

*Ultra-violet Absorption Spectra of Some Organic Hypohalites.*

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The ultra-violet absorption spectra of some derivatives of hypochlorous and hypobromous acids were determined in several organic solvents. The spectra were compared with those of the free acids and halogen monoxides. The spectra of hypochlorous and hypobromous acid were examined in aqueous media over a wide range of hydrogen-ion concentration. No spectrophotometric evidence could be found for the existence of  $H_2OCl^+$  and  $H_2OBr^+$ , even in the most acid solutions.

In connection with a study of the mechanisms of reaction of organic hypohalites (preceding paper) the absorption spectra in the range 2050—5000 Å of a number of organic hypohalites, hypohalous acids, and halogen monoxides have been determined. The compounds studied include ethyl hypochlorite and hypobromite, *tert.*-butyl hypochlorite and hypobromite, 3 : 3 : 3-trichloro-1-methylpropyl hypochlorite, acetyl hypochlorite and hypobromite, and hypochlorous and hypobromous acid, in all cases, except for the acids, in carbon tetrachloride solution. The spectra of *tert.*-butyl hypochlorite and of acetyl hypochlorite and hypobromite were also measured in acetic acid and heptane solution. The absorption spectra of hypohalous acids were determined in aqueous solution over a pH range from N-sodium hydroxide to 7.5N-perchloric acid.

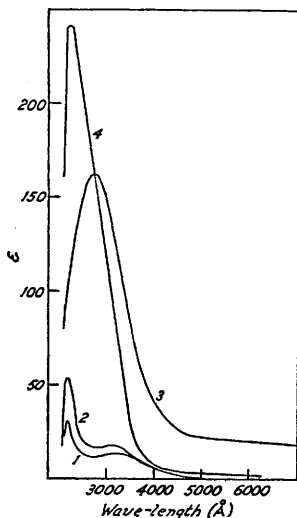
The spectra of hypochlorous and hypobromous acid and of ethyl hypochlorite have been previously investigated. Schaeffer (*Z. physikal. Chem.*, 1919, **93**, 312) reports the absorption spectra of hypochlorous and hypobromous acids in aqueous N-sodium hydroxide and in neutral solution, and that of ethyl hypochlorite in light petroleum-ether. That of aqueous hypochlorous acid was reinvestigated by Fergusson, Slotin, and Style (*Trans. Faraday Soc.*, 1936, **32**, 956). That of hypobromous acid in aqueous N-sodium hydroxide and in aqueous solution has been reported by Farkas and Klein (*J. Chem. Phys.*, 1948, **16**, 886).

The spectra of the hypochlorites and hypobromites in carbon tetrachloride solutions are given in Figs. 1 and 2. The strong band at about 2600 Å is characteristic of the hypochlorite and is present also in the spectrum of chlorine monoxide (Fig. 3). In hypochlorous acid in water the same band appears shifted to 2300 Å (Fig. 4). Substitution of the electron-attracting trichloromethyl group for one of the methyl groups of *tert.*-butyl broadens this band and shifts it to 2880 Å (Fig. 1). In the simple alkyl hypochlorites another weaker maximum is observed around 3100 Å. However, this band is poorly resolved, and with those compounds which show strong absorption in the 2600-Å region the maximum may be absorbed into the base of the bigger peak. Thus, acetyl hypochlorite and 3 : 3 : 3-trichloro-1-methylpropyl hypochlorite show only one strong absorption band, at 2640 Å. The general appearance of the spectra of hypobromites is similar to that of the hypochlorites, but the high peak is shifted to about 2800 Å (cf. Fig. 2), and the other maximum is displaced to 3400 Å. The same maxima appear in hypobromous acid which shows peaks at 2600 and 3200 Å in aqueous solution. No direct comparison of the spectra of hypohalous acids and of hypohalites in the same solvent is possible. However, when due allowance is made for the effect of the change in the solvent, the spectra of hypochlorous and hypobromous acid are seen to be similar to those of their simple alkyl derivatives.

The positions of the bromine monoxide and chlorine monoxide maxima appear to be identical with those of acetyl hypobromite and hypochlorite respectively. This is probably fortuitous, for, although the positions of the maxima are identical, the magnitude of the extinction coefficients is different, that of the halogen monoxides being more than twice that of the corresponding acetyl hypohalites. Another indication that the two spectra belong to different chemical entities is obtained from the fact that on addition of a small quantity of anhydrous acetic acid to a solution of chlorine monoxide in carbon tetrachloride a turbidity is produced which is due to water. When the mixture is clarified by anhydrous sodium sulphate, the spectrum is that of acetyl hypochlorite prepared by

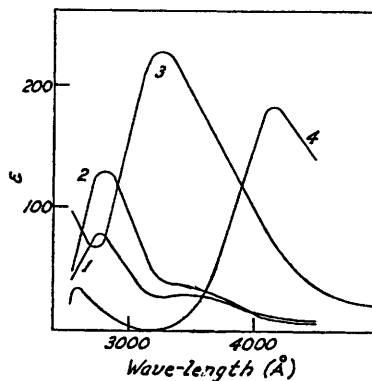
other methods. The reaction taking place is evidently  $\text{Cl}_2\text{O} + 2\text{HOAc} \rightarrow 2\text{ClOAc} + \text{H}_2\text{O}$ . We have succeeded in measuring only one band of bromine monoxide, at  $3200 \text{ \AA}$  (in  $\text{CCl}_4$ ) (Fig. 3), corresponding to the short wave-length maximum of a hypobromite. It should

FIG. 1.



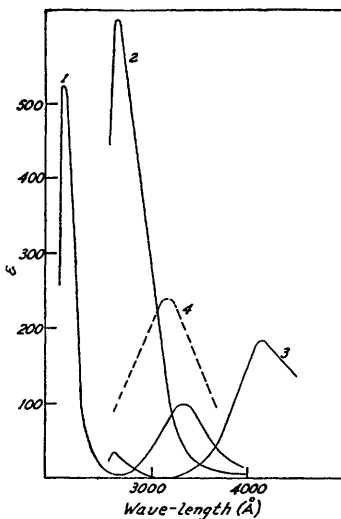
1, Ethyl hypochlorite; 2, tert.-butyl hypochlorite; 3, 3:3:3-trichloro-1-methylpropyl hypochlorite; 4, acetyl hypochlorite. (All in  $\text{CCl}_4$ .)

FIG. 2.



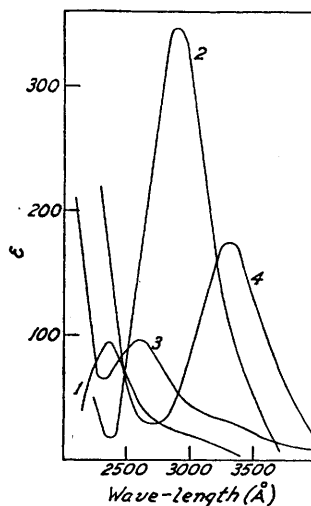
1, Ethyl hypobromite; 2, tert.-butyl hypobromite; 3, acetyl hypobromite; 4, bromine. (All in  $\text{CCl}_4$ .)

FIG. 3.



1, Chlorine; 2, chlorine monoxide; 3, bromine; 4, bromine monoxide. (All in  $\text{CCl}_4$ .)

FIG. 4.



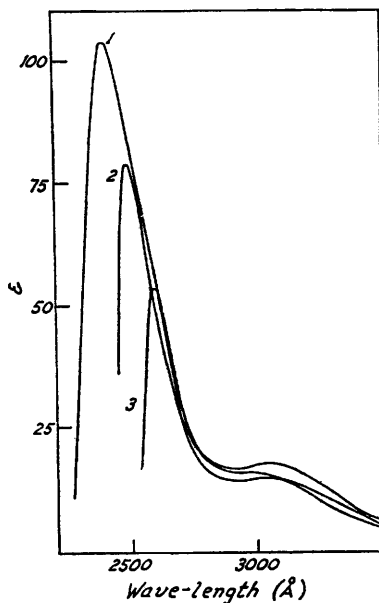
1, Hypochlorous acid; 2, hypochlorite ion; 3, hypobromous acid; 4, hypobromite ion. (All in  $\text{H}_2\text{O}$ .)

be noted that while the strong maximum at the short wave-length is very sensitive to variations in the solvent (Fig. 5), that at  $3100 \text{ \AA}$  changes only slightly either in intensity or in position.

The spectra of the hypohalite ions differ greatly from those of the un-ionised acids (see Figs. 6 and 4), both hypochlorite and hypobromite ions in aqueous solution showing one strong maximum, at  $2920$  and  $3330 \text{ \AA}$  respectively. The dissociation constant of

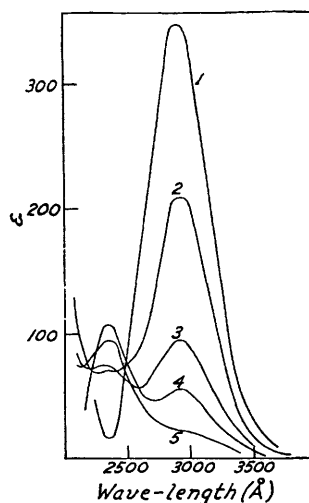
the acid can be determined from the variation in the spectra with change in the acidity of the solution (see Fig. 4). In this way the value of 7.38 for the  $pK$  of hypochlorous acid at room temperature was obtained, in good agreement with the values obtained by other methods (*e.g.*, by Shilov and Gladtschikova, *J. Amer. Chem. Soc.*, 1938, **60**, 490; Skrabal and Berger, *Monatsh.*, 1937, **70**, 168). In order to investigate the behaviour of hypohalous acid in strongly acid solution, the extinction curves were determined in aqueous solution containing up to 7.5*N*-perchloric acid. The curves obtained did not differ from those of the hypohalous acid in weakly acid solutions. This indicates either that the concentration of  $H_2OCl^+$  or  $H_2OBr^+$  is too small to be detected or that the absorption spectra of those species do not differ greatly from those of the unprotonated hypohalous acids.

FIG. 5.



tert.-Butyl hypochlorite in: 1, n-heptane; 2, acetic acid; 3, carbon tetrachloride.

FIG. 6.



Hypochlorous acid at:

pH .....	14.0	7.4	6.8	6.4	1.0
Curve no. ...	1	2	3	4	5

#### EXPERIMENTAL

**Materials.**—The solvents used were all of analytical grade. Carbon tetrachloride was purified further by washing it with 10% sulphuric acid and then 10% sodium hydroxide solution and water; after being dried ( $CaCl_2$ ), it was fractionated through a 20-plate column. Anhydrous acetic acid was prepared by adding a slight excess of acetic anhydride to analytical-grade acetic acid, and fractionated through a 12-plate column. *n*-Heptane was purified by shaking it with fuming sulphuric acid and then 10% sodium hydroxide solution and water; after being dried ( $CaCl_2$ ), it was fractionated through a 20-plate column. The lowest limits of measurement with these solvents were 2540 Å for carbon tetrachloride, 2420 Å for acetic acid, and 2040 Å for heptane.

**Preparation of Compounds.**—Hypochlorous and hypobromous acid were prepared by several methods, generally that of Jakowkin (*cf. Z. physikal. Chem.*, 1899, **29**, 613) based on the action of the halogen on an aqueous suspension of freshly prepared mercuric oxide. The crude hypohalous acid was redistilled at 5 mm. into a trap cooled with liquid nitrogen. Identical spectra were obtained with hypohalous acid prepared by other methods (Shilov and Kanyiaev, *J. Phys. Chem. U.S.S.R.*, 1934, **5**, 655; hydrolysis of *tert.*-butyl hypochlorite or *N*-chlorosuccinamide).

Chlorine monoxide and bromine monoxide in carbon tetrachloride solution were prepared by Schumacher and Townend's method (*Z. physikal. Chem.*, 1933, **20**, B, 375). Bromine monoxide could be obtained free from bromine by this method (see Brenshede and Schumacher, *ibid.*, 1935, **29**, B, 356; *Z. anorg. Chem.*, 1936, **226**, 370).

*tert.*-Butyl hypochlorite was prepared by three different methods: (a) Chlorine was passed through a cooled alkaline solution of *tert.*-butanol (*Org. Synth.*, 1952, 32, 20). (b) Carbon tetrachloride was shaken with aqueous 0.4N-hypochlorous acid (200 ml.) containing *tert.*-butanol (5 ml.). The carbon tetrachloride layer containing *tert.*-butyl hypochlorite was separated and dried ( $K_2CO_3$ ). The yield based on the alcohol is quantitative. (c) Excess of *tert.*-butanol was added to 0.24N-solution of chlorine monoxide in the solvent (50 ml.), and the mixture dried with anhydrous sodium sulphate. A solution of *tert.*-butyl hypochlorite in carbon tetrachloride was obtained in quantitative yield as shown by the complete disappearance of the spectrum of the monoxide. No difference could be detected in spectra of *tert.*-butyl hypochlorite prepared by the various methods.

Ethyl hypochlorite was prepared by methods similar to (a) and (b) for *tert.*-butyl hypochlorite.

3 : 3 : 3-Trichloro-1-methylpropyl hypochlorite was prepared by method (b) as for *tert.*-butyl hypochlorite.

Acetyl hypochlorite in acetic acid solution was obtained by passing chlorine into a solution either of mercuric acetate in acetic acid (cf. De La Mare, Ketley, and Vernon, *Research*, 1953, 6, 125) or of silver acetate in acetic acid (cf. Bockenmuller and Hoffmann, *Annalen*, 1935, 519, 165). A solution in carbon tetrachloride was obtained by (a) shaking a solution of chlorine in carbon tetrachloride with excess of silver acetate or mercuric acetate (with the latter a quantitative yield is obtained, whereas with the former it was not possible to obtain a preparation free from chlorine), or (b) adding a slight excess of acetic acid to a solution of halogen monoxide in carbon tetrachloride, and drying ( $Na_2SO_4$ ) (cf. Schutzenberger, *Compt. rend.*, 1861, 52, 135).

Ethyl hypobromite and *tert.*-butyl hypobromite in carbon tetrachloride were prepared by shaking aqueous hypobromous acid, the corresponding alcohol, and carbon tetrachloride together. The carbon tetrachloride layer was separated and dried.

*Measurements of Absorption Spectra.*—These were measured in silica cells of 10-mm. optical path with a Beckman model DU Spectrophotometer, modified to increase its sensitivity (cf. Anbar and Dostrovsky, preceding paper). The concentration of hypochlorites in solution was determined iodometrically.