Fourier Transform Infrared Spectrometry/Attenuated Total Reflectance Study of the Reaction of Pentanal and Propanal with 2-(Hydroxymethyl)piperidine

EUGENE R. KENNEDY and KEVIN ASHLEY*

US Department of Health and Human Services,† Centers for Disease Control, National Institute for Occupational Safety and Health, 4676 Columbia Pkwy., Cincinnati, Ohio 45226

The reactions of propanal and pentanal with 2-(hydroxymethyl)piperidine were investigated by Fourier transform infrared spectrometry/attenuated total reflectance in both the solution phase and at the gas/solid interface. The reactions were studied with the use of a flow-through cylindrical internal reflection ("circle") cell. Reaction intermediates were tentatively identified by their characteristic infrared absorption frequencies. At the gas/solid interface the reaction is thought to yield a hemiaminal intermediate. In the solution phase a hemiaminal intermediate is believed to form initially, followed by loss of water to generate an enamine product. In both gas-phase and solution-phase studies, an oxazolidine product is prepared only after an ultrasound treatment. The FT-IR/ATR technique reveals detailed mechanistic information concerning reactions between aldehydes and ethanol amines.

Index Headings: **Analyses for aldehydes; ATR spectroscopy; Infrared; Spectroscopic techniques.**

INTRODUCTION

Airborne aldehydes are potential occupational hazards in a number of industries, and many efforts have been conducted to sample and analyze these compounds in the workplace. For example, the reaction of secondary ethanolamines with aldehydes has been used as the basis for several sampling and analytical methods for aldehydes in air.[1-3] In this previous work an ethanolamine-coated sorbent, 2-(hydroxymethyl)piperidine, was packed into tubes through which aldehyde-containing air was drawn.[1,3] The aldehyde reacted with the coating and was analyzed as an oxazolidine derivative by gas chromatography after solvent desorption. The method proved successful for several aldehydes but, for other aldehydes such as 2-methylpropanal and propanal, the reaction efficiency of the reagent-coated sorbent was significantly reduced.[3] With many of the aldehydes studied, the maximum rate at which air could be drawn through the sorbent tubes without breakthrough was limited. This prompted a study of the reaction mechanism outlined in Fig. 1.[4,5] In the proposed mechanism the reaction of the aldehyde with amine yields first a hemiaminal intermediate, which may then lose a water molecule to form an enamine. The enamine can subsequently undergo rearrangement to an oxazolidine product.

Since reaction mechanisms in solution may differ from gas-phase mechanisms due to solvent interactions, it was not entirely clear how the reaction between the aldehyde and 2-(hydroxymethyl)piperidine progresses.[1,3] On the one hand, the reaction may go to completion totally on the reagent-coated sorbent; conversely, the reaction may take place partially on the collection sorbent and partially during the solvent desorption step. Additionally, little is known regarding the identities and lifetimes of intermediates in the reaction sequence. In this work an oxazolidine product was desorbed from the sorbent only after the exposed sorbent was immersed in desorption solvent in an ultrasonic bath. Ultrasound is commonly used to aid in the desorption of analytes from sorbents, but also may be employed to accelerate reactions, such as the N-alkylation of amines.[6]

In order to study the reaction of representative aldehydes with 2-(hydroxymethyl)piperidine as it was occurring at the gas/solid interface and during solvent desorption, Fourier transform infrared spectrometry with an attenuated total reflectance attachment (FT-IR/ATR) was used.[7] A cylindrical internal reflection ATR element, or "circle" cell,[8,9] was employed for these studies. FT-IR/ATR has been used previously to investigate a number of other reaction sequences in various systems. Examples include those involving high-pressure catalysis,[10] solution decomposition,[11] biological systems,[12] surface-mediated reactions,[13] and electrochemical systems,[14-16] to name a few. The methodology allows for the characterization of all infrared absorption bands due to reaction intermediates formed, provided they exist in sufficient concentration and have long enough lifetimes to be observed spectroscopically.

In this study, the time dependence of the FT-IR spectra due to the reaction of the aldehydes with 2-(hydroxymethyl)piperidine was monitored. Also, the reaction of pentanal with 2-(ethyl)piperidine was investigated, for purposes of comparison with the reaction of aldehyde with the ethanolamine. Since the reactions were found to be relatively slow (i.e., they went to completion on a time scale of an hour or more), it was possible to follow the infrared bands arising from intermediates in the reaction sequence.

EXPERIMENTAL

Reagents. Pentanal (99%), propanal (99%+), and 2-(ethyl)piperidine (98%) were purchased from Aldrich and used as received. Ultrapure benzene, isooctane, and toluene were obtained from Burdick and Jackson and used as received. 2-(Hydroxymethyl)piperidine (93%) came from Aldrich and was recrystallized from isooctane 2–3 times before use.

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* Author to whom correspondence should be sent.

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Apparatus. Infrared spectra were recorded with a Nicolet 60SX FT-IR spectrometer equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Nicolet 1280 data system. A NICOS (Nicolet) operating system was employed, and all software used for data collection was supplied by Nicolet. Spectra consisting of 4 to 8 signal averaged scans at 4 cm^{-1} resolution were taken approximately every second. Data reduction and display Fortran programs (PKHTS, HIDE.FCP, and ANALYS) were obtained from Nicolet, with additional modifications implemented in the laboratory. The sample cell used was a 3-mL flow-through cylindrical internal reflectance ("circle") cell equipped with a zinc selenide rod crystal (Spectra-Tech). Kinetic data for gas-phase reactions were obtained by monitoring infrared spectral peak heights using this cell.

Pentanal vapor was generated by injecting liquid pentanal at room temperature into a heated injection block (135°C) by syringe pump (Sage model 355). The vapor was flushed from the block with dry nitrogen at 500 cm^3/min into the "circle" cell. Concentration was determined (calibrated) by syringe pump delivery rate and a photoionization detector (AID Model 590 OVM). Propanal vapor was generated by passing nitrogen at 500 cm^3/min over two diffusion tubes which were held at 20°C and filled with propanal.

Procedure. 2-(Hydroxymethyl)piperidine was coated onto the zinc selenide crystal of the "circle" cell by dipping the ATR crystal into a saturated solution of the ethanolamine and allowing the coating to dry. Alternatively, a 1-mL aliquot of this solution was rinsed through the cell and allowed to dry. 2-(Ethyl)piperidine was coated onto the crystal by applying 10 μL of the liquid directly and allowing it to run over the surface of the crystal. The reagent loadings obtained with these procedures were in the microgram range.

For experiments conducted in toluene and benzene solutions, single-beam spectra were taken over time, ratioed to a background of the cell filled with either benzene or toluene, and converted to absorbance. To study the reaction in the solution phase (i.e., the aldehyde dissolved in toluene or benzene), we filled the cell with 2.0 mL of either solvent containing 25 mg/mL of 2-(hydroxymethyl)piperidine. A 2-mL syringe was used to inject 1.0 mL of a toluene or benzene solution of 40 mg/mL pentanal into the cell. Spectra were then collected over time to study the intermediates formed.

For gas-phase data, the single-beam spectral data were ratioed to the background spectra of the 2-(hydroxymethyl)piperidine-coated rod crystal and converted to absorbance for further data reduction. In this manner, the consumption of the 2-(hydroxymethyl)piperidine coating was indicated by the presence of negative peaks in the spectra, while the formation of the reaction intermediates was indicated by the growth of positive peaks.

To determine peak heights and peak areas, we manually determined start and end points for peak baselines and entered them into the Fortran data reduction program, PKHGT. The program then would collect the necessary data from spectral files, and peak height and area information was stored in a data file. This file was subsequently accessed by the program ANALYS to prepare plots of data (peak height or peak area) vs. time. Peak height values for 2-(hydroxymethyl)piperidine were assumed to be representative of the initial concentration of this compound, since the actual amount of reagent on the crystal was difficult to determine. Also, since the data reduction software was only able to process positive peaks, the growth of negative peaks due to the consumption of starting material was studied by multiplying the spectra by -1, causing the negative peaks to appear positive.

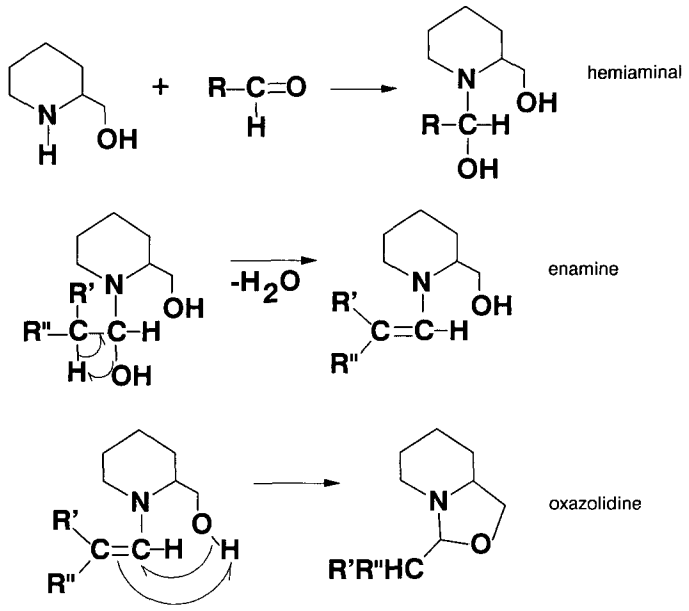

FIG. 1. Proposed mechanism for the reaction of aldehyde with 2-(hydroxymethyl)piperidine.

RESULTS AND DISCUSSION

Solution-Phase Studies. Reactions of solutions of 2-(hydroxymethyl)piperidine and pentanal in toluene or benzene were studied with the use of the "circle" cell. Comparison of separate infrared spectra of the amine reagent and the oxazolidine reaction product, 9-butyl-1-aza-8-oxabicyclo[4.3.0]nonane, yielded absorptions at about 1200 cm^{-1} (assigned to cyclic C-O-C band) and 1135 cm^{-1} (triplet, O-C-N moiety), which were unique to the oxazolidine. These spectral features were used as indicators of oxazolidine formation in the reaction.

One of the interesting observations in the spectra was the appearance of absorbance bands at ~1400, 1550, and 1640 cm^{-1} after the addition of pentanal solution to the 2-(hydroxymethyl)piperidine solution in the "circle" cell (Figs. 2A and 2B). During the course of the reaction, the bands at about 1400 and 1550 cm^{-1} first grew and then decreased in absorbance with time, ultimately reaching a constant absorbance value. In contrast, the absorbance at ~1640 cm^{-1} continued to grow, as did a water band (O-H stretch) at ~3400 cm^{-1} (not shown). The peak at about 1720 cm^{-1}, attributed to the aldehyde (C=O stretch), increased quickly and then disappeared at long periods of time. No peaks assignable to oxazolidine species appeared in the spectra, even after very long periods of time (tens of minutes). The absorbance at 1640 cm^{-1} was interpreted as characteristic of an enamine[17-19] C=C stretch; this was supported by IR spectra of representative enamine compounds.[20] The bands at about 1550

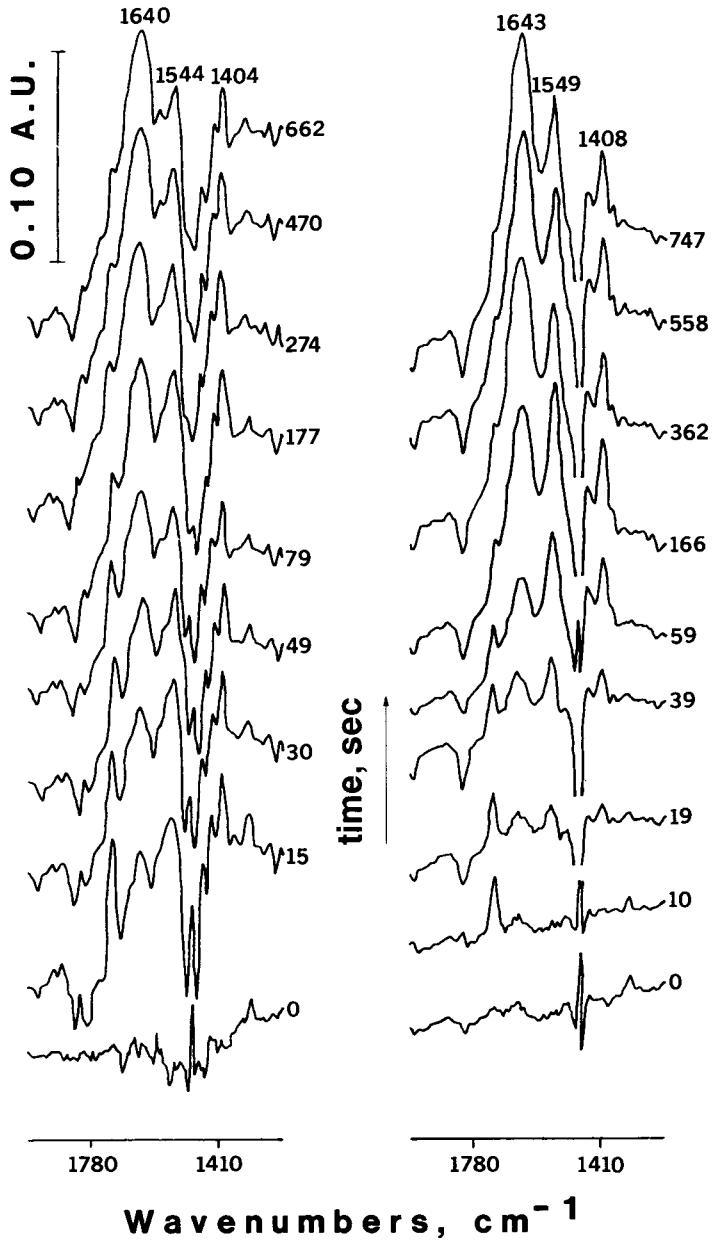

FIG. 2. Spectra obtained as a function of time from a "circle" ATR cell coated with 2-(hydroxymethyl)piperidine in (**A**) toluene and (**B**) benzene solutions containing 40 mg/mL of pentanal. The resolution was 4 cm^{-1}, and the time scale for successive spectra, obtained after initial exposure of the ethanolamine to aldehyde, is in seconds.

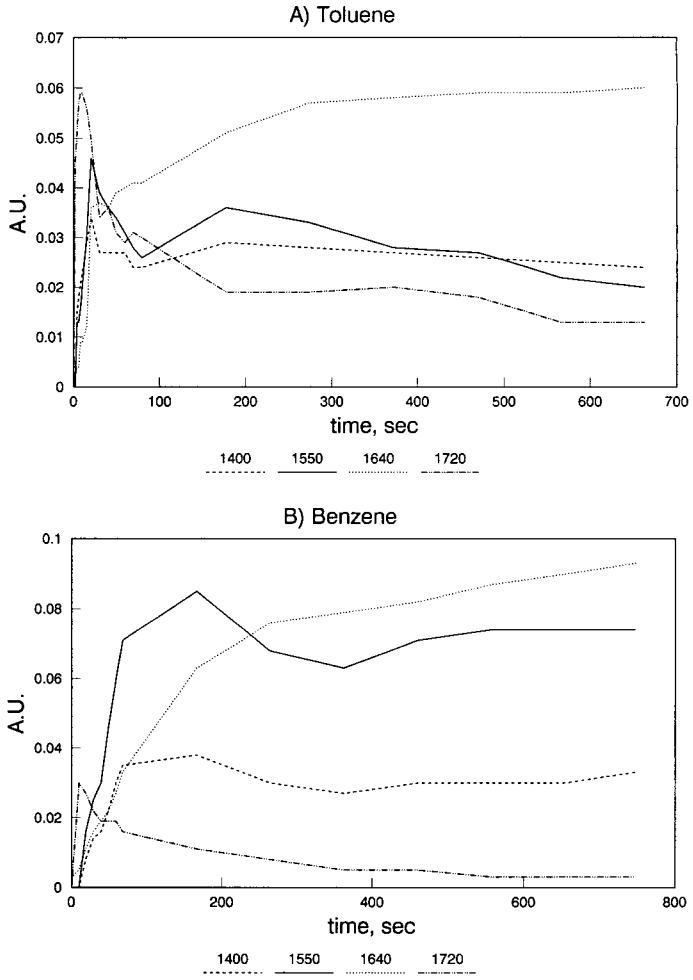

FIG. 3. Absorbance vs. time behavior of various IR bands observed during the reaction of 40 mg/mL pentanal and 2-(hydroxymethyl)piperidine in (**A**) toluene and (**B**) benzene. IR peak heights are in absorbance units (A.U.), and frequencies listed are in units of cm^{-1}.

and 1400 cm^{-1} may be due to either an aminal[21] or more likely a hemiaminal,[5] but little information on the characteristic infrared absorbances of this class of compounds was available to aid in spectral interpretation. Representative IR spectra of aminals derived from piperidines and substituted piperidines showed no peaks in the vicinity of 1400 or 1550 cm^{-1},[22] so the implication is that the most likely intermediate formed is the hemiaminal. We therefore tentatively attribute the bands observed near 1400 and 1550 cm^{-1} to a hemiaminal intermediate structure. This information is consistent with the mechanism proposed in Fig. 1.

The behavior of each spectral feature of interest can be seen more clearly in kinetic plots of absorbance vs. time (Figs. 3A and 3B), and offers further support for the mechanism outlined in Fig. 1. As the aldehyde reacts with the ethanolamine, intermediate peaks (1400 and 1550 cm^{-1}) grow simultaneously and then level off in absorbance as a steady-state concentration is reached. Concurrently, water (3400 cm^{-1}) and enamine (1640 cm^{-1}) product peaks grow on a similar time scale. This result is consistent with the idea that a hemiaminal intermediate undergoes dehydration to yield the enamine (Fig. 1). As can be seen from the plots of absorbance vs. time (Figs. 3A and 3B), the reaction to form hemiaminal proceeds more quickly when toluene is used as the solvent rather than benzene. We have no explanation for these reactivity differences in the two solvents, for the polarities and donor-acceptor properties of benzene and toluene are similar.[23]

It was further observed that the band at 1640 cm^{-1} did not decay appreciably over a day, indicating that the enamine product was stable. Even after this very long time period, no absorbance attributable to oxazolidine (at 1135 and 1200 cm^{-1}) appeared in the IR spectra. Additional spectroscopic studies of the reaction of neat

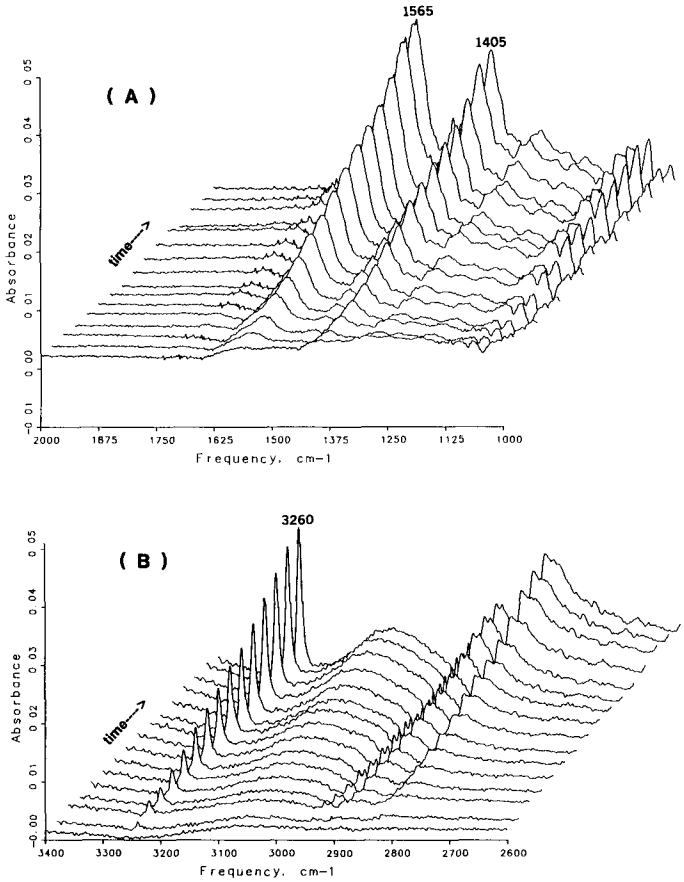

FIG. 4. Three-dimensional plot of spectra vs. time obtained from 150 ppm pentanal vapor reacting with 2-(hydroxymethyl)piperidine coating the "circle" ATR element. (A) 1000–2000 cm^{-1} region; (B) 2600–3400 cm^{-1} frequency range (spectrum is multiplied by −1 to make negative peaks appear positive). Time resolution is 0.25 min per spectrum, and spectral resolution was 4 cm^{-1}.

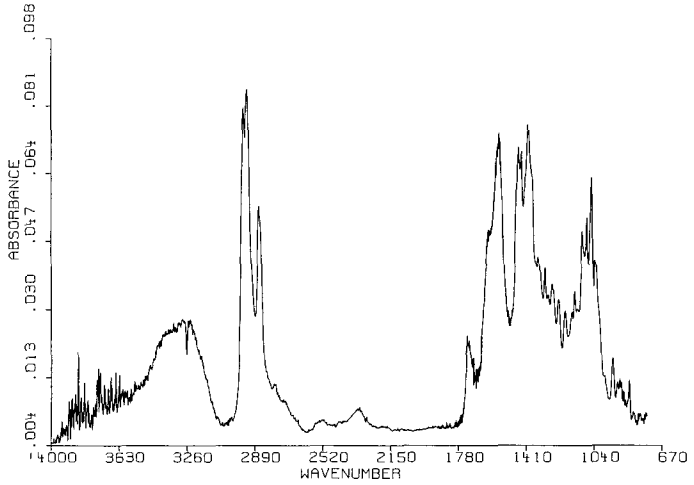

FIG. 5. Enhanced FT-IR spectrum obtained from the reaction of gaseous pentanal (100 ppm) with 2-(hydroxymethyl)piperidine. The negative contribution of the reagent to the spectrum of the reaction mixture was removed by adding a spectrum of 2-(hydroxymethyl)piperidine.

2-(ethyl)piperidine with pentanal also exhibited the 1640-cm^{-1} band. Since the enamine was the main product expected from this reaction[24] and was structurally similar to the proposed 2-(hydroxymethyl)piperidine-based enamine, this offers further support for the enamine structure.

Because of the apparent stability of the enamine, additional energy may be needed to drive the reaction to the oxazolidine product. Agitation for 30 min in an ultrasonic bath was necessary to obtain good recovery of the oxazolidine from the sorbent. Prior to this study, the need for this treatment was thought to be required only for complete desorption of the analyte from the sorbent. The results from the FT-IR/ATR investigation suggested that an ultrasound treatment may be necessary to cause the enamine to undergo further reaction to the oxazolidine.

Gas-Phase Studies. To study the reaction of pentanal with 2-(hydroxymethyl)piperidine as it may occur on the reagent-coated sorbent, we coated the ethanolamine onto the ZnSe crystal of the "circle" cell (in the manner specified in the Experimental section), and pentanal vapor was passed over the coated crystal. As with the solution-phase data, absorbance bands were observed to grow at ~1565 and 1405 cm^{-1} (Fig. 4A). Small differences in peak frequencies (on the order of 5–20 cm^{-1}), compared to those observed in solution, are attributed to the lack of solvation effects in the gas phase. Accompanying the increased absorbances at about 1400 and 1560 cm^{-1} was a decrease in absorbance at 3260 cm^{-1} (N-H stretching mode), due to the loss of 2-(hydroxymethyl)piperidine reagent as it reacted with the aldehyde (Fig. 4B). Unlike the solution-phase data, the bands near 1405 and 1565 cm^{-1} were not accompanied by the growth of a peak at ~1640 cm^{-1}. This result suggests that the hemiaminal structure proposed in the solution experiments was the major product, and that enamine was not formed until much later, if at all.

Further support for the existence of a hemiaminal intermediate was the observation of a broad positive band around 3250 cm^{-1} (Fig. 5), which can be attributed to the O-H stretch of the intermediate. In all spectra (even those obtained at very long periods of time, i.e., days later) peaks at 1135 and 1200 cm^{-1} were absent, indicating that, if oxazolidine is formed on the sorbent, the amount formed is below the detection limit (~0.1%). On the basis of the results obtained in both solution phase and at the gas/solid interface, it appears that the addition of solvent (toluene or benzene) during the desorption step may be responsible for the formation of enamine, since the enamine was observed to form quite readily in the solution phase. Subsequently, the addition of ultrasonic energy may drive the enamine to form the oxazolidine product.

Plots of absorbance vs. time for various IR bands observed in the gas-phase data are shown in Fig. 6. Intermediate bands at ~1560 and 1400 cm^{-1} grow for some time and then slowly decay, while the reagent continues to react. This is indicated by continued absorbance decrease at 3260 cm^{-1}. However, the reagent reacts much more slowly after the decay of the intermediate (after about 1 h). It was not possible to assign bands to an ultimate reaction product since negative bands due to the 2-(hydroxymethyl)piperidine reagent ultimately overwhelmed the spectra. We note that the reaction rates observed in solution (Figs. 2 and 3) were much greater than those observed at the gas/solid interface (Figs. 4

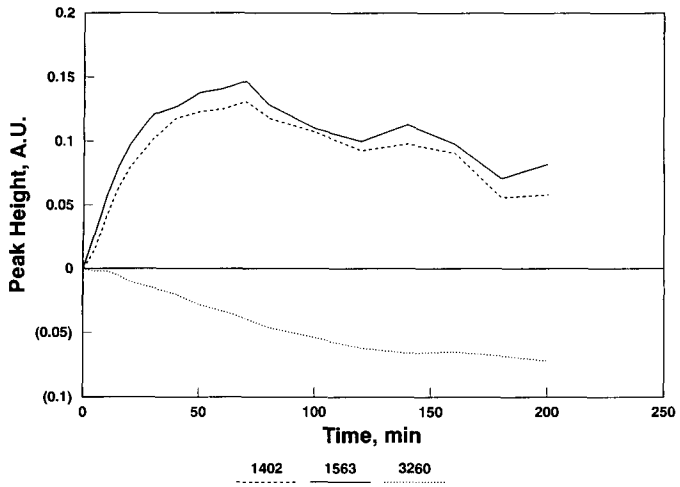

FIG. 6. Absorbance vs. time plots of various IR bands observed during the reaction of 100 ppm gaseous pentanal with 2-(hydroxymethyl)piperidine. Peak frequencies are in units cm^{-1}, and peak heights are in absorbance units (A.U.).

and 6). It is apparent that the presence of solvent not only favors an enamine product but also speeds up the reaction by facilitating the dehydration of the hemiaminal intermediate. Similar results were obtained from experiments in which the aldehyde concentration was varied from 50 to 500 ppm.

Additional vapor-phase experiments in which pentanal (500 ppm) was reacted with 2-(ethyl)piperidine coating the ATR "circle" cell gave an adduct with IR bands similar to those observed in experiments with 2-(hydroxymethyl)piperidine (approx. 1560 and 1410 cm^{-1}). It was hypothesized that these features were also due to the formation of a hemiaminal intermediate structure.

When the "circle" cell coated with 2-(hydroxymethyl)piperidine was exposed to pentanal at high concentrations (~500–5000 ppm), an absorption due to the carbonyl stretch at about 1725 cm^{-1} was observed to grow and subsequently decline. This peak is probably due to physical adsorption of the aldehyde onto the crystal before reaction with the ethanolamine sorbent. This observation was consistent with a slow reaction of pentanal with the 2-(hydroxymethyl)piperidine coating. The subsequent decay of the absorbance may be due to a phase change in the crystal coating. Prior to experimental runs, the 2-(hydroxymethyl)piperidine coating on the "circle" ATR cell appeared needle-like, but after exposure to pentanal, the needle-like crystal coating had disappeared and was replaced by a liquid. The change of coating from solid to liquid may shorten the reaction, as observed by the decrease in the carbonyl absorbance with time. However, as the coating becomes less viscous, the absorbance due to the amine reagent overwhelms the IR spectra since the effective penetration depth of the IR beam through the reagent coating is decreased. Hence, it becomes more difficult for the IR beam to sample the reaction occurring at the interface between the reagent and gas phase. This effect is thought to be responsible for the decay observed in the intermediate peaks at ~1400 and 1560 cm^{-1} (Fig. 6).

In an earlier study, sorbent breakthrough experiments with aldehydes indicated that the 2-(hydroxymethyl)piperidine-coated sorbent had a larger capacity for pentanal than for propanal.[3] It was hoped that a comparison of the reaction kinetics for the two aldehydes would help explain this capacity difference. Time-resolved FT-IR/ATR spectra obtained during the reaction of propanal with the ethanolamine closely resembled spectra obtained during exposure of the ethanolamine to pentanal, with a sharp negative band appearing at 3260 cm^{-1} (N-H stretch of the amine reagent) and strong positive peaks showing up at ~1400 and 1560 cm^{-1} (intermediate bands). A broad positive absorption centered around ~3300 cm^{-1} was also observed, which is attributed to the O-H stretching mode of the hemiaminal intermediate. However, there were substantial differences in the reaction rates between the two aldehydes. The 3260-cm^{-1} N-H stretching and ~1560-cm^{-1} intermediate bands were used to obtain estimates of the reaction rates of the respective aldehydes with 2-(hydroxymethyl)piperidine, assuming the following kinetic model.

In the experiment, vapor-phase aldehyde, $RCHO_{vap}$, which is present at a constant concentration, is passed over the surface of the ethanolamine reagent. Some of this aldehyde can become adsorbed onto the surface ($RCHO_{ads}$), where it may either react with the amine reagent or partition back into the vapor phase. The rate of the reaction between the adsorbed aldehyde and the amine reagent can be expressed:

$$\text{Rate} = k_r[RCHO_{ads}][\text{amine}] \quad (1)$$

where k_r is the rate constant for the reaction of adsorbed aldehyde with amine. If we assume a steady-state coverage (concentration) of $RCHO_{ads}$, then the rate of formation of adsorbed aldehyde equals its rate of depletion, i.e.,

$$k_1[RCHO_{vap}] = k_{-1}[RCHO_{ads}] + k_r[RCHO_{ads}][\text{amine}] \quad (2)$$

where k_1 is the rate constant for adsorption of the aldehyde onto the surface, and k_{-1} is the rate constant for desorption of surface aldehyde. Rearrangement of Eq. 2 gives

$$[RCHO_{ads}] = k_1[RCHO_{vap}]/(k_{-1} + k_r[\text{amine}]), \quad (3)$$

so that we now may write

$$\text{Rate} = \frac{k_1 k_r[RCHO_{vap}][\text{amine}]}{k_{-1} + k_r[\text{amine}]}. \quad (4)$$

If $k_{-1} \gg k_r[\text{amine}]$, then

$$\text{Rate} = (k_1/k_{-1})k_r[RCHO_{vap}][\text{amine}]. \quad (5)$$

On the other hand, if $k_r[\text{amine}] \gg k_{-1}$, then

$$\text{Rate} = k_1[RCHO_{vap}]. \quad (6)$$

It is now desirable to evaluate whether Eq. 5 or Eq. 6 is the appropriate rate law for the aldehyde/amine system in question.

Typical pseudo-first-order kinetic plots for the reaction of the 2-(hydroxymethyl)piperidine with pentanal and propanal are shown in Figs. 7A and 7B, and results from rate constant calculations are summarized in Table I. The data show that the overall reaction rate of propanal with the ethanolamine is nearly an order of mag-

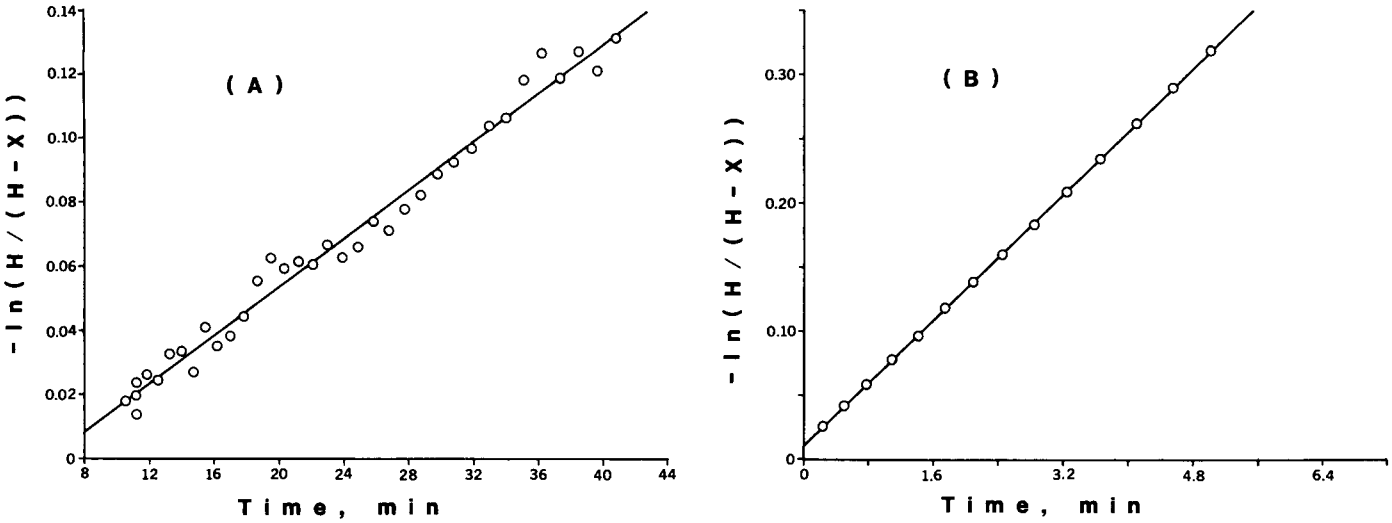

FIG. 7. Normalized pseudo-first-order kinetic plots of: (A) 3260-cm^{-1} absorbance peak, 100-ppm gaseous pentanal experiment; and (B) 1565-cm^{-1} peak, 150-ppm gaseous propanal experiment. H represents the maximum peak height (in A.U.) of the peak, and the quantity (H − X) is the difference in peak height at each time increment. The spectra in A were multiplied by −1 to make negative peaks appear positive.

nitude greater than the reaction of the amine with pentanal. The data appear to fit Eq. 5, i.e., pseudo-first-order in [amine], with [$RCHO_{vap}$] effectively constant. In both Eq. 5 and Eq. 6, the rate constant for adsorption of the aldehyde (k_1) appears, so the experimentally determined rate constant necessarily contains k_1. Therefore, the experimental rate constant does not enable high reactivity to be distinguished from a favorable $RCHO_{ads}$/$RCHO_{vap}$ equilibrium. The implication is that the observed differences in reaction rates are not responsible for the better capacity of the coated sorbent for pentanal. Other factors, such as lower volatility of pentanal (b.p. 102–103°C) over propanal (b.p. 49°C), may play a larger role (than relative reaction rates) in the observed capacity differences.

Since the volatility of pentanal is lower than that of propanal, it is probable that the quotient k_1/k_{-1} is greater for pentanal. The measured pseudo-first-order rate constant, $(k_1/k_{-1})k_r[RCHO_{vap}]$, is greater for propanal, so k_r must also be larger for propanal. Because the ethanolamine sorbent has a higher capacity for pentanal, volatility must be a more important factor than reactivity in determining the capacity of the reagent.

CONCLUSIONS

Time-resolved FT-IR/ATR spectra of the reaction of propanal and pentanal with 2-(hydroxymethyl)piperidine show conclusively that an oxazolidine derivative is not formed in the initial reaction. Instead, at the gas/solid interface, a stable hemiaminal intermediate is apparently the favored product, while in solution this hemiaminal may undergo dehydration to give an enamine product, which in turn is stable. An oxazolidine is formed only after desorption of the intermediate from the sorbent and subjection of the mixture to an ultrasound treatment. This study has provided detailed mechanistic insight into how the 2-(hydroxymethyl)piperidine-coated sorbent interacts with various aldehydes to which it may become exposed.

An interplay of adsorption kinetics, reaction rates, and aldehyde volatility is responsible for the capacity of the sorbent. These contributions must be evaluated for each aldehyde under study in order to fully understand how the coated sorbent interacts with the analyte.

TABLE I. Pseudo-first-order rate constants (calculated from 3260-cm^{-1} and ~1560-cm^{-1} peaks) for the reaction of propanal and pentanal with 2-(hydroxymethyl)piperidine.

Aldehyde	Conc. (ppm)	Time (min)	Rate const., M^{-1} sec^{-1} (3260 cm^{-1})	(~1560 cm^{-1})
Propanal	150	0–20	74 ± 5	69 ± 8
	300	0–20	71 ± 5	112 ± 9
Pentanal	50	0–40	6.4 ± 0.6	9.0 ± 0.9
	100	0–40	7.0 ± 0.05	9.5 ± 0.8
	150	0–40	11 ± 1	13 ± 2
	500	0–40	7.3 ± 0.7	8.5 ± 0.9

ACKNOWLEDGMENTS

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