

Kinetics of Quadricyclene-Norbornadiene Isomerization Reaction for Use in Modeling Supported Liquid-Phase Catalysis

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The isomerization kinetics of quadricyclene (tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane) to norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) was chosen as a reaction appropriate to the study of supported liquid-phase catalysis (SLPC). An infrared spectrophotometer, modified to permit measurement of reaction rates with half-lives of ~ 1 sec, was used to determine the intrinsic rate constant and its temperature dependence. These quantities are essential in evaluating SLPC systems.

INTRODUCTION

Homogeneous liquid-phase catalysis has found widespread use in chemical synthesis. Compared to heterogeneous catalysis, homogeneous catalysts offer significant advantages. However, the difficulties in separating catalyst from product as well as the loss of expensive catalyst by entrainment are severe drawbacks in many applications. A supported liquid-phase catalyst (SLPC) provides a method for eliminating these disadvantages.

Catalysts of this type, in which the pore walls of the porous support are coated with a catalytic liquid as shown in Fig. 1, have been considered in several experimental studies, and at least three investigators have presented mathematical models for predicting effectiveness factors in SLPC (1-4). To date, the testing of such models has been mainly qualitative and at best semiquantitative, indicating the need for a more quantitative method. The difficulties of conducting such a test include: (i) adequate representation of the homoge-

neous kinetics, (ii) maintenance of catalyst stability, and (iii) elimination of gas-film diffusion resistance as well as other problems typical of heterogeneous kinetics. Initiation of a test requires the acquisition of a catalyst-solvent reaction system with the following desirable properties: (i) The homogeneous reaction within the liquid phase must take place at a rate sufficiently high so that intrapellet gas-phase diffusion limitations exist. (ii) The reaction rate must be variable over a wide range so as to approximate the restriction on liquid-phase diffusion rates incorporated within the models. (iii) The intrinsic homogeneous kinetics must be well known to allow proper interpretation of SLPC results. (iv) Catalyst activity must be constant during the time required to reach steady state and to measure conversion. (v) The reaction condition must exist for which there are no bulk diffusion resistances in the liquid phase.

To simplify the transport equations and the mathematical computations, it is highly

desirable but not essential that a test system for SLPC models also be characterized as follows: (i) There should be only two diffusion components. (ii) There should be no change in mole number or in molecular weight upon reaction. (iii) The reaction should be pseudo-first order. (iv) The solvent for the catalyst should be non-volatile at the reaction conditions. (v) To avoid hindered diffusion in small pores, the reactants and products should have a small molecular size relative to the pore structure. (vi) To permit satisfactory catalyst distribution, the catalyst and solvent molecules should not be too large relative to the support pore structure. (vii) The catalyst solution should be stable for long periods of time.

APPROPRIATE REACTION SYSTEM

An applicable reaction of interest for evaluating SLPC behavior is the valence isomerization of quadricyclene to norbornadiene (C_7H_8) catalyzed homogeneously by cobalt tetraphenylporphyrin (CoTPP). The structural rearrangement is shown in Fig. 2.

This reaction is of considerable interest mechanistically in that it is "thermally forbidden" by the Woodward-Hoffman rules. The literature of the past 10 years is replete with discussions of possible mechanisms for this and similar reactions (5-9);

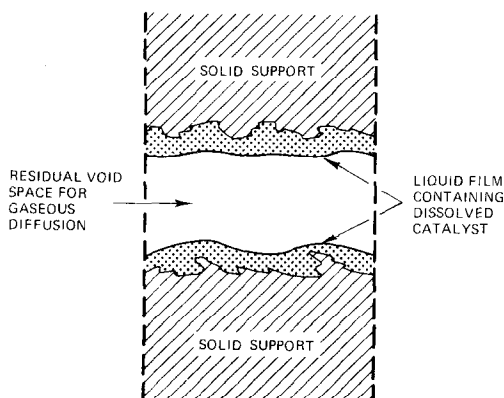


Fig. 1. Section of typical pore in a porous solid support containing liquid catalyst on the pore walls.

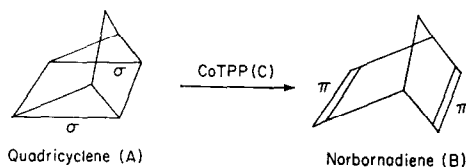


Fig. 2. Structural rearrangement in the isomerization of quadricyclene to norbornadiene.

yet there is a paucity of corroborating rate data. Since this reaction has potentially desirable properties as a model reaction with which to study SLPC and because of its fundamental value in elucidating catalytic mechanisms, it is of particular interest to measure and describe the kinetics of reaction by means of a rate law.

The thermal isomerization of quadricyclene proceeds very slowly. Hammond *et al.* (10) determined a half-life of 14 hr for the thermal reaction at 140°C. Volger and Hogeveen (9) first reported the homogeneously catalyzed isomerization at -26°C. The half-life was determined to be 45 min in a 2% (mole basis) catalyst solution. Manassen (6) reported the isomerization of quadricyclene via CoTPP (concentration 0.01 mol/liter) at 35°C. He found that the rate was too high to measure by the procedures used in his analysis. Consideration of this information resulted in the conclusion that the reaction possesses many properties of interest in regard to studies in SLPC.

The choice of catalyst, cobalt tetraphenylporphyrin, was based on the studies of Manassen (6) who showed that it is extremely efficient for the isomerization. The studies of Rothmund and Menotti (11) showed that CoTPP is extremely stable and that it is a good dye, thus making its concentration easy to determine. In addition, it is relatively soluble in a number of nonpolar organic solvents.

The choice of solvent was dictated by several criteria. Primarily, the solvent must dissolve the catalyst to an appreciable extent, must wet the pore walls of the support material, and must have a viscosity on

the order of water. Secondly, the solvent must have an ir transmission window in an appropriate range to permit kinetic data acquisition by techniques used in the present study. Finally, to be appropriate to SLPC, the vapor pressure of the solvent should be extraordinarily low and certainly no greater than that of ethylene glycol, the solvent used by Acres *et al.* (12) and by Abed and Rinker (1). Moreover, this solvent should not present a significant health hazard. One solvent which satisfies all of these criteria is 1-chloronaphthalene.

EXPERIMENTAL

The synthesis of quadricyclene in the present study follows mainly from the procedure of Manassen (6) except that pretreatment of pentane, used as a solvent, was different. The pretreatment consisted of acid washing the pentane with reagent grade H_2SO_4 and then neutralizing it with NaOH. The pentane was finally water washed and distilled. Use of the modified Manassen procedure gave a yield of about 50 g of 99% quadricyclene by starting with 100 g of norbornadiene. The identification and purity of quadricyclene were obtained by NMR.

The synthesis of cobalt tetraphenylporphyrin follows exactly from the procedure of Rothmund and Menotti (11). A yield of 1 g of CoTPP was obtained by starting with 1.0 g of TPP and 0.5 g of cobalt acetate. The identity of the CoTPP was verified by its visible spectrum which agreed with the previously reported spectrum of Dorough *et al.* (13). TPP in 20% yield was obtained by the procedure of Adler *et al.* (14).

Norbornadiene and 1-chloronaphthalene in 99% purity and pentane in spectrophotometric grade were obtained from Aldrich Chemical Co. Chloroform and carbon tetrachloride were obtained from Mallinckrodt, Inc., in analytical reagent-grade form.

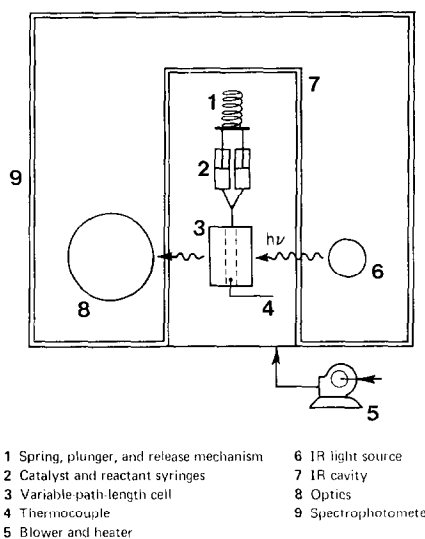


FIG. 3. Schematic of experimental equipment.

The reaction vessel is a variable-path-length liquid ir cell with KBr windows. The cell was obtained from Beckman-RIIC, Inc., and is Model VT-02. Its design is such that it may be readily placed in one of the light paths of a dual beam instrument. A similar cell containing a blank solution may be placed in the second light path and the difference in transmission between the contents of the two cells can be observed. Window parallelism and path-length calibrations were verified by measuring interference fringes during an ir scan.

The cell path-length, though variable, is usually less than 1 mm. This dimension essentially prohibits stirring the contents of the cell; it is necessary that the contents be mixed rapidly and well prior to entering. This process was assured through the use of spring-loaded syringes to force the solutions of reactant and catalyst through a mixing line and into the cell. By means of such an arrangement, 2 ml of solution were mixed and injected into the cell in times less than 0.3 sec and with Reynolds numbers in excess of 4000. A schematic of the experimental equipment is shown in Fig. 3.

When in use, the ir cell is located in a cavity which normally has an increasing

TABLE 1
Range of Reaction Conditions

Solvent	Catalyst concentration (mmol/liter)	Initial quadricyclene concentration (mol/liter)	Temperature (°C)	k' (sec ⁻¹)
Carbon tetrachloride	0.39-0.83	0.025-0.10	22.0-44.0	0.05-0.13
Chloroform	2.1-27.3	0.025-0.10	22.0-42.0	0.06-0.99
1-Chloronaphthalene	2.2-13.4	0.025-0.10	21.8-50.0	0.08-0.41

temperature as a result of infrared heating. To compensate for this nonisothermal behavior, an enclosure was built to isolate the cavity from the ambient, and a centrifugal blower was attached to circulate air through the isolated cavity. The throughput of the blower is in excess of 340 liters/min. In addition, a heater was added to permit control at temperatures above ambient. With this arrangement, it was possible to monitor the reaction over the temperature range of 21 to 50°C. For all but two runs, the temperature inside the reaction cell remained constant within $\pm 0.2^\circ\text{C}$ during the course of the entire run. During the two runs in question, the isomerization rate in 1-chloronaphthalene was measured at low catalyst concentration, thus requiring more than 10 min to complete. In these cases, because of the dipole heating of the solvent, the reaction temperature increased about 1°C during a typical run. Temperatures inside the ir cell were measured with an iron-constantan thermocouple placed inside the cell and in contact with the reaction solution.

The transmission of the cell was monitored with a modified Perkin-Elmer Model 257 dual-beam infrared spectrophotometer. Details of the modifications to permit use of the instrument in rate measurements are given elsewhere (15). This instrument was used for *in situ* concentration measurements of the norbornadiene and to provide identification of product distribution. Prior to each run, a calibration curve for norbornadiene in a particular solvent was established. Solutions of norbornadiene and

quadricyclene were prepared in advance and stored at 5°C . These solutions were stable for several months.

One of the injection syringes, with a capacity of 1 ml, was filled with a quadricyclene solution, and the other syringe was filled with CoTPP dissolved in the same solvent. Both were allowed to equilibrate in the ir cavity until reaction temperature was reached. The chart recorder was started and the spring was released, thus forcing the reactants into the cell. The appearance of norbornadiene was monitored by observing the change in transmission at 1313 cm^{-1} .

Before, during, and after each run, the temperature of the reacting system was recorded. Also, after each run, the reaction mixture was diluted with solvent and the concentration of catalyst was determined by measuring its absorbance on a Bausch and Lomb Model 20 spectrophotometer.

RESULTS

The isomerization of quadricyclene was studied in the range of catalyst conditions shown in Table 1. Three different solvents, including 1-chloronaphthalene, were used to elucidate the solvent effect if any. The reaction was conducted at atmospheric pressure, and the only product formed was norbornadiene.

Using an integral analysis, the first-order dependence of the isomerization reaction on quadricyclene concentration in each solvent at constant temperature and catalyst concentration is shown for typical runs in Fig. 4. A derivative analysis of the data

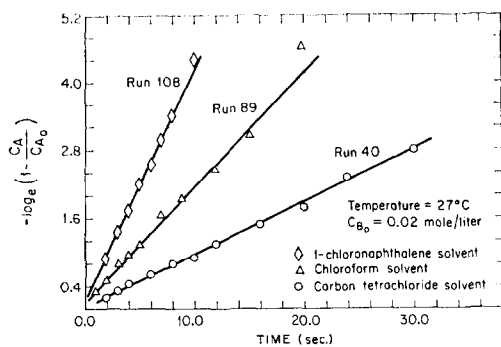


FIG. 4. Integral first-order behavior of quadricyclene isomerization in various solvents.

yields essentially the same result and is shown elsewhere (15). A pseudo-first-order rate constant, k' , was calculated by a non-linear least-squares fit of the data to Eq. (1):

$$C_B/C_{B_0} = 1 - e^{-k't}. \quad (1)$$

The effect of catalyst on the reaction rate in each solvent is shown in Figs. 5 and 6. Note that the reaction is second order with respect to catalyst concentration in 1-

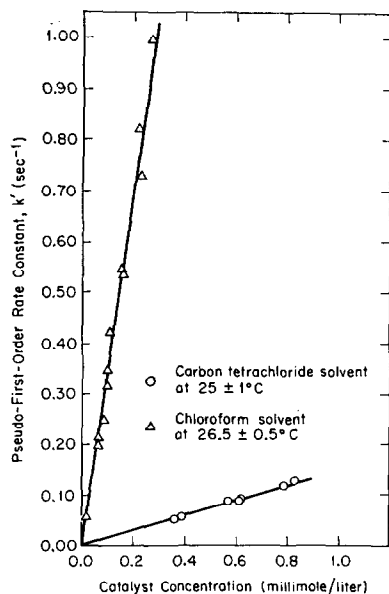


FIG. 5. Effect of catalyst concentration on the specific rate, k' , in carbon tetrachloride and in chloroform.

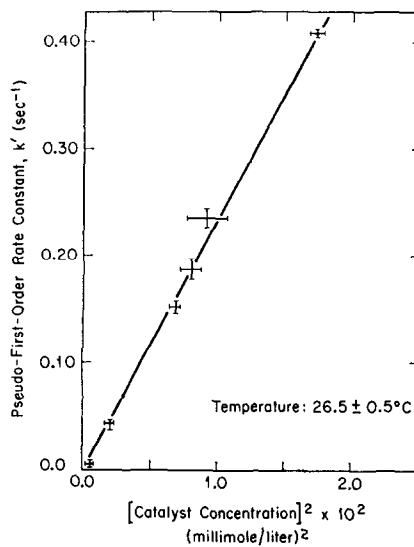


FIG. 6. Effect of catalyst concentration on the specific rate, k' , in 1-chloronaphthalene.

chloronaphthalene and is first order with respect to catalyst concentration in chloroform and in carbon tetrachloride.

The effect of solvent on the temperature dependence of the reaction rate is shown in Fig. 7, wherein the logarithm of the rate constant, k' , is plotted versus reciprocal of

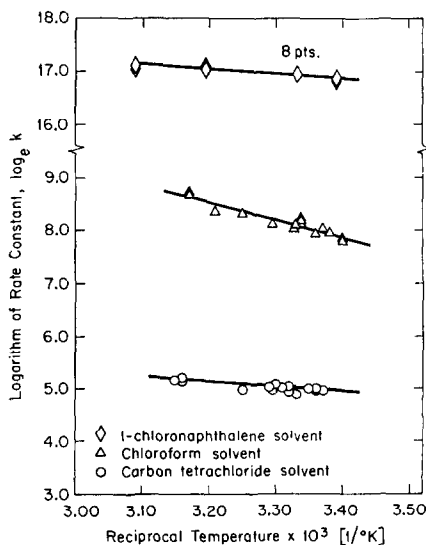


FIG. 7. Effect of solvent and temperature on the specific reaction rate, k .

TABLE 2
Thermal Parameters with 95% Confidence Limits

Solvent	k_0	$\Delta H^\ddagger \times 10^{-3}$ (cal/mol)	n	$\Delta E \times 10^{-3}$ (cal/mol)	ΔS^\ddagger (cal/mol °K)
Carbon tetrachloride	$2.6 \pm 0.30 \times 10^8$ liters mol ⁻¹ sec ⁻¹	1.73 ± 0.18	1	2.32 ± 1.8	-42.8 ± 2.0
Chloroform	$1.75 \pm 0.25 \times 10^8$ liters mol ⁻¹ sec ⁻¹	6.43 ± 1.2	1	7.02 ± 1.2	-20.9 ± 3.0
1-Chloronaphthalene	$3.48 \pm 0.15 \times 10^8$ liters ² mol ⁻² sec ⁻¹	1.61 ± 0.15	2	2.2 ± 0.15	-19.0 ± 1.0

the temperature to form the conventional Arrhenius plot. It is of interest to note that there is only a small temperature dependence in each solvent and that the Arrhenius activation energy, ΔE , is moderately dependent on solvent composition.

The rate of isomerization of quadricyclene for the conditions listed in Table 1 is correlated by Eq. (2).

$$r = k'CA = kCAC^n \\ = k_0 \exp(-\Delta H^\ddagger/RT)CAC^n, \quad (2)$$

where $\Delta H^\ddagger = \Delta E - RT$ and where k_0 is defined by Eq. (3):

$$k_0 = (\bar{k}T/h) \exp(\Delta S^\ddagger/R). \quad (3)$$

The parameters k_0 , ΔE , n , ΔH^\ddagger , and ΔS^\ddagger are listed in Table 2.

Replicate trials indicated that the pseudo-first-order rate constants were reproducible with a standard deviation of 0.01 sec⁻¹ which is seemingly independent of the magnitude of k' within the range of values listed in Table 1. The major sources of uncertainty in the data arose from measurement of catalyst concentration at low concentration levels and from sensitivity of the calculated constant, k' , to the measured parameter, C_{B_w} .

DISCUSSION AND CONCLUSIONS

The isomerization of quadricyclene via CoTPP in 1-chloronaphthalene is a reaction appropriate for use in testing transport models of SLPC. The intrinsic rate for this

reaction is well described by data contained herein. The data indicate that near ambient temperature the reaction rate can be varied over a wide range including the range appropriate for discriminating among various transport models in SLPC. The reaction system also possesses most of the properties desired so as to simply modeling.

Problems encountered by previous workers have been considered and essentially eliminated. An important potential problem which is still unresolved is the question of catalyst deactivation. The reported SLPC systems observed to date have encountered rapid deactivation of the catalyst. That question will not be answered until the present catalyst is tested in a continuous system. Since this catalyst forms no products which attack it, there is a good chance that it will remain relatively stable.

The valence isomerization was also studied in carbon tetrachloride and in chloroform. An effect of solvent was observed. Not only do the transition-state parameters ΔH^\ddagger and ΔS^\ddagger change as a result of different solvents but also the form of the rate law changes. In the solvents investigated, the linear Arrhenius relationship is an adequate representation of the rate dependence on temperature.

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