[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE MATHIESON ALKALI WORKS, INC.]

HYPOCHLOROUS ACID AND THE ALKYL HYPOCHLORITES

BY M. C. TAYLOR, R. B. MACMULLIN AND C. A. GAMMAL

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Our knowledge of the alkyl hypochlorites begins with the work of Sandmeyer[1] in 1885 who prepared methyl hypochlorite by chlorinating a mixture of alcohol and sodium hydroxide. The esters are relatively insoluble in water, and separate as yellow oils, unstable towards heat and light and possessing very irritating odors. Very recently Chattaway and Backeberg[2] described other hypochlorites including the various isomeric propyl, butyl and amyl hypochlorites. They found that the hypochlorites of tertiary alcohols are much more stable than those of the corresponding primary or secondary alcohols.

The work on alkyl hypochlorites at the Mathieson Laboratory, which was begun about two years prior to the publication of Chattaway, was a part of the research program on the development of pure calcium hypochlorite. The immediate problem was to find a compound of hypochlorous acid whose physical properties would allow it to be separated from the water solution of chloride formed by the hydrolysis of chlorine and whose chemical properties would permit reconversion to hypochlorous acid after separation. Preliminary tests showed that ethyl hypochlorite as prepared by Sandmeyer satisfied both of these conditions. The unstable nature of the pure material made it unsuitable for use in a technical process, but it was found that a solution of the ester in carbon tetrachloride, or any other inert solvent immiscible with water, was stable for several hours below 25°.

These preliminary observations led to the following simple and rapid method of preparing a comparatively stable solution of ethyl hypochlorite. Twenty to 25 g. of precipitated chalk or ground limestone is added to a liter of water and the mixture chlorinated with stirring until about 25 g. of chlorine has been absorbed. With this excess of chalk, the available chlorine is present almost entirely as hypochlorous acid. The excess of carbonate is then filtered off and the filtrate shaken immediately with an equal volume of carbon tetrachloride containing about 2% or more of ethyl alcohol. About two minutes of shaking is sufficient to cause reaction between the hypochlorous acid and alcohol to such an extent that the greater portion of the available chlorine is removed as ethyl hypochlorite from the water to the solvent layer which can then be separated. This solvent contains then some dissolved carbon dioxide and traces of free chlorine. The former can be eliminated, if desired, by subjection of the chlor-

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[1] Sandmeyer, *Ber.*, **18**, 1767 (1885); **19**, 857 (1886).

[2] Chattaway and Backeberg, *J. Chem. Soc.*, **123**, 2999 (1923).

inated carbonate solution to evacuation before shaking it with the solvent. The chlorine is most easily removed from the solvent by shaking the ethyl hypochlorite solution with a solution of sodium bicarbonate and again separating. A pure solution of ethyl hypochlorite in carbon tetrachloride made in this way lost only 10% of this available chlorine on standing for two days at 20° in the diffused light of the laboratory.

Such a solution of ethyl hypochlorite liberates iodine quantitatively from potassium iodide and acetic acid. It reacts rapidly with phenol, aniline, methylaniline, sodium picrate and similar easily oxidized substances and in general shows most of the reactive properties of hypochlorous acid. When ethylene is passed into a mixture of ethyl hypochlorite, slightly acidified water and carbon tetrachloride, absorption occurs with the probable formation of ethylene chlorohydrin, which dissolves in the carbon tetrachloride. We did not, however, carry this experiment to the point of isolating the chlorohydrin.

Ethyl hypochlorite decomposes on standing, giving high yields of ethyl acetate, probably by the following steps: $C_2H_5OCl \longrightarrow CH_3CHO + HCl$; $CH_3CHO + C_2H_5OCl \longrightarrow CH_3COOC_2H_5 + HCl$.

Ethyl hypochlorite reacts with alkali to form alkali hypochlorite free from chlorides. Practically pure calcium hypochlorite can be prepared if such a water solution be evaporated to dryness under a vacuum. A more suitable technical way of making solid calcium hypochlorite is described in United States Patents, Nos. 1,481,039 and 1,481,040. Dry, 200-mesh hydrated lime is added to carbon tetrachloride containing an excess of ethyl hypochlorite. A quantity of water sufficient to form the trihydrate of calcium hypochlorite is introduced slowly with violent agitation. This water appears to be necessary to get good conversion, although too much water wets the lime particles and hinders conversion. The alcohol regenerated remains in the carbon tetrachloride, which solution is used over again to extract more hypochlorous acid from chlorinated carbonate solution. This process illustrates the possibility of employing a comparatively unstable organic chemical to produce a very stable inorganic commodity—calcium hypochlorite containing 75 to 90% of available chlorine.

We wish to call attention to the fact that a solvent solution of ethyl hypochlorite is easily obtainable, sufficiently stable for use in organic synthesis, and moreover is anhydrous, thus permitting organic oxidation with hypochlorous acid in the presence of regulated amounts of water. If a small amount of water is desired, it is best to choose an inert solvent which will dissolve water to the required extent. In those cases where greater stability is required, we suggest the use of tertiary amyl hypochlorite. Tertiary amyl alcohol is easily prepared from fusel oil by the method described by Adams, Kamm and Marvel.[3]

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[3] Adams, Kamm and Marvel, THIS JOURNAL, 40, 1950 (1918).

Study of the Alkyl Hypochlorites

The constitution of the ethyl hypochlorite has been shown by our work to be that of a true ester. The oil was prepared by the method of Sandmeyer, washed with sodium bicarbonate solution and dried with calcium chloride. It was kept in the dark at 0° during analysis. Six different determinations of chlorine content were made, of which the average value is 44.13% as compared with the calculated value of 44.05. The percentage of available chlorine found was 88.4 as compared with 88.10 calculated. The Victor Meyer vapor-density determination gave a molecular weight of 81.8 as compared with a calculated value of 80.5. Cryoscopic lowering in benzene gave a molecular weight of 79.2.

If the substance had been a double compound of one molecule of alcohol to one of acid, EtOH.HOCl, the molecular weight would have been 98.5. This shows that the compound which we have assumed to be ethyl hypochlorite is a true ester. Although, as will be shown below, hypochlorite is largely hydrolyzed in water, its insolubility in water permits esterification by removing the reaction product from the water phase. Solvents aid in this removal of the ester from the water, giving even greater yields of ester than when no solvent is used.

We investigated the formation of the hypochlorous acid esters of various alcohols by the method which Sandmeyer used for preparing ethyl and methyl hypochlorite. Yellow, insoluble, unstable oils were obtained with propyl, *iso*propyl, *iso*butyl, *sec*.butyl, *tert*.butyl, *iso*amyl, *sec*.amyl and *tert*.amyl alcohols. Benzyl alcohol is oxidized to benzaldehyde by

TABLE I

REACTION OF VARIOUS ALCOHOLS WITH HYPOCHLOROUS ACID

All values are for 5cc. samples, using 0.1 *N* thiosulfate solution

	Distribution of available chlorine					
Alcohol used	Water layer Thiosulfate Cc.	Solvent layer Thiosulfate Cc.	Total Thiosulfate Cc.	Total avail. Cl before shaking	Removal %	Loss %
Methyl	8.1	18.7	26.8	28.9	70	7
Ethyl	3.3	24.1	27.4	28.9	88	5
*n*Propyl	6.1	21.7	27.8	28.9	78	4
*iso*Propyl	4.5	23.5	28.0	28.9	84	3
Amyl	7.3	20.7	28.0	28.9	74	3
Benzyl	6.7	20.8	27.5	28.9	76	5
Ethylene chlorohydrin	12.1	11.0	23.1	23.6	48	2
Glycol	18.0	2.9	20.9	23.6	14	11
Fusel oil	7.4	20.1	27.5	28.9	73	5
sec.Butyl	1.5	22.1	23.6	27.4	94	14
tert.Butyl	1.6	25.5	27.1	27.4	94	1
sec.Amyl	3.7	21.4	25.1	27.4	85	8
tert.Amyl	3.4	22.9	26.3	27.4	87	4
Glycerol	17.5	3.1	20.6	27.4	15	25
Blank	24.9	2.2	27.1	27.4	8	1

hypochlorous acid. Glycerol, glycol and ethylene chlorohydrin gave no appreciable amounts of an immiscible oil.

A further study of ester formation was made by shaking various alcohols with carbon tetrachloride and hypochlorous acid. Transference of available chlorine to the solvent layer was taken as an indication of ester formation. Forty cc. of carbon tetrachloride and 0.8 cc. of the alcohol were shaken for two minutes with an equal volume of hypochlorous acid solution, and the two layers analyzed for available chlorine. The results, which are given in Table I, show that all the monohydric alcohols react with hypochlorous acid to give alkyl hypochlorites, but that the dihydric and trihydric alcohols either do not react or else their hypochlorites are very soluble in water. These results do not indicate the relative distribution between solvent and water of all the alcohols, as equimolecular quantities of alcohol were not used. Separate experiments indicate, however, that the higher the molecular weight, the greater the distribution in favor of the solvent. For instance with ethyl hypochlorite the ratio of the concentration of available chlorine in the solvent to that in water is 4.0; for *tert.*butyl hypochlorite it is 45; and for *tert.*amyl hypochlorite it is 237; these values refer to a temperature of 25° and a total hypochlorite (OCl) concentration of about 0.3 *M*.

The comparative stabilities of water solutions and of carbon tetrachloride solutions of primary, secondary and tertiary amyl and butyl hypochlorites was obtained by allowing these solutions to stand in ordinary, colorless glass bottles in the diffused light of the laboratory at room temperature.

TABLE II

STABILITY OF ALKYL HYPOCHLORITES

In cc. of 0.1 *N* sodium thiosulfate per 5cc. sample

IN CARBON TETRACHLORIDE

Alkyl OCl, hours	Start	5	19	40	64	97	121	162	282
Ethyl..........	19.2	18.6	18.5	18.2	17.5	4.4	3.3	2.5	1.0
*iso*Butyl	20.0	20.0	19.2	18.3	4.4	1.2	..	..	..
*sec.*Butyl.......	19.3	19.3	0.1	..	..	..	..	..	..
*tert.*Butyl.......	19.6	19.6	19.1	18.6	17.8	14.3	10.8	7.5	3.7
*iso*Amyl........	19.2	19.2	18.7	18.4	12.7	0.3	..	..	..
*sec.*Amyl	17.3	0.1	0.1	..	..	..	..	..	..
*tert.*Amyl.......	18.3	18.2	18.0	18.1	17.7	17.2	17.0	16.4	16.2

IN WATER

The value at the start was 30.2 cc.

Alkyl OCl, hours	2	18	42	162
Methyl.......	23.5	3.0	..	...
Ethyl.........	24.0	0.2	..	...
*iso*Propyl	6.1	.3	..	...
*iso*Butyl	22.5	.2	..	...
*sec.*Butyl......	4.0	.0	..	...
*tert.*Butyl.....	25.9	24.6	19.1	8.7
*iso*Amyl	16.2	1.6	..	...
*sec.*Amyl......	7.1	2.2	..	...
*tert.*Amyl......	24.8	22.5	19.0	5.4
Benzyl.......	2.3	.0	..	...
Blank HOCl..	29.9	27.4	..	...

Portions were analyzed for available chlorine at intervals as indicated in Table II. The results plainly show that secondary hypochlorites are the most unstable, *iso* and *n* primary hypochlorites more stable and tertiary hypochlorites very stable. This bears out the findings of Chattaway.[2]

The Hydrolysis of Ethyl Hypochlorite

When ethyl hypochlorite is shaken with water and carbon tetrachloride the hypochlorite radical (OCl) is distributed between the two phases as shown below in Cols. S and C of Table IV which represent respectively the hypochlorite radical concentrations in the solvent and water layers. If the logarithm of the S value is plotted against that of C an approximately straight line is obtained whose equation is $\log C = 0.538 \log S + 0.1416$. Therefore $C = 0.1416\ S^{0.538}$, where C is the moles of hypochlorite radical per liter in the water and S that in the solvent. The fact that the C values increase approximately as the square roots of the values of S can be explained either on the basis of association to double molecules in the solvent (as in the case of benzoic acid in benzene) or on the basis of nearly complete hydrolysis in the water phase. That this latter is the correct explanation is proved by the freezing-point lowering of water by ethyl hypochlorite. Pure ethyl hypochlorite prepared as described above was dissolved in water and the freezing-point lowering determined. From this the degree of hydrolysis was calculated as shown in Table III. The percentage hydrolyzed, as given by this method, is probably high, because inevitably a slight decomposition not exceeding 0.5% always took place in the water before analysis.

TABLE III

CRYOSCOPY OF ETHYL HYPOCHLORITE IN WATER

EtOCl, g. per kg. of water	Δt °C.	M	h %
23.4	1.000	43.4	85.5
16.18	0.710	42.3	90.3
5.17	.234	41.0	96.3
15.52	.659	43.7	84.2

$\Delta t°$ is the freezing-point lowering, M the apparent mol. wt. of ethyl hypochlorite and h the degree of hydrolysis at 0°.

Jakowkin[4] has studied the hydrolysis of chlorine by the distribution between water and carbon tetrachloride. We have applied this method to the hydrolysis of ethyl hypochlorite as follows. Hypochlorous acid is insoluble in carbon tetrachloride. The distribution ratio of ethyl alcohol between water and carbon tetrachloride has been found to be 100 to 1 in favor of the water. Therefore it may be safely assumed that the concentrations of hypochlorous acid and alcohol in the water phase resulting

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[4] Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

from hydrolysis are equal. We may then represent the relation between the various concentrations mathematically as follows.

Let C equal the moles per liter of hypochlorite radical in the water phase, S the moles in the solvent phase, k the distribution ratio of unhydrolyzed ethyl hypochlorite between carbon tetrachloride and water, K the equilibrium constant of the reaction, $EtOCl + H_2O = HOCl + EtOH$ and h the fraction hydrolyzed in the water phase.

Then $(EtOH)_{water} = (HOCl)_{water} = h\,C;\qquad (EtOCl)_{water} = (1-h)C$

$(EtOCl)_{solvent} = S$

$$k = \frac{(EtOCl)_{solvent}}{(EtOCl)_{water}} = \frac{S}{C(1-h)} \tag{1}$$

$$K = \frac{(HOCl)_{water}\,(EtOH)_{water}}{(EtOCl)_{water}} = \frac{h^2C}{(1-h)} \tag{2}$$

From equation (1) $$h = \frac{Ck - S}{Ck} \tag{3}$$

Substituting in (2) $$K = \frac{(Ck - S)^2}{Sk} \tag{4}$$

In order to determine the constants k and K at any particular temperature it is necessary only to determine S and C accurately in two distinct experiments made at that temperature. If we denote the variables in one of the experiments by primes,

$$\frac{(Ck - S)^2}{S} = \frac{(C'k - S')^2}{S'} \tag{5}$$

Solving for k; $$k = \frac{S - \sqrt{SS'}}{C - C'\sqrt{\frac{S}{S'}}} \tag{6}$$

Carbon tetrachloride containing ethyl hypochlorite was prepared by the method heretofore described. It was shaken with saturated sodium bicarbonate solution immediately before use in order to remove free chlorine and any small amount of alcohol remaining. To 250 cc. of this solvent solution in a wide mouthed Erlenmeyer flask of about 530cc. capacity was added 250 cc. of distilled water. The flask was closed with a rubber stopper provided with stirrer, thermometer and sampling tube, placed in a water-bath maintained at the desired temperature and the contents stirred until equilibrium was reached. Samples of the water and solvent layer were withdrawn at intervals and analyzed for available chlorine. Stirring was continued until two successive analyses gave the same value for the ratio S/C. The time required to reach equilibrium varied from about 90 minutes at 5.0° to only 10 to 15 minutes at 36°. The decomposition occurring during the course of the stirring was less than 0.5% in all cases. The equilibrium values and the constants calculated therefrom are given in Table IV. Three different experiments were made at each temperature, permitting three combinations in calculating the constants k and K. The values for k at each temperature thus calculated are not identical. This is explained by Equation 6, the denominator of which approaches zero when the degree of hydrolysis is high.

This is the case with ethyl hypochlorite and therefore the accuracy of the method is not sufficient to establish the exact relation between hydrolysis and temperature. However, the results do indicate, first that for concentrations of the hypochlorite radical in the water of less than 0.08 mole per liter hydrolysis is over 90% complete; even in a saturated solution of ethyl hypochlorite in water which contains 0.464 mole of hypochlorite radical per liter we calculate that 69% is hydrolyzed; second, that the effect of temperature on the amount of hydrolysis is not pronounced; third, that the distribution of ethyl hypochlorite between carbon tetrachloride and water is more than 20 to 1 in favor of the carbon tetrachloride.

TABLE IV

DISTRIBUTION OF ETHYL HYPOCHLORITE BETWEEN CCl_4 AND H_2O

Temp. °C.	S	C	k	K	Av. k	Av. K	Fract. hydr. in H_2O layer h
5.0	0.3355	0.0805	36 (2–3)	0.62	..	..	0.90
5.0	.1583	.0541	60 (1–2)	.64	40	0.62	.92
5.0	.0690	.0341	23 (1–3)	.61	..	..	.96
22.5	.3499	.08019	70 (4–5)	.71	..	..	.92
22.5	.1997	.0597	41 (4–6)	.72	47	0.71	.95
22.5	.0637	.0321	31 (5–6)	.70	..	..	.98
36.0	.3121	.0759	50 (7–8)	.87	..	..	.93
36.0	.1642	.0540	57 (7–9)	.87	55	0.87	.96
36.0	.0692	.0344	57 (8–9)	.87	..	..	.99

The figures in parentheses indicate the experimental pairs used in calculations.

As a further check on the accuracy of the above conclusions a series of experiments similar to those already described was made in which alcohol was added to the system. By the use of the average values for k and K it is possible to calculate the value of C for any given value of S as follows.

Let f equal the moles of alcohol added per liter of water in the system and let $e = (\mathrm{EtOH})_{\mathrm{water}}$. From Equation 1 $(\mathrm{EtOCl})_{\mathrm{water}} = S/k$.

$S + \frac{S}{k} + e$ = total moles of ethyl alcohol and ethyl hypochlorite present.

$S + C$ = moles of ethyl present if no alcohol had been added as such.

Therefore $f = \frac{S}{k} + e - C$ and $e = f + C - \frac{S}{k}$

$(\mathrm{HOCl})_{\mathrm{water}} = C - \frac{S}{k}$

Therefore, from Equation 2

$$K = \frac{e\left(C - \frac{S}{k}\right)}{\frac{S}{k}} = \frac{\left(f + C - \frac{S}{k}\right)\left(C - \frac{S}{k}\right)}{\frac{S}{k}} \qquad (7)$$

Solving for C

$$C = \frac{2S - kf \pm \sqrt{K^2f^2 + 4kSK}}{2k} \qquad (8)$$

The data and calculated results of Table V show that the experimental values of C can be predicted with a considerable degree of accuracy.

TABLE V

DISTRIBUTION OF ETHYL HYPOCHLORITE BETWEEN CARBON TETRACHLORIDE AND WATER, WITH EXCESS OF ALCOHOL

Temp. °C.		S	C observed	C calculated[a]	Value of C if no alcohol had been added
22.5	0.0794	0.3702	0.0557	0.0528	0.0832
22.5	.0745	.2217	.0369	.0363	.0625
22.5	.0388	.0795	.0254	.0220	.0372
36.0	.0745	.3265	.0508	.0497	.0776
36.0	.0685	.1638	.0318	.0301	.0532

[a] At 22.5°, $K = 0.71$, $k = 47$; at 36.0°, $K = 0.87$, $k = 55$.

A direct application can be made of this idea of hydrolysis and distribution to the quantitative determination of ethyl alcohol in spirituous liquors. Where an accuracy of 5% is all that is desired, the following simplified method of analysis is recommended. A sample of alcohol containing from 0.04 to 0.60 g. of ethanol is added to a freshly chlorinated limestone solution, the total volume being made equal to 40 cc. This is shaken for two minutes at 20–25° with 40 cc. of pure carbon tetrachloride in a stoppered flask. After settling, samples are withdrawn from each phase and analyzed iodimetrically for available chlorine. The total available chlorine present in both phases and the percentage of the total that is transferred to the carbon tetrachloride are then calculated. In the accompanying nomograph, Fig. 1, when these points on the corresponding scales are connected with a straight-edge, the intersection with the center scale gives the total grams of ethyl alcohol in the original sample. The method has been successfully applied to mixtures of water and alcohol, of carbon tetrachloride and alcohol and wines, but not so successfully with whisky. Its chief advantage is that the sample required for the determination is

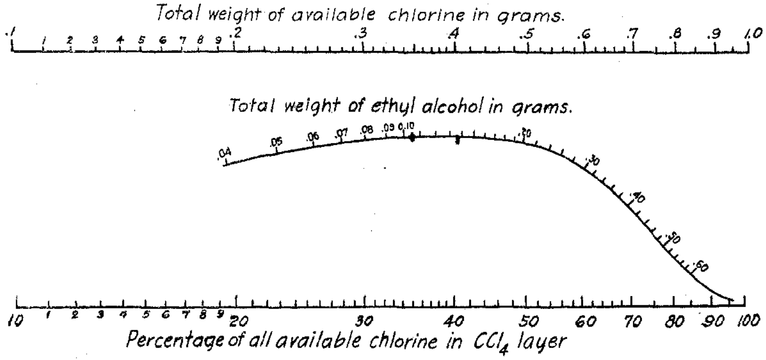

Fig. 1.—Nomograph for alcohol determination.

very small compared with that necessary in the regular density test which involves distillation of a 100cc. sample.

Summary

1. In general, hypochlorous acid reacts with monohydric alcohols to form esters. The hypochlorites of dihydric or trihydric alcohols could not be prepared.

2. Tertiary alcohols were found to give more stable esters than either primary or secondary alcohols.

3. The constitution of ethyl hypochlorite has been proved to be that of a true ester.

4. Ethyl hypochlorite readily hydrolyzes in water, even in its saturated solution, to the extent of 69%.

5. A simple method of preparing solvent solutions of alkyl hypochlorites has been described.

6. A new method for the approximate determination of alcohols has been described.

Niagara Falls, New York

[Contribution from the Chemistry Laboratory of the University of Hawaii]

SYNTHESIS OF THE ANHYDRIDE OF HYDROXYMERCURI-ETHOXY-CHAULMOOGRIC ACID AND ETHYL ACETOXYMERCURI-ETHOXY-CHAULMOOGRATE

By A. L. Dean, R. Wrenshall and G. Fujimoto

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While the administration of the mixed ethyl esters of the fatty acids from chaulmoogra oil in the treatment of leprosy has produced highly gratifying results,[1] and derivatives of the acids of the chaulmoogric series have been shown, both *in vitro*[2] and *in vivo*[3] to possess unique therapeutic value against the lepra bacillus, these products should by no means be considered an absolute specific against the disease.

While practically all the patients who have received this treatment at the United States Leprosy Investigation Station, Honolulu, Hawaii, have shown marked improvement, a considerable number of them have come to a standstill after a few months, and even in the cases where apparent cures have been effected, the treatment is a slow one, usually requiring from one to two or more years.

To improve the present method for treating leprosy, compounds of higher therapeutic value than these chaulmoogra esters will be required. For

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[1] McDonald, *J. Am. Med. Assoc.*, **75**, 1483 (1920).

[2] Walker and Sweeney, *J. Infectious Diseases*, **26**, 238 (1920).

[3] McDonald and Dean, *J. Am. Med. Assoc.*, **76**, 1470 (1921) and *Pub. Health Repts.*, Aug. 20, **1920**, 1959.