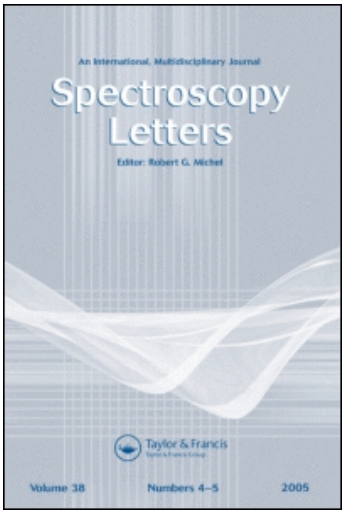

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VYCOR POROUS GLASS (THIRSTY GLASS) AS A REACTION MEDIUM FOR OPTICAL WAVEGUIDE BASED CHEMICAL VAPOR DETECTORS

Key Words: VYCOR porous glass, 1,3-diisonitrosoacetone, 4,4-bis-(diethylamino)benzophenone oxime, 2,6-dichloroquinone-4-chloroimide, 4-(p-nitrobenzyl)-pyridine, methanesulfonyl chloride, 1-butanethiol, 2-chloroethylethylsulfide, dimethylsulfate

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ABSTRACT

Vycor Porous Glass (Thirsty Glass) has been studied as a reaction medium for several model chemical vapor detection reactions. It was also compared with Celgard 2400 microporous propylene film as a reaction medium. Using Thirsty Glass as the reaction support for the detector reagent 2,6-dichloroquinone-4-chloroimide, 1-butanethiol was detected at concentrations as low as 0.1 ppm. With either 4,4'-bis(diethylamino)benzophenone oxime or 1,3-diisonitrosoacetone as the detector reagent, methanesulfonyl chloride was detected at concentrations in air as low as 1 ppm. When 4-(p-nitrobenzyl)pyridine was the detector reagent, high detection sensitivities for 2-chloroethylethylsulfide and dimethylsulfate were achieved only when a two-step test procedure was used.

INTRODUCTION

There is considerable interest in chemical vapor detection devices that exhibit both specificity and high sensitivity. Chemical sensors based on fiber optics may satisfy this need (1). A critical component of a fiber optic detection device is the optical element that conveys the detection signal to the transducer. Frequently, consolidated (non-porous) glasses are used for this purpose. These materials have at least two disadvantages when used as the optical element for a guided-wave device for the detection of chemical vapors that are of interest to us; these are: (a) the detector reagents of interest do not adhere well to the glass unless they are applied in combination with a chemical binder with resultant loss of detection sensitivity, and (b) consolidated glasses do not provide an appropriate environment for many chemical vapor detection reactions. Consequently, we are interested in other media that might serve as the optical element for waveguide detection devices.

Vycor porous glass (Code 7930) is a product of Corning Glass Works. It is manufactured by (a) making a homogeneous borosilicate glass at high temperature, (b) carrying out a phase separating procedure at a lower temperature, and (c) acid leaching the glass after it has cooled. A particularly interesting property of this glass is its ability to attract organic vapors from the atmosphere (2). Also, the glass is very hygroscopic and, depending on the humidity, it can retain absorbed water up to 25% of its

dry weight (3). Because of its water-retaining characteristics, Vycor porous glass is frequently called "Thirsty Glass".

Studies of photochemical reactions carried out in Thirsty Glass have been reported (4). Also, it has been shown that porous glass can be used in fabricating optical elements for guided-wave devices (5). To our knowledge, no results have previously been reported for the use of this material as a medium for chromogenic detection of chemical vapors. Therefore, the aim of this paper is to illustrate how Thirsty Glass serves as a reaction medium for several model chromogenic reactions that are used in detection of chemical vapors.

The model reactions included in this study were (1) the reaction of 1,3-diisonitrosoacetone with methanesulfonyl chloride vapor, (2) the reaction of 4,4'-bis(diethylamino)benzophenone oxime with methanesulfonyl chloride vapor, (3) the reaction 2,6-dichloroquinone-4-chloroimide with 1-butanethiol vapor, and (4,5) the reactions of 4-(p-nitrobenzyl)pyridine with 2-chloroethyl-ethylsulfide vapor and with dimethylsulfate vapor.

In several experiments, Thirsty Glass was compared with Celgard 2400 microporous polypropylene film as the reaction medium. The Celgard film was selected for the comparison because it is similar to Thirsty Glass in that it is a porous medium that is transparent to light in the visible range of the spectrum, but differs significantly in that it is non-polar, and hence, contains much less water. Therefore, by making this comparison it was

possible to determine the effect of support polarity and/or water on the reaction.

MATERIALS AND METHODS

Materials

1,3-Diisonitrosoacetone quanidinium salt was obtained from Polysciences, Inc., Warrington, PA. 4,4'-Bis(diethylamino)benzophenone oxime was from a custom synthesis carried out by H.I. Laboratories, Whitmore Lake, MI. 2-Chloroethylethylsulfide was from Fairfield Chemical Co., Blythewood, SC. 1-Butanethiol, dimethylsulfate, methanesulfonyl chloride, 2,6-dichloroquinone-4-chloroimide, and 4-(p-nitrobenzyl)pyridine (NBP) were from Aldrich Chemical Co., Milwaukee, WI.

Precut pieces of Thirsty Glass (Code 7930) 2" x 1/2" x 1/16" were obtained from Corning Glass Works, Corning, NY. Celgard 2400 microporous polypropylene film was from Celanese Plastics, Inc., Charlotte, NC. Celgard film is described in reference 6.

Spectrophotometric Procedure

The spectrophotometric measurements were carried out with a Cary 17 spectrophotometer using the cell shown in Fig. 1. A 250 cc jar (Cat. No. 02-892DD) from Fisher Scientific, Springfield, NJ) was modified for use as the spectrophotometric cell. A glass microscope slide was glued to the inside surface of the cover with epoxy cement. The bottom of the jar was glued to a piece of cardboard that was cut to the exact size of the bottom of the cell compartment of the spectrophotometer. Prior to gluing, the jar was aligned so that when the cover was screwed on tightly, the light beam of the spectrophotometer passed directly through

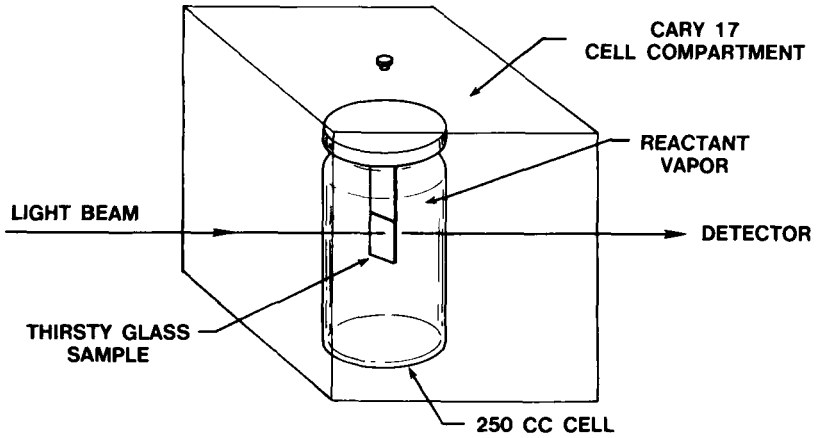


FIG. 1. Sketch of Glass Jar Modified for Use as the Spectrophotometric Cell.

the location on the microscope slide where the detector reagent impregnated portion of the solid support was to be positioned. The portion of the microscope slide surrounding the area through which the light beam passed was covered with an inert black tape. Thus, the tape served as a guide when applying the detector reagent solution. By using the tape, it was possible to deposit the reagent only on the portion of the support through which the light beam passed. In all cases, the detector reagents were applied to the supports in ca. 10 microliters of solution. The diisonitrosoacetone salt was dissolved in water and the other detector reagents were dissolved in acetone.

All spectrophotometric measurements were made at room temperature (ca. 25°C) using a Cary 17 spectrophotometer equipped with a repetitive scan accessory. The step-by-step procedures are given below.

Thirsty Glass Support

The Thirsty Glass samples were extracted for a minimum of 16 hours (overnight) with water and then stored in distilled water. Immediately before use, the samples were dried in a desiccator under vacuum and then allowed to equilibrate at ambient conditions for at least one hour. Pieces cut to size (1" x 1/2" x 1/16") were used in the tests. These were made by scoring each of the original pieces of glass at the center with a file and bending the glass carefully so that it broke cleanly along the mark. Then, using a piece of cellophane tape, a cut piece of Thirsty Glass was attached to the bottom of the microscope slide that had been glued to the cover of the jar.

The detector reagent solution was carefully applied to the Thirsty Glass sample so that only that portion of the glass through which the light beam passed was coated. This was done by rubbing the end of a Pasteur pipet (or a microcap) containing ca. 10 microliters of the detector reagent solution back and forth on the surface of the glass so that only the portion (1/2" x 1/4") outlined by the black tape was treated. (In experiments where sodium cyanide was used, the Thirsty Glass was wet with a 0.2% aqueous solution of sodium cyanide and dried prior to applying the detector reagent). The thread on the jar was tightly covered with teflon tape to insure that reactant vapor did not escape when the jar was covered. After the cover was screwed on, the jar was oriented so that the light beam of the spectrophotometer passed directly through the portion of the Thirsty Glass sample that had been treated with the detector reagent. The cell was then placed

in the sample compartment and the compartment was covered. A piece of Thirsty Glass taken from the same batch as the one placed in the sample compartment served as the reference for the double beam spectrophotometric measurement.

To establish a baseline for the measurement, scans were run between 700 nm and 400 nm at 2 minute intervals until no change was observed in three successive scans. The cell was then removed from the sample compartment to add the test vapor. The vapor phase reactant was added as a neat liquid or in solution, as appropriate, and allowed to evaporate. This was accomplished by injecting the desired amount of reagent (typically 1-10 microliters) as a neat liquid or in dichloromethane solution from a 10-microliter syringe so that it wet the side of the jar about halfway between top and bottom. The cover was quickly screwed on. The cell was then placed in the sample compartment of the spectrophotometer and the compartment was covered. Spectra were then obtained at regular intervals.

Celgard 2400 Support

The spectrophotometric procedure used with Celgard 2400 film differed from the one outlined for Thirsty Glass in the following respects. The Celgard 2400 film was not extracted or dried. It was simply cut to size and glued with cellophane tape to the bottom of the microscope slide that was fastened to the cover of the jar that served as the cell. A piece of Celgard 2400 film served as the reference for the double beam measurement. When the results of the experiments were to be compared with those carried out with Thirsty Glass, care was taken to insure that an identical

quantity of detector reagent solution was applied to approximately the same area on each support.

NBP Tests

When the one-step test procedure was used, dry pieces of Thirsty Glass that had been cleaned by extraction with water were treated with a 3% aqueous solution of potassium carbonate. After the samples were dried, the same procedure followed for the other Thirsty Glass samples was used. In these experiments, spectra were obtained at 30 minute intervals.

When the two-step test procedure was used, the NBP impregnated Thirsty Glass samples did not develop color during the vapor exposure step. To develop color, samples exposed to the test vapor for a 30-minute period were treated with 1M aqueous NaOH (one drop per sample). Prior to measuring the color spectrophotometrically, the samples were allowed to stand for one minute.

RESULTS AND DISCUSSION

Reaction of 2,6-Dichloroquinone-4-chloroimide with 1-Butanethiol Vapor

This reaction has not been reported previously; however, a similar reaction involving thiophenol has been reported (7). The reaction probably occurs by an addition-elimination mechanism. It produces a yellow product which can be monitored spectrophotometrically at 430 nm. Fig. 2 shows the effect of 1-butanethiol vapor concentration on the reaction 2,6-dichloroquinone-4-chloroimide carried out on Thirsty Glass. The absorbance measurements were taken after 15 minutes reaction at each vapor concentration.

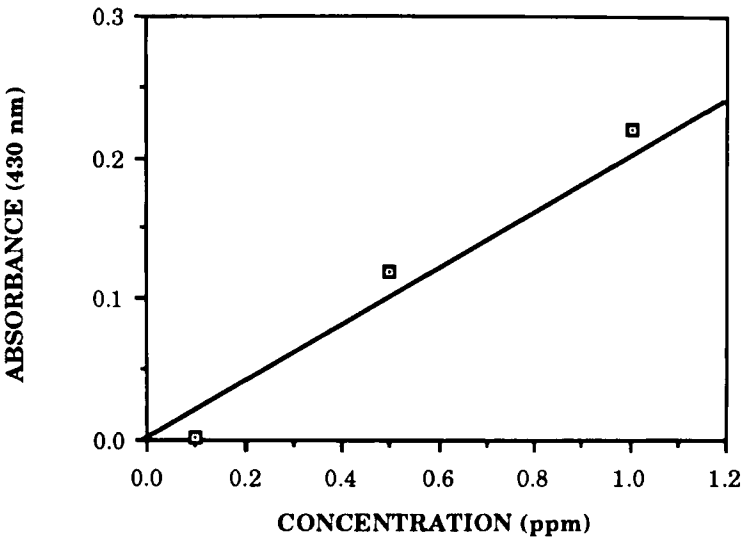


FIG. 2. Effect of 1-Butanethiol Concentration on the Reaction of 1-Butanethiol Vapor with 2,6-Dichloroquinone-4-chloroimide on Thirsty Glass Support.

A significant response (0.001 absorbance units) was obtained at a 1-butanethiol vapor concentration as low as 0.1 ppm. Thirsty Glass was also compared with Celgard 2400 microporous polypropylene film as the reaction support. The properties of Thirsty Glass and of Celgard film ar compared in Table 1.

The supports differ in their polarity, and consequently, their affinity for water. Thirsty Glass is polar and very hygroscopic; depending on the humidity, it can absorb water up to 25% of its dry weight. In contrast, Celgard film is non-polar and hydrophobic. At the same humidity, it would be expected to retain much less water. When performing tests using these supports we observed that the reaction of 2,6-dichloroquinone-4-

TABLE 1

Properties of Solid Supports

	Thirsty Glass	Celgard 2400 Film
Composition	96% SiO_2 + 3% B_2O_3	Polypropylene
Density	1.45 - 1.50	0.6
Void Space	28% of Volume	38% of Volume
Pore Size	40-50 Angstroms	0.02 x 0.2 Micrometers
Surface Area	200 Sq Meters/Gm	70 Sq Meters/Gm
Color	Slightly Opalescent	Opalescent
Water Content	Up to 25% of Dry Weight	Low - Hydrophobic

chloroimide with 1-butanethiol vapor occurred at a much faster rate when it was carried out on Thirsty Glass. The initial color formation plotted for this reaction carried out on the two supports is shown in Fig. 3.

While the reactions carried out on the two supports were at somewhat different 1-butanethiol concentration levels, it's clear that the reaction proceeded ca. 10 times faster on Thirsty Glass. The higher rate of color formation produced on the Thirsty Glass is probably due to the higher polarity and/or the higher water content of the glass.

Reaction of 4,4'-Bis(diethylamino)benzophenone Oxime with Methanesulfonyl Chloride Vapor

Using Thirsty glass at the support, the reaction of 4,4'-bis(diethylamino)benzophenone oxime with methanesulfonyl chloride vapor was successfully monitored at concentrations in air as low

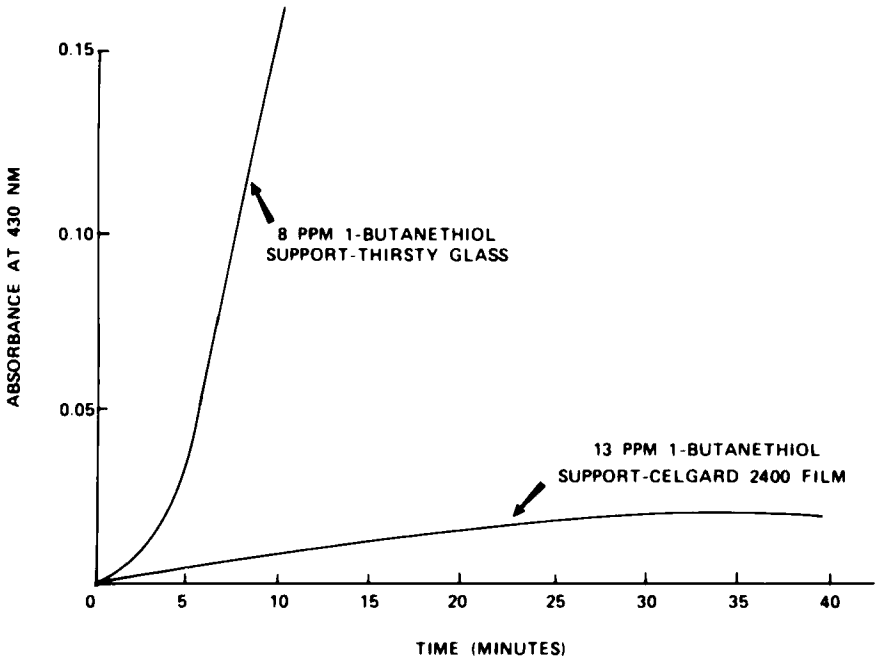


FIG. 3. Comparison of Initial Color Formation Resulting from the Reactions of 1-Butanethiol Vapor with 2,6-Dichloroquinone-4-chloroimide Carried Out on Thirsty Glass and on Celgard 2400 Film.

as 1 ppm. Fig. 4 shows the effect of methanesulfonyl chloride vapor concentration on the reaction of 4,4'-bis(diethylamino)-benzophenone oxime carried out on Thirsty Glass. The absorbance measurements were taken after 15 minutes reaction at each vapor concentration.

This reaction has been studied previously by Porier and Morin (8). They reported the formation of a Beckmann intermediate and the involvement of cyanide in the formation of the colored product. Therefore, we expected that addition of a cyanide salt

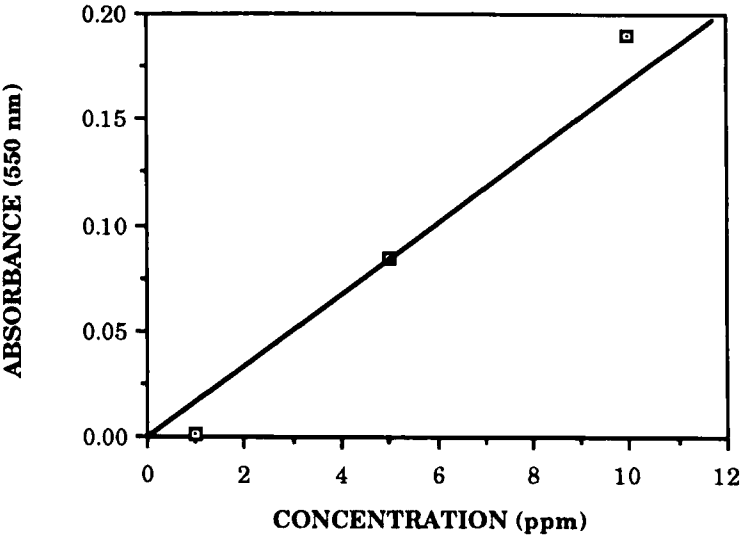


FIG. 4. Effect of Methanesulfonyl Chloride Concentration on the Reaction of Methanesulfonyl Chloride Vapor with 4,4'-Bis-(Diethylamino)benzophenone Oxime on Thirsty Glass.

to the oxime reagent impregnated on the Thirsty Glass support would result in some enhancement of the rate of formation of colored product. When we investigated this possibility we did not observe any acceleration in the rate of color formation; as a matter of fact, the addition of the cyanide salt appeared to slow the rate of color formation somewhat. At this time, we do not have an explanation for this observation.

When the reaction of 4,4'-bis(diethylamino)benzophenone oxime with methanesulfonyl chloride vapor was studied using both Thirsty Glass and Celgard 2400 film as the reaction supports, we observed significant differences in the spectra. Spectra obtained using Thirsty Glass and Celgard film as reaction supports are shown in

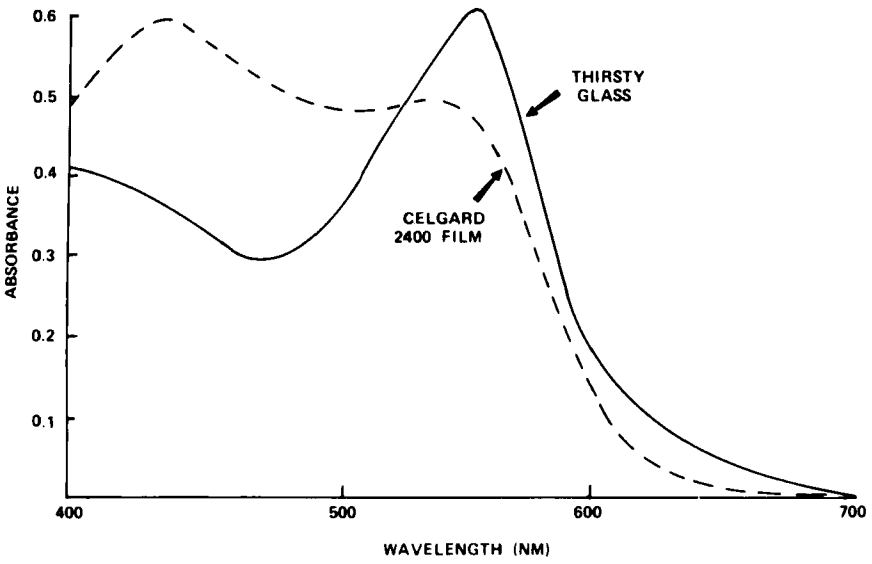


FIG. 5. Comparison of Spectra Resulting from the Reactions of 4,4'-Bis(diethylamino)benzophenone Oxime with Methanesulfonyl Chloride Vapor Run on Thirsty Glass and on Celgard 2400 Film.

Fig. 5. These spectra were obtained after a 30 minute reaction period at a methanesulfonyl chloride concentration of 4000 ppm. When the reaction was run on either support, prominent absorptions were observed near 550 nm and below 400 nm. As the reaction progressed, the absorption below 400 nm decreased and a new absorption near 430 nm became evident. The decrease in the absorption below 400 nm was much slower when Thirsty Glass was the support. Consequently, after a 30 minute reaction period the spectrum of the colored product on the Celgard film showed prominent absorptions at both 550 nm and 430 nm, while the colored product on the Thirsty Glass showed a prominent absorption at 550 nm, but only a shoulder at 430 nm.

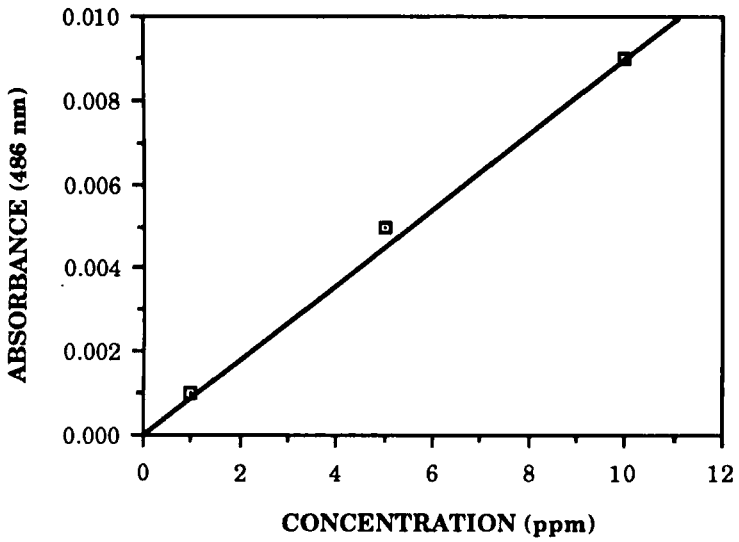
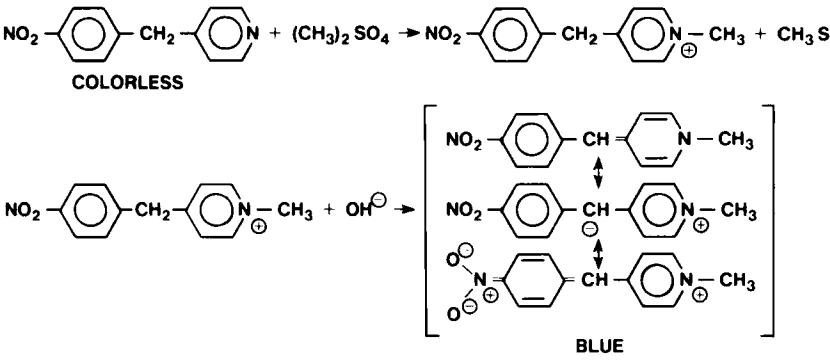


FIG. 6. Effect of Methanesufonyl Chloride Concentration on the Reaction of Methanesulfonyl Chloride Vapor with 1,3-Diisonitroso-acetone (Guanidinium Salt) on Thirsty Glass.

Reaction of 1,3-Diisonitrosoacetone with Methanesulfonyl Chloride Vapor

This reaction has been described by Sass and coworkers (9). It produces a magenta colored product with an absorption maximum at 486 nm. The change in absorbance at 486 nm that occurred over a 15 minute reaction period when 1,3-diisonitrosoacetone treated Thirsty Glass was exposed to vapors of methanesulfonyl chloride vapor is shown in Fig. 6. This reaction was monitored at a vapor concentration of methanesulfonyl chloride in air as low as 1 ppm. The colored product was produced at about the same rate when either Thirsty Glass or Celgard film were the reaction supports.



Eq 1

Eq 2

Reaction of 4-(p-Nitrobenzyl)pyridine with Vapors of Alkylating Agents

4-(p-Nitrobenzyl)pyridine (NBP) has been reported to be a useful analytical reagent for use in the detection of alkylating agents. Mustard gas is among the analytes that can be detected with NBP (10). The chemistry involved in the tests that utilize NBP for the detection of the alkylating agent, dimethylsulfate, is described in the equations below.

In equation 1, dimethylsulfate undergoes a nucleophilic attack by the NBP to form a colorless pyridinium salt. Then, in equation 2, a strong base is added to deprotonate the pyridinium salt and produce a blue anion that can be seen at low levels due to its high molar absorptivity.

While this test is normally carried out using a two-step procedure (i.e., exposure of the NBP reagent to the test vapors followed by treatment of the reagent with base) the test could conceivably be simplified and improved if it were possible to utilize the reagent on a support that had been pretreated with

base. Use of the NBP reagent in this simplified (one-step) fashion would be particularly advantageous if the reagent, for example, were to be used as an alkylating agent-sensing coating in an optrode. Therefore, we studied the NBP reagent using both the two-step and the one-step test procedures. The alkylating agents that were investigated were dimethylsulfate and 2-chloroethyl-ethylsulfide. The two-step procedure involved a vapor exposure step in which pieces of Thirsty Glass impregnated with NBP were exposed to vapors of alkylating agent, and a basification step in which the exposed samples were subsequently treated with aqueous NaOH solution to produce the color body. Thirsty Glass samples for the one-step test procedure were prepared by treating pieces of the glass with aqueous potassium carbonate, drying, and then applying the NBP. By using a layer of dry potassium carbonate beneath the NBP reagent layer, it was hoped that as the NBP became alkylated, the pyridinium salt that formed would be immediately deprotonated by the carbonate to produce the colored product. The results of the tests that involved the two-step test procedure are shown in Figs. 7 and 8. They are also compared with the results of tests carried out with the one-step test procedure in Table 2. It's evident from these results that although a color change signalling detection of the alkylating agents can be obtained with the one-step procedure, the detection sensitivities for both dimethylsulfate and 2-chloroethylethylsulfide are much poorer than those obtained with the two-step procedure. Poorer sensitivities in the one-step tests are probably due to deprotonation of the

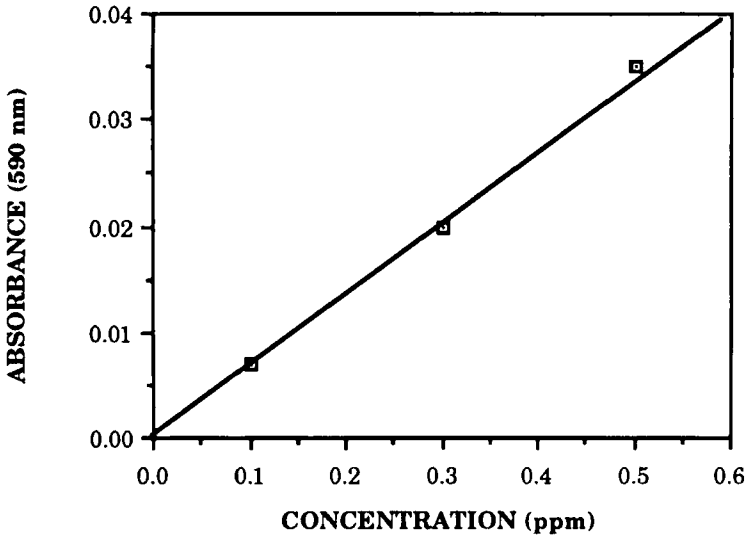


FIG. 7. Effect of Dimethylsulfate Concentration on the Detection of Dimethylsulfate Vapor with 4-(p-Nitrobenzyl)pyridine on Thirsty Glass (Two-Step Test Procedure).

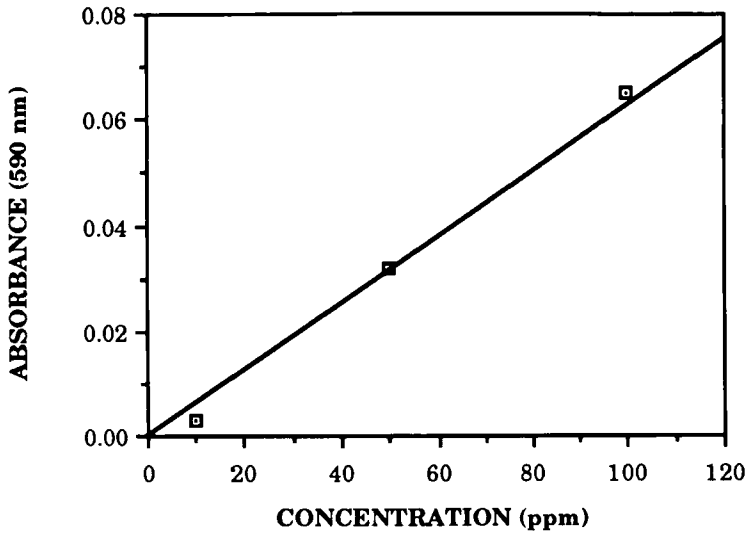


FIG. 8. Effect of 2-Chloroethylethylsulfide Concentration on the Detection of 2-Chloroethylethylsulfide Vapor with 4-(p-Nitrobenzyl)pyridine on Thirsty Glass (Two-Step Test Procedure).

TABLE 2

Effect of Test Procedure on the Sensitivity of Detection of Alkylating Agents

Vapor	Sensitivity of Detection (ppm)	
	Two-Step Test Procedure	One-Step Test Procedure
DimethylSulfate	< 0.1	1000
2-Chloroethyl-ethylsulfide	10	1000

pyridinium salt occurring only at the interface of the layers of NBP and base. Hence, when the one-step procedure was used, color formation was observed only when the concentration of test vapor was high. These results show that while the NBP test can be carried out on Thirsty Glass using either method, high detection sensitivities result only when the two-step procedure is used. Consequently, NBP does not appear promising as a reagent for use as an optrode coating for sensing alkylating agents.

CONCLUSIONS

Thirsty Glass has been shown to be a suitable reaction support for model chromogenic detection reactions. In the model reactions, 2,6-dichloroquinone-4-chloroimide was used to detect 1-butanethiol vapor, and 4,4'-bis(diethylamino)benzophenone oxime as well as 1,3-diisonitrosoacetone were used to detect methanesulfonyl chloride vapor. While Thirsty Glass can also serve as a

reaction medium for 4-(p-nitrobenzyl)pyridine, which is used to detect vapors of alkylating agents, high detection sensitivities are possible only when a two-step test procedure is used.

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