[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Thermal Decomposition of Ald-chlorimines[1]

BY CHARLES R. HAUSER, ATHEY G. GILLASPIE AND JOHN W. LEMAISTRE

It has been shown previously[2] that ald-chlorimines (RCH=NCl) readily undergo thermal decomposition. Nitriles and hydrogen chloride have been qualitatively identified as primary products.

In this paper is reported the synthesis of some new ald-chlorimines and the results of a study of the relative thermal stabilities of these and other ald-chlorimines. The products of thermal decomposition of certain of these compounds have been determined semi-quantitatively at temperatures where their decomposition is practically instantaneous.

Experimental

Reagents.—Most of the aldehydes used in this work were Eastman or Kahlbaum products. Solids were recrystallized if melting points were low. Liquids were redistilled before use. Eastman 4-methylbenzaldehyde was purified through a crystalline addition product with phosphoric acid.[3] 2-Bromo-[4] and 3-bromo-[5] benzaldehydes, and 4-nitrocinnamaldehyde[6] were synthesized by methods described in the literature. 3-Nitrocinnamaldehyde was prepared by a method similar to that used for the preparation of the para isomer.

Monochloramine was prepared as described previously,[2] by mixing equivalent amounts of molar solutions of sodium hypochlorite[7] and ammonium hydroxide containing crushed ice.

Preparation of Ald-chlorimines.—The following general method includes certain modifications of the one previously described.[2] Six grams of a liquid aldehyde was shaken with 400 cc. of freshly prepared monochlorimine solution containing about 100 g. of crushed ice. If a solid product formed it was coagulated by shaking and then filtered rapidly with suction. The product was washed free from alkali with cold water. If no solid had formed within a short time (five to twenty minutes) the oil was extracted with ether or drawn off with a pipet. Throughout the procedure the reaction mixture should be kept at 0°.

A modified procedure was used for solid aldehydes, the latter being dissolved in 30–40 cc. of ether and the solution added to 400 cc. of aqueous monochloramine reagent so that two layers formed. The mixture was then shaken vigorously. A precipitate formed almost immediately. After it had coagulated the product was filtered and washed. Ethyl acetate was used as solvent instead of ether for the nitrobenzaldehydes, and dioxane for the nitrocinnamaldehydes. The yields of crude products were generally 75–85% of the theoretical quantities.

The solid chlorimines were recrystallized from alcohol and acetone as described previously.[2] They were pressed on porous plates and kept over potash in a desiccator in a refrigerator. Certain chlorimines have been purified by precipitating them from chloroform solutions by the addition of ligroin. Liquid chlorimines could not be purified since attempts to distil them even under reduced pressure resulted in decomposition. They were dissolved in ether, dried over sodium sulfate, and the ether removed *in vacuo*.

The chlorimines were analyzed for active chlorine by dissolving weighed samples in glacial acetic acid or in a mixture of alcohol and acid, adding potassium iodide solution, and titrating with standard thiosulfate in the usual manner. Near the end of the titration water and starch indicator were added. Many of the chlorimines were further identified by converting them into their corresponding imine hydrochlorides by passing dry hydrogen chloride into their ether solutions.

The following crystalline compounds which have been prepared previously[2] were used in this work: 2-chloro-,

TABLE I

NEW CHLORIMINES, R—CH=NCl

	Chlorimine	M. p., °C.	Active chlorine, % Calcd.	Found
1	3-Bromobenzal-	21	16.24	16.18
2	3-Chlorobenzal-	15	20.38	20.10
3	3-Methoxybenzal-	Oil	20.92	20.82
4	2-Bromobenzal-	48	16.24	15.85
5	4-Methylbenzal-	20	23.10	23.00
6	3-Nitro-4-methoxybenzal-	86–87	16.54	16.48
7	4-Nitrobenzal-	213 (dec.)[a]	19.22	19.20
8	Cinnamal-	52	21.42	21.22
9	2-Nitrocinnamal-	124 (dec.)[a]	16.84	16.68
10	3-Nitrocinnamal-	140–142 (dec.)[a]	16.84	16.76
11	4-Nitrocinnamal-	153–155 (dec.)[a]	16.84	16.80

[a] The solid melted with instantaneous decomposition on the melting point bar used for the determination of the decomposition temperature. When a sample of *p*-nitrobenzalchlorimine was heated in a bath from room temperature in the usual manner the substance melted at about 120° with frothing.

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[1] This paper is from portions of theses presented by A. G. Gillaspie and John W. LeMaistre in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Duke University.

[2] Hauser, Hauser and Gillaspie, THIS JOURNAL, **52**, 4158 (1930).

[3] Raikow and Schtarbanow, *Chem.-Zeit.*, **25**, 1135 (1901).

[4] Brady, Cosson and Roper, *J. Chem. Soc.*, **127**, 2429 (1925). The procedure was modified, 10 g. of chromium trioxide being dissolved in 30 g. of acetic anhydride instead of glacial acetic acid as recorded in this reference.

[5] Einhorn and Gernsheim, *Ann.*, **284**, 141 (1894).

[6] Fecht, *Ber.*, **40**, 3893 (1907).

[7] A convenient source of hypochlorite was found to be "H. T. H.," a calcium hypochlorite product of the Mathieson Alkali Works. An aqueous solution of "H. T. H." was treated with sodium carbonate, the precipitate allowed to settle, and the sodium hypochlorite siphoned off as required.

4-chloro-, 4-bromo-, 2-nitro-, 3-nitro-, 2-methoxy-, 4-methoxy-, 3,4-methylenedioxy- and 2-chloro-5-nitrobenzalchlorimines. The melting points and analytical data for new compounds are listed in Table I. 3-Bromo-, 3-chloro-, 3-methoxy- and 4-methyl-benzalchlorimines were colorless oils at room temperature. Cinnamalchlorimine and its nitro derivatives were obtained as pale yellow crystals. Benzalchlorimine and 2-furfuralchlorimine have been obtained as oils, 85 and 80% pure, respectively, calculated from their active chlorine contents.

Condensation of Monochloramine with Aldehydes.—Alkali favors the condensation of monochloramine with aldehydes. However, since ald-chlorimines are decomposed by bases[8] they cannot be prepared in alkaline solution except with conditions under which the product precipitates promptly. It has been found that 4-chlorobenzaldehyde condensed very little with monochloramine in neutral aqueous alcoholic solution. In the presence of sodium bicarbonate the chlorimine was obtained. Under these conditions, however, the reaction required about one and one-half hours, whereas in the presence of 0.5 *N* sodium hydroxide the condensation was complete within a few minutes.

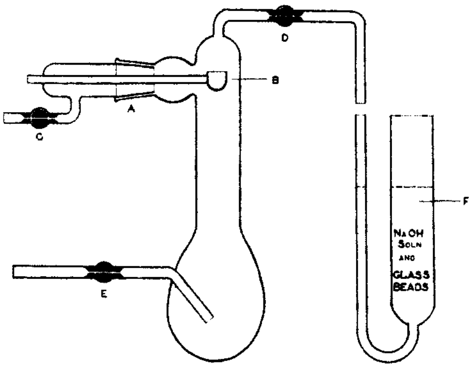

Fig. 1.

It has been found that some aldehydes could not be condensed with monochloramine. When ether or ethyl acetate solutions of 2,4-dinitro-, 2,4,6-trinitrobenzaldehydes, 4-methoxy-1-naphthaldehyde or alpha-bromocinnamaldehyde were shaken with alkaline monochlorimine reagent the aldehydes were recovered practically unchanged. Alpha-chlorocinnamaldehyde gave a product containing about 18% of the chlorimine. Certain aldehydes that condensed very little by this method have been converted partially to chlorimines by allowing the reaction to take place in aqueous alcoholic solution in the presence of sodium bicarbonate for several hours, but this method was not satisfactory since low yields and impure products were obtained.

Products of Thermal Decomposition.—The apparatus shown in Fig. 1 consisted of a Kjeldahl flask to which was sealed a ground glass joint (A). The movable inner cone of this joint carried a spoon (B), and a stopcock tube (C) through which this part of the vessel could be swept out. To the neck of the flask was sealed a stopcock tube (D) which was used as an outlet. To the bulb of the flask was attached a stopcock tube (E) through which the gas used for sweeping out the apparatus could be introduced. The absorption vessel (F) was filled with dilute sodium hydroxide solution (0.1 to 0.2 normal).

The sample used in these experiments was usually about 0.2 g. The use of smaller samples added considerably to the analytical difficulties and the use of larger samples made it difficult to obtain instantaneous decomposition. The apparatus was swept out with 7 to 8 liters of nitrogen gas which had been passed through towers containing sulfuric acid, soda lime and calcium chloride. An accurately weighed sample of pure chlorimine was then placed in the spoon (B). The floor of the flask was heated by a bath of Wood's metal to a temperature above that where the chlorimine decomposed instantaneously, keeping stopcocks (D) and (E) open. The absorption vessel was connected to the apparatus, stopcock (E) closed, and the sample dropped to the hot floor of the flask by turning the ground glass joint. Sudden decomposition occurred at this point, and when the first flow of gases had ceased, stopcock (D) was closed, and the apparatus allowed to cool. When at room temperature the apparatus was swept out with 7 to 8 liters of dry nitrogen, the gases passing out at (D) into the absorption vessel.

The alkaline solution was washed out of the absorption vessel and made up to definite volume. Aliquot portions were acidified, potassium iodide added and the solution titrated with sodium thiosulfate in the usual manner. In other aliquot portions the chlorine was reduced with ammonia.[9] These solutions were then acidified with nitric acid and titrated for chloride ion by Volhard's method.

The residue left in the decomposition vessel was washed thoroughly with hot benzene, the solution filtered and the filtrate evaporated in a tared vessel. The product was weighed and shown by the mixed melting point method to consist of practically pure nitrile in each case. A very small amount of the residue was insoluble in benzene and consisted presumably of the imine hydrochloride. It was treated with water and the aqueous solution titrated for chloride ion by Volhard's method. In several cases the aldehyde corresponding to the chlorimine used was identified in the products of hydrolysis. No other substance was found. The results are given in Table II.

The products obtained in the thermal decomposition of ald-chlorimines are accounted for by two reactions (I) and (II).

$$\mathrm{RCH{=}NCl} \longrightarrow \mathrm{RCN} + \mathrm{HCl} \qquad \text{(I)}$$

$$\mathrm{RCH{=}NCl} + 2\mathrm{HCl} \longrightarrow \mathrm{RCH{=}NH{\cdot}HCl} + \mathrm{Cl_2} \qquad \text{(II)}$$

The extent of the primary decomposition (I) can be calculated from the amount of nitrile obtained, or from the hydrogen chloride found in the gaseous products plus that used up in the secondary reaction (II). By inspection of equation (II) it can be seen that the amount of hydrogen chloride used in the secondary reaction should be equivalent to the free chlorine produced. Thus the value for the total chloride ion found in the gaseous products after reduction of the free chlorine with ammonia should correspond to the

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[8] Hauser and Moore, THIS JOURNAL, **55**, 4526 (1933).

[9] Treadwell-Hall, "Analytical Chemistry," etc., Vol. II, p. 291.

TABLE II

PRODUCTS OF THERMAL DECOMPOSITION OF SUBSTITUTED BENZALCHLORIMINES

Substituent	Temp., °C.	Millimoles of chlorimine used	Total Cl in gaseous product	RCN	Cl_2	RCH=NH·HCl	Percentage decomposition (I)	(II)
2-Nitro-	275	1.23	1.11	1.16	0.087	0.057	92[b]	5.9
3-Nitro-	274	0.959	0.846	0.716	.080	.076	88	8.1
4-Methoxy-	195	1.23	.997	.64[a]	.065	.059	81	5.0
2-Chloro-	275	1.17	1.02	1.02	.033	.072	87	4.5
4-Chloro-	235	3.70	3.33	3.31	.18	..	90	4.8

[a] In this experiment the residue was somewhat charred. [b] This value was calculated from the average of the figures for hydrogen chloride and nitrile.

hydrogen chloride produced in the primary decomposition. These values have been used to calculate the extent of the primary decomposition. The extent of the secondary reaction (II) has been calculated from the average of the figures obtained for free chlorine and imine hydrochloride.

It can be seen from Table II that at temperatures where the decomposition of the ald-chlorimines was practically instantaneous, reaction (I) was predominant, occurring in general to the extent of about 90%, whereas reaction (II) took place to only a small extent. It might have been supposed that an ald-chlorimine would decompose to give an aldazine and chlorine ($2RCH{=}NCl \longrightarrow RCH{=}N{-}N{=}HCR + Cl_2$). However, no evidence of the occurrence of such a reaction was found.

The decomposition at elevated temperatures appears to follow the same course as that at lower temperatures. At lower temperatures, however, where the life of the chlorimine is relatively long, there is more opportunity for hydrogen chloride to come into contact with unchanged chlorimine than at higher temperatures where the life of the chlorimine is short. Accordingly, more of the secondary products have been found[10] at lower temperatures.

Stabilities of Ald-chlorimines.—The relative thermal stabilities of these compounds have been determined in the following manner. Small samples (2 to 5 mg.) of an ald-chlorimine were sprinkled along a heated melting point bar of the type described by Dennis and Shelton,[11] and the temperature recorded at which the compound decomposed without detectable lapse of time. The sudden decomposition, accompanied by the evolution of a cloud of hydrogen chloride, was easily recognized. In this manner a characteristic temperature, reproducible in general to within ±5°, which has been called the "instantaneous decomposition temperature," has been determined for each compound.[12] The results are given in Table III. These values seem to be practically independent of the presence of impurities. Experiments with mixtures of chlorimines and their corresponding aldehydes or nitriles containing 20–25% of the impurity, gave values which were approximately the same as those obtained when the pure chlorimine was used. It should be pointed out that all of the compounds that were solid at room temperatures, with the exceptions of *p*-nitrobenzalchlorimine and the nitrocinnamalchlorimines, melted at temperatures below those at which they decomposed instantaneously.

TABLE III

INSTANTANEOUS DECOMPOSITION TEMPERATURES OF CHLORIMINES

Cinnamal-	120
2-Furfural-	165
Benzal-	170
3-NO_2-4-OMe-benzal-	168
3,4-H_2CO_2-benzal-	170
3-Cl-5-NO_2-benzal-	215

	o	*m*	*p*
Nitrocinnamal-	124	142	143
Methoxybenzal-	172	177	163
Methylbenzal-	..	...	178
Nitrobenzal-	180–200	213	213
Chlorobenzal-	215	215	195
Bromobenzal-	215	215	213

Although the rates of decomposition of these compounds at room temperatures are complicated by secondary reactions, especially in the case of the liquids, certain regularities are evident on comparing these rates with the results given in

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(10) The decomposition of *p*-methoxybenzalchlorimine at room temperatures gave nearly two-thirds as much imine hydrochloride as nitrile. Hauser and Hauser, THIS JOURNAL, **52**, 2053 (1930).

(11) Dennis and Shelton, *ibid.*, **52**, 3128 (1930).

(12) Although the heats of fusion and heat conductivities of the liquid or solid compounds on the bar are unknown quantities it would seem that under the conditions of decomposition these factors should be comparable if not negligible. The copper bar has a high heat reserve because of its large mass which would appear to be adequate to maintain the temperature level, at least approximately, when so little a quantity as a few milligrams of chlorimine is used. The fact that no variation in decomposition temperature is observed for varying quantities of material within limits of 2–5 mg. would seem to support this.

Table III. It has been shown[2] that 2- and 4-chloro-, 4-bromo- and 3-nitrobenzalchlorimines, compounds that have relatively high decomposition temperatures, are changed only slightly at 30° within a few hours, whereas the 2- and 4-methoxy and 3,4-methylenedioxy derivatives, which have somewhat lower decomposition temperatures, are decomposed almost completely at 30° during the same time. Moreover, cinnamalchlorimine, which has the lowest decomposition temperature of any of the compounds listed in Table III, decomposes vigorously within thirty minutes when allowed to stand at room temperatures. *o*-Nitrobenzalchlorimine, however, seems to be exceptional in that decomposition temperatures have been found ranging from 180–200°; also, at 30°, it decomposes much more rapidly than its isomers.

The writers wish to express their indebtedness to Dr. L. A. Bigelow and Dr. P. M. Gross, whose valuable suggestions have contributed to the progress of the work.

Summary

1. Eleven new ald-chlorimines have been synthesized.

2. The products formed by the instantaneous decomposition of certain ald-chlorimines have been determined. In general, 90% of a chlorimine decomposed to form primary products, nitrile and hydrogen chloride, and only about 5% to form the secondary products, imine hydrochloride and free chlorine.

3. The temperatures of instantaneous decomposition of 22 ald-chlorimines have been measured. They are reproducible to within ±5° and range from 120 to 215°.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

The Preparation of Sodium Alkyl Sulfonates

BY R. M. REED WITH H. V. TARTAR

A method for the preparation of high molecular weight alkyl sulfonic acids has been described recently by Noller and Gordon.[1] They prepared the corresponding alkyl mercaptans and then oxidized the lead mercaptides to sulfonates with 50% nitric acid. Collins, Hilditch, Marsh and McLeod[2] later described a similar method in which alkyl mercaptans or disulfides were oxidized to the corresponding sulfonic acids by powdered potassium permanganate in acetone or acetic acid solution. These methods were both modifications of those of Reychler[3] and Norris.[4]

Norris reported that many unsuccessful attempts were made to prepare cetyl sulfonic acid from cetyl iodide by using sulfite or bisulfite with solvents such as water, methyl alcohol, ethyl alcohol, acetone and ether. Collins and his co-workers verified this report of Norris as follows: "We confirmed the statement of Norris that the alkyl iodides do not yield the sulfonic acid salts when heated with ammonium sulfite under pressure."

The reaction referred to by these workers

$$RI + (NH_4)_2SO_3 = RSO_3NH_4 + NH_4I$$

is known as the Strecker reaction, and was reported as early as 1868 by Strecker[5] and various other workers. It has been applied successfully to the preparation of sulfonates from such substances as methyl and ethyl iodides, chloroform, ethylene bromide, chlorinated quinones, benzyl chloride and many others, but until very recently had never been used with alkyl halides of high molecular weight (such as octyl or cetyl iodides). It was known, however, that any of the halides could be used in the reaction, and that sodium, potassium and ammonium sulfites were all effective in the sulfonation.

Although Collins and his co-workers were unsuccessful in applying the Strecker reaction to the preparation of alkyl sulfonic acids of high molecular weight, its successful use in such cases had been reported in the patent literature some time previously.[6] These references describe the preparation of such typical high molecular weight

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[1] Noller and Gordon, THIS JOURNAL, **55**, 1090 (1933).

[2] Collins, Hilditch, Marsh and McLeod, *J. Soc. Chem. Ind.*, **52**, 272T (1933).

[3] Reychler, *Bull. soc. chim. Belg.*, **27**, 110, 217, 300 (1913).

[4] Norris, *J. Chem. Soc.*, **121**, 2161 (1922).

[5] Strecker, *Ann.*, **148**, 90 (1868).

[6] (a) French Patent 711,210, *C. A.* **26**, 1732 (1932); (b) French Patent 716,715, *ibid.*, **26**, 2288 (1932); (c) British Patent 360,539, *ibid.*, **27**, 575 (1933); (d) British Patent 369,301, *ibid.*, **27**, 2661 (1933).