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MECHANISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION

LEVEL III

FINAL REPORT

by

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July 1977

DREXEL UNIVERSITY

Philadelphia, PA 19104

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
Chemical Systems Laboratory
Aberdeen Proving Ground, Maryland 21010

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Phenyl sulfone	Sebaceous oils	Benzene sulfonamide (cont)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

These investigations covered two distinct subjects: activated charcoal degradation by perspiration and decomposition of chloramine B. Both untreated and treated activated charcoal samples were exposed to synthetic sweat solutions or aqueous solutions of individual components of synthetic sweat. Change in activated charcoal capacity was measured using carbon tetrachloride pick-up measured under static conditions. Gas chromatography was also used for dynamic measurements to determine if individual components could be ranked as to their poisoning effects. Neither static or dynamic tests uncovered any material which could

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Item 19 continued

Inorganic salts
Activated charcoal

Item 20 continued

be positively identified as causing capacity reduction. The studies showed that "poisoning" effects could be reduced by pretreating the charcoal with a pH 7 buffer or by coating the charcoal with hydrophobic substances.

Thermal decomposition of chloramine B was studied in two temperature ranges: low (ambient to $100^\circ C$) and high ($100^\circ C$ to $185^\circ C$). In the low range, decomposition was determined to be the result of hydrolysis of the chloramine B salt. In the high range, decomposition was violent with the generation of a large amount of heat, characteristic of N-Cl compound decomposition.

PREFACE

The work reported in this document was authorized by Task 1L762710A09506, Body Protection Investigations. It was carried out from July 1975 to June 1976.

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CONTENTS

MECHANISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION

(CHLORAMINE B THERMAL DECOMPOSITION MECHANISMS)

I. BACKGROUND

Having had considerable experience with determining the chemical and thermochemical characteristics of ASC Whetlerite solutions and ASC Whetlerite impregnated carbons, [1] our research group at Drexel University was asked by Mr. Charles Keck and Mr. Thomas Mitchell of Edgewood Arsenal (Clothing and Decontamination Section, Physical Protection Branch, Development and Engineering Directorate) if we could come up with answers to a very pressing problem involving self-ignition of packaged kits labeled XXCC3 (used as an external dusting powder to protect against mustard gas damage to exposed surfaces of the human body.) [2] We were able to solve this problem by finding the sources of ignition; additionally we were able to develop considerable chemical insight on the behavior of the N-Cl bond as a function of temperature. Part of this research resulted in a published paper whereby the reactivity of the N-Cl bond in chloramines is delineated. [3]

Subsequently, we were invited by this same group to research a problem concerning the perspiration damage of the activated carbon layer used in a protective uniform. However, before our research was to begin on "sweat poisoning," another urgent problem arose involving the heating and explosion of sealed glass ampoules in which chloramine B (the sodium salt of N-chloro-benzenesulfonamide) was stored. Consequently about 80% of the contract time and funds intended for sweat poisoning were devoted to the chloramine B problem, concluding about December 31, 1975 whereby the contract specified a termination date of February 28, 1976. With only two months to spend on sweat poisoning we continued our research on a nonfunded extension basis until the end of December 1976. Overall, our studies on sweat were not as intensive as planned because of a distinct lack of funds. However, we have reached some conclusions which are on much firmer ground than those arrived at by previous investigators, and we can make some suggestions for further study which should produce beneficial results.

II. DISCUSSION

Although our research started with chloramine B and ended with sweat "poisoning," I shall discuss sweat poisoning first (being the principal goal.)

A. Perspiration Effects on Activated Carbon

1. Preliminary Information

Activated carbon is a well known absorbent for gases and

has been used extensively for removal of toxic agents from air samples. A layer of activated carbon granules is one of several layers associated with the construction of protective clothing for military personnel. Because of the nature of such garments, being very heavy in combination with airtight seals to the body, the wearer is quickly subjected to profuse sweating. Such sweating affects the activated carbon granules so that they rapidly lose their adsorptive capabilities. [4]

A great deal of precedential work has been done on this problem but as yet nothing specifically useful can be extracted. Indeed, it is impossible to draw reasonable, workable conclusions from all the published work done so far. A great deal of the research is at best piecemeal and one often meets contradictions.*

The sweats used in most of the studies were simulations of the real thing. These synthetic sweats varied from one investigation to another but were basically defined in a study by Frank and Bruic.**

The significant variations were not so much found in the types of compounds but in their relative concentrations. None of the formulations have included body oils (sebum) although addition to synthetic sweat formulation of lanolin or oleates have been made.

Ths substances present in the largest amounts and common to most formulations are inorganic salts such as NaCl, KCl, $Ca_3(PO_4)_2$, $CaCO_3$, and $KHCO_3$. The organic material common to all formulations and in the highest concentration is lactic acid--but generally lower in concentration than NaCl by a factor of 0.05. Also common to all formulations as organic components and in concentrations approximately 10% of the lactic acid are urea, uric acid, formic acid, and sugars such as ribose and glucose. Some formulations recognized that amino acids are essential real sweat components** and used what they consider one representative of that class, d,l-valine. We have chosen to use a formulation which has by far the largest number of components principally through the addition of about 20 amino acids. [5] In this synthetic sweat, the lactic acid concentration is about 100 ppm and the amino acids are each in the range of 5-10 ppm, so that the sum total is roughly equivalent to the lactic acid concentration.

None of the earlier studies went beyond the use of synthetic sweat in order to determine the source of activated carbon degradation. There appeared to be two "schools of thought" present when we began our studies: (a) The carbon is poisoned by lactic acid [6] and (b) the internal pores are simply filled with sweat solution and leave no room for gas adsorption. The former notion had more support than the latter when we first met the problem at Edgewood Arsenal. With this, the solution to the problem should be stated simply -- keep

*
Poziomek, E. J., Trip Report, SAREA-CL, Edgewood Arsenal, Subject: Update on In-House Research on Sweat Degraded Activated Carbon, 2 October 1974

**
Frank, G. B. and Bruic, R. P., Edgewood Arsenal, Special Scientific Report, Preparation of a Synthetic Sweat, 1 February 1953.

the lactic acid component from reaching the carbon. The latter thought ('b') was principally represented by several different investigators who felt that the addition of a hydrophobic coating to the activated carbon granule would reduce water uptake and by this increase gas adsorption capacity.

A substantial part of the persistent variability in the earlier reports can certainly be due to the "nature of the beast itself." Our own past experiences have shown quite often that broad deviations can occur even when measurements are made on activated carbon samples drawn from the same one pound canister. The usual analytical practice of duplicate and triplicate determinations on a single sample are by no means enough when handling activated carbons. We feel that much of the previous work on the sweat degradation of activated carbons did not take this into account. In our own work on this problem we have tried to use sextuplicate determinations, using as much carbon per run as possible within each experiment. Needless to say it was very time consuming, but necessary. In our studies, on many occasions, control samples of PAC Lot 7502 have shown as high as a 50% deviation in CCl_4 vapor uptake on a dry, untreated basis. We had to constantly run measurements on controls alone and within each experiment. Everything possible was done in an attempt to limit the effects of the intrinsic heterogeneity of activated carbon.

As in all previous works, static measurements using CCl_4 vapor uptake by plain and treated carbons were used to evaluate various experimental situations impressed on the activated carbons. Because of this, we have only determined adsorptive capacity and not adsorption rate. It was hoped that rate measurements could be made using gas chromatography techniques. However, the time limitation imposed by the work precluded such.

Hydrophobic surfactants, particularly silicones, have been added to activated carbon by solution and vapor deposition techniques.[4, 6] However, such methods of application have not resulted in a reproducibly good, water resistant carbon. We have developed a method of applying a silicone grease to the outer surface only by tumbling a batch of carbon in a cylindrical tube whose walls have been coated with a thin layer of silicone grease. With this process, we can produce a good hydrophobic external surface coating which also allows for unhindered access by gases to the pores of a carbon.

2. Conclusions Based on Our Experimentation

As far as our experimental measurements are concerned, we see absolutely no reason to suspect lactic acid as a poison. Indeed, lactic acid itself appears to be neutral in its effects on carbon. In fact, synthetic sweat itself reduced the static CCl_4 adsorption of activated carbon over that of pure water alone by only 4.5%. Thus our experimentation casts doubts on the further use of all known synthetic sweats as valid models for determining the source of sweat damage to carbons. In fact, in every experiment using a pretreated carbon, the

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effect of synthetic sweat versus plain water on degradation was to about the same degree and in the same direction (except for the silicone pretreated carbon, whereby the direction was reversed.) It is especially noteworthy that the carbons which had been pretreated with the individual components in aqueous solution almost always showed a substantial increase in degradation over those exposed to the whole sweat and also pure water. These carbons generally held onto the impregnating solution much more tenaciously and this was particularly noticeable with the bulk of amino acid treated carbons. Of all the components used, the amino acids, individually, produced a degradation that one could best associate with a "poisoning" effect -- especially when it is noted that their concentrations in solution are in the lowest range of all components, about 5-10 ppm. However, again, this effect did not show up with whole sweat solutions, at least by the testing procedures we've used. These results suggest that if there is a "poisoning" mechanism operating on a carbon layer in a protective garment that it most likely occurs by having one component (or class of components) arrive at first at the activated carbon surface. Of the candidates we've surveyed, the amino acids are pretty much by themselves at the top of the list with lactic acid close to the bottom.

With these data, it appears that when whole synthetic sweat is absorbed by a carbon granule, the many components, especially those in high concentration, very effectively compete for active surface sites in the carbon pores and greatly hinder the "poisoning" rates of the amino acid components. Indeed, competition is only one of many mechnaisms that can operate in this system to delay the effects of "poisons." Although, by necessity, I have focused on amino acids in this discussion, it must be stated that there are many components in human sweat which we have not been able to touch on but I anticipate the same mechanism to apply for any one or group of these.

On several occasions, activated carbon was coated on its external surface only, using dimethylpolysiloxane grease by the process described in the last paragraph of section II A. 1. An extremely hydrophobic carbon was produced which consistently took on about 20% less sweat solution than pure water. Further work using this technique is encouraged not only using silicones but also oleophobic and hydrophobic fluorocarbon surfactants and oils.

Gas chromatography studies were conducted with the hope that the various volatile components (and components of appreciable volatility at relatively low ambient temperatures) of real sweat could be partitioned using a column packed with activated carbon. Success in this endeavor would have resulted in assigning retention values to these materials and, by this, significant insight as to the existence of volatile poisons in sweat. It became apparent rather quickly that too much additional time was needed to pin down the necessary analytical

parameters. Using gas chromatography, a very direct and important experiment could be conducted whereby carbon saturated with human sweat beforehand then laid down onto a column packed with a variety of polar and nonpolar stationary phases will, I'm certain, produce the first really useful dynamic data about human sweat and activated carbon "poisoning." Followup experimentation would focus on what is most tenaciously bound to human-sweated carbon by successive extractions with water, by heat treatment and by cold trapping components away from these carbons.

In summary, while the precedential literature is convincing regarding the deleterious effect of human sweat on the adsorptive capability of activated carbon, there is also a decided scarcity of information which is substantive toward solving the problem or pointing out ways to solutions. Lactic acid, heretofore regarded as the poison, has been found in this study to be neutral in its effect on activated carbon. In fact, synthetic sweat formulations, including ours, appear not to produce a significant increase in their negative effect in carbon over that of plain water. However, many individual components of synthetic sweat, particularly amino acids, show a decided reduction in the amount of CCl_4 taken up by the static testing procedure. The effect of amino acids deserves special attention because their concentrationa are in the lowest range of 5-10 ppm in water and it is tempting to use the word "poison" here. From this a mechanism of degradation is strongly suggested which requires that one component or class of components is able to get to the activated carbon first, i.e., before the bulk of the sweat arrives. With a real human sweat situation it may not be an amino acid(s), but perhaps a volatile ester of an amino acid, or formic acid, or uric acid, even lactic acid, or some combination of organic acid esters. Also, other degradation mechanisms are suggested through some kind of chromatographic partitioning process taking place with human sweat as it passes through whatever layers of material which separate the carbon layer from the skin.

Silicone hydrophobic coatings, when applied to the outer surface of a carbon granule by our tumbling method, do result in reproducible carbons which take on much less synthetic sweat solution than plain water. Whether or not this silicone treated carbon will behave effectively under human sweat conditions remains to be studied.
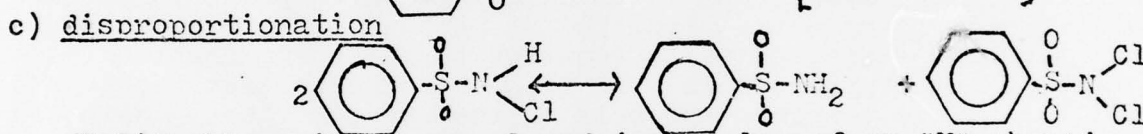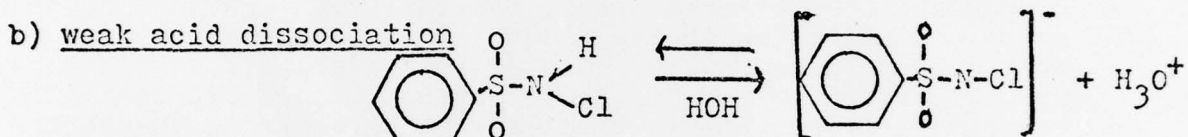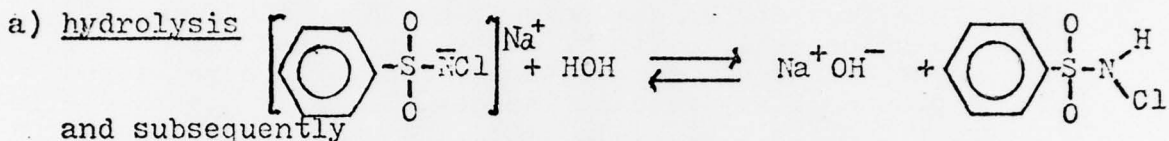
B. Chloramine B

1. Thermal Decomposition Mechanisms; Low Temperature Range

Sealed glass ampoules of chloramine B, which were used as a part of a skin decontamination kit, were subjected to mild heating and, after some short number of days, exploded. Mr. Charles Keck of the Clothing and Decontamination Section (EWA) reported to us that this had not happened previously. The
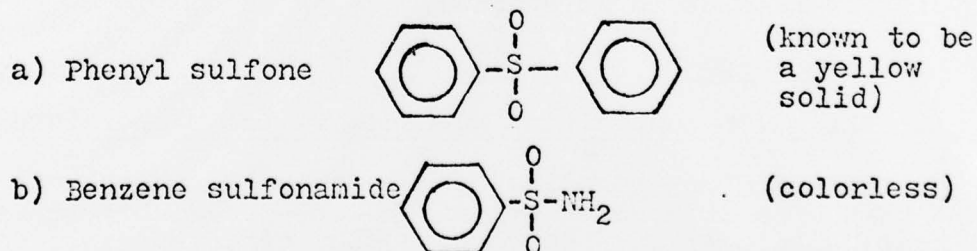
success that we experienced with XXCC3 ignition was called upon to solve this problem.

The thermal characteristics of chloramine B were outlined using a Thermal Gravimetric Analyzer. There were two distinct regions where thermal decomposition occurred. From room temperature to about $100^{\circ}C$ there was a gradual decomposition associated with a slow loss in mass. Above $100^{\circ}C$ no further decomposition occurred until $175^{\circ}-185^{\circ}C$ at which point a violent burning took place. The first decomposition step appeared to be associated with the hydrolysis of the chloramine B salt. The second decomposition step has every characteristic of N-Cl compound "burns" in which a great deal of heat is generated.

Chloramine B is the salt of a strong base and a weak acid and is subject to several aqueous equilibria such as:
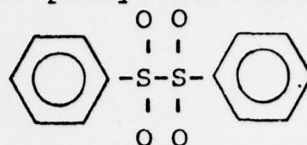
a) <u>hydrolysis</u>

$$\left[C_6H_5 - \overset{O}{\underset{O}{S}} - \overline{N}Cl \right] Na^+ + HOH \rightleftharpoons Na^+ OH^- + C_6H_5 - \overset{O}{\underset{O}{S}} - N \overset{H}{\underset{Cl}{}}$$

and subsequently

b) <u>weak acid dissociation</u>

$$C_6H_5 - \overset{O}{\underset{O}{S}} - N \overset{H}{\underset{Cl}{}} \underset{HOH}{\rightleftharpoons} \left[C_6H_5 - \overset{O}{\underset{O}{S}} - N-Cl \right]^- + H_3O^+$$

c) <u>disproportionation</u>

$$2\, C_6H_5 - \overset{O}{\underset{O}{S}} - N \overset{H}{\underset{Cl}{}} \longleftrightarrow C_6H_5 - \overset{O}{\underset{O}{S}} - NH_2 + C_6H_5 - \overset{O}{\underset{O}{S}} - N \overset{Cl}{\underset{Cl}{}}$$

Solid chloramine B was placed in one leg of an "H" shaped glass tube which was filled with H_2O carefully so that the bulk of the chloramine B was not dissolved. In about 6 hours a measurable amount of gas was trapped beneath the fibreglass plug in that leg of the "H" tube. This gas was directly withdrawn using a GC gas syringe and injected into a Gas Chromatograph having a column packed with molecular sieve. The gas sample contained 91% N_2 and 9% O_2. This experiment was quite reproducible. The solid chloramine B at the bottom of the "H" tube took on a yellow-tan color with time. This residue was analyzed using IR and mass spectra and two components were determined:

a) Phenyl sulfone $\quad C_6H_5 - \overset{O}{\underset{O}{S}} - C_6H_5 \quad$ (known to be a yellow solid)

b) Benzene sulfonamide $\quad C_6H_5 - \overset{O}{\underset{O}{S}} - NH_2 \quad$ (colorless)

The same "H" tube experiment was conducted whereby the tube was placed in an oil bath and heated to $60^{\circ}C$. At the start of heating, considerable gas was evolved but the rate of evolution ceased as the chloramine B went into solution.

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At 60°C a deep brown solid precipitated and when subjected
to analysis was found not to contain any of the two ingre-
dients above, but rather phenyl disulfone,

$$\left\langle\bigcirc\right\rangle - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - \left\langle\bigcirc\right\rangle \quad .$$

The above experiments were conducted using pH-7 buffer
(a mixture of KH_2PO_4 and KOH) in place of water and in each
situation no gas evolved and no precipitation occurred even
though the temperature was raised to 95°C in the latter case.

The evolution of N_2 and O_2 from the thermal and hydro-
lytic treatment of chloramine B in the low-temperature range
can be best understood by considering three concurrent reac-
tions (or reaction mechanisms) and the gases evolved:

a) Hydrolysis of chloramine B resulting in production of
a reactive intermediate, HOCl, which decomposes to
give O_2 (called the acid path).

b) Hydrolysis of chloramine B resulting in the production
of a reactive intermediate, NaOCl, which decomposes to
give O_2 (called the base path), and the predominant
reaction.

c) Dissociation of chloramine B in water resulting in the
production of a <u>nitrene</u> radical and NaOCl.

The NaOCl decomposes to give O_2 and a pair of nitrene radicals
condense to give an unstable sulfazo bridged compound which
decomposes with the production of N_2. An overall view of the
lower temperature decomposition along with indicated (*) iso-
lated and characterized products is presented in the figure.

The amount of N_2 gas that could be obtained from 18 g. of
chloramine B is 820 ml. (at S.T.P.) if decomposition was com-
pletely efficient.

Fresh samples of chloramine B supplied to us by MSA did
contain about 0.1% water insoluble material which we identi-
fied as phenyl sulfone (yellow-tan) and benzenesulfonamide.
Each one of these compounds is not known to possess any unu-
sual instability -- wet or dry.

Attempts to isolate pure chloramine B by successive re-
crystallization only resulted in an increased build up of in-
solubles (phenyl sulfone and benzenesulfonamide).

2. Thermal Decomposition Mechanisms; Higher Temperature Range

Chloramine B was heated in an evacuated system at various
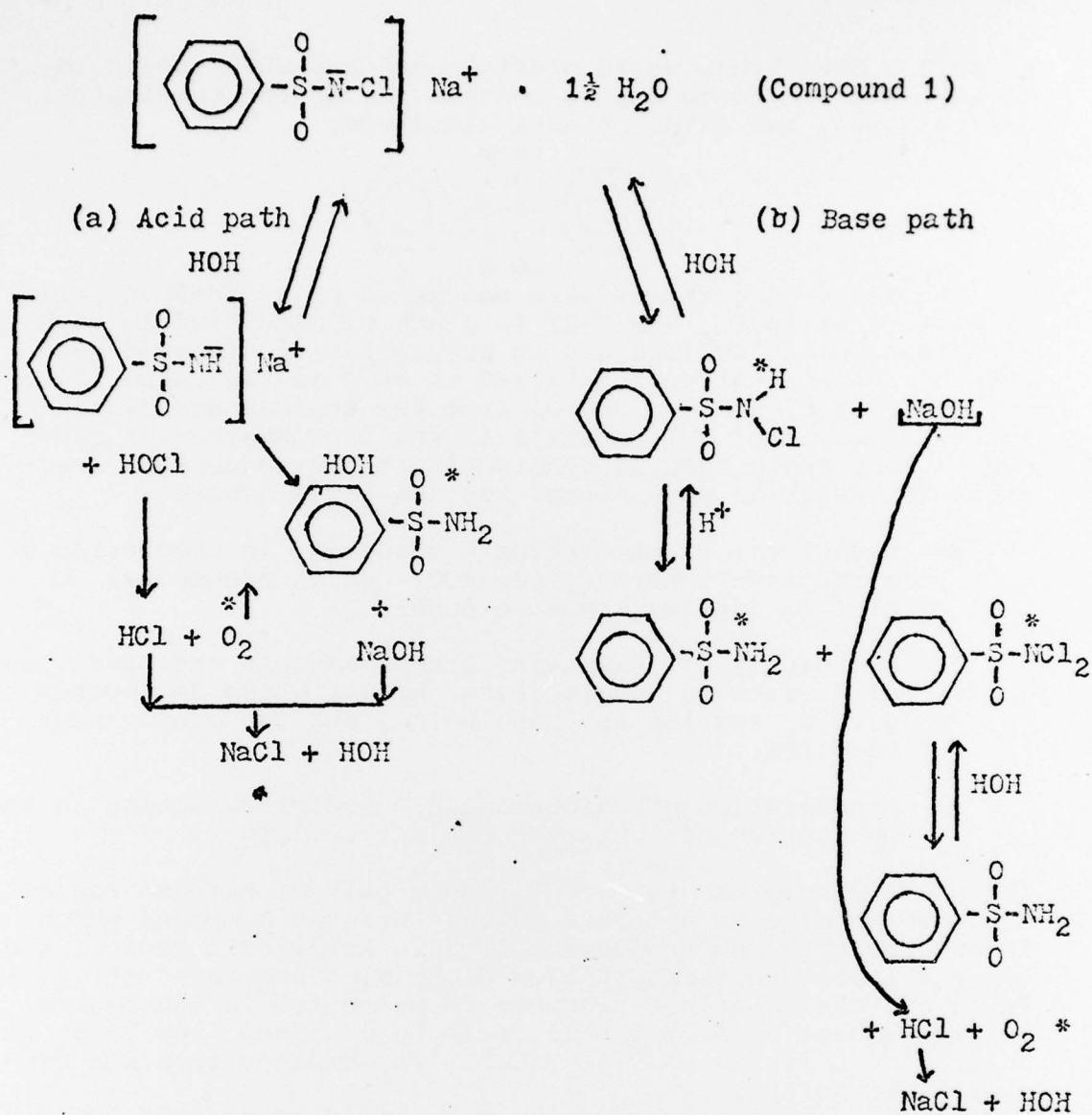
Figure

Reactions: Chloramine B; room temperature to about 100°C.

* = identified products

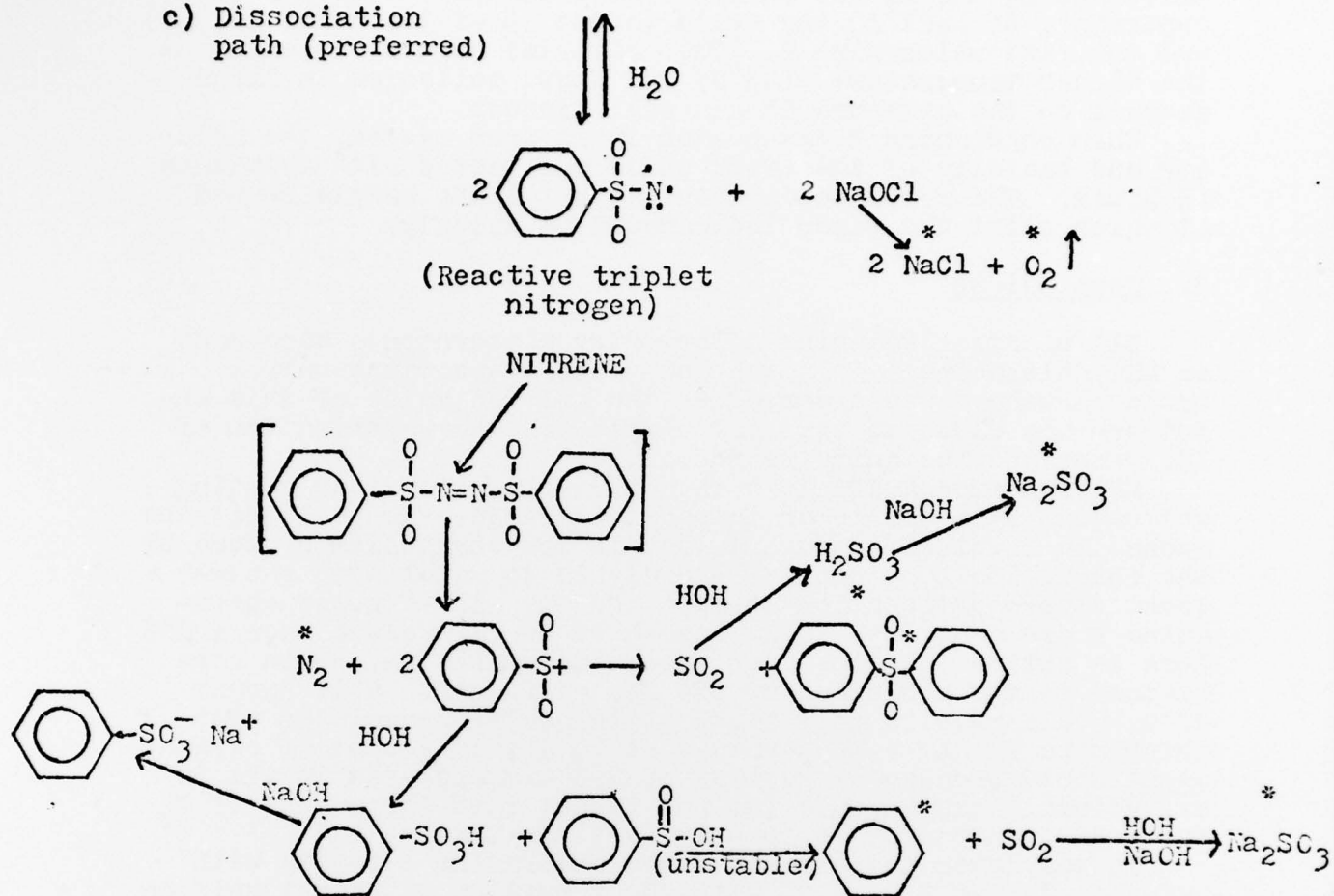Compound I

c) Dissociation
path (preferred)

Figure   Continued

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temperatures up to about 185°C. The lower temperature range, discussed previously, produced a dehydration without the formation of N_2 and O_2 gas in measurable amounts. There was the appearance of NaCl in the solid (about 3% of the total weight) and the rest chloramine B. This material burned violently at the higher temperature (185°C) and H_2SO_4 collected in large amounts on the attached IR gas cell windows.

When chloramine B was heated in an open system, the acidity and basicity of the vapor phase was tested with moistened pH paper. The response was neutral until the sample burned at which point the paper indicated high acidity.

3. Conclusions

Differential Scanning Calorimetry measurements were made on MSA chloramine B. In the low temperature range only a broad endotherm was observed -- the caloric value of this endotherm was close to that calculated for the vaporization of 12% water and was quite reproducible.

MSA reported a 20% loss in active chlorine after heating chloramine B in the lower temperature range. We feel that the mechanism involved in such a loss is the conversion of some of the chloramine B by partial hydrolysis to NaOCl with subsequent disproportionation to NaCl and O_2. If 18 g. of chloramine B are contained in an ampoule of 30 ml. volume then a 20% loss in active chlorine, per the above mechanism, would correspond to the evolution of 166 ml. of O_2 gas. This amount of O_2 would require only 14.2% of the water associated with chloramine B. At a temperature of 70°C this amount of oxygen alone would produce a pressure of 7.44 atmospheres in the 30 ml. volume glass ampoule. (do not forget that the amount of N_2 evolved concurrently is roughly 10 times that of O_2).

In the lower temperature range chloramine B reacts with water to evolve N_2 and O_2 with the formation of phenyl sulfone and benzenesulfonamide. If the water of crystallization is allowed to escape freely as heat is applied, the conversion of chloramine B to these aforementioned products is very small (negligible) but the dehydrated solid that remains is now capable of the higher temperature violent, exothermic burn which will occur at 70°C if enough time is given. If chloramine B is placed under water (large excess) then hydrolysis occurs to produce N_2, O_2, phenyl sulfone, and benzenesulfonamide but this reaction ceases rapidly at elevated temperature with the solution of chloramine B. It would seem from this that the worst possible system is that in which the water of crystallization is not allowed to escape and yet is not enough to cause solution of the chloramine B -- such is the case of the MSA sealed ampoule. Even if only 14.2% of the water in the chloramine B is consumed by hydrolysis this will result in the production of a partial pressure of oxygen at 70°C. As to prevention of this phenomenon, the following are dictated by the data available:

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a. The repression or elimination of chloramine B <u>hydrolysis</u> -- apparently a neutral buffer solution is effective here.

b. Avoid dehydration and also storage of hydrated salt in a sealed system.

c. If H_2O is necessary, then solutions of chloramine B appear safer by far at conditions other than those in b above -- especially if the storage container can allow for a water vapor pressure blowoff and self-equilibration at elevated temperature.

d. All in all, storage of ampoules of chloramine B at the lowest possible temperature is strongly recommended.

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