Steric Factors Affecting the Discrimination of Isomeric and Structurally Related Olefin Gases and Vapors with a Reagent-Coated Surface Acoustic Wave Sensor

Edward T. Zellers* and Guo-Zheng Zhang

University of Michigan, Department of Environmental and Industrial Health, School of Public Health,
1420 Washington Heights, Ann Arbor, Michigan 48109-2029

An investigation of steric factors affecting the olefin–olefin selectivity of a surface acoustic wave (SAW) sensor coated with reagents of the general formula *trans*-$PtCl_2$(ethylene)(substituted-pyridine) is described. Detection is based on the mass increase accompanying replacement of ethylene by other gas-phase olefins to form the corresponding olefin-substituted products. Selectivity depends on the relative reaction rates of the different olefins. Within series of structurally similar butenes, acrylates, and aromatic olefins, unusually high selectivity is observed for the less hindered olefins and complete discrimination of isomers is achieved in certain cases. Replacing pyridine by 2-methylpyridine and 2,6-dimethylpyridine in the reagent complex progressively reduces the sensor response. Sensitivities increase with increasing temperature and limits of detection ranging from about 2 to 70 μg/L are achieved with modest heating (30–40 °C) using a 30-MHz SAW oscillator. Initial results with a 52-MHz sensor show a 3.4-fold increase in sensitivity compared to the 30-MHz sensor in rough agreement with theory.

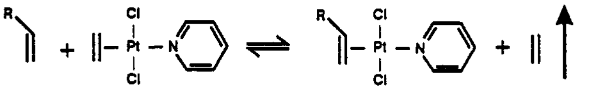
INTRODUCTION

The surface acoustic wave (SAW) chemical sensor has emerged as a useful tool for the characterization of thin films[1,2] and the measurement of atmospheric gases, vapors, and aerosols.[3–5] The analytical versatility of the SAW sensor stems largely from the generic nature of its predominant transduction mechanism, i.e., its sensitivity to surface mass changes. For the case of gas and vapor measurements, this feature, coupled with the ability to adjust the response of the sensor through the use of different surface coatings, results in a broad range of detectable analytes.

We are primarily interested in the development of SAW sensors for environmental and industrial monitoring of toxic organic gases and vapors whose moderate-to-low reactivity can preclude direct or selective measurement by other sensor technologies. To date, the most common approach to measuring organic vapors with SAW sensors has been to use a sorptive polymer coating to concentrate the vapor(s) near the sensor surface.[3,6–8] The partition coefficient of the vapor, which reflects the magnitude of the sensor response at a given vapor concentration, will depend on the strength of the solubility interactions between the vapor and the polymer.[8,9] By use of an array of SAW sensors coated with polymers of different structures and solubility properties, a collective response pattern can be obtained that is characteristic of a given type of vapor.[6,10] Discrimination between the components of simple vapor mixtures is also possible.[11]

Due to the low energies associated with these solubility interactions, however, there is a limit to both the sensitivity and selectivity achievable with this approach. Thus, structural isomers and homologues with very similar solubility properties will not be easily discriminated. In addition, most organic gases and many volatile solvents have very low partition coefficients at ambient temperatures.[12] As a result, detection limits for these compounds using polymer-coated SAW sensors can be rather high. For detection in the range of many environmental and occupational health standards, this approach may not provide adequate sensitivity without sample preconcentration.[13]

We recently reported the selective measurement of vinyl acetate[14] and styrene[15,16] vapors using a SAW sensor coated with the Pt–olefin π-complex *trans*-$PtCl_2$(ET)(pyr) (ET = ethylene, pyr = pyridine). The trapping reaction is shown in general form by eq 1, where R represents the substituent on the target olefin. The rate of frequency change was related to the olefin vapor concentration by means of a power-law kinetic model, and real-time measurement of olefin vapor concentrations was possible. In addition, the initial trapping reagent was regenerable following exposure by treatment with ET in situ. Complete selectivity in the presence of non-ole-



(1)

---

(1) Frye, G. C.; Martin, S. J.; Ricco, A. J.; Brinker, C. J. In *Chemical Sensors and Microinstrumentation*; Murray, R. W. Ed.; ACS Symposium Series 403; American Chemical Society: Washington, DC, 1989; pp 208–221.

(2) Ballantine, D. S., Jr.; Wohltjen, H. In *Chemical Sensors and Microinstrumentation*; Murray, R. W. Ed.; ACS Symposium Series 403; American Chemical Society: Washington, DC, 1989; pp 222–236.

(3) Nieuwenhuizen, M. S.; Venema, A. *Sens. Mater.* **1989**, *5*, 261.

(4) Bowers, W. D.; Chuan, R. L. *Rev. Sci. Instrum.* **1989**, *60*, 1297–1302.

(5) Bowers, W. D.; Chuan, R. L.; Duong, T. M. *Rev. Sci. Instrum.* **1991**, *62*, 1624–1629.

(6) Rose-Pehrsson, S. L.; Grate, J. W.; Ballantine, D. S., Jr.; Jurs, P. C. *Anal. Chem.* **1988**, *60*, 2801.

(7) Ballantine, D. S., Jr.; Rose, S. L.; Grate, J. W.; Wohltjen, H. *Anal. Chem.* **1986**, *58*, 3058.

(8) Grate, J. W.; Snow, A.; Ballantine, D. S., Jr.; Wohltjen, H.; Abraham, M. H.; McGill, A.; Sasson, P. *Anal. Chem.* **1988**, *60*, 869.

(9) Grate, J. W.; Abraham, M. H. *Sens. Actuators* **1991**, *B3*, 85–112.

(10) Wohltjen, H.; Ballantine, D. S., Jr.; Jarvis, N. L. In *Chemical Sensors and Microinstrumentation*; Murray, R. W. Ed.; ACS Symposium Series 403; American Chemical Society: Washington, DC, 1989; pp 157–175.

(11) Zellers, E. T.; Pan, T. S.; Patrash, S.; Han, M.; Batterman, S. *Sens. Actuators*, submitted for publication.

(12) Zellers, E. T.; Patrash, S.; Zhang, G. Z. *Proc. 1991 Int. Conf. Solid-State Sensors and Actuators–Transducers '91*; San Francisco, June 24–27, 1991; pp 998–1001.

(13) Grate, J. W.; Klusty, M.; Rose-Pehrsson, S. Presented at the 42nd Pittsburgh Conference and Exposition, Chicago, IL, March 3–8, 1991.

(14) Zellers, E. T. In *Chemical Sensors and Microinstrumentation*; Murray, R. W. Ed.; ACS Symposium Series 403; American Chemical Society: Washington, DC, 1989; pp 176–190.

(15) Zellers, E. T.; White, R. M.; Rappaport, S. M. *Anal. Chem.* **1990**, *62*, 1223–1227.

(16) Zellers, E. T.; Hassold, N. C.; White, R. M.; Rappaport, S. M. *Anal. Chem.* **1990**, *62*, 1227–1232.

0003-2700/92/0364-1277$03.00/0

fin organic vapors was observed. High selectivity in the presence of certain other olefins was also observed and was tentatively attributed to steric and electronic factors that favored reaction with the target olefins.

This paper describes a more systemmatic study of the influence of steric factors on the rates of olefin substitution reactions in complexes of the general formula *trans*-$PtCl_2(ET)(R_n\text{-pyr})$ (R = H or CH_3, $n = 1$–3) and the corresponding selectivity obtained when these coatings are used in SAW sensors for measuring the concentrations of various olefin gases and vapors. The response of a 30-MHz SAW sensor coated with *trans*-$PtCl_2(ET)(pyr)$ to vapors of ethyl acrylate (EA) is first characterized over a range of concentrations and temperatures. Data are presented confirming the selectivity for EA in the presence of several non-olefin organic vapors. Then, for series of acrylate (including EA), butene, and aromatic olefin isomers and derivatives, the effects of steric hindrance in both the reagent coating and olefin analytes on the olefin–olefin selectivity of the coated sensor are described. Sensitivities and limits of detection (LOD) using this type of reagent coating are compared to those obtained using a sorptive polymer coating of poly(isobutylene) (PIB). Preliminary results obtained with a 52-MHz reagent-coated SAW sensor are also presented to demonstrate the effect on sensitivity of increasing the sensor operating frequency.

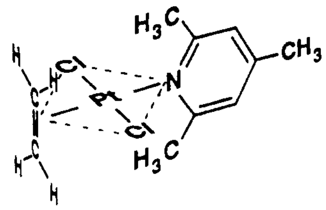
Sensor Configuration and Trapping Reaction. As in most reported chemical sensing applications,[3] we use the coated SAW device as the frequency-controlling element in a feedback oscillator circuit and monitor the oscillation frequency. The response of the SAW oscillator to changes of surface mass can be described by the following approximate expression:[17]

$$\Delta f = K f_0^2 \Delta m/a \qquad (2)$$

where Δf is the frequency change (sensor response), K is a negative substrate constant, f_o is the initial operating frequency, and $\Delta m/a$ is the change of mass per unit area caused by deposition of the coating film and by subsequent interactions of the coating with a gas or vapor.

In the coating reagents, bonding between ET and Pt(II) occurs through donation of electron density from the filled p_π-orbital of the ET to the Pt via a σ bond as well as through back-bonding from the filled orbitals on the Pt to the antibonding π^* orbitals of the ET via a π bond.[18] Similar σ and π bonding interactions occur between Pt and pyr. The strength of the Pt–ligand bonds will depend on the relative energies and overlaps of the orbitals involved. One consequence of the trans configuration of these ligands is that substituents on pyr can affect the bonding to ET (and vice versa). This, in turn, can affect the susceptibility of the complex to nucleophilic attack by other olefins. Both steric and electronic factors can be important, and although it is often difficult to completely separate the influences of these factors, an attempt has been made here to focus on systems where steric factors are predominant. An investigation of substituent-related electronic factors affecting the responses of these complexes as SAW sensor coatings is currently being performed and will be the topic of a separate report.

Crystallographic studies of Pt(II)–ET complexes have shown that the C=C bond axis is nearly perpendicular to the Pt–Cl–N–Cl plane.[19] The angle between the pyr ring and this plane can vary significantly with different pyr substituents. For the 4-methylpyridine (4-Mepyr) complex this angle is 50°, whereas for the 2,6-dimethylpyridine (2,6-Me_2pyr) and the 2,4,6-trimethylpyridine (2,4,6-Me_3pyr) complexes this angle is about 90°. Interestingly, the C=C, Pt–N and (C=C)–Pt bond lengths are nearly identical in these three structures. Although no crystallographic data are available for the 2-methylpyridine (2-Mepyr) complex, one would expect some intermediate value for the ring–plane angle.



Olefin substitution reactions proceed by an associative pathway.[18] Attack by the entering olefin occurs from above or below the Pt–Cl–N–Cl plane, and the two olefins and the pyr comprise the base of the trigonal-bipyramidal transition state. It is not difficult to envision how substituents in the 2- and 6-positions on the pyr ring would inhibit the reaction through crowding in the transition state. Similar crowding would be expected for olefins having bulky substituents on the double-bonded carbons.

Miya et al.[20] reported a significant decrease in the olefin substitution rate with *trans*-$PtCl_2$(2-methyl-2-butene)(pyr) for more sterically hindered olefins, but only a few olefins were examined in that report. Additional evidence of steric effects is found in studies of exchange rates between free and bound ET in solutions of *trans*-$PtCl_2(ET)(R_n\text{-pyr})$ where the activation energies for the exchange process were in the order 2,4,6-Me_3pyr > 2-Mepyr > 4-Mepyr ~ pyr.[21,22] Thermodynamic studies have revealed a consistent trend toward lower equilibrium formation constants for more hindered olefins in Pt(II)–olefin complexes[19,23] as well as in olefin complexes of Ag(I),[24] Rh(I),[25] and Pd(II).[26] In the case of the Pt(II)–olefin complexes, NMR[27] and X-ray[23,28] data have revealed that substituents on the olefin double bonds are invariably bent away from the metal (i.e., out of the C=C plane) presumably to minimize repulsions between the olefin substituents and either the metal or the adjacent ligands.

The goal of the work described in this paper was to determine the extent to which steric factors could be exploited to obtain selectivity for unhindered olefins in the presence of hindered olefins with these reagents coated on a SAW sensor.

EXPERIMENTAL SECTION

Sensor Coatings. All synthetic reagents, gases, and solvents were of 97% or higher purity and were used as received. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Infrared spectra were obtained with a Perkin-Elmer 775B spectrophotomer using thin-film samples deposited on KBr disks. Particle-size analyses were performed using an

---

[17] Wohltjen, H. *Sens. Actuators* **1984**, *5*, 307.

[18] Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1965; Chapter 2.

[19] Hartley, F. R. In *Comprehensive Organometallic Chemistry—The Synthesis, Reaction and Structures of Organometallic Compounds*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 6, pp 614–754.

[20] Miya, S.; Kashiwabara, K.; Saito, K. *Inorg. Chem.* **1980**, *19*, 98–101.

[21] Natile, G.; Maresca, L.; Cattalini, L. *J. Chem. Soc.*, Dalton *Trans.* 1977, 651–655.

[22] Chottard, J. C.; Mansuy, D.; Bartoli, J. F. *J. Organomet. Chem.* **1974**, *65*, C19–C22.

[23] Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163–190.

[24] Muhs, M. A.; Weiss, F. T. *J. Am. Chem. Soc.* **1962**, *84*, 4697–4705.

[25] Cramer, R. *J. Am. Chem. Soc.* **1967**, *89*, 4621–4626.

[26] Ban, E.; Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1974**, *69*, 455–472.

[27] Cooper, D. G.; Powell, J. *Inorg. Chem.* **1976**, *15*, 1959–1968.

[28] Mura, P.; Spagna, R.; Ughetto, G.; Zambonelli, L. *J. Cryst. Mol. Struct.* **1977**, *7*, 265–274.

Table I. Analytical Data for *trans*-$PtCl_2$(Olefin)(Amine) Complexes

			elemental analysis					
			found			theoretical		
olefin	amine	mp,[a] °C	C	H	N	C	H	N
ET	pyr	112	22.50	2.50	3.70	22.53	2.43	3.75
ET	2-Mepyr	97	24.82	2.86	3.62	24.88	2.84	3.75
ET	4-Mepyr	118	24.82	2.86	3.62	24.90	2.90	3.60
ET	2,6-Me_2pyr	155	26.94	3.27	3.49	26.89	3.30	3.46
ET	2,4,6-Me_3pyr	151	28.93	3.64	3.37	29.10	3.70	3.30
EA	pyr	–[b]	26.98	2.94	3.15	27.08	3.13	2.94
MA	pyr	–[b]	25.07	2.57	3.25	24.32	2.69	3.30

[a] All compounds melted with decomposition. [b] Not determined.

Olympus Model BHA optical microscope according to established methods.[29]

Coating reagents, *trans*-$PtCl_2$(ET)(R_n-pyr), were synthesized by the addition of 1 equiv of the amine to a stirred aqueous solution of $KPtCl_3$(ET) (Aldrich) at room temperature.[30] The solid precipitates which formed immediately were isolated, rinsed with water, dried, and then recrystallized from a minimum of methylene chloride by addition of hexane to the cloud point. The resulting products were typically yellow crystalline solids soluble in moderately polar organic solvents (e.g., methylene chloride and toluene). The 2-Mepyr complex would often precipitate as an oil that could be eventually crystallized following slow evaporation of the solvents. *trans*-$PtCl_2$(ethyl acrylate)(pyr) and *trans*-$PtCl_2$(methyl acrylate)(pyr) were prepared from methylene chloride solutions of the corresponding ET complex by adding an excess of the acrylate and refluxing for 1 h. Both acrylate complexes were isolated as viscous yellow oils by addition of hexane. The products could not be recrystallized but did become semisolid on standing for several days. Table I lists the reagents investigated along with the corresponding melting points and elemental analyses.

Previous work showed that combining the Pt–olefin complexes with the amorphous rubbery polymer PIB resulted in more uniform and adherent coating films than those obtained using the solid complexes alone.[15] Films were deposited by solvent casting from solutions containing 6 mg/mL of each component in 2:1 toluene–hexane. The amount deposited was estimated by eq 2 from the net frequency shift after evaporation of the casting solvent. Frequency shifts due to the coating films were typically in the range of 280 ± 30 kHz. It has also been shown previously that coating the reference SAW device with PIB and measuring the difference frequency between the two sensors masked the response due to sorption and desorption of vapors by the polymer on the sensing oscillator.[15] For measurements described here only the single-oscillator output was monitored, and the steady-state response was determined after establishment of sorption equilibrium at a given olefin concentration.

Apparatus. Most experiments were performed using a 30-MHz SAW oscillator (active area = 1.5 cm^2) fabricated on an ST-quartz substrate (Valpey-Fischer, Hopkinton, MA). Additional experiments were performed using a 52-MHz SAW oscillator (active area = 0.63 cm^2) purchased from Microsensor Systems, Inc. (Bowling Green, KY). Sensor frequencies were monitored with a digital frequency counter (Hewlett-Packard Model 5384A) and logged on a personal computer via an IEEE-488 interface. Frequency measurements were collected every 10 s with a resolution of 1 Hz, and the net 1-min frequency shifts were averaged over a given exposure interval.

The sensor was placed on a Teflon pedestal in a 240-cm^3 stainless-steel exposure chamber wrapped with heating tape to control the temperature. A thermocouple was used to monitor the temperature at the surface of the sensor. Test atmospheres of the vapors were generated by passing nitrogen gas through a bubbler containing the liquid solvent and then into a dilution-air stream. For the gases investigated, a syringe pump was used to meter the gas into the dilution stream. Dilution-air flow and temperature were controlled with a Miller-Nelson Research HCS 301 control unit, and the relative humidity was maintained below 10%. Part of the contaminated air stream was directed through the exposure chamber and the remainder through an infrared gas analyzer (Foxboro, MIRAN 1A) used for continuous monitoring of solvent vapor concentrations. The exhaust from both streams was then vented to a fume hood. At the flow rates used, the theoretical mixing time in the exposure chamber was 8 s.[31] For binary-mixture exposures the infrared gas analyzer was calibrated for each component of the mixture at a common absorbance wavelength. Following establishment of a constant concentration for the initial component, the second component was introduced and the increase in absorbance was used to determine its concentration.

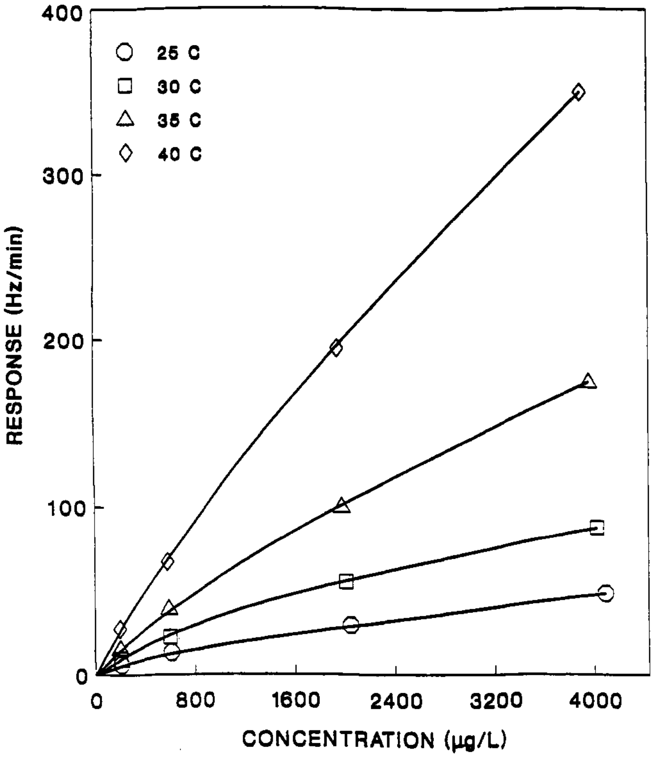


Figure 1. Response to ethyl acrylate from 25 to 40 °C using *trans*-$PtCl_2$(ET)(pyr) coating.

RESULTS AND DISCUSSION

Response to Ethyl Acrylate. Figure 1 shows the response of the sensor coated with *trans*-$PtCl_2$(ET)(pyr) to EA as a function of concentration and temperature. Each point on the curves represents the mean steady-state rate of frequency change observed at each concentration. Exposures were limited to 20 min at each concentration to avoid any significant

---

(29) Taylor, D. G. *NIOSH Manual of Analytical Methods*, 2nd ed.; USDHEW-NIOSH: Cincinnati, OH, 1977; Vol. 1, pp 239(1)–239(21).

(30) Orchin, M.; Schmidt, P. J. *Inorg. Chim. Acta Rev.* **1968**, 123–135.

(31) Nelson, G. O. *Controlled Test Atmospheres*; Ann Arbor Press: Ann Arbor MI, 1976.

Table II. Response to EA in the Presence of Other Solvent Vapors Using *trans*-$PtCl_2$(ET)(pyr) Coating

interferent	concn, μg/L	mean response (std dev) to 800 μg/L of EA,[a] Hz/min
–	–	29 (1)
hexane	3600	27 (2)
toluene	3800	31 (2)
tetrahydrofuran	3200	29 (1)
ethyl acetate	4100	30 (3)
chloroform	6900	29 (2)
acetone	4000	28 (3)
methanol	1400	27 (3)

[a] 15–20-min exposure.

depletion of the reagent (see below). The standard deviations around each point ranged from 1–3 Hz/min at low concentrations to about 6 Hz/min at the higher concentrations. Results were quite reproducible, with differences of less than 10% being observed at a given concentration for duplicate coating films. Response times and recovery times ranged from about 20 to 45 s.

The nonlinear response vs concentration curves presented in Figure 1 are typical of those observed for all of the olefins tested and reflect the heterogeneous nature of the gas–solid trapping reaction which is the rate-limiting step in the overall interaction of the olefins with the sensor coating. For a given temperature a plot of log concentration vs log response gave a straight line ($r^2 > 0.998$) in accordance with a power-law kinetic model.[32] Linear regressions of Arrhenius plots at several different concentrations ($r^2 > 0.994$) yielded a mean thermal activation energy of 21.9 ± 2.4 kcal/mol. This value is close to that determined from similar experiments with styrene (22.8 kcal/mol)[15] and those previously reported for analogous olefin-substitution reactions studied in solution (13–20 kcal/mol).[20] LODs were defined as $3s_n$/sensitivity, where s_n is the standard deviation of oscillator noise measured each minute for 10–15 min before and after exposure and the sensitivity is the slope of the response curve at low concentrations. LODs ranged from 102 μg/L at 25 °C to 22 μg/L at 40 °C.

A persistent drift in the postexposure baseline was observed following exposure to EA at 40 °C. To determine whether the complex was hydrolyzing or otherwise decomposing, a thin film of the complex was deposited on a KBr plate and exposed to air at 40% RH at 40 °C for several hours. IR spectra taken before and after exposure of the sample were indistinguishable. If hydrolysis to acrylic acid or polymerization of the EA were occurring it was evidently at a very low rate. Our previous studies suggested that the olefin substitution reaction can cause slight changes in the packing density of the solid. It is possible that subtle postexposure structural relaxations could be responsible for the observed drift. Despite the baseline drift, the response to EA did not change upon repeated exposure. Lowering the temperature to 30 °C eliminated the postexposure drift but raised the LOD to 67 μg/L.

Table II presents the results of simultaneous exposure to 800 μg/L of EA and each of several non-olefin organic solvent vapors at 30 °C. As shown, there were no effects on the response to EA even at the high interferent concentrations tested. These results were not unexpected since the interfering vapors cannot react with the trapping agent. A high degree of selectivity for EA in the presence of other acrylates was also observed and is discussed below in the context of steric effects.

For continuous exposure to 1100 μg/L of EA, the sensor response remained constant (within 5%) for over 2 h and then began to gradually decline, reaching about 70% of the initial response after 4 h. This reflects the depletion of the reagent and, possibly, the added diffusional resistance associated with an increasingly thick product layer around a core of unreacted reagent.[16,33] Regeneration of the reagent by exposure to pure ET was only partially successful after such prolonged exposure—the sensor response for the regenerated coating was considerably lower than that for the fresh coating. For repeated exposures of shorter duration (~1.5 h at 200–4800 μg/L), however, regeneration yielded responses that were within 7% of those for the fresh coating.

Steric Effects of Attacking Olefins. The effect of olefin steric hindrance on the response of the *trans*-$PtCl_2$(ET)(pyr)-coated sensor was examined for three series of olefins in which the number and/or geometry of substituents adjacent to the olefin double bond were varied. Experiments were performed by exposing a freshly coated sensor to each of the olefins individually over a range of concentrations. Additional experiments were then performed for certain binary olefin mixtures. As above, the duration of exposure at a given olefin concentration (≤20 min) was limited to avoid reagent depletion: relative standard deviations at a given concentration were invariably below 10%. Continued exposure at high concentrations, however, did lead to a reduction in response. The reproducibility of responses to a given olefin for different coating films was similar to that described above for EA.

Acrylate Series. The first series consisted of the isomers EA, methyl crotonate (MC), and methyl methacrylate (MMA), as well as methyl acrylate (MA). As shown in Figure 2a, the responses were in the order EA > MA ≫ MC > MMA (exposure temperature = 30 °C). The greater response for EA compared to MA is due in part to its slightly higher mass (i.e., for the same rate of reaction, substitution of ethylene by EA would produce a larger frequency shift). However, this factor alone does not account for the observed difference in sensitivity. Since the steric environment of the double bond is similar in each of these olefins, the difference in response (i.e., reactivity) probably has an electronic origin. A previous report on the MA complex showed that the carbonyl group is not involved in the bonding to Pt,[34] and our own IR spectra confirm this. Nevertheless, conjugation of the double bonds with the carbonyl groups will cause some electron delocalization of the olefin π cloud in both compounds. The increased reactivity found with EA is assumed to arise from the subtle difference in the field/inductive effects of the methyl and ethyl esters.[35]

The responses for EA and MA were much higher than those for the remaining acrylates, MC and MMA. MC gives a low concentration-dependent response but the response to MMA could not be differentiated from the baseline noise. In MMA, the pendant methyl group and the ester group are on the same carbon atom of the double bond. In MC, the olefin substituents are on different carbon atoms. Thus, it appears that vicinal substitution presents less steric hindrance than geminal substitution in the formation of the Pt–olefin complexes. Differences in the rates of diffusion of the vapors into the surface of the solid reagent would also contribute to the observed order of responses, since the more highly branched MMA and MC would be expected to have smaller diffusion coefficients than the other acrylates. The potential

---

(32) Hayward, D. M.; Crowell, A. D. *Chemisorption*, 2nd ed.; Butterworths: London, 1964; Chapter 1.

(33) Levenspiel, O. *Chemical Reaction Engineering*; Wiley, New York, 1972; Chapter 12.

(34) Meester, M. A. M.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* **1977**, *21*, 251–258.

(35) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

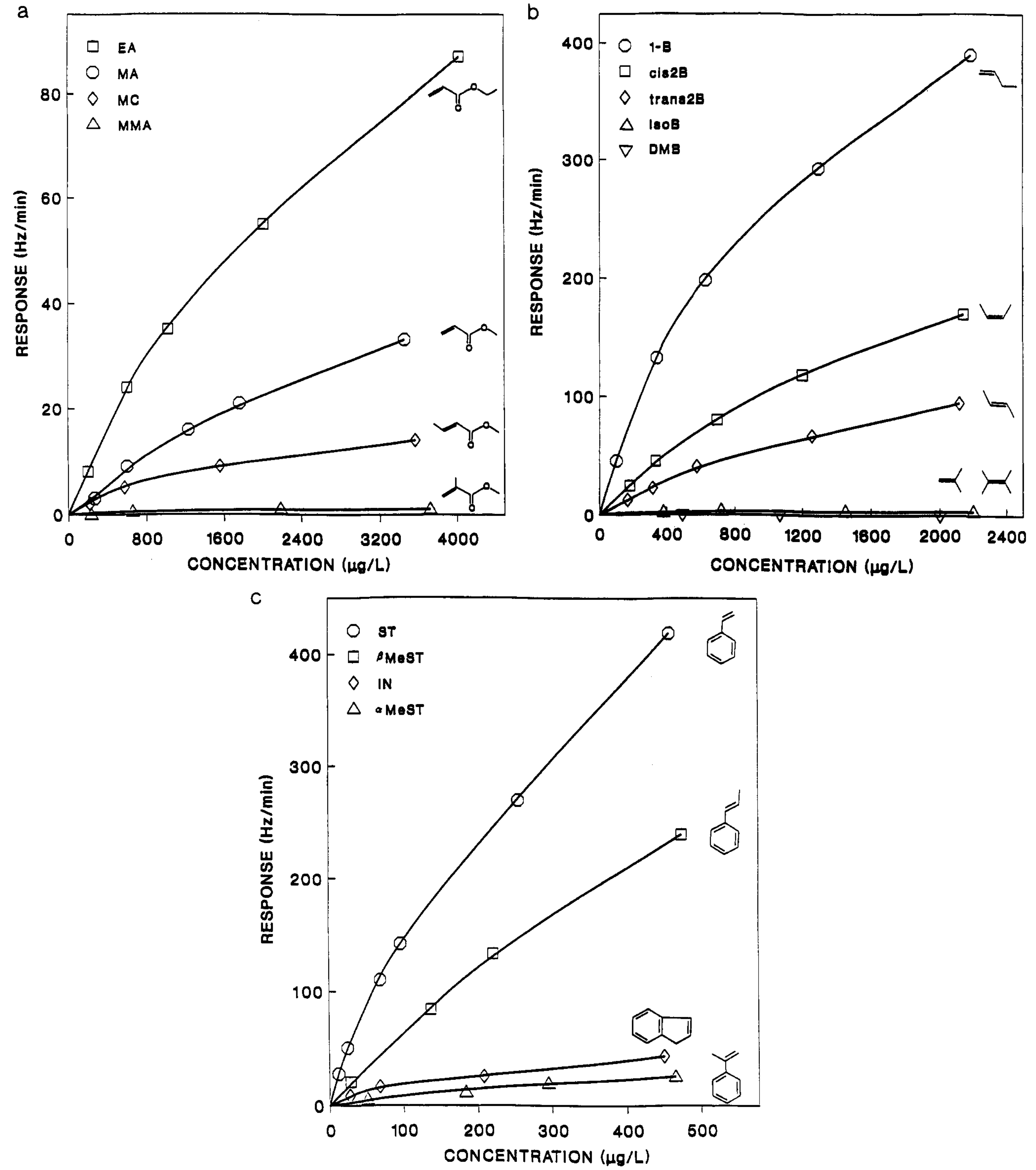


Figure 2. Responses using *trans*-PtCl$_2$(ET)(pyr) coating for series of (a) acrylates at 30 °C; (b) butenes at 40 °C; and (c) aromatic olefins at 40 °C.

role of diffusional effects is discussed in more detail in the next section.

Coexposure to EA and MMA did not affect the response to EA, even up to a concentration ratio of 2:1 (MMA:EA). MC only affected the response to EA at relatively high MC concentrations: an increase of about 13% in the response to 2000 μg/L of EA was observed upon coexposure to 5000 μg/L of MC (note: analogous results were obtained for the complex where 4-Mepyr was the amine ligand). Similarly, coexposure to MA and MMA did not affect the response to MA. The response to MA increased by about 20%, however, upon introduction of an equivalent concentration of MC.

Coexposure to EA and MA revealed a preferential response to EA. At equivalent concentrations, MA did not affect the response to EA. But at a concentration ratio of 2:1 (MA:EA), the response increased by 30% due to MA. The combined response was somewhat less than the sum of the individual responses measured at the same concentrations. To further probe this issue, coatings of *trans*-PtCl$_2$(EA)(pyr) and *trans*-PtCl$_2$(MA)(pyr) were tested for reactivity toward MA and EA, respectively. No response was observed for either combination at concentrations as high as 4800 μg/L, indicating that these olefins are competing for displacement of ET from its complex and are not displacing each other.

It should be mentioned that this is the first report of the complex *trans*-$PtCl_2$(EA)(pyr), although the corresponding MA complex is known.[34] That olefins with electron-withdrawing ester substituents can so readily displace ET by nucleophilic attack on Pt is quite remarkable, particularly in light of our previous results showing that electron-deficient olefins (e.g., vinyl chloride, acrylonitrile) do not react with *trans*-$PtCl_2$(ET)(pyr).[16]

Butene Series. Responses of the *trans*-$PtCl_2$(ET)(pyr)-coated sensor to the butenes and substituted butenes examined were in the order 1-butene (1-B) > *cis*-2-butene (cis2B) > *trans*-2-butene (trans2B) ≫ isobutylene (isoB) ~ 2,3-dimethyl-2-butene (DMB), as shown in Figure 2b for exposure at 40 °C. No responses were observed for the latter two olefins at concentrations up to 2200 μg/L. Limits of detection for the former three olefins ranged from 15 μg/L for 1-B to 45 μg/L for trans2B, and response times were <30 s.

The order of responses follows the same trend as that observed for the acrylates, with increases in methyl substitution on the double bond leading to decreases in the rate of reaction. Comparison of the results for isoB and either cis2B or trans2B shows that, again, geminal substitution results in significantly lower reactivity than vicinal substitution.

The difference in responses between cis2B and trans2B is consistent with the general finding that cis isomers form more stable metal–olefin complexes than trans isomers,[19] which can be ascribed to two effects. First, cis olefins are generally more strained than trans olefins, as indicated by their higher heats of hydrogenation,[36] and coordination with the metal relieves the strain because the bond order is lowered (i.e., the C=C bond length is increased and takes on slightly more sp^3 character). Second, the metal–olefin bonds are stronger in the case of cis isomers, owing to the ability for rotation about the C=C axis to minimize repulsive nonbonded interactions between the methyl substituents and the other ligands (e.g., the Cl atoms in the Pt complexes considered here).[28] For trans isomers, additional rotation about the olefin–Pt bond axis is necessary to relieve these interactions with a resultant reduction in overlap between the filled d orbitals of the Pt and the π^* orbitals of the olefin. This reduces considerably the overall bond strength.[19] For isoB, neither type of rotation would lead to significant reductions in these repulsive interactions with the Cl ligands in the complex, hence the lack of response for this isomer.

Addition of isoB at concentrations up to 2200 μg/L to atmospheres of 200–1000 μg/L of 1-B, cis2B, or trans2B did not affect the responses to the latter olefins. Coexposure to cis2B and trans2B gave a response that was roughly equal to the sum of the individual responses at a given concentration. Addition of either cis2B or trans2B to an atmosphere of 1-B also caused an increase in response, but there was an apparent preference for the 1-B. From a practical standpoint, although monitoring 1-B, cis2B, or trans2B in the presence of isoB (and probably DMB) would be possible, discrimination of the former three isomers in the presence of each other would not be possible with a single sensor.

Aromatic Olefin Series. The aromatic olefins examined gave the following order of responses with the *trans*-$PtCl_2$(ET)(pyr) coating: styrene (ST) > *trans*-β-methylstyrene (βMeST) > indene (IN) ~ α-methylstyrene (αMeST). Figure 2c shows the response curves for these vapors at 40 °C. Here again, the geminally substituted αMeST gives a lower response than its vicinally substituted βMeST isomer. The low response for IN is contrary to expectations based on steric factors, since the cis configuration of IN is less sterically hindered than the trans configuration of βMeST. Based on the NMR and X-ray data cited previously (see Introduction), we speculate that the rigidity of the IN structure reduces the extent to which the subsituents on the double bond can bend away from the Pt or the Cl ligands. The greater repulsion would destabilize both the transition state and the product.

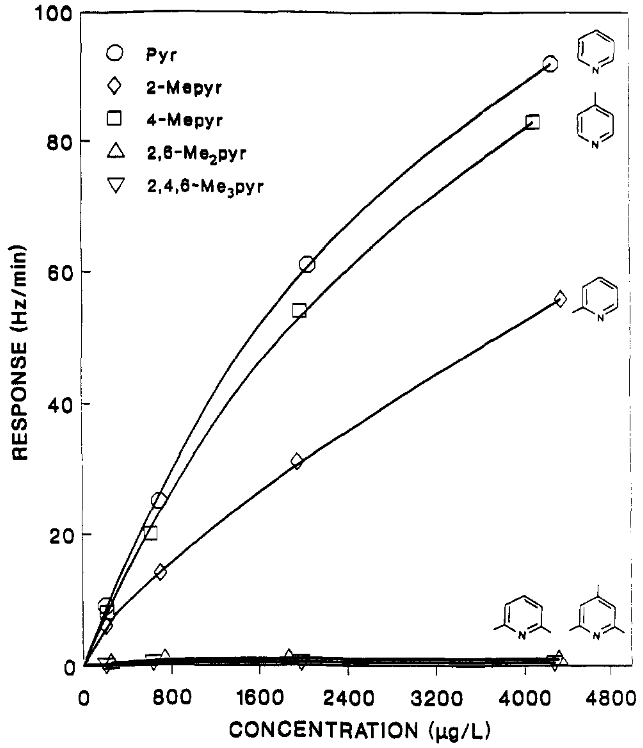


Figure 3. Responses to EA at 30 °C using *trans*-$PtCl_2$(ET)(R_n-pyr) coatings (R = H, CH_3; n = 1–3).

Responses to αMeST were observed to decline by several percent even over the short exposure periods of 15–20 min at a given concentration. These results suggest that diffusional resistance in the solid reagent may be more important for this molecule. This is further supported by the observation that the difference in responses between ST and αMeST showed a marked temperature dependence. At 25 °C the ratio of responses to 200 μg/L of each vapor (for separate exposures) was only about 3:1 (ST:αMeST), but at 40 °C this ratio increased to about 10:1. To the extent that the reaction is limited by diffusion of the vapors into the solid reagent, there would be a smaller temperature dependence for the overall response since diffusion generally involves a lower activation energy than chemical reaction. That diffusional effects are more important in the interaction with αMeST is consistent with its lower reactivity and more highly branched structure. This factor enhances the selectivity for styrene. Coexposures to equivalent air concentrations of styrene and αMeST gave responses that were only 5–10% higher than the responses to styrene alone.

***trans*-$PtCl_2$(ET)(R_n-pyr).** To further investigate the effects of steric hindrance, several of the olefins were exposed to the sensor coated with complexes having 2-Mepyr, 2,6-Me_2pyr, or 2,4,6-Me_3pyr ligands trans to the ET. To account for the slight electron-donating effect of the methyl substituents, the complex with a 4-Mepyr ligand was also included in this series. Substitution in the 4-position allows resonance interaction through the aromatic ring (as with the 2-methyl isomer) but does not exert any steric influence.

Figure 3 shows the sensor response to EA at 30 °C with coatings of the different complexes. The pattern of responses is consistent with the progressive increase in steric hindrance. Thus, the 2-Mepyr complex exhibits considerably less sensitivity than the pyr and 4-Mepyr complexes. Remarkably,

---

(36) Turner, R. B.; Nettleton, D. E.; Perelman, M. *J. Am. Chem. Soc.* 1958, *80*, 1430–1439.

adding a second methyl group at the 6-position of the pyridine (i.e., 2,6-Me_2pyr) completely precludes reaction. Similarly, no response was obtained with 2,4,6-Me_3pyr as the trans ligand. The dramatic difference is attributed to the exclusion of EA attack from both above and below the square plane for the 2,6-Me_2pyr and 2,4,6-Me_3pyr complexes. In addition, to the extent that the 2-Mepyr ring is rotated toward the square plane (see Introduction), the steric hindrance from the 2-methyl group would be reduced. For 2,6-Me_2pyr and 2,4,6-Me_3pyr, the rings are perpendicular to the square plane and the pendant methyl groups would exert more steric influence.

Similar orders of response were observed for MA and MC. None of the complexes gave responses to MMA. Contrary to expectations, use of the 2-Mepyr complex did not enhance the selectivity for the unhindered EA and MA relative to the more hindered MC. That is, the ratios of responses of the former acrylates to the latter were reduced for the 2-Mepyr complex. We also noted somewhat poorer reproducibility with this reagent.

Results for the butene series were similar to those for the acrylate series. For the relatively unhindered 1-B and cis2B the responses decreased in the order pyr > 4-Mepyr > 2-Mepyr ≫ 2,6-Me_2pyr, with no response being observed for the latter complex. Interestingly, at low concentrations of trans2B, the 2-Mepyr complex gave responses that were slightly higher than those for the pyr and 4-Mepyr complexes. The slope of the 2-Mepyr response curve was quite shallow, however, and responses at higher trans2B concentrations were lower than those for the pyr and 4-methylpyridine complexes. Use of the 2-Mepyr complex also reduced the differences in responses between 1-B, cis2B, and trans2B. In fact, responses to the cis and trans isomers could not be differentiated with this reagent.

The aromatic olefins showed response trends similar to those just described. ST and βMeST gave the following overall order of responses: pyr > 4-Mepyr > 2-Mepyr ≫ 2,6-Me_2pyr ~ 2,4,6-Me_3pyr. However, at low vapor concentrations of both ST and βMeST, responses with the 2-Mepyr complex were similar to those for the pyr and 4-Mepyr complexes. At higher vapor concentrations, higher responses were obtained with the latter complexes. For αMeST and IN the responses with the 2-Mepyr complex, while still quite low, were consistently higher than those for the pyr and 4-Mepyr complexes over the entire concentration range examined. No responses were observed for any of the aromatic olefins with the 2,6-Me_2pyr or the 2,4,6-Me_3pyr complexes.

The results for the 2-Mepyr complex reveal a consistent trend across all three series of olefins: the more hindered olefins give responses that are higher than expected. For most of the olefins this effect is seen only at low concentrations, while for IN and αMeST this effect extends over a fairly large concentration range. These results support the notion that diffusional resistance may be an important covariable affecting the responses to certain vapors.

Microscopic inspection of the 2-Mepyr complex coating films showed that it formed a mixture of solid crystals and oil droplets, consistent with the difficulty encountered in recrystallizing the reagent following synthesis. The other reagents formed solids in all cases. For olefins whose interactions with the reagent are limited by the rate of reaction, the physical state of the reagent would be less critical. But for olefins whose interactions were at least partly diffusion-limited, the physical state would be important since diffusion rates would be higher into an oil than into a solid. For the least hindered (and most diffusive) olefins the responses to the 2-Mepyr complex were consistently lower than for the pyr and 4-Mepyr complexes, indicating that the chemical reaction is rate-limiting. For the more hindered olefins, which would have lower diffusion coefficients due to higher branching, diffusion into the reagent complexes becomes increasingly important in the rate of the overall interaction. This leads to the initially higher responses for the partially-liquid 2-Mepyr complex relative to the solid pyr and 4-Mepyr complexes even though the reaction rates are higher for the latter complexes. As the olefin concentration increases at the surface of the reagents, the relative influence of diffusional effects declines and the reaction rates predominate for all but the least diffusive vapors (i.e., IN and αMeST).

Particle Size. With the exception of the 2-Mepyr complex, responses obtained for successive coatings of the same reagent were quite reproducible at the low concentrations examined. The amount of coating deposited affected the capacity (i.e., service life) but had little effect on responses for short-term exposures. The somewhat poorer reproducibility with the 2-Mepyr complex is consistent with its variable composition as discussed above.

Given the heterogeneous nature of the trapping reactions, we considered the possibility that particle size might be contributing to some of the differences observed between the coating reagents (notwithstanding the results for the 2-Mepyr complex). Investigations of this issue were hampered by differences in the morphologies of the reagents in the coating films: although the methyl-substituted pyr complexes generally precipitated at discrete nucleation sites on the surface of the sensor, the pyr complex formed a mixture of discrete crystals and intricate crystalline networks. As a result, the distribution of particle sizes could not be accurately determined by microscopic analyses for coating films of the pyridine complex.

For the remaining complexes the size distributions of the solid particles (or solid/oil mixtures, in the case of the 2-Mepyr complex) were all approximately lognormal, i.e., skewed toward smaller diameters. The 2- and 4-Mepyr complexes gave similar geometric mean diameters (d_g) of about 4 μm, whereas the remaining complexes gave d_g values ranging from 1.1 to 1.4 μm. For similar deposited masses, smaller particle sizes would lead to a larger total surface area for reaction. If surface area were a predominant factor, the latter complexes would have given higher responses. For the 4-Mepyr complex an additional experiment was performed to compare a solvent-cast coating to a coating applied with an air brush. The former gave a d_g of 4.3 μm and the latter gave d_g of 1.2 μm, yet the responses to EA were nearly identical. From these data and estimates of the amount of reagent consumed it is apparent that at the relatively low olefin concentrations examined there is an excess of reagent surface area available for adsorption/reaction.

Polymer Sorption vs Chemical Reaction. The advantage of using these reagent coatings to improve selectivity are clear from the data just presented. It should also be stressed that this approach can have advantages in terms of sensitivity compared to the more common approach of using a polymer-coated sensor where equilibrium sorption determines the sensor response. This is particularly true for more volatile compounds and can be illustrated by comparison of the responses to 1-B using the *trans*-$PtCl_2$(ET)(pyr) coating and a coating of PIB alone.

Several factors must be considered in order to make a fair comparison between these coatings. One factor is the affinity of the polymer for 1-B. Given the similarity in the structures of 1-B and PIB, the solubility interactions should be quite strong and the polymer/air partition coefficient for 1-B in PIB should be relatively high. That is, polymers containing polar functional groups would probably interact less with

1-B than would PIB. Another factor is the exposure temperature. Since sorption decreases exponentially with increasing temperature, operating a polymer-coated sensor at elevated temperatures would decrease the sensitivity and increase the LOD. A temperature of 25 °C is suitable for most practical air-monitoring applications (note: cooling to subambient temperatures is possible but can lead to problems such as condensation of atmospheric humidity). Finally, for a given partition coefficient the sensor response will increase linearly with the amount of coating deposited.[37] In practice, however, there is a limit to the amount of coating that can be applied without completely dampening the oscillator. Typical coatings reported in the literature[6,37] are on the order of a few percent of the acoustic wavelength in nominal thickness, which corresponds to frequency shifts of 200–300 kHz for polymers having densities near 1 g/cm^3.

With these factors in mind, a coating of 250 kHz of PIB was used, and the response to 1-B was determined at a temperature of 25 °C. Exposure to several concentrations in the range of 250–4600 μg/L resulted in a linear sorption isotherm having a slope (i.e., sensitivity) of 0.008 Hz/(μg/L) and a corresponding limit of detection of about 374 μg/L (note: at 40 °C the LOD was well above 1000 μg/L). The sensitivity using the pyr complex decreases slightly with increasing concentration (i.e., the response isotherm is concave downward, see Figure 2b), but at low concentrations it is nearly constant: a value of 0.21 Hz/((μg/L)/min) was obtained for 1-B at 40 °C. The LOD was about 15 μg/L, as mentioned above. Thus, the reagent coating provides about a 25-fold sensitivity and detection-limit advantage for 1-B.

The relatively poor sensitivity of the PIB coated sensor to 1-B arises from its low molecular weight and high volatility. For higher-molecular-weight (and less-volatile) compounds, responses using polymer-coated sensors generally increase. The sensitivity of the PIB-coated sensor to ST, for example, was about 1 Hz/(μg/L) at 25 °C. The corresponding value for the pyr complex was 2.2 Hz/((μg/L)/min). Although the reagent coating still provides higher sensitivity, the difference is much smaller than for 1-B.

Sensor Operating Frequency. From eq 2 it can be seen that the mass sensitivity of the SAW device increases with the square of the operating frequency. According to this equation, using a SAW oscillator that operates at twice the frequency should lead to a 4-fold increase in mass sensitivity. However, the sensitivity to vapors will not necessarily increase proportionally. For polymer coatings the response to the vapor is dependent on the amount of polymer on the device. As just mentioned, there is a limit to the amount of coating that can be tolerated without loss of oscillation. This limit will decrease as the frequency of the SAW device increases (and the acoustic wavelength decreases). Grate and Klusty recently examined this issue and found for SAW devices operating at frequencies ranging from 158 to 400 MHz that if a polymer coating causing the same frequency shift is used on these devices then the sensitivity to organic vapors is the same regardless of the operating frequency.[37] Their report also confirmed that vapors penetrate into the bulk of the polymer film rather than adsorbing at the surface.

In contrast to the case of polymer coatings, for the reagent coatings used here the responses involve interfacial phenomena. As a result, increases in sensor frequency should lead to increases in sensitivity. From preliminary tests of a 52-MHz sensor having acoustic dimensions similar to the 30-MHz device (i.e., similar active areas as measured in terms of the acoustic wavelength) the sensitivity to EA using the pyr complex was found to be about 3.4 times that of the 30-MHz device over the concentration range of 200–1200 μg/L. According to eq 2, an increase of $52^2/30^2 = 3$ would be expected theoretically, which is in reasonable agreement with the data.

CONCLUSIONS

The use of a SAW sensor coated with reagents of the general formula *trans*-PtCl$_2$(ethylene)(substituted-pyridine) for real-time measurement of various olefin gases and vapors has been described. It has been shown that subtle differences in the steric properties of olefins lead to a high degree of selectivity for the relatively unhindered olefins. Positional isomers can be completely discriminated, and appreciable differences in response are seen even for geometric (cis/trans) isomers. The consistent trend observed across three series of olefins indicates that the steric effects are quite general. Thus, similar molecular selectivity would be expected within other groups of olefins.

As shown here for ethyl acrylate, and previously for styrene[16] and vinyl acetate,[14] use of Pt–olefin π complexes as SAW sensor coatings provides responses to olefins that are unaffected by the presence of a range of non-olefin organic vapors. These findings thus also appear to be general. While not unexpected, the practical significance of these results should not be underemphasized since this degree of selectivity is not generally possible with commercial organic vapor detectors.

The ability to regenerate the reagent complex by exposure to ethylene gas was demonstrated following exposure to ethyl acrylate. For prolonged exposure, the response of the regenerated coating was lower than that of the original coating owing, presumably, to structural changes within the reagent solid. For short-term exposures, however, the regenerated-coating responses were the same as the original coatings. In practice a means for periodic regeneration would be necessary to maintain the initial calibration for extended monitoring periods.

This work highlights several advantages of reagent SAW sensor coatings over sorptive-polymer coatings for measurement of this class of organic compounds. In addition to the unusually high selectivity obtained, the reagent coatings allow detection of low concentrations of gases which have small polymer/air partition coefficients and therefore low responses with polymer-coated sensors. Increasing the temperature of the reagent-coated sensor leads to increased sensitivity (and selectivity, in some cases) whereas increasing the temperature of polymer-coated sensors decreases sensitivity. This adds a measure of flexibility to the reagent-coating approach. Finally, increasing the operating frequency of the sensor increases the sensitivity of responses using the reagent coating, in contrast to polymer-coated sensors.

The influence of electronic factors was apparent in some of the results obtained in this study. A more systematic investigation of substituent-related electronic factors is currently being performed, and preliminary results indicate very large differences in response depending on the electron-withdrawing/donating strengths of substituents on both of the olefins and the pyridine–ligand in the complex. Once the influence of these factors are more completely characterized, it may be possible to modulate both steric and electronic effects by judicious of ligands in the complex to provide even greater control over the response selectivity of the sensor.

ACKNOWLEDGMENT

This work was supported by research grant 5-RO1-2663-02 from the National Institute for Occupational Safety and Health of the Centers for Disease Control.

RECEIVED for review December 11, 1991. Accepted March 17,1992.

---

[37] Grate, J.; Klusty, M. *Anal. Chem.* **1991**, *63*, 1719–1727.