coefficient of chloride ion, f_{Cl}, from the e.m.f. data, using the equation

$$E^0_c - E^0_c(\mathrm{HOH}) = -0.05915 \log (f_H f_{Cl}) \quad (5)$$

and available values of f_H for lyonium ion.[12] The pertinent data at various rounded solvent compositions are given in Table II, which also lists values of f_{OH} for lyate ion.[12] It is seen that the solvent dependence of f_{Cl} closely resembles that of f_{OH}, but departs grossly from that of f_H. The results corroborate the view, based on entirely different evidence,[13] that solvation energies of anions in hydroxylic media are much less sensitive to solvent change than those of cations.

TABLE I

DATA FOR CELL 1 IN THE SYSTEM ETHANOL–WATER AT 25.0°

Ethanol, mole %	D^a	s (Å.)	$K(M)$	E^0_c (mv.)	Ref.
0.00	78.48	4.95[b]	Large	221.5	10
4.17	72.99	5.00	Large	214.9	5
		5.32		215.4	6
8.91	67.54	5.32	Large	207.0	5
		4.95		209.1	6
25.00	51.35	5.45	Large	184.6	4
50.00	36.60	5.93	0.176	143.3	4[c]
72.75	29.68	5.99	.0546	....	11
75.00	29.18	5.98	.0502	87.4	4
92.27	25.77	5.65	.0251	....	11
100.00	24.306	3.60	.00915	−88.6	9

[a] Reference 8. [b] G. J. Hill and D. J. G. Ives, *J. Chem. Soc.*, 318 (1951). [c] This research.

TABLE II

VALUES OF f_{Cl}

Ethanol, wt. %	E^0_c	$\log f_H{}^a$	$\log f_{Cl}$	$\log f_{OH}{}^a$
0.0	221.5	0.000	0.000	0.00
20.0	208.0	.008	.220	.32
35.0	195.8	.042	.392	.53
50.0	180.0	.251	.451	.63
65.0	157.9	.542	.533	.75
80.0	119.2	1.152	.577	.76
100.0	−88.6	4.707	.536	.8

[a] Reference 12.

The authors are indebted to the Research Corporation and to the Florida State University Research Council for financial support, and to Drs. J. L. Hall and H. Phillips for permission to quote their dielectric constant data.

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(12) B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 565 (1953).

(13) P. M. Gross, *Chem. Revs.*, **13**, 99 (1933).

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Tertiary Butyl Hypochlorite as an N-Chlorinating Agent

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RECEIVED MARCH 15, 1954

It has recently been shown that *t*-butyl hypochlorite (TBH) can be used in place of inorganic hypochlorites in the synthesis of hydrazine from either ammonia or urea.[1,2] Spectroscopic investigation of the corresponding reaction mixtures showed that the N-chloro compounds, that is, chloramine and N-chlorourea, are formed as the intermediate products. Although neither one of the N-chloro compounds was isolated in these instances it was considered highly probable that TBH might serve as an effective N-chlorinating agent. The general usefulness of TBH for this purpose has now been demonstrated by the synthesis of a number of typical N-chlorinated derivatives, examples of which are listed in Table I.

TABLE I

PREPARATION OF N-CHLORO COMPOUNDS USING *t*-BUTYL HYPOCHLORITE

Compound	Melting point (boiling point)	Yield, %
N-Chlorophthalimide	181–183	74.6
N-Chlorosuccinimide	150–151	35.2
N-Chloro-*o*-toluenesulfonamide (Na salt·$2H_2O$)	~170 dec.	83.9
N-Chloroacetanilide	91[a,b]	22.7
N-Dichloro-*t*-octylamine	98.5–100.5 at 18 mm.	74.8
N-Dichloro-*t*-butylamine	~30 at 16 mm.	60.5

[a] The larger part of the product mixture was converted into 4-chloroacetanilide, m.p. 173–174°; rearrangement takes place readily upon the addition of acetic acid. If the reaction is carried out in acetic acid as the solvent, only the 4-chloroacetanilide is obtained. [b] A parallel experiment with sodium hypochlorite as the chlorinating agent gave a 33.2% yield of 4-chloroacetanilide.

t-Butyl hypochlorite also may be used to prepare N-dichloro derivatives. This was accomplished specifically in the synthesis of two previously unknown N-dichloro-*t*-alkylamines. In effecting the N-chlorination of *t*-octylamine, an amount of *t*-butyl alcohol corresponding to that required by the following equation was recovered by distillation from the reaction mixture

$$\mathrm{RNH_2 + 2ROCl \longrightarrow RNCl_2 + 2ROH}$$

In effecting the synthesis of N-chlorosuccinimide by the action of TBH upon succinimide a more extensive investigation was carried out to determine the influence of such variables as temperature, solvent and time. Results are summarized in Table II.

TABLE II

PREPARATION OF N-CHLOROSUCCINIMIDE

Expt. no.	Reaction time, hr.	Temp., °C.	Mole ratio TBH: succinimide	Solvent	Yield, %
A	1	0	1:1	Acetic acid, saturated with sodium acetate	Trace
B	1	0	1:1	$HC_2H_3O_2$	14.8
C	6.5	0	2:1	$HC_2H_3O_2$	34
D	1	0	1:1	50% $HC_2H_3O_2$ in H_2O	31.3[a]
E	1	25	1:1	50% $HC_2H_3O_2$ in H_2O	36.5
F	1	0	1:1	Tetrahydrofuran	None

[a] In carrying out a comparable experiment using aqueous sodium hypochlorite in place of TBH a 35.2% yield of the desired product was obtained.

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(1) L. F. Audrieth, E. Colton and M. M. Jones, THIS JOURNAL, **76**, 1428 (1954).

(2) E. Colton, M. M. Jones and L. F. Audrieth, *ibid.*, **76**, 2572 (1954).

It is interesting to point out that only traces of the desired product are obtained when the components are brought together in a "strongly basic solution" comprising a saturated solution of sodium acetate in glacial acetic acid.

When pure acetic acid is used as the solvent the yield is found to depend upon the reaction time and the mole ratio of TBH: succinimide (experiments B and C). Aqueous acetic acid appears to be a better solvent medium for the reaction than pure acetic acid (compare experiments D and E with B and C). None of the N-chloro compound was obtained when tetrahydrofuran was used as the solvent.

As an N-chlorinating agent TBH possesses certain advantages over an inorganic hypochlorite: (a) it can be prepared readily as a pure substance and can be stored for months in an ice chest without suffering appreciable deterioration; (b) no contaminants are introduced into the synthesis solution; (c) it can be used along with only small quantities of solvent thus greatly simplifying preparation and isolation of the desired product; (d) reaction is carried out in homogeneous solution.

Experimental

t-Butyl hypochlorite was prepared according to the method of Teeter, *et al.*[3] Yields of pure product exceeded 90%. All starting materials were recrystallized (or distilled) before use. Composition of previously unknown N-chloro derivatives was verified by iodometric analysis for active chlorine content.

N-Chlorosuccinimide.—A solution of 4.96 g. (0.05 mole) of succinimide in a mixture consisting of 17 ml. of acetic acid and 15 ml. of water was treated with 5.6 g. of TBH (0.05 mole of 92% material) and was allowed to stand at 0° for one hour. The resulting precipitate was removed by filtration and dried in a vacuum desiccator; yield 2.07 g. (31.3%), m.p. 149–150°.[4]

Sodium Salt of N-Chloro-*o*-toluenesulfonamide.—A solution containing 8.5 g. (0.05 mole) of *o*-toluenesulfonamide, 100 ml. of 1 *N* sodium hydroxide, 100 ml. of *t*-butyl alcohol and 5.6 g. of TBH (0.05 mole of 92% material) was warmed for one hour on a water-bath. The solution was then cooled in the ice chest and the resulting precipitate recovered by filtration and dried in a desiccator over calcium chloride. The product, weighing 11.05 g., was found to decompose violently at 170°.[5]

Anal. Calcd. for $(C_7H_7SO_2NCl)Na\cdot 2H_2O$: Cl, 13.44. Found: Cl, 13.74.

N-Chloroacetanilide.—A suspension of 6.6 g. of acetanilide in 100 ml. of 0.5 *N* sodium hydroxide was cooled to 0° and then treated with 5.6 g. (0.05 mole of 92% material) of TBH. The mixture was allowed to stand in the dark for one hour after which a small amount of the precipitate was removed by filtration. The latter gave a strong positive iodide reaction and after recrystallization from chloroform was found to have a melting point of 88–90°.[6] The remainder of the suspension was acidified by the addition of acetic acid and warmed to room temperature to effect solution of the product and rearrangement to the more stable compound, 4-chloroacetanilide. A yield of 1.93 g. (22.7%) of the latter was isolated, m.p. 171–173°.[7]

N-Chlorophthalimide.—A solution consisting of 7.36 g. (0.05 mole) of phthalimide, 5.6 g. of TBH (0.05 mole of 92% material), 50 ml. of water and 25 ml. of *t*-butyl alcohol was stirred for one hour at room temperature. The resulting precipitate was then removed by filtration and dried upon a clay plate. (The mother liquor still gave a very weak reaction when tested with iodide indicating that complete interaction (chlorination) of phthalimide had not taken place.) The product was recrystallized to give 6.5 g. of N-chlorophthalimide, m.p. 181–183°.[8]

N-Dichloro-*t*-octylamine.—A solution of 6.5 g. (0.05 mole) of tertiary octylamine in 100 ml. of ether was cooled to 0° and treated over a period of 20 minutes with 11.5 g. of TBH (approximately 0.1 mole 92% material) which was added dropwise to the solution. The ether was then removed by evaporation on the water-bath and the remaining liquid subjected to vacuum distillation. The major fraction consisting of a viscous yellowish liquid distilled at 99.5–100.5° at 18 mm.; n^{19}_{D} 1.4780, yield 7.81 g. (74.8%).

Anal. Calcd. for $C_8H_{17}NCl_2$: Cl, 35.79. Found: Cl, 35.62.

N-Dichloro-*t*-butylamine.—This substance was prepared from 7.3 g. (0.1 mole) of *t*-butylamine and 23 g. (0.2 mole of 92% material) of TBH in 200 ml. of ether. The product was recovered by vacuum distillation as a yellowish liquid, possessing a very irritating odor, which could not be distilled completely without some decomposition; n^{19}_{D} 1.4639; yield 8.6 g. (60.5%).

Anal. Calcd. for $C_4H_9NCl_2$: Cl, 49.93. Found: Cl, 47.03.

Acknowledgment.—The technical assistance of Mrs. Marlies Zimmer and Mr. Ervin Colton is acknowledged with gratitude. This investigation was carried out under the sponsorship of the Office of Ordnance Research as one phase of a fundamental study of the synthesis of hydrazine, Contract No. DA-11-022-ORD-828.

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[3] H. M. Teeter, R. C. Bachmann, E. W. Bell and J. C. Cowan, *Ind. Eng. Chem.*, **41**, 849 (1949).

[4] G. Bender, *Ber.*, **19**, 2272 (1886), m.p. 148°.

[5] F. D. Chattaway, *J. Chem. Soc.*, 145 (1905), dec. 170–175°.

[6] W. J. Jones and J. P. Orton, *ibid.*, 1056 (1909), m.p. 91°.

[7] C. K. Ingold, E. W. Smith and C. C. N. Vass, *ibid.*, 1245 (1927).

[8] J. Tscherniac, *Ber.*, **34**, 4209 (1901), m.p. 183°.