24. *The Absorption Spectra of Mono-, Di-, and Tri-chloroamines and Some Aliphatic Derivatives.*

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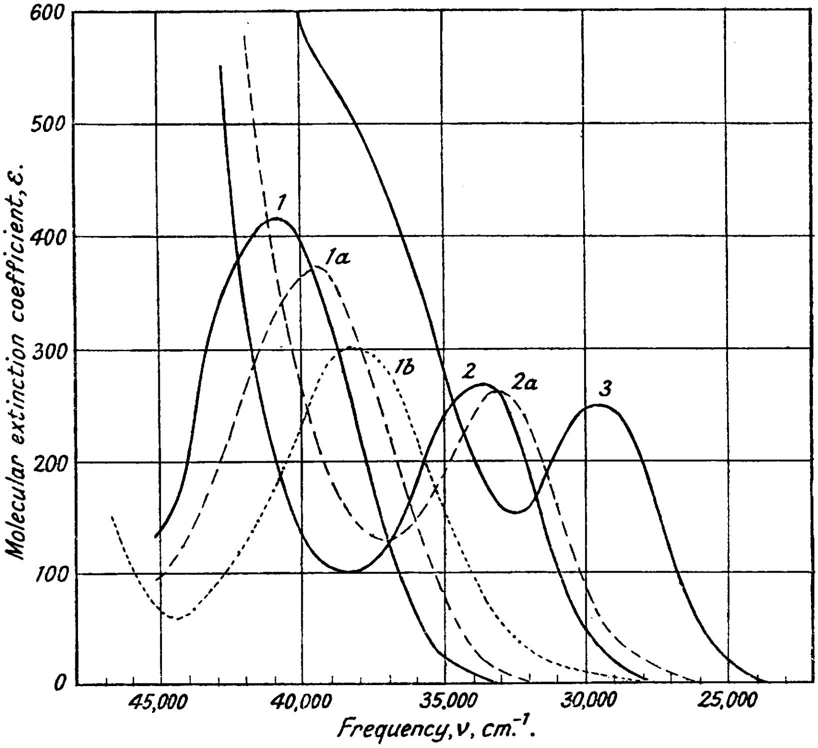
The chloroamines examined show a characteristic absorption band lying between the limits $\nu_{\max.} = 40800$ cm.$^{-1}$, $\varepsilon_{\max.} = 416$, and $\nu_{\max.} = 29400$ cm.$^{-1}$, $\varepsilon_{\max.} = 255$. The less the polarisability of the groups attached to the >N–Cl chromophore, the greater is the frequency of maximum absorption.

IN view of the fact that most chloroamines are unstable and sensitive to light, their spectra were examined in aqueous solution, which was circulated through the absorption cell of a sector photometer attached to a small quartz spectrograph. The solution passed through the cell sufficiently rapidly to prevent appreciable photochemical decomposition.

FIG. 1.



In order to keep a constant check on the concentration of the solution, it was collected after circulation in a device arranged to deliver aliquot portions. These were run into an acidified solution of potassium iodide and the iodine liberated was titrated with 0·01N-sodium thiosulphate.

The chloroamine solutions were obtained by adding hypochlorous acid to a solution of the appropriate amine buffered with acetate or phosphate mixtures. These buffered solutions gave an improved yield of chloroamine, and a more stable solution. The substances chosen for the buffer are stable to chlorine and sufficiently transparent to ultra-violet light.

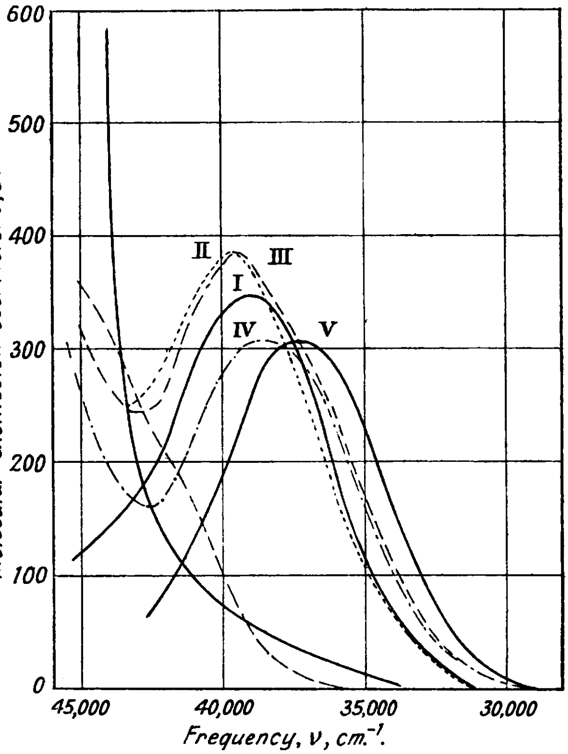
The concentration of chloroamine as measured by titration falls on standing, but the molecular extinction coefficient $\varepsilon = (1/cd) \log I_0/I$ was found not to vary as the solution decomposed, provided that the value of c was taken as the concentration of chloroamine measured by titration. This proves that products formed by the decomposition of chloroamines have a negligible effect on the absorption spectra of the solutions. Deviations were observed in solutions whose titre had fallen to half the original value, but such solutions were not used for measurements. The yield of chloroamine obtained on mixing the amine with hypochlorous acid was always greater than 90% of the theoretical.

Solutions of hypochlorous acid and ammonia show the spectrum of hypochlorite ions at p_H greater than 14, of chloroamine over the range 14—7·5, of dichloroamine from 5·5 to 3, and of nitrogen trichloride at p_H less than 2·8. This equilibrium and those of other amines are now being studied. The spectra are quite constant over a range of p_H. Chapin (*J. Amer. Chem. Soc.*, 1929, **51**, 2113), by extraction with chloroform, has isolated the chloroamines formed at various hydrogen-ion concentrations, and has confirmed their identity analytically. Similarly, methylchloroamine is prepared in 0·1N-alkali, whereas methyldichloroamine is obtained in a solution buffered at p_H 7.

All other chloroamines were prepared in solutions buffered at p_H 7, save *N*-chloroacetamide which was prepared as pure crystals and dissolved in water.

The values of the wave-length, frequency, and molecular extinction coefficient are listed in the table. Fig. 1 shows the absorption curves for the alkyl-substituted chloroamines, and Fig. 2 those of more complex chloroamines, which show only minor differences from the spectra of the corresponding alkyl compounds. Methyl, ethyl, and *n*-propyl derivatives have spectra identical within the experimental error.

FIG. 2.



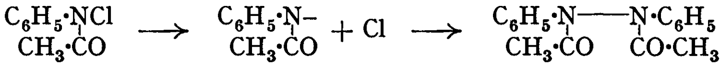
	$\lambda_{max.}$, A.	$\nu_{max.}$, cm.$^{-1}$.	$\varepsilon_{max.}$.	Fig.*
Chloroamine	2450	40,800	416	1
Monosubstituted chloroamines :				
Methylchloroamine	2530	39,500	372	1*a*
N-Chloroglycine	2560	39,100	350	I
N-Chloroalanine	2530	39,500	385	II
N-Chloroaspartic acid	2540	39,400	380	III
Disubstituted chloroamines :				
Dimethylchloroamine	2630	38,000	300	1*b*
Diethylchloroamine	2630	38,000	300	1*b*
Di-*n*-propylchloroamine	2630	38,000	300	1*b*
N-Chloromorpholine	2600	38,500	312	IV
N-Chlorosarcosine	2680	37,300	310	V
Dichloroamine	2970	33,700	265	2
Monosubstituted dichloroamines :				
Methyldichloroamine	3030	33,000	260	2*a*
Ethyldichloroamine	3030	33,000	260	2*a*
Trichloroamine :				
(Nitrogen trichloride)	3400	29,400	255	3

* Arabic numerals refer to Fig. 1 and Roman numerals to Fig. 2.

Discussion.—The frequencies of the maxima lie in groups corresponding to the number and type of the atoms attached to the >NCl chromophore. In order of decreasing frequency (and also, incidentally, of decreasing intensity) these groups are : chloroamine, alkylchloroamines, dialkylchloroamines, and trichloroamine (nitrogen trichloride). A carbonyl group adjacent to the nitrogen atom of the >NCl chromophore removes selective absorption from the region studied. If, however, the carbonyl group is separated by a carbon atom from the chromophore as in *N*-chloroglycine, the spectrum is little different from that of the corresponding alkylchloroamine.

The frequencies of the maxima are in the inverse order of the polarisabilities of the groups $-H$, $-CH_3$, $-Cl$ (cf. Ingold, *Chem. Rev.*, 1939, **15**, 255) attached to the chromophore.

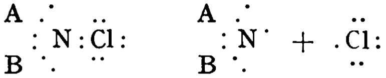
From the work of Hodges (J., 1933, 240), who has shown that diacetylhydrazobenzene is formed in the photochemical decomposition of *N*-chloroacetanilide, thus :



$$\underset{CH_3\cdot CO}{C_6H_5\cdot NCl} \longrightarrow \underset{CH_3\cdot CO}{C_6H_5\cdot N-} + Cl \longrightarrow \underset{CH_3\cdot CO}{C_6H_5\cdot N}\text{——}\underset{CO\cdot CH_3}{N\cdot C_6H_5}$$

it is probable that the absorption of ultra-violet light by chloroamines results in the disruption of the >NCl bond. Price (*Ann. Reports*, 1939, **36**, 58) considers that absorption in the near ultra-violet by polyatomic molecules is usually due to a transition from a bonding to an antibonding orbital causing disruption in the case of a single bond.

If we represent this disruption thus,



$$\begin{array}{lcl} A\ .\dot{} & & A\ .\dot{} \\ \quad :N:\overset{..}{\underset{..}{Cl}}: & & \quad :N^{\cdot} + .\overset{..}{\underset{..}{Cl}}: \\ B\ \dot{}. & & B\ \dot{}. \end{array}$$

then the more the groups A and B are able to provide electrons to the nitrogen atom, the more readily will dissociation take place. Hence, the energy required for the dissociation is less, and light is absorbed at lower frequencies, the more polarisable are the groups attached to the chromophore.

The attraction of the carbonyl group for electrons may also account for the removal of absorption to the extreme ultra-violet region in the cases of *N*-chloroacetamide and *N*-chloroacetylglycine, although in these spectra the characteristic maximum was not observed.

Similar shifts in the spectra of water, hydrogen sulphide, and ammonia have been observed on alkyl substitution. In these instances the spectra lie at higher frequencies and dissociation does not necessarily occur. Price (*loc. cit.*) considers the shift here to be due to accumulation of negative charge on the oxygen, sulphur, or nitrogen atom, respectively.

With formaldehyde the spectra are also shifted towards the visible by alkyl substitution, but are moved in the opposite direction by chlorine substitution (*i.e.*, in carbonyl chloride) (Henri; quoted by Mulliken, *J. Physical Chem.*, 1935, **3**, 572). Here the excited electron is in a non-bonding oxygen orbital, and is, therefore, separated by a carbon atom from the chlorine atom. The negative nature of chlorine with respect to carbon decreases the negative charge on the oxygen atom, and the spectrum moves to higher frequencies. In the case of substitution of hydrogen by chlorine in chloroamine, however (where, incidentally, the >N–Cl bond is practically non-polar (Pauling, *J. Amer. Chem. Soc.*, 1932, **54**, 3582)), the excited electron is probably in a bonding orbital, which is in closer proximity to the readily polarisable chlorine atom. Here, as we have observed, the spectrum moves considerably towards the visible.

The author's thanks are due to Prof. F. G. Soper for suggesting the subject and for his continued interest and helpful advice; and to the University of Otago for the award of the George Young and the Duffus Lubecki Scholarship.

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[*Received, December* 1*st*, **1941**.]