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STUDY OF THE KINETICS FOR A CATALYZED REACTION USING GAS CHROMATOGRAPHY

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SUMMARY

A technique was used which allowed us to study the kinetics of vapor phase catalysis reactions occurring in a gas chromatographic column. The chemical "reactor" is actually the front section of the chromatographic column in the injection port of the chromatograph. The first order decomposition of isopropanol over MnO was the model reaction with which the system is demonstrated. A series of experiments at various flow-rates and temperatures was conducted in order to obtain the kinetic data. Analysis of these data indicated excellent agreement with literature values for the activation energy of the reaction.

INTRODUCTION

In recent years gas chromatography (GC) has been recognized by the catalyst industry as a powerful tool having both analytical and non-analytical applications in the research and development of catalysts. One important non-analytical application is the determination of mechanisms, kinetics and thermodynamics of chemical reactions.

There are two approaches to the utilization of GC in studies of kinetics and catalysis. The first is the microcatalytic technique developed by Kokes et al.[1]. In this method the effluent from a micro-reactor chamber is diverted to a gas chromatograph which is fitted with an analytical column used for separating the products and reactants. In the second method, the on-column catalysis or chromatographic reactor approach, both the catalytic effect and the chromatographic separating power of the catalyst are used simultaneously. Bassett and Habgood[2] pointed out that in this technique one could determine the extent of adsorption of the reactant under experimental conditions and thus, the rate constant for the reaction at the catalytic surface.

In the described work a very simple combination of the two techniques was used in order to study the kinetics of a vapor phase catalysis reaction. A small amount of catalyst was placed in the front section of a chromatographic column. The injection port of the gas chromatograph controlled the temperature of the catalyst bed.

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The catalyst bed was followed immediately by an analytical column for the separation of products from unreacted starting material. A small glass-wool plug was used to separate the catalyst bed from the analytical column. In order to test the feasibility of this system, the decomposition of isopropanol over MnO was studied. This reaction is frequently used as a model in studies of catalytic activity of non-metallic catalysts[3,4].

EXPERIMENTAL

Chromosorb W AW DMCS (60–80 mesh) obtained from Supelco (Bellefonte, PA, U.S.A.) was used as the inert support for the analytical column. The liquid stationary phases, SP-2401 and Carbowax 1500 also purchased from Supelco, were coated on the support with loadings of 20 and 0.1 %, respectively. The coated material was packed in a 12 ft. × 0.25 in. O.D. glass column, leaving only the section that fits into the injection port to be filled with the catalyst. Manganese(II) oxide (99 %+) was obtained from Chemetals Corporation (Baltimore, MD, U.S.A.) and sieved to a constant mesh range size (60–80 mesh) suitable for packing in the chromatographic column. The front of the column was packed with 1.110 g of this catalyst. The temperature of the catalyst bed was monitored by a thermocouple pyrometer with parallax correction mirror. For measurements of retention volume of the reactant on the catalyst, a 15 in. × 2 mm I.D. glass column packed with 2.596 g of MnO was used. A Varian Model 1840-1 gas chromatograph equipped with dual flame-ionization detectors was connected to a Vidar Autolab digital integrator. The helium carrier gas was dried and purified over molecular sieve and indicating calcium chloride and regulated by a differential flow controller.

Isopropanol and acetone were "Photrex" reagent-grade (suitable for use in ultraviolet spectrophotometry) and obtained from J. T. Baker (Phillipsburg, NJ, U.S.A.). Pure reactant vapor was injected by means of a 500-μl Hamilton gas-tight syringe (with a Chaney adapter) after sampling the headspace of a previously evacuated, carefully thermostatted vial fitted with a screw cap Mininert valve. The vial was completely filled with the pure isopropanol liquid and after putting the Minenert value in place, a large bore syringe needle was inserted through the septum. Approximately half the liquid in the vial was withdrawn by vacuum into a trap. This ensures that the entire headspace above the remaining liquid is pure isopropanol vapor in equilibrium with isopropanol liquid. The vial and gas-tight syringe were then thermostatted at 31.0°C, just slightly above ambient temperature. Because of the small difference in temperature, problems such as condensation or adsorption of the reactant vapor on the syringe wall were not encountered. The gas-tight syringe, block heater for thermostatting, vial and Mininert valve were all obtained from Supelco. This headspace sampling was necessary so as to remain within the linear region of the adsorption isotherm and not overload the column and/or the detector.
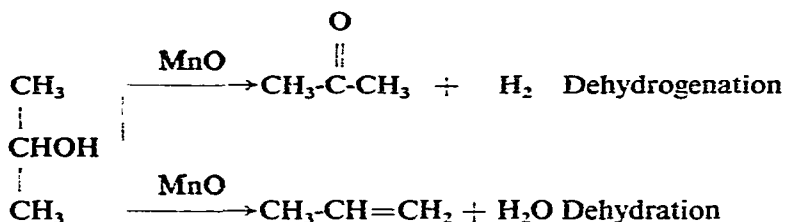
RESULTS AND DISCUSSION

Several workers[5–7] have described experimental set-ups for studying reaction kinetics using GC. These often require special switching valves, pressure regulators,

traps for products and reactants prior to separation and other equipment modifications. Even a set-up such as that described by Choudary[8], in which no modifications of the GC unit itself are made, still requires special valves and design of an appropriate microreactor chamber.

In this work a study was undertaken to determine the feasibility of using a single GC column filled with an analytical packing and a small amount of catalyst in the injection port section of the column, for obtaining kinetic data on vapor phase catalysis reactions. Injections would be made via a gas-tight syringe and no special traps would be necessary. Initial reservations regarding inadequate temperature control of the catalyst bed by the injection port heater were proven to be unfounded.

In using the GC method for kinetic measurements, generally only first-order or pseudo first-order reactions permit quantitative studies. This is because the partial pressure of the reactant varies from point to point through the reactant pulse, and it is only for a first-order reaction that the fractional conversion of reactant to products is independent of pressure. A second criterion for using the GC method for kinetic studies is that the rate of adsorption must be fast relative to the rate of the surface reaction for the latter to be the rate controlling stop. With this in mind the reaction chosen for this investigation was the catalytic decomposition of isopropanol vapor on manganese(II) oxide. The two main paths of this decomposition are:

$$
\begin{array}{c}
\text{CH}_3 \\
| \\
\text{CHOH} \\
| \\
\text{CH}_3
\end{array}
\quad
\begin{array}{c}
\xrightarrow{\text{MnO}} \text{CH}_3\text{-C-CH}_3 \;+\; \text{H}_2 \quad \text{Dehydrogenation} \\
\overset{\overset{\text{O}}{\|}}{} \\
\\
\xrightarrow{\text{MnO}} \text{CH}_3\text{-CH}=\text{CH}_2 + \text{H}_2\text{O} \quad \text{Dehydration}
\end{array}
$$

The dehydrogenation reaction predominates at all temperatures with an average selectivity of 0.80 (ref. 4). However, under the conditions of the reaction in this investigation only the dehydrogenation and not the dehydration reaction was observed.

Initially, a series of injections of varying amounts of pure isopropanol vapor were made in order to determine an amount that would be consistent with remaining on the linear portion of the adsorption isotherm, since this is a requirement for the subsequent data analysis. This study revealed that this could be accomplished only by head-space sampling of pure isopropanol vapor. The amount of reactant (isopropanol) injected is then calculated by using the ideal gas law ($PV = nRT$), where P is the vapor pressure of the pure vapor at the temperature at which the vials are thermostatted and V is the volume injected from the gas-tight syringe. Corrections for deviations from ideality by use of virial coefficients were found to be unnecessary.

The catalysis was carried out at five different flow-rates from 10 to 40 cm^3/min of helium at a constant injector temperature, in order to test the first order rate law and determine the rate constant for the surface reaction. Fig. 1 shows a sample reaction chromatogram. As will be seen later, it was necessary to collect experimental data to obtain values for a Van 't Hoff plot. This experiment consisted of determination of the corrected retention volumes of the reactant on the catalyst at a series of temperatures and constant flow-rate. Values for the Arrhenius plot were determined
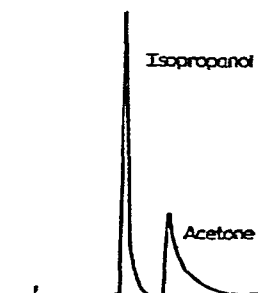
Fig. 1. Chromatogram of unreacted isopropanol plus product (acetone) from the dehydrogenation of isopropanol on MnO. Operating conditions: column, 12 ft. × 1/4 in. O.D. × 2 mm I.D. glass, packed with 20 % SP 2401 + 0.1 % Carbowax 1500; amount of catalyst, 1.110 g 60–80 mesh MnO. Flow-rate, 28.3 cm³/min; helium; injector (catalyst) temperature, 198°C; column temperature, 100°C. Amount injected: 400 μl of isopropanol vapor maintained at 31.0°C.

by varying the temperature of the catalyst bed between 150 and 200°C at a constant flow-rate.

Calibration of the resultant chromatographic peaks was accomplished by injection of controlled amounts of acetone at the conditions of each catalysis run. Again, it was necessary to use headspace sampling so as to remain within the linear region of the adsorption isotherm. Acetone may undergo condensation reactions on MnO, but under the conditions used in this investigation (198°C) these were not observed. A material balance of product and reactant was calculated in order to confirm this.

Analysis of the chromatographic data was performed according to the treatment outlined by Bassett and Habgood[2]. Briefly the treatment is as follows. For a rate-controlled surface reaction, the instantaneous rate of reaction of the adsorbed reactant in a section of catalyst is given by:

$$(-) \frac{dn}{dt} = \frac{kKnRT}{(V_g + V_r)} \tag{1}$$

where k is the first-order rate constant of the surface reaction, K is the adsorption equilibrium constant given by $K = V_r/(RT)$, n is the number of moles of reactant, R is the gas constant, and T is the temperature of the catalyst. V_g is the volume of gas space in a section of the reactor containing 1 g of catalyst and V_r is the chromatographic retention volume for 1 g of catalyst, measured at column temperature and corrected for column dead space. Summing over the catalytic reactor and integrating gives an equation of the form:

$$\ln [1/(1 - x)] = \frac{kKRT}{(V_g + V_r)} t \tag{2}$$

where x is the fractional conversion and t the residence time of the pulse. If the flow-rate of carrier gas in the reactor is F (cm³/sec) at column temperature, T, and mean pressure, P, and W is the total weight of catalyst, t can be given by:

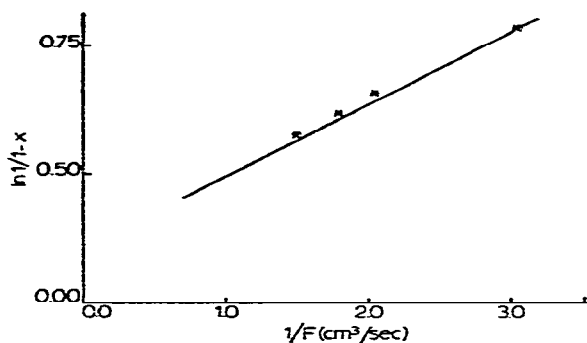$$t = \frac{(V_g + V_r) W}{F} \tag{3}$$

Fig. 2. Plot of ln $[1/(1 - x)]$ *vs.* $1/F$ for decomposition of isopropanol on 1.110 g MnO at 192°C. $kK = 2.72 \cdot 10^{-6}$ mole/atm·g·sec.

Substituting for t gives:

$$\ln [1/(1 - x)] = \frac{RTW}{F} kK \tag{4}$$

This result is analogous to the equation giving the conversion in a conventional flow reactor under steady state conditions, and holds for a catalyst column of any length.

Once x has been calculated from the chromatographic data, it can be seen from eqn. 4 that a plot of ln $[1/(1 - x)]$ *vs.* $1/F$ will yield a straight line whose slope is proportional to the product of the rate constant for the surface reaction and the adsorption equilibrium constant. Fig. 2 depicts this plot, with the product kK equal to $2.72 \cdot 10^{-6}$ mole/atm·g·sec.

In order to determine k one must first find the value of K from a plot of ln V_r^0 *vs.* $1/T$, as shown in Fig. 3. From the slope of this plot one can also determine ΔH_{ads} for the reaction.

The apparent activation energy, E_a, may be obtained from the slope of a plot of ln kK *vs.* $1/T$, and at constant flow-rate, this is equivalent to a plot of ln $[\ln 1/(1 - x)]$ *vs.* $1/T$ (Fig. 4). For the isopropanol decomposition on MnO the apparent activation energy obtained from this graph is 29.1 kcal/mole. One can subseuqently determine
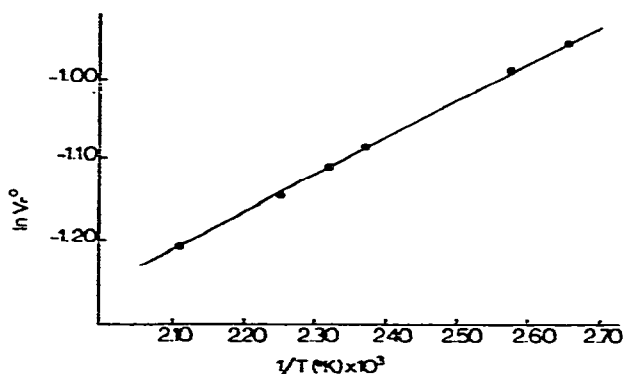

Fig. 3. Plot of ln V_r^0 *vs.* $1/T$. $\Delta H_{ads} = 0.847$ kcal/mole; $K = 3.498 \cdot 10^{-6} e^{847/RT}$.

the activation energy of the surface reaction (29.9 kcal/mole) by summing the apparent activation energy and the heat of adsorption from the plot of ln V_r vs. $1/T$. This value is in good agreement with the value of 30 ± 2 kcal/mole found for a steady-state flow reactor[4] and the earlier value of 31.9 kcal/mole from adsorption coefficients[9].
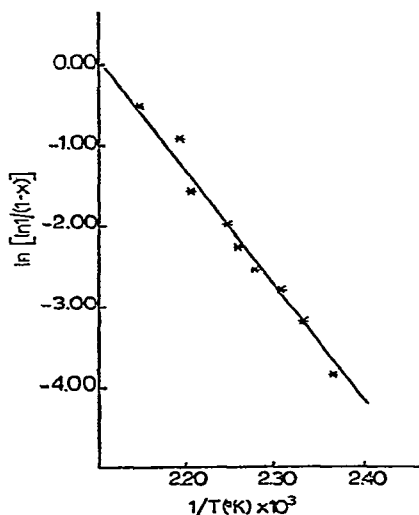

Fig. 4. Arrhenius plot at constant helium flow-rate (27.5 cm³/min). Energy of activation equals 29.1 kcal/mole.

CONCLUSION

The kinetics of a reaction occurring in the vapor phase on a non-metallic catalyst may be determined using a very simple GC technique. Control of the various parameters (e.g., flow-rate, temperature, pressure, weight of catalyst and amount of reactant) enables one to calculate reliable data from a dynamic system. Hopefully, the applications of this technique may be extended to studies of catalyst selectivity and predictions of optimum conditions as well as the best possible catalyst for a given reaction.

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