate for our purposes. It will be seen that of the fifteen reactions studied, eleven have values of P equal to unity within a factor of 10, which probably represents the uncertainty in our estimates of P. Of the remaining four reactions, three have low values of P and one a high value of P. In none of these four cases, however, is the deviation of P from unity very large. All the reactions may in fact be regarded as having speeds practically equal to those predicted by the simple collision theory.

The exact mechanisms of these reactions are not known. If one assumes that the rate-determining step in the amine reactions is an addition process, then the results are of interest since addition reactions of similar type (for example, the Menschutkin reaction) have hitherto been studied only in organic solvents, in which the rates (and P) are low, usually increasing with increasing polarity of the solvent.¹⁵ Hawkins ¹⁶ found that for the addition reaction between pyridine and alkyl iodide in the polar solvent C_2H_5OH , P has a value approaching unity. It is therefore in agreement with expectation that in the highly polar solvent water the reactions of CNI and CNBr with amines-assuming them to be addition reactions—have also values of P of the order of unity. From the data presented above it is not possible to obtain with any degree of certainty correlations between the parameters E and P of the Arrhenius equation, since the overall changes in P and E are small. It would appear, however, from Table VIII that: (a) in the methylamine re-actions with CNI, E is practically constant and P increases as we pass from primary to tertiary amine, and (b) by comparison of the reactions of CNI with CNBr the larger $E_{CNI} - E_{CNBr}$ is, the greater is the ratio P_{CNI}/P_{CNBr} . This has the effect of tending to maintain the relative rates of corresponding reactions at a constant value.

> ¹⁵ Pickles and Hinshelwood, J.C.S., 1936, 1353. ¹⁶ Hawkins, J.C.S., 1922, **121**, 1170.

Summary.

The kinetics have been studied and the critical increments determined of the following reactions in aqueous solution :

CNI with OH^- , NH_3 , the three methylamines, the three ethylamines and triethanolamine;

CNBr with OH⁻, CO₃⁻⁻, NH₃, CH₃NH₂, C₂H₅NH₂ and triethanolamine.

Each reaction is of second order with the steric factor of the simple collision theory approximately unity.

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