

SULFUR COMPOUNDS AS CATALYST MODIFIERS
IN THE SELECTIVE HYDROGENATION OF 1,5
CYCLOOCTADIENE TO CYCLOOCTENE

By

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ABSTRACT

Selective hydrogenation of cyclic-diolefins to cyclo-monoenes is a basic route to reactive olefin intermediates for the synthesis of C_8 or C_{12} lactams, dicarboxylic acids, and their derivatives. Frequently the yield to the desired olefin can be improved by the addition of a small amount of material that modifies the system. Sulfur compounds in small amounts have been suggested for this purpose but the type of sulfur compound and the concentration required to enhance the selectivity has not been reported for a palladium catalyst.

Experiments were conducted in a 300 ml autoclave at room temperature, about 25°C , under the hydrogen pressure of 413.7 kPa (60 psig). The results show that the detailed reaction sequence fits the experimental data well when the individual reaction steps are considered first order. With the sulfur containing compounds used in this study, thiophene, C_4H_4S , and mercaptan, $C_{10}H_{21}SH$, thiophene was the best reagent to enhance the selectivity and increase the yield of desired product, cyclooctene. However, the concentration of thiophene should be controlled in a range between 10 to 40 ppm. If excessive amounts of thiophene are employed the reaction remains very selective, but the rate of conversion of 1,5 cyclooctadiene is dramatically reduced; consequently, a low net yield of cyclooctene is obtained. The results also indicate that, at the same sulfur content, the mercaptan, $C_{10}H_{21}SH$, immediately poisoned the catalyst and sharply retarded the hydrogenation rate, resulting in significant low net yields to cyclooctene.

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NOMENCLATURE

C_i	Concentration of compound i, mole/litre
f	Conversion of 1,5 cyclooctadiene
$k', k_1, k_2, k_3, k_4, k_5, k_6$	First order rate constant, $\text{min}^{-1} \text{ g}_{\text{cat}}^{-1}$
t	Time, min.

Subscripts

A	1,5 cyclooctadiene
B	1,4 cyclooctadiene
C	1,3 cyclooctadiene
D	cyclooctene
E	cyclooctane

Superscripts

$^{\circ}$	Initial state
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CHAPTER I

INTRODUCTION/LITERATURE REVIEW

The objective of this work was to investigate the use of sulfur compounds to improve the selectivity for preparing cyclic-monoenes by hydrogenation of the corresponding cyclodiolefins over supported palladium catalyst in the liquid phase. Selective hydrogenation of cyclo-diolefins to cyclic-monoenes is the basic route to prepare a reactive intermediate for the synthesis of C_8 or C_{12} lactams, dicarboxylic acids, and their derivatives (Hanika et al., 1981; Nowack et al., 1985). One of the potential uses of cyclooctene (COE) is its oxidation to suberic acid which can be used for synthesis of special oils, plasticizers, polyesters, polyimides, etc. In spite of the fact that the sulfur compounds are known poison for the hydrogenation reaction, a number of previous investigations (Genas et al., 1967; Komiyama et al., 1975; Karanth et al., 1975; Lechercq et al., 1981; Pearce et al., 1981; Hughes, 1984) have indicated that a small amount of sulfur compounds improved the selective hydrogenation of diolefins to monoenes. However, no systematic study of the various types of the sulfur compounds such as sulfide, mercaptan, and disulfide has been reported. Therefore, a systematic study of the effect of the sulfur compounds on the selective hydrogenation was made and the effect of the various types of sulfur compounds on rate reaction and selectivity clarified.

This study resulted in a recommendation that thiophene is the most effective type of sulfur compound for selective hydrogenation. In addition, the previously advanced reaction mechanism reactions for preparation of cyclic-olefins were tested and compared with the results obtained during this investigation with and without sulfur compounds.

The selective hydrogenation of cyclooctadienes (COD) using soluble transition metal complexes was extensively studied (Itatani et al., 1972; Terasawa et al., 1978; Fuji et al., 1978; Strukul et al., 1979; Hirai et al., 1981; Fragale et al., 1984) with a wide variety of catalysts such as $\text{NiI}_2(\text{O}_3\text{P})_2$, $\text{PtCl}_2(\text{O}_3\text{P})_2 + \text{SnCl}_2$, $\text{PdCl}_2(\text{O}_3\text{P})_2 + \text{SnCl}_2$, $[\text{Ir}(\text{COD})\text{L}_2]\text{PF}_6$, etc. The homogeneous catalysts have been studied more extensively than any heterogeneously catalyzed hydrogenation reactions (Johnson et al., 1972; Johnson et al., 1975; Hanika et al., 1980; Ruman et al., 1982; Morelli et al., 1974; Lalancette, 1974; Pickles, 1967).

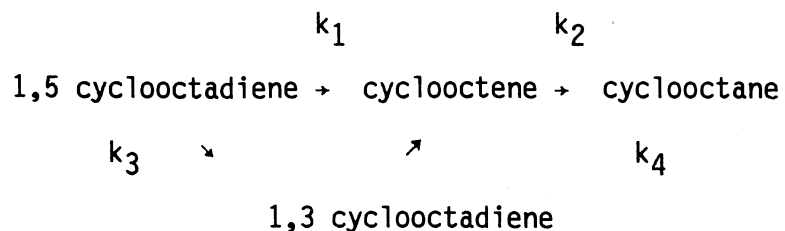
In all of these catalytic reactions, isomerization took place with or preceded hydrogenation. The rates of isomerization of 1,5 cyclooctadiene to 1,4 and 1,3 isomers on the platinum catalyst were measured and the composition of an equilibrium mixture was determined by Tayim et al. (1957). Also, isomerization with the nickel catalyst and those containing platinum was reported and compared by Itatani et al. (1967). Itatani indicated that nickel catalyst resulted in less isomerization than either platinum or palladium catalysts. They also pointed out that the rapid migration of double bonds of 1,5 cyclooctadiene occurs to form the conjugated 1,3 cyclooctadiene and the succeeding hydrogenation to cyclooctene, but not to cyclooctane (COA), followed pseudo first-order kinetics, after a short induction period.

In addition to the transition soluble metal complexes, the selective hydrogenation of cyclooctadienes catalyzed by colloidal palladium in Poly (n-vinyl-2 pyrrolidone) was investigated by Hirai et al. (1981). Their results showed that, for the hydrogenation of 1,5 cyclooctadiene, the catalytic activity of the colloidal palladium was 2.7 times greater than that of 0.5% palladium on activated charcoal and the selectivity of cyclooctadiene to cyclooctene was much higher with the colloidal catalyst than with the homogenous palladium complex and polymer-bound Pd(II) complexes.

The isomerization of 1,5 cyclooctadiene to cis-Bicyclo [3.3.0] oct-2-ene, 1,4 cyclooctadiene, and 1,3 cyclooctadiene catalyzed by transition metal complexes, such as Pd(II), Rh(I), Ru(II), Pt(0), Pt(II), Mn(II), and Ni(II) complexes was studied by Nishiguchi et al. (1975) under various reaction conditions.

In their studies, Ni(II) complexes were found to have excellent catalytic activities for the isomerization to the bicyclic compound. The effect of reaction solvent, additives, reaction temperature, reaction time, catalyst concentration, and 1,5 cyclooctadiene concentration were investigated using $\text{NiBr}_2(\text{PBU}_3)_2$ as a catalyst. A modified π -allyl mechanism was also proposed for the isomerization.

Hanika et al. (1981) studied the kinetics of hydrogenation of 1,3 cyclooctadiene, 1,5 cyclooctadiene, and cyclooctene on supported palladium catalysts. The rates of hydrogenation of cyclooctadiene isomers and cyclooctene were measured and compared. The reaction system could be well described by a kinetic model, depicted below, in which the individual reaction steps were assumed the 1st order.



Moreover, the highest selectivity for hydrogenation of 1,5 cyclooctadiene to cyclooctene was obtained with a Pd/Al₂O₃ catalyst similar to those used in this study. It was also observed that 1,3 cyclooctadiene was hydrogenated 3.5 time faster than 1,5 cyclooctadiene, probably owing to the favorable effect of the double bond conjugation in 1,3 cyclooctadiene. Therefore, they suggested that the migration of the double bonds was induced by the strain in eight membered ring with two double bonds and the tendency to form a system of conjugated double bonds, which necessarily involved interim formation of the 1,4 isomer. Their results also indicated that the rate of hydrogenation of 1,5 cyclooctadiene on the supported catalysts was 3-4 times higher than the rate of isomerization and the subsequent hydrogenation of cyclooctene was essentially slower. Thus, the high and flat maximum for the concentration of cyclooctene was achieved and it was possible to obtain cyclooctene in the reaction mixture at the olefin concentration of 97-99% mol.

In addition to the kinetics of hydrogenation of cyclooctadiene isomers, Hanika et al. (1981) investigated the effect of internal diffusion on the selective hydrogenation of 1,5 cyclooctadiene to cyclooctene using both powder and tablet catalysts with 0.6% (by wt.) palladium on Al₂O₃. The results obtained showed that the retarding effect of intra-particle diffusion of the reaction components in porous catalysts. The results showed both the expected lowering of the

reaction rates and a significant selectivity decrease to cyclooctene with the use of tablet catalyst. To avoid these intraparticle diffusion effects and accompanying decrease in selectivity (Tamaru., 1951; Mars et al., 1964), catalyst with all the palladium deposited in the outside surface of the catalyst particles are used for the industrial preparation of the cyclic-olefin from the corresponding diolefin.

Ruman et al. (1982) studied the hydrogenation of 1,5 cyclooctadiene to cyclooctene at 68-70°C and 0.25 MPa in the presence of a palladium catalyst. The hydrogenation was accompanied by isomerization of 1,5 cyclooctadiene to 1,3 cyclooctadiene and 1,4 cyclooctadiene. The formation of cyclooctane under the given condition was low with 97% conversion of 1,5 cyclooctadiene and 94% selectivity to cyclooctene.

Nowack et al. (1986) investigated the selective hydrogenation of 1,5 cyclooctadiene to cyclooctene in a very high yields. In their experiments, 1,4 cyclooctadiene was hydrogenated in the presence of a catalyst composition comprising palladium on alumina and on an aluminum phosphate support, $\text{Pd}/\text{Al}_2\text{O}_3$ and Pd/AlPO_4 respectively. The palladium content ranged from about 0.1 to about 20% wt. at the pressure range from 15 psia to 5,000 psia and the reaction temperature from 16°C to 93°C. The experimental results showed that, at equal conversion of 1,5 cyclooctadiene, the selectivity to cyclooctene was higher for Pd/AlPO_4 catalyst than for $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst. Moreover, the selectivity to cyclooctene at comparable conversion of 1,5 cyclooctadiene to cyclooctene on Pd/AlPO_4 catalyst was even higher when lithium methoxide or lithium methoxide plus a small amount of carbon monoxide, CO, was used with the Pd/AlPO_4 catalyst. This work was directed at optimizing the large scale production of cyclooctene from cyclooctadiene and

pointed out the effect of catalyst modifier such as CO to increase selectivity. The addition of sulfur compound to improve the selectivity to cyclooctene was not considered by Nowack.

CHAPTER II

EXPERIMENTAL SYSTEM AND PROCEDURE

The basic objective of this study was to investigate the effects of sulfur compounds, thiophene and 1-decanethiol, on the hydrogenation of 1,5 cyclooctadiene using palladium on $\gamma\text{-Al}_2\text{O}_3$ as a catalyst. The dependence of selectivity to cyclooctene on the various concentrations of the sulfur compounds was studied and the kinetic models previously described in the literature were used to determine the rate constants for the separate steps.

Experimental

Chemicals

1,5 cyclooctadiene (Eastman Kodak Company), b.p. 149°C lit., n_D^{20} 1.4931, density 0.882

Cyclohexane 99% mol pure (Fisher Scientific), b.p. $80.7 \pm 0.1^\circ\text{C}$, density 0.779

Hydrogen (Big 3 Industries, Inc., Houston, Texas) UN 1049, 99.9% mol.

Thiophene b.p. 84°C , n_D^{20} 1.5278, density 1.070

1-decanethiol, 97% mol pure, b.p. $114^\circ/13\text{ mm}$, n_D^{20} 1.4536, density 0.841

Catalyst

S. D. 143, 0.3% palladium on γ - Al_2O_3 (Calsicat Chemical Company), pellet 3.5 mm in diameter, specific surface area $31 \text{ m}^2/\text{g}$, pore volume 0.036 ml/g , pore diameter 462°A . The catalysts were crushed and screened prior to use (grain size between $149 \text{ }\mu\text{m}$ and $1000 \text{ }\mu\text{m}$.) All the palladium was deposited on the surface of the catalyst.

Apparatus and Procedure

In each experiment, a constant volume batch reactor, a 300 ml Autoclave Engineer, connected to a hydrogen source was charged with 1.0 gram of 0.3% palladium on γ - Al_2O_3 catalyst, 90 ml of cyclohexane, and 10 ml of 1,5 cyclooctadiene. The hydrogen pressure was held constant at 413.7 kPa (kN/m^2).

In examining the dependence of the selective hydrogenation of 1,5 cyclooctadiene to cyclooctene on the amount of sulfur compounds, various amounts of thiophene: $1.0 \text{ }\mu\text{l}$; $3.0 \text{ }\mu\text{l}$; $6.0 \text{ }\mu\text{l}$, and 1-decanethiol: $1.0 \text{ }\mu\text{l}$; $7.9 \text{ }\mu\text{l}$, were added into the solution of 90 ml of cyclohexane and 10 ml of 1,5 cyclooctadiene with 1.0 gram of 0.3% palladium on γ - Al_2O_3 as a catalyst.

The reactor was flushed free of air by repeatedly filling with hydrogen, H_2 , and venting to the atmosphere several times. After that, hydrogen was charged into the reactor in such a fashion that a constant pressure at 413.7 kPa (60 psig) was held in the reactor. Then the mixture was stirred at 600 rpm and at room temperature. During the experiment, the progress of the reaction was monitored by periodically sampling the reaction mixture, every hour, until 1,5 cyclooctadiene was almost completely converted to products.

Analyses

The progress of the reaction was monitored by periodically sampling the reaction mixture. One micro litre samples were injected into a Hewlett Packard 5880 A gas-chromatograph equipped with a Hewlett-Packard 5880 A integrator. A 9.0 meter Carbowax column was used with helium as a carrier gas.

The relative retention times: cyclooctane 1.0, cyclooctene 1.11, 1,3 cyclooctadiene 1.3, 1,4 cyclooctadiene 1.4, 1,5 cyclooctadiene 1.76.

Products were identified by direct comparison with actually prepared samples made with reagent grade starting reactants. GC/MS was run on one of the samples at Phillips Petroleum to verify the identification.

CHAPTER III

RESULTS AND DISCUSSION

Run 6 (Preliminary Experiment)

A preliminary experiment was made to select a suitable hydrogen pressure and an appropriate amount of catalyst for use in this study to convert all of the 1,5 cyclooctadiene to products in a reasonable period of time. The hydrogenation of 1,5 cyclooctadiene was first studied in the absence of a sulfur compound using 1.0 gram of 0.3% wt. Pd/Al₂O₃ catalyst with 90 ml of cyclohexane and 10 ml of 1,5 cyclooctadiene in a 300 ml autoclave at room temperature, about 25°C, under the hydrogen pressure of 413.7 kPa (60 psig). After 1440 minutes, the 1,5 cyclooctadiene was completely converted to products as shown in Figure 1. The concentration of cyclooctene obtained was 94.4% mol, and the concentration of cyclooctane was 5.7% mol. The amount of cyclooctane increased rapidly after the disappearance of 1,5 and 1,4 cyclooctadiene. At this point, $t = 1440$ minutes, the selectivity to cyclooctene of the obtained product was 94.4%. The selectivities to cyclooctene and the corresponding conversions of 1,5 cyclooctadiene are tabulated in Table I and also plotted in Figure 2. As may be seen from examinations of this figure, the selectivity to cyclooctene was very high at low conversion of 1,5 cyclooctadiene and progressively decreased with increased conversion.

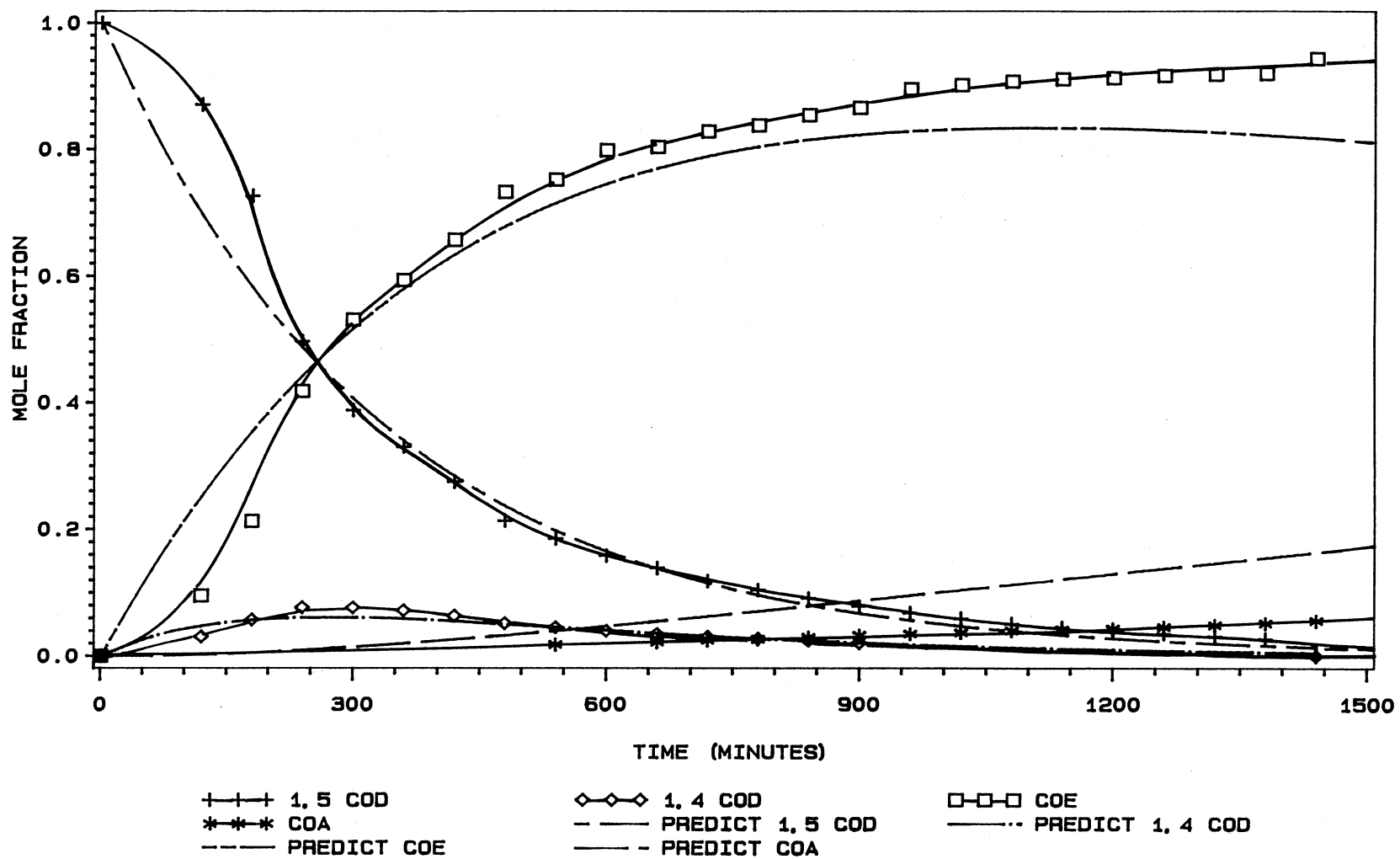


Figure 1. Hydrogenation of 1,5 Cyclooctadiene in Run 6

TABLE I
RUN 6 (NO SULFUR COMPOUND)

Time (min)	% Conversion 1,5 Cyclooctadiene	% Selectivity to Cyclooctene*	Conversion f	$\ln \frac{1}{(1-f)}$
240	50.4	--	0.504	0.703
420	72.5	--	0.725	1.212
660	86.1	97.8	0.861	1.973
780	89.6	96.8	0.896	2.214
900	92.1	96.6	0.921	2.538
1020	94.0	96.0	0.940	2.814
1140	95.5	95.5	0.955	3.101
1260	96.5	95.2	0.965	3.352
1380	97.8	94.8	0.973	3.612
1440	--	94.4	--	--

* Cyclooctene yield divided by total yield of cyclooctene and cyclooctane.

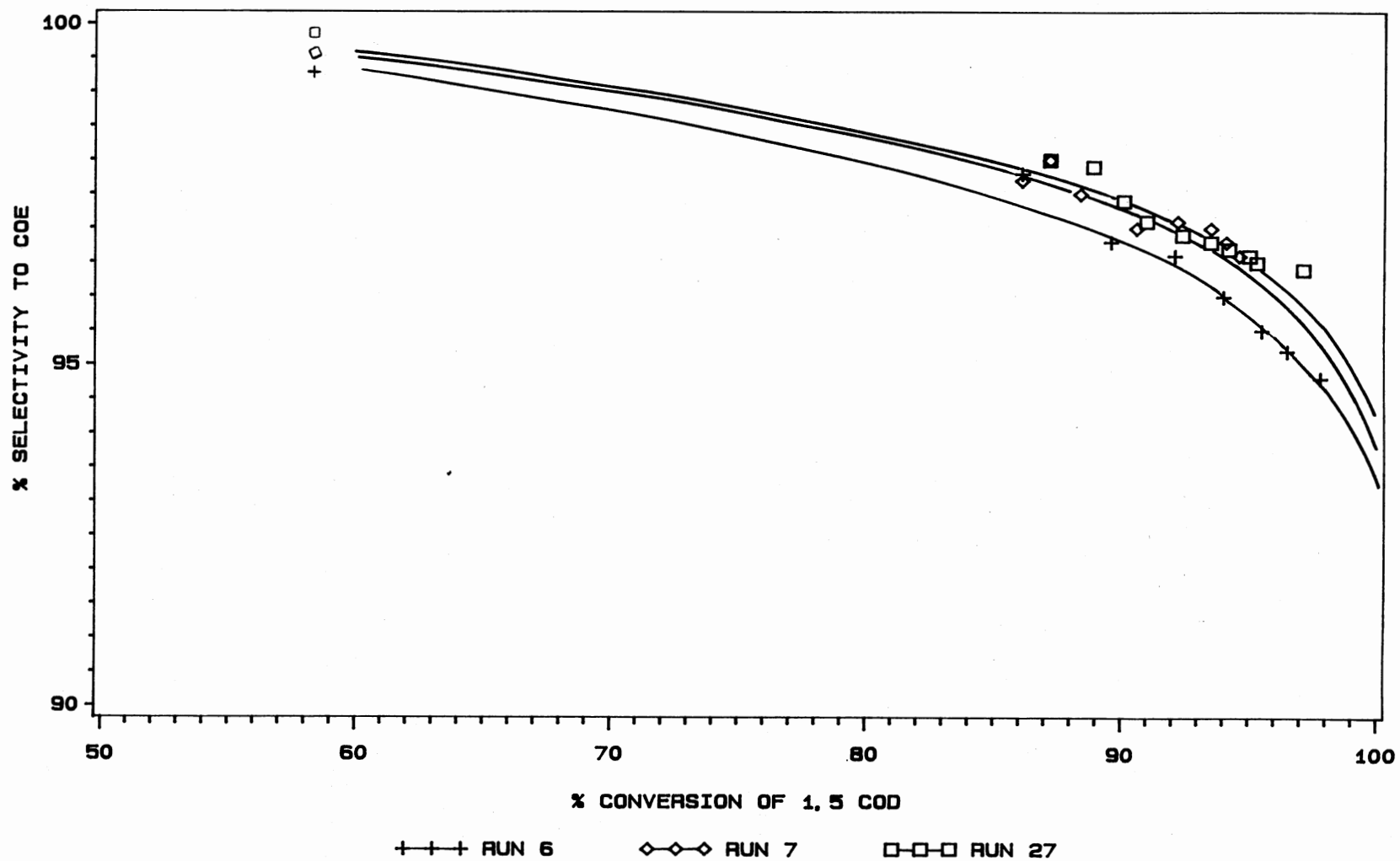


Figure 2. % Selectivity to COE vs. % Conversion of 1.5 COD

Analyses of the reaction mixture by gas chromatography clearly indicated the formation of 1,4 cyclooctadiene in the earlier stages of the hydrogenation reaction. The maximum concentration of 1,4 cyclooctadiene obtained was about 8% mol at $t = 240$ minutes and 1,4 cyclooctadiene was virtually absent after 960 minutes. However, 1,3 cyclooctadiene was not detected in the reaction mixture at any time during this run. This suggests that the rate of hydrogenation of 1,3 cyclooctadiene was much faster than that of the isomerization of 1,5 cyclooctadiene to 1,3 cyclooctadiene.

The first order rate constants for the individual reaction steps in this run agree well with those arrived at assuming that hydrogenation of 1,5 cyclooctadiene follows first order kinetics as shown in Figure 1 and Table II. The reaction scheme is shown in Appendix A.

TABLE II
VALUES OF THE RATE CONSTANTS OF THE INDIVIDUAL REACTION STEPS

Sulfur Compound			Rate Constant, min ⁻¹ g _{cat} ⁻¹					
			k1	k2	k3	k4	k5	k6
RUN 6	--	--	6.3x10 ⁻⁴	4.6x10 ⁻³	--	--	2.37x10 ⁻³	1.7x10 ⁻³
RUN 7	40.7 ppm,	C ₄ H ₄ S	8.0x10 ⁻⁴	3.48x10 ⁻³	--	--	2.1x10 ⁻³	3.0x10 ⁻⁴
RUN 9	81.3 ppm,	C ₄ H ₄ S	3.65x10 ⁻⁴	1.02x10 ⁻³	3.6x10 ⁻⁵	--*	1.03x10 ⁻³	--
RUN 10	84.2 ppm,	C ₁₀ H ₂₁ SH	5.0x10 ⁻⁵	4.0x10 ⁻⁵	--	--	5.4x10 ⁻⁵	--
RUN 11	10.7 ppm,	C ₁₀ H ₂₁ SH	2.19x10 ⁻⁴	6.669x10 ⁻⁴	4.23x10 ⁻⁵	--*	7.27x10 ⁻⁵	--
RUN 27	13.6 ppm,	C ₄ H ₄ S	8.9x10 ⁻⁴	3.56x10 ⁻³	--	--	2.2x10 ⁻³	7.8x10 ⁻⁵

* The order of magnitude of k value is very small, in the order of 10^{-7}

Run 7

A small amount of thiophene, C_4H_4S , a concentration approximately 40.7 ppm, was added into the mixture of 10 ml of 1,5 cyclooctadiene solution in 90 ml of cyclohexane using 1.0 gram of 0.3% wt. Pd/Al_2O_3 catalyst, and the hydrogenation was conducted at the same condition used previously with no added sulfur compound. The conversion of 1,5 cyclooctadiene was again followed as a function of time. The formation and loss of the various C_8 olefins with time is shown in Figure 3.

At this concentration of thiophene, the results were very similar to those obtained earlier in run 6, in the absence of a sulfur compound. After 1380 minutes, the conversion of 1,5 cyclooctadiene was 94.6% mol, the concentration of cyclooctene in the obtained product was 89.1% mol, and the cyclooctane was 3.1% mol. At this point, the selectivity to cyclooctene was 96.6%, which was somewhat greater than the selectivity obtained in run 6 at equal conversion of 1,5 cyclooctadiene. The selectivities of cyclooctene and the corresponding conversion of 1,5 cyclooctadiene are tabulated in Table III and also plotted in Figure 2. The data plotted in Figure 2 clearly show that the selectivity to cyclooctene was higher, at comparable conversion of 1,5 cyclooctadiene, for run 7 with 40.7 ppm of thiophene, than for run 6, with no sulfur compound, especially at conversions of 1,5 cyclooctadiene greater than 90% mol.

Analyses of the reaction mixture by gas chromatography also indicated the formation of 1,4 cyclooctadiene in the earlier stages of the hydrogenation reaction. The maximum concentration of 1,4 cyclooctadiene, obtained at $t = 240$ minutes, was about 10% mol, more

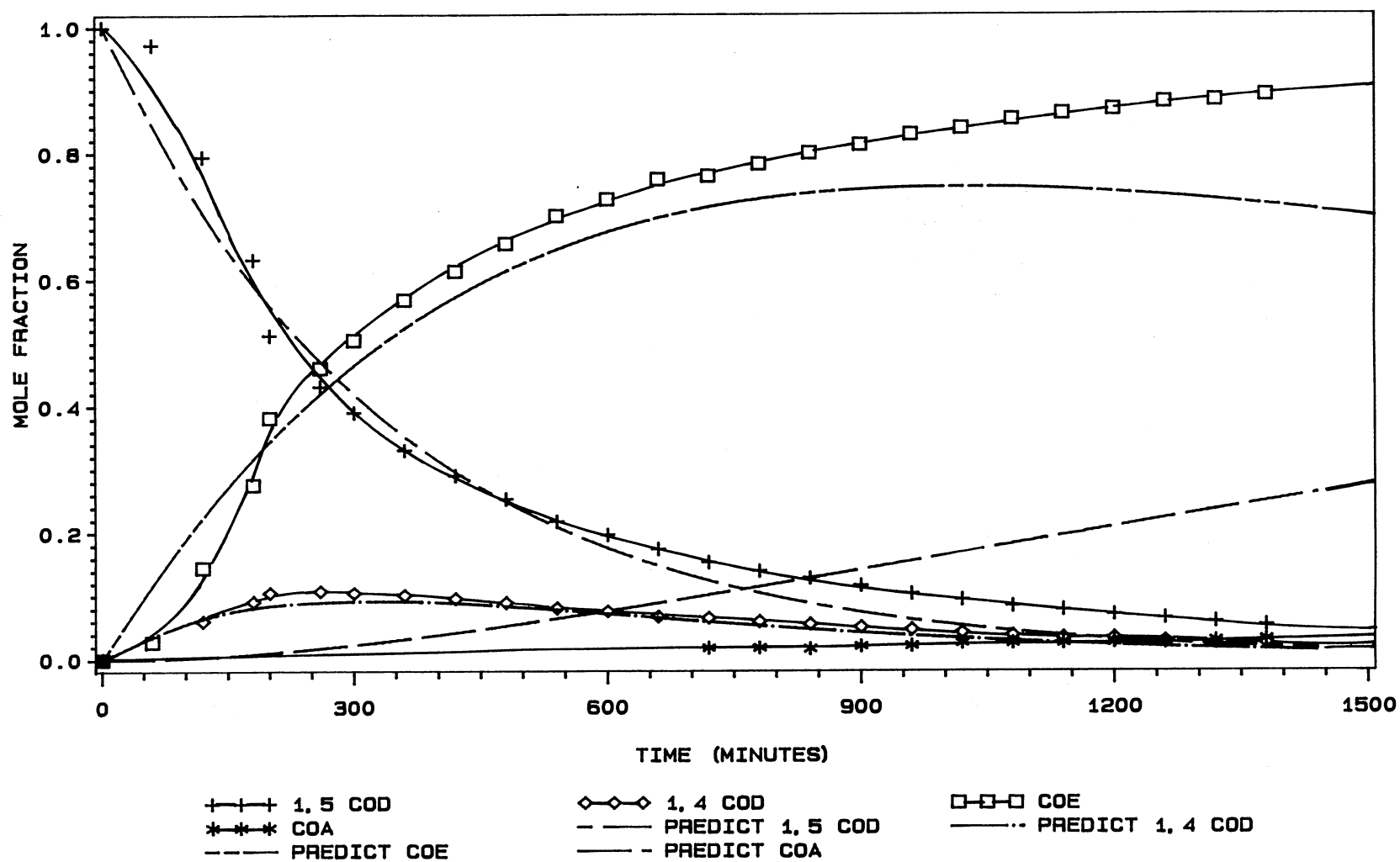


Figure 3. Hydrogenation of 1,5 Cyclooctadiene in Run 7

TABLE III
 RUN 7 (40.7 PPM of THIOPHENE, C₄H₄S)

Time (min)	% Conversion 1,5 Cyclooctadiene	% Selectivity to Cyclooctene	Conversion f	$\ln \frac{1}{(1-f)}$
200	48.7	--	0.487	0.67
420	71.0	--	0.710	1.24
660	82.6	--	0.826	1.75
780	86.1	97.7	0.861	1.97
840	87.2	98.0	0.872	2.06
900	88.4	97.5	0.884	2.15
1020	90.6	97.0	0.906	2.36
1140	92.2	97.1	0.922	2.55
1260	93.5	97.1	0.935	2.73
1320	94.1	96.8	0.941	2.83
1380	94.6	96.6	0.946	2.92

than obtained in the absence of sulfur compound. However, 1,3 cyclooctadiene was not detectable in the reaction mixture at any time.

The concentration versus time data for the reaction steps agree well with the assumption that the hydrogenation of 1,5 cyclooctadiene follows the 1st order kinetics as shown in Figure 3 and Table II.

Run 9

A small amount of thiophene, C_4H_4S , a concentration approximately 81.3 ppm, was added into the 300 ml autoclave containing 10 ml of 1,5 cyclooctadiene, 90 ml of cyclohexane, and 1.0 gram of Pd/Al_2O_3 catalyst. The hydrogenation of 1,5 cyclooctadiene was done at room temperature ($25^\circ C$) under the hydrogen pressure of 413.7 kPa, and the course of the reaction was followed as a function of time. The dependence of the reaction mixture composition versus time is shown in Figure 4.

At this concentration of thiophene, 81.3 ppm, the rate of hydrogenation of 1,5 cyclooctadiene was obviously slower than for run 6 and run 7. At $t = 3540$ minutes, with the conversion of 1,5 cyclooctadiene of 94.3%, most of the product was cyclooctene (88.5% mol) with lesser amounts of 1,4 cyclooctadiene (3.8% mol) and 1,3 cyclooctadiene (2.0% mol), and a negligible quantity of cyclooctane.

Analyses again indicated the formation of 1,4 cyclooctadiene and some 1,3 cyclooctadiene. The maximum concentration of 1,4 cyclooctadiene obtained was about 12.5% mol, at $t = 520$ minutes, higher than the concentration obtained in either run 6 and run 7.

The concentration versus time data support the assumption that the hydrogenation of 1,5 cyclooctadiene follows the 1st order kinetics as shown in Figure 4 and Table II.

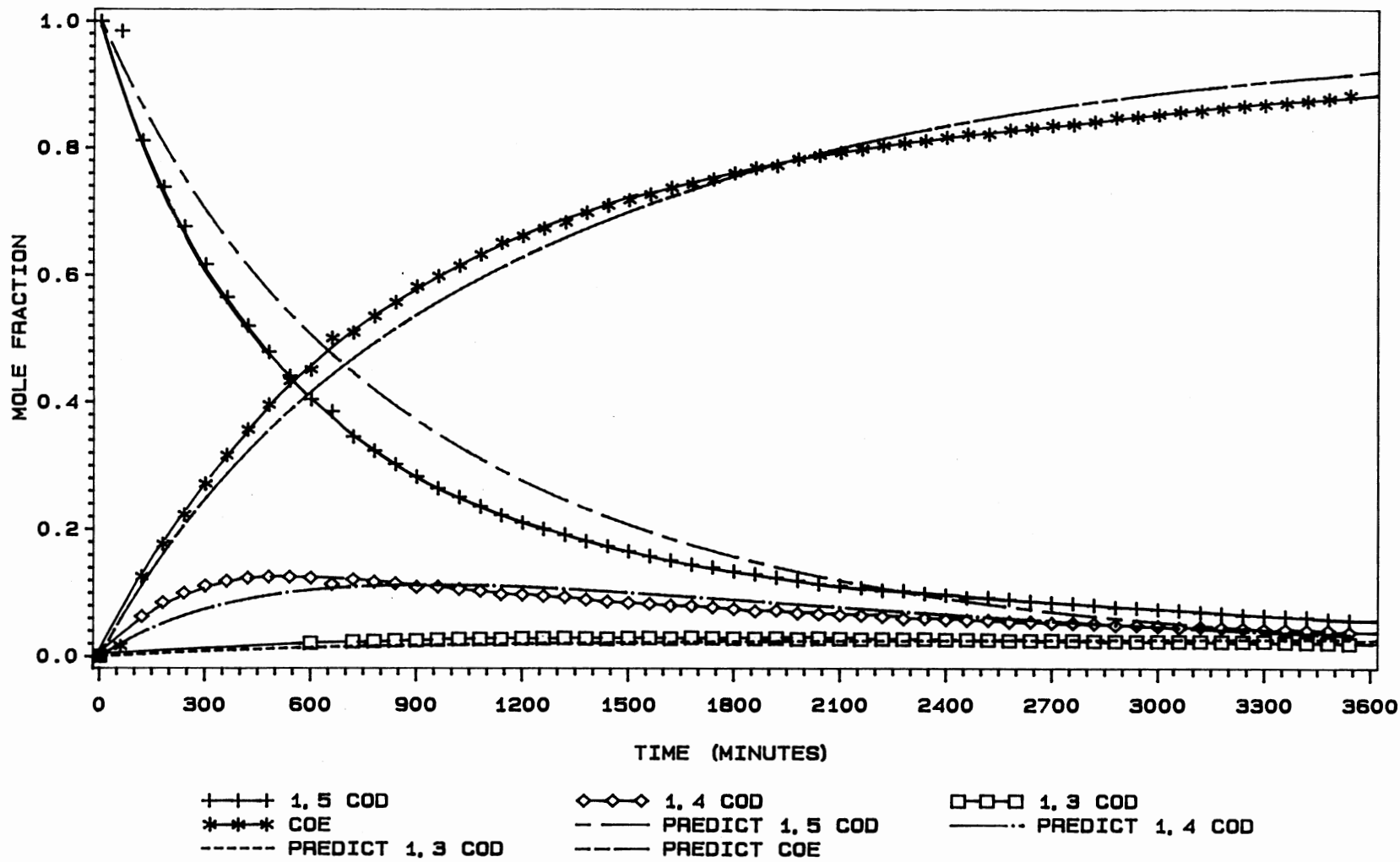


Figure 4. Hydrogenation of 1,5 Cyclooctadiene in Run 9

Run 10

A small amount of 1-decanethiol, $C_{10}H_{21}SH$, a concentration about 84.2 ppm, was added into the mixture of 10 ml of 1,5 cyclooctadiene and 90 ml of cyclohexane. The hydrogenation of 1,5 cyclooctadiene was done in the autoclave using 1.0 gram of 0.3% Pd/Al_2O_3 catalyst at room temperature ($25^{\circ}C$) under the hydrogen pressure of 413.7 kPa (60 psig).

At this concentration of 1-decanethiol, 84.2 ppm, the rate of hydrogenation of 1,5 cyclooctadiene was remarkably slow as shown in Figure 5. Analyses of the reaction mixture by gas-chromatography indicated the formation of 1,4 cyclooctadiene; however, no 1,3 cyclooctadiene and cyclooctane appeared during this experiment. The rate of hydrogenation of cyclooctene to cyclooctane and the rate of isomerization of 1,5 cyclooctadiene to 1,4 and 1,3 cyclooctadiene were sharply retarded by 1-decanethiol apparently due to immediately poisoning of the active sites on the catalyst.

No attempt was made to continue this experiment after 1800 minutes because of the low conversion of 1,5 cyclooctadiene and very low yield of cyclooctene obtained when this amount of 1-decanethiol was present. The values of the rate constants of the individual reaction steps are tabulated in Table II.

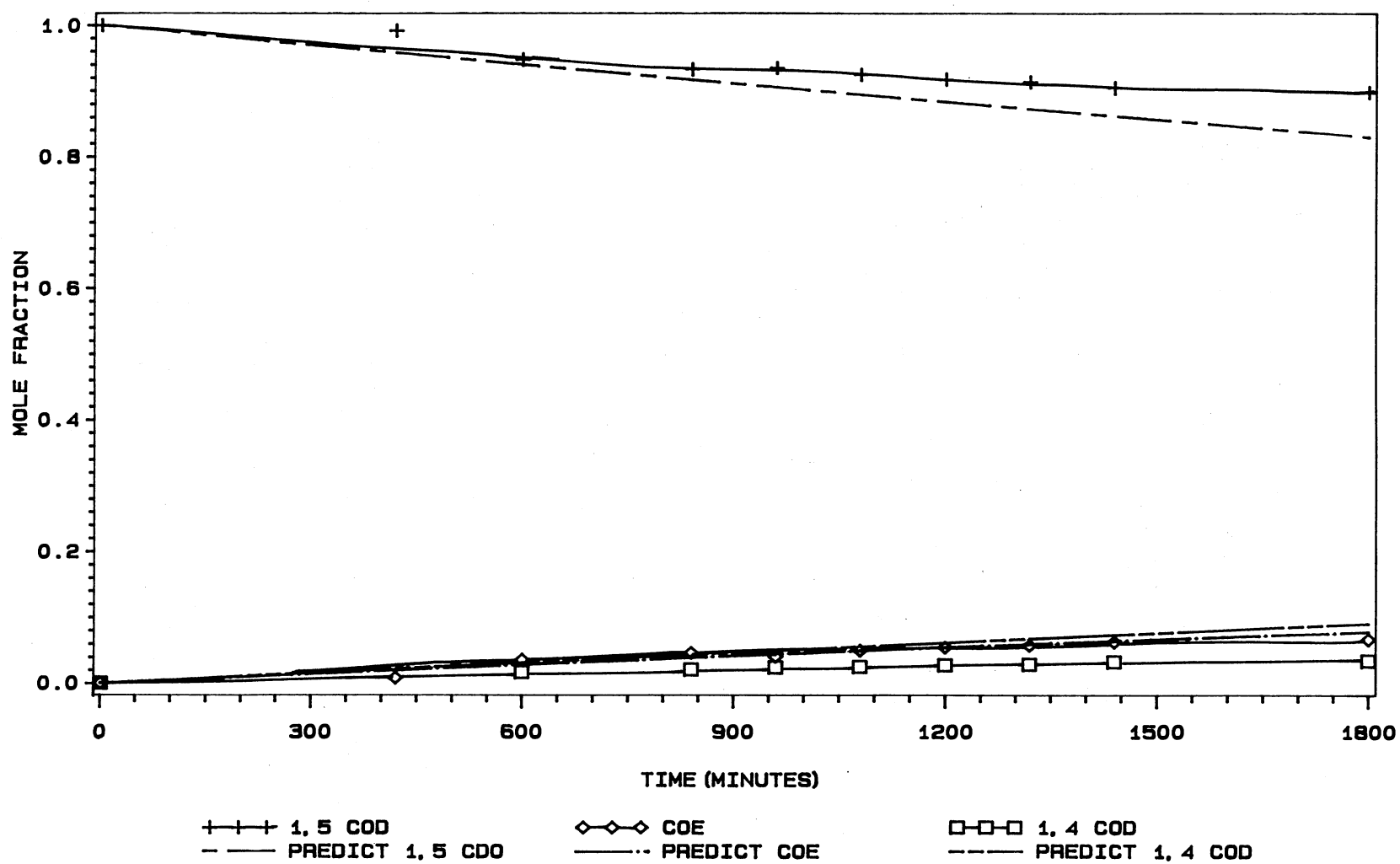


Figure 5. Hydrogenation of 1,5 Cyclooctadiene in Run 10

Run 11

A small amount of 1-decanethiol, $C_{10}H_{21}SH$, a concentration approximately 10.7 ppm, was added into the 300 ml autoclave containing 10 ml of 1,5 cyclooctadiene, 90 ml of cyclohexane as a solvent, and 1.0 gram of 0.3% wt. Pd/Al_2O_3 catalyst. The hydrogenation of 1,5 cyclooctadiene was done at the standard test conditions of room temperature and under the hydrogen pressure of 413.7 kPa (60 psig). The conversion of 1,5 cyclooctadiene was again followed as a function of time.

The dependence of the variations in the reaction mixture composition on time during the hydrogenation of 1,5 cyclooctadiene is shown in Figure 6. At this concentration of 1-decanethiol, the results were similar to those obtained in run 10. The rate of hydrogenation of 1,5 cyclooctadiene was obviously slow. After 3460 minutes, the conversion of 1,5 cyclooctadiene was 55.1% mol, and the concentration of cyclooctene was 27.3% mol.

Analyses of the reaction mixture by gas-chromatography indicated the formation of 1,4 cyclooctadiene and 1,3 cyclooctadiene during the hydrogenation of 1,5 cyclooctadiene. However, no cyclooctane was formed in the system, probably due to complete poisoning of the catalyst. The rate constant values of the individual reaction steps in this run are tabulated in Table II and then plotted in Figure 6.

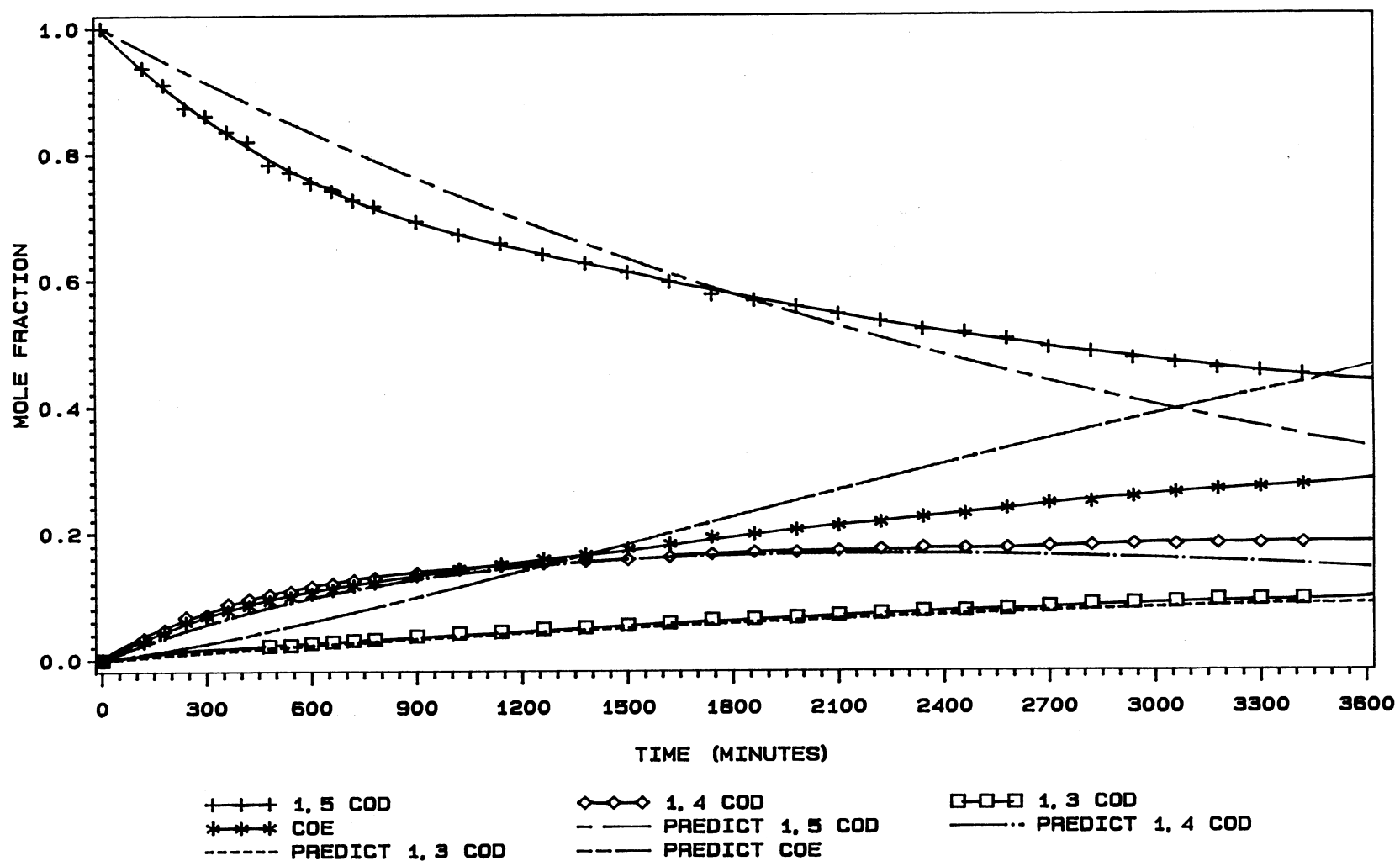


Figure 6. Hydrogenation of 1,5 Cyclooctadiene in Run 11

Run 27

A small amount of thiophene was added into the mixture of 10 ml 1,5 cyclooctadiene and 90 ml of cyclohexane with 1.0 gram of 0.3% Pd/Al₂O₃ catalyst. The thiophene concentration was 13.6 ppm. The reactant was stirred in the absence of hydrogen gas at atmospheric pressure and room temperature (about 25°C) for 1 hr and then hydrogenated at the hydrogen pressure of 413.7 kPa (60 psig).

After 2520 minutes, 1,5 cyclooctadiene was converted completely. With this amount of thiophene, time require was 1.75 time longer than when no sulfur compound was present. Figure 7 illustrates the dependence of the variations in the reaction mixture composition with time during the hydrogenation of 1,5 cyclooctadiene. At the concentration of thiophene, 13.6 ppm, the results were similar to those obtained in run 6, in the absence of a sulfur compound, and run 7, with 40.7 ppm of thiophene. The concentration of cyclooctene obtained, after the disappearance of 1,5 and 1,4 cyclooctadiene, was 95.6% mol, and the cyclooctane was 4.4% mol and increasing. Therefore, selectivity to cyclooctene in the product was 95.6% for this run. This was more selective than for run 6 at equal conversion of 1,5 cyclooctadiene. The selectivities to cyclooctene and the corresponding conversion of 1,5 cyclooctadiene are tabulated and compared with the previous runs in Table IV and then plotted in Figure 2. The graph plotted in Figure 8 clearly shows that the selectivity to cyclooctene was higher at comparable conversion of 1,5 cyclooctadiene for run 27, with 13.6 ppm of thiophene, than for run 6, with no sulfur compound and roughly equal to the selectivity for run 7, with 40.7 ppm of thiophene. The hydrogenation of 1,5 cyclooctadiene with 13.6 ppm of thiophene was

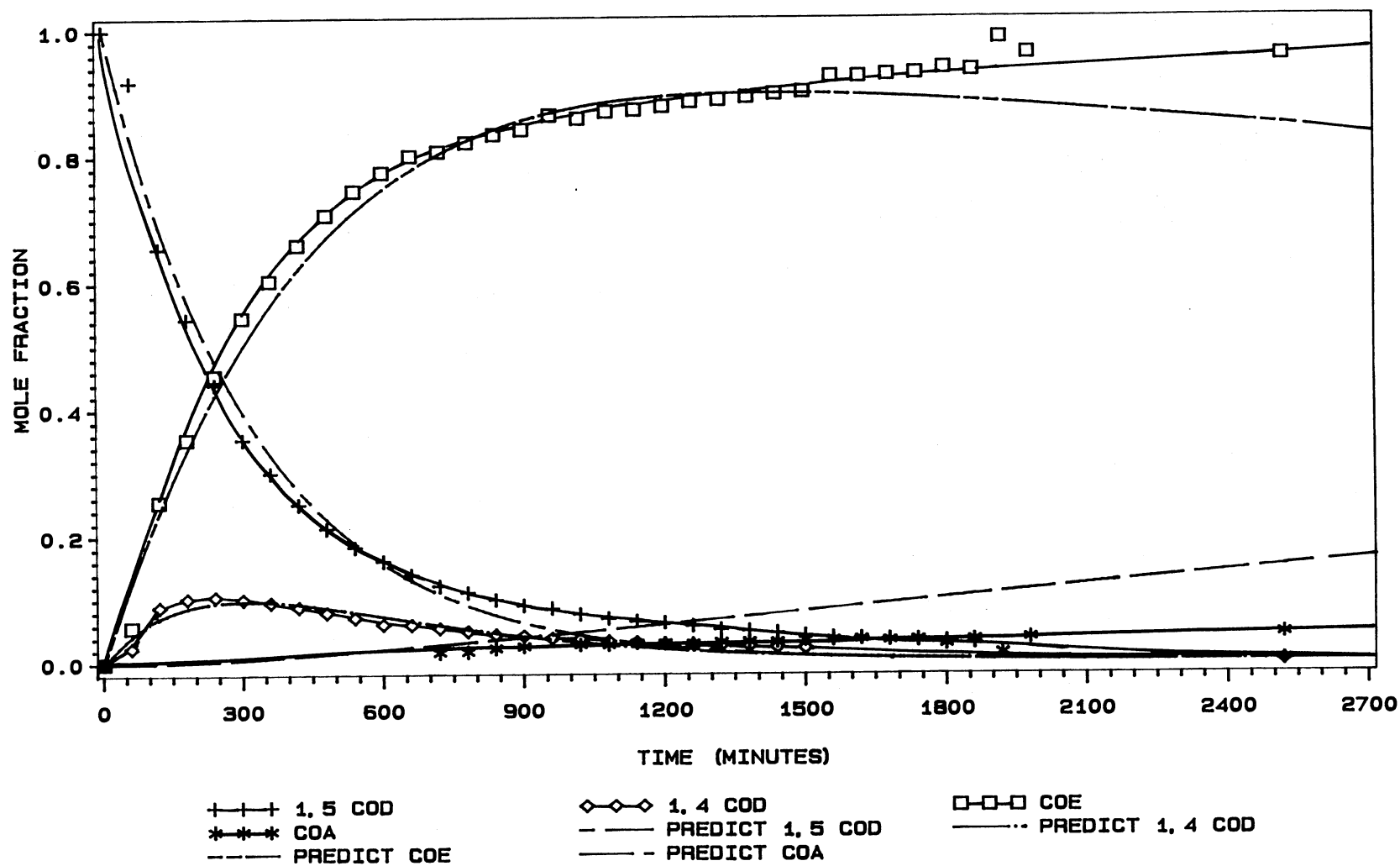


Figure 7. Hydrogenation of 1,5 Cyclooctadiene in Run 27

TABLE IV
 RUN 27 (13.6 PPM OF THIOPHENE, C₄H₄S)

Time (min)	% Conversion 1,5 Cyclooctadiene	% Selectivity to Cyclooctene	Conversion f	$\ln \frac{1}{(1-f)}$
240	56.0	--	0.560	0.82
420	75.0	--	0.750	1.38
660	86.1	--	0.861	1.97
720	87.2	98.0	0.872	2.11
780	88.9	97.9	0.889	2.2
840	90.1	97.4	0.901	2.31
900	91.0	97.1	0.910	2.40
1020	92.4	96.9	0.924	2.57
1140	93.5	96.8	0.935	2.73
1260	94.2	96.7	0.942	2.85
1380	95.0	96.6	0.950	3.00
1440	95.3	96.5	0.953	3.06
1860	97.1	96.4	0.971	3.53
2520	--	95.6	--	--

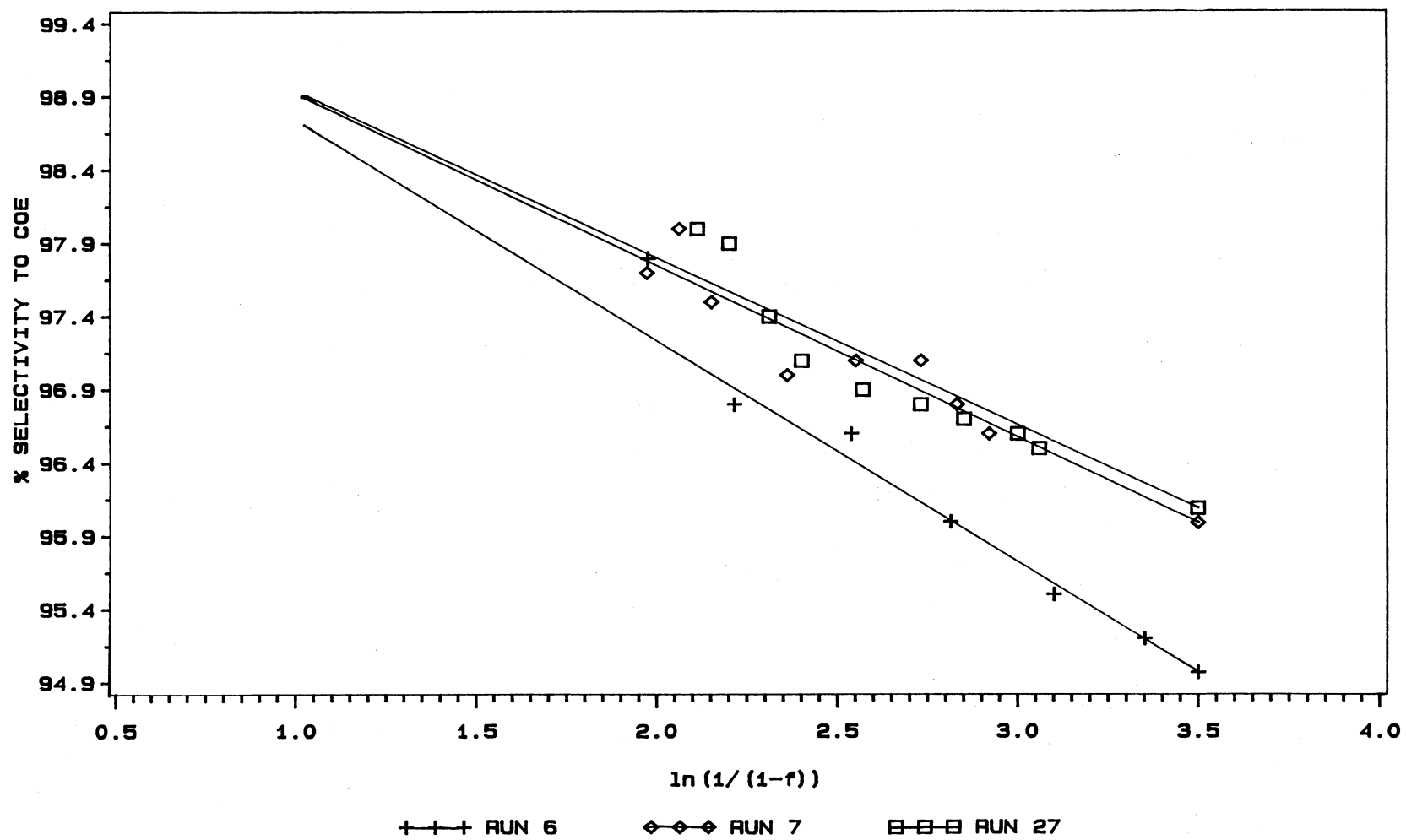


Figure 8. % Selectivity to COE vs. $\ln(1/(1-f))$

somewhat faster in this run (run 27) than with 40.7 ppm of thiophene in run 7 as expected, due to less amount of sulfur compound poisoning the catalyst.

Analyses of the reaction mixture by gas-chromatography also showed the formation of 1,4 cyclooctadiene with the maximum concentration of 11.1% mol in the earlier stage of hydrogenation about $t = 240$ minutes.

Similar to run 6 and run 7, 1,3 cyclooctadiene was not detectable in the reaction mixture, probably owing to rapid rate of hydrogenation of 1,3 cyclooctadiene. The rate constants of the individual reaction steps obtained for hydrogenation of 1,5 cyclooctadiene, 1,4 cyclooctadiene and cyclooctene are again in very good mutual agreement as showed in Figure 7.

In Figure 8, the graph of % selectivity vs. $\ln\left(\frac{1}{1-f}\right)$ clearly illustrates that for every point of the experimental data, the selectivity to cyclooctene in the systems containing sulfur compounds is always higher than in the one without a sulfur compound. On error analysis in selectivity to cyclooctene cannot be easily applied to this selectivity-conversion plot.

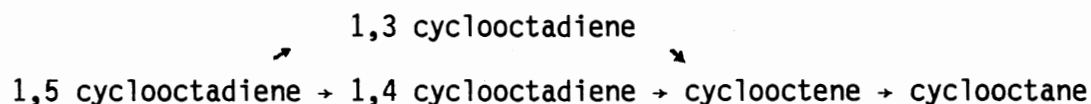
There is also a significant difference between the values of the individual rate constant from cyclooctene to cyclooctane, k_6 , in the presence and absence of sulfur, as shown in Table II. This indicates that % selectivity to cyclooctene in the system with a small amount of sulfur compound is much higher than the system in the absence of sulfur compound.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

The selective hydrogenation of 1,5 cyclooctadiene to cyclooctene with a supported palladium catalyst (0.3% Pd/Al₂O₃) was studied in solutions of cyclohexane at room temperature and a hydrogen pressure of 413.7 kPa using a 300 ml batch autoclave reactor.

1. The detailed reaction sequence, depicted below, fits the experimental data well when the individual reaction steps are considered 1st order.



2. The addition of small amounts of sulfur compounds, thiophene, C₄H₄S, and mercaptan, C₁₀H₂₁SH, into the reaction mixture considerably improved the selectivity to cyclooctene at comparable conversion of 1,5 cyclooctadiene, compared with the reaction in the absence of sulfur compound.

3. For sulfur containing compounds considered in this study, thiophene, C₄H₄S, and mercaptan, C₁₀H₂₁SH, thiophene was the best reagent to enhance the selectivity and increase the yield of desired product, cyclooctene. The optimum content of thiophene was in the range of 10 to 40 ppm under these experimental conditions. If the excessive amounts of thiophene are employed in the hydrogenation of 1,5

cyclooctadiene, the reaction remains very selective, but the rate of conversion of cyclooctadienes is dramatically reduced due to poisoning of the catalyst. Therefore, the concentration of thiophene must be controlled in a range between 10 to 40 ppm to obtain high selectivities and reasonable rates of hydrogenation. Compared with mercaptan, $C_{10}H_{21}SH$, thiophene had considerably less effect on the rate of reaction. At the same sulfur content, approximately 10 ppm, the mercaptan immediately poisoned the catalyst, resulting in significant lower rates of the hydrogenation of cyclooctadiene; consequently, a low net yield of cyclooctene was obtained in the reaction product with the mercaptan.

As described above, not all sulfur compounds can be used to enhance the selective hydrogenation of cyclo-diolefins to cyclo-olefin. Some compounds have a dramatic effect on the rate of hydrogenation. For example, mercaptan and disulfide severely poison the catalyst; apparently they are absorbed very tightly and remove active sites from participation in the reaction. This results in a low rate of hydrogenation, and small changes in the selectivity to the desired intermediate, cyclooctene.

For this reason, thiophene probably remains the ideal sulfur-compound for a catalyst modifier in the selective hydrogenation of diolefins to olefin, especially with cyclohexane as a solvent. It appears that thiophene is reversibly chemisorbed on the active site, not permanent poison, and while it competes with diolefins for sites, also markedly reduces olefin adsorption and subsequent hydrogenation to saturates. However, it must be used carefully; if excessively added, thiophene can also sharply retard the hydrogenation rate.

The other advantage that makes thiophene attractive as a catalyst modifier is its similarity in boiling point to cyclohexane, a widely used solvent for diolefin hydrogenation. The boiling points of thiophene and cyclohexane are almost the same (the boiling point of thiophene is 84°C and cyclohexane is 80.7°C). Thus, cyclohexane and added thiophene can be easily separated from C_8 products by overhead distillation and the mixed thiophene-cyclohexane solvent can be recycled many times without adding fresh thiophene.

For many purposes, thiophene would be the catalyst modifier of choice for use in selective hydrogenation reaction, particularly when cyclohexane is the solvent.

Recommendations

Thiophene would be the reagent of choice to improve the selective hydrogenation of cyclic-diolefins to monoenes. It is reversibly adsorbed by the catalyst and improves the selectivity of the reaction. Other sulfur compounds are less effective. It is likely that other sulfides, such as dimethyl sulfide and diethyl sulfide would react with catalyst in the same manner as thiophene. That is, they would not permanent poison the catalyst and reversibly chemisorbed on the active sites (proprietary data, as shown in Appendix G). Thus they function a similar manner and in some instances would offer some possible advantages in separation of the product from the solvent. These materials should be tested in future work along with carbonyl sulfide, COS, which is normally a gas and could be used effectively in flow reactors and recycled with the excess hydrogen. Mercaptans and disulfides are strongly adsorbed by the catalyst and dramatically reduce

catalyst activity. Their use as a catalyst modifier is not recommended.

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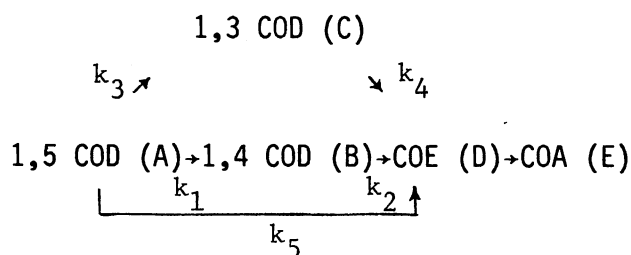
APPENDIXES

APPENDIX A

REACTION SCHEME

REACTION SCHEME

In this work, the following reaction scheme for hydrogenation of 1,5 cyclooctadiene has been proposed:



For a constant volume of the reaction mixture and constant hydrogen pressure, the following system of equations can be written for hydrogenation of 1,5 cyclooctadiene in a constant volume batch reactor.

$$\frac{dC_A}{dt} = - (k_1 + k_3 + k_5) C_A \quad (\text{A-1})$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad (\text{A-2})$$

$$\frac{dC_C}{dt} = k_3 C_A - k_4 C_C \quad (\text{A-3})$$

$$\frac{dC_D}{dt} = k_2 C_B + k_4 C_C + k_5 C_A - k_6 C_D \quad (\text{A-4})$$

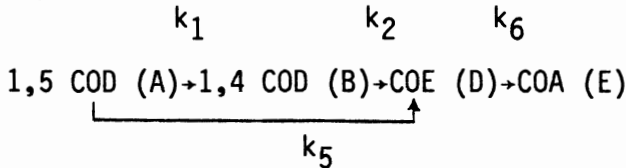
$$\frac{dC_E}{dt} = C_A^0 - C_A - C_B - C_C - C_D \quad (\text{A-5})$$

with the initial conditions

$$t = 0, C_A = C_A^0, C_B = C_C = C_D = C_E = 0 \quad (\text{A-6})$$

The system of differential equations were solved by analytical method as following cases:

Case I. For the system without 1,3 cyclooctadiene occurring, such as run 6, run 7 and run 27, the following reaction scheme for hydrogenation can be shown as:



The concentrations of each component can be determined by using equation A-1 through A-6 as follows:

$$C_A = C_A^0 e^{-k' t} \quad (A-7)$$

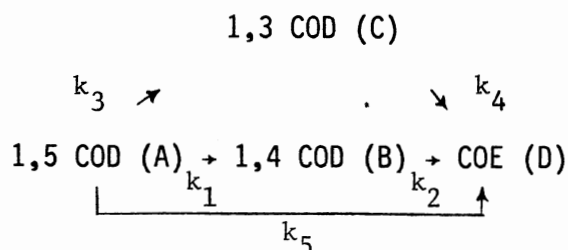
where $k' = k_1 + k_5$

$$C_B = \frac{k_1 C_A^0}{(k_2 - k')} [e^{-k't} - e^{-k_2 t}] \quad (A-8)$$

$$C_D = \frac{(k_1 k_2 + k_2 k_5 - k' k_5) C_A^0}{(k_2 - k') (k_6 - k')} [e^{-k' t} - e^{-k_6 t}] + \frac{k_1 k_2 C_A^0}{(k_2 - k') (k_6 - k')} [e^{-k_6 t} - e^{-k_2 t}] \quad (A-9)$$

$$C_E = \frac{k_6(k_1k_2 + k_2k_5 - k'k_5)C_A^0}{(k_2 - k')(k_6 - k')} \left[\frac{e^{-k_6t}}{k_6} - \frac{e^{-kt}}{k'} \right] + \frac{k_1k_2k_6}{(k_2 - k')(k_6 - k_2)} C_A^0 \left[\frac{e^{-k_2t}}{k_2} - \frac{e^{-k_6t}}{k_6} \right] + \frac{(k_1k_2 + k_2k_5 - k'k_5) C_A^0}{k'(k_2 - k')} - \frac{k_1 C_A^0}{(k_2 - k')} \quad (A-10)$$

Case II. For the system without cyclooctane appearing in the reaction mixture, such as run 9 and run 11, the following reaction scheme for hydrogenation can be depicted as:



The concentrations of each component can be obtained as follows:

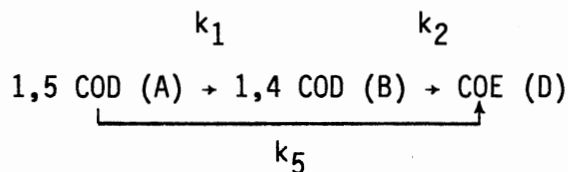
The concentration of A can be obtained from equation A-7.

The concentration of B can be calculated from equation A-8.

$$C_C = \frac{k_3 C_A^0}{(k_4 - k')} [e^{-k't} - e^{-k_4 t}] \quad (\text{A-11})$$

$$\begin{aligned}
 C_D = & \left[\frac{k_1 k_2}{(k_2 - k')} + \frac{k_3 k_4}{(k_4 - k')} + k_5 \right] \frac{C_A^0}{k'} (1 - e^{-k't}) \\
 & + \frac{k_1 C_A^0}{(k_2 - k')} (e^{-k_2 t} - 1) + \frac{k_3 C_A^0}{(k_4 - k')} (e^{-k_4 t} - 1)
 \end{aligned} \quad (\text{A-12})$$

Case III. For the system without 1,3 cyclooctadiene and cyclooctane present in the reaction mixture, such as run 10, the following reaction scheme for hydrogenation can be depicted as:



The concentrations of each component can be obtained as follows:

The concentration of A can be obtained from equation A-7.

The concentration of B can be calculated from equation A-8.

$$C_D = \frac{k_1 k_2}{(k_2 - k')} \left[\frac{(e^{-k_2 t} - 1)}{k_2} - \frac{(e^{-k' t} - 1)}{k'} \right] - \frac{k_5}{k'} C_A^0 (e^{-k' t} - 1) \quad (A-13)$$

K values of each individual reaction step are fitted the experimental data by using Nonlinear Regression Analysis by Marquardt method.

APPENDIX B

COMPUTER PROGRAM FOR CONCENTRATION AND
INDIVIDUAL RATE CONSTANT

```

C234567
1      REAL KD,K1,K2,K3,K4,K5,K6
2      INTEGER NCASE,TS,TE,NT,RUN
C*****
C
C      DATA RUN
C      INPUT RUN #
3      RUN =
C
C      INPUT INITIAL CONCENTRATION
4      CAO =
C
C      INPUT K VALUE
5      KD =
6      K1 =
7      K2 =
8      K3 =
9      K4 =
10     K5 =
11     K6 =
C
C      INPUT STARTING TIME
12     TS =
C
C      INPUT ENDING TIME
13     TE =
C
C      INPUT INCREASING TIME
14     NT =
C*****
C      INPUT CASE #
C      CASE I
C      1,5 COD → 1,4 COD → COE → COA
C      |
C      |
C      CASE II
C      1,3 COD
C      /      \
C      1,5 COD → 1,4 COD → COE
C      |
C      |
C      CASE III
C      1,5 COD → 1,4 COD → COE
C      |
C      |
C*****
C
15     NCASE =

```

```

C
C
16 WRITE(6,1) RUN
17 1 FORMAT(3X,'RUN = ',I5,/)
18 WRITE(6,5) KD,K1,K2,K3,K4,K5,K6
19 5 FORMAT(3X,'K = ',F10.7,3X,'K1 = ',F10.7,
$      3X,'K2 = ',F10.7,3X,'K3 = ',F10.7,/,
$      3X,'K4 = ',F10.7,3X,'K5 = ',F10.7,
$      3X,'K6 = ',F10.7,/)
20 DD2 = K2-KD
21 DD4 = K4-KD
22 DD6 = K6-KD
23 D26 = K6-K2
C
24 T12 = K1*K2
25 T25 = K2*K5
26 TD5 = KD*K5
27 T34 = K3*K4
C
28 D1 = (T12+T25-TD5)/(DD2*DD6)
29 D2 = T12/(DD2*D26)
C
30 GO TO (10,100,200),NCASE
C
C CASE I
C -----
C
31 10 WRITE(6,15)
32 15 FORMAT(3X,'T(MIN)',2X,'1,5 COD',3X,'1,4 COD',
$      5X,'COE',7X,'COA'/)
33 DO 50 I=TS,TE,NT
34 EKD = EXP(-KD*I)
35 EK2 = EXP(-K2*I)
36 EK4 = EXP(-K4*I)
37 EK6 = EXP(-K6*I)
38 CALL AI(EKD,CAO,CA)
39 CALL BI(EKD,EK2,K1,DD2,CAO,CB)
40 CALL DI(EKD,EK2,EK6,D1,D2,CAO,CD)
41 CALL EI(EKD,EK2,EK6,D1,D2,DD2,KD,K1,K2,K6,
$      T12,T25,TD5,CAO,CE)
C*****
C
C CA = CONCENTRATION OF 1,5 COD
C CB = CONCENTRATOIN OF 1,4 COD
C CC = CONCENTRATION OF 1,3 COD
C CD = CONCENTRATION OF COE
C CE = CONCENTRATION OF COA
C*****
C
C CONVERT CA,CB,CD,CE INTO MOLE FRACTION
C*****
C
42 CT = CA+CB+CD+CE
43 AA = CA/CT
44 BB = CB/CT
45 DD = CD/CT
46 EE = CE/CT
47 WRITE(6,20) I,AA,BB,DD,EE

```

```

48      20  FORMAT(3X,I5,3X,F7.4,3X,F7.4,
$        3X,F7.4,3X,F7.4)
49      50  CONTINUE
50      STOP

C
C      CASE II
C      -----
51      100 WRITE(6,110)
52      110 FORMAT(3X,'T(MIN)',2X,'1,5 COD',3X,'1,4 COD',
$        3X,'1,3 COD',5X,'COE')
53      DO 150 I=TS,TE,NT
54          EKD = EXP(-KD*I)
55          EK2 = EXP(-K2*I)
56          EK4 = EXP(-K4*I)
57          CALL AI(EKD,CAO,CA)
58          CALL BI(EKD,EK2,K1,DD2,CAO,CB)
59          CALL CII(EKD,EK4,DD4,K3,CAO,CC)
60          CALL DII(EKD,EK2,EK4,DD2,DD4,KD,K1,K3,K5,
$        T12,T34,CAO,CD)
61          CT = CA+CB+CC+CD
62          AA = CA/CT
63          BB = CB/CT
64          CC = CC/CT
65          DD = CD/CT
66          WRITE(6,120) I,AA,BB,CC,DD
67      120  FORMAT(3X,I5,3X,F7.4,3X,F7.4,
$        3X,F7.4,3X,F7.4)
68      150  CONTINUE
69      STOP

C
C      CASE III
C      -----
70      200 WRITE(6,210)
71      210 FORMAT(3X,'T(MIN)',2X,'1,5 COD',3X,'1,4 COD',
$        5X,'COE')
72      DO 250 I=TS,TE,NT
73          EKD = EXP(-KD*I)
74          EK2 = EXP(-K2*I)
75          CALL AI(EKD,CAO,CA)
76          CALL BI(EKD,EK2,K1,DD2,CAO,CB)
77          CALL DIII(EKD,EK2,DD2,KD,K2,K5,T12,CAO,CD)
78          CT = CA+CB+CD
79          AA = CA/CT
80          BB = CB/CT
81          DD = CD/CT
82          WRITE(6,220) I,AA,BB,DD
83      220  FORMAT(3X,I5,3X,F7.4,3X,F7.4,3X,F7.4)
84      250  CONTINUE
85      STOP
86      END

C*****
C
C      SUB AI
C
C      CALCULATION OF 1,5 COD CONCENTRATION IN CASE I
C
C*****
C

```

```

87      SUBROUTINE AI(EKD,CAO,CA)
88      REAL EKD,CAO,CA
89      CA = CAO*EKD
90      RETURN
91      END
C*****
C
C      SUB BI
C
C      CALCULATION OF 1,4 COD CONCENTRATION IN CASE I
C
C*****
C *

92      SUBROUTINE BI(EKD,EK2,K1,DD2,CAO,CB)
93      REAL EKD,EK2,K1,DD2,CAO,CB
94      B1 = K1*CAO/DD2
95      B2 = EKD-EK2
96      CB = B1*B2
97      RETURN
98      END
C*****
C
C      SUB DI
C
C      CALCULATION OF COE CONCENTRATION IN CASE I
C
C*****
C

99      SUBROUTINE DI(EKD,EK2,EK6,D1,D2,CAO,CD)
100     REAL EKD,EK2,EK6,D1,D2,CAO,CD
101     CD = CAO*(D1*(EKD-EK6)+D2*(EK6-EK2))
102     RETURN
103     END
C*****
C
C      SUB EI
C
C      CALCULATION OF COE CONCENTRATION IN CASE I
C
C*****
C

104     SUBROUTINE EI(EKD,EK2,EK6,D1,D2,DD2,KD,K1,K2,K6,
$          T12,T25,TD5,CAO,CE)
105     REAL EKD,EK2,EK6,D1,D2,DD2,KD,K1,K2,K6,
$          T12,T25,TD5,CAO,CE
106     CE1 = K6*D1*(EK6/K6-EKD/KD)
107     CE2 = K6*D2*(EK2/K2-EK6/K6)
108     CE3 = (T12+T25-TD5)/(KD*DD2)
109     CE4 = K1/DD2
110     CE = (CE1+CE2+CE3-CE4)*CAO
111     RETURN
112     END
C*****
C
C      SUB CII
C
C      CALCULATION OF 1,3 COD IN CASE II
C*****

```



```

C
C*****
C
113      SUBROUTINE CII(EKD,EK4,DD4,K3,CAO,CC)
114      REAL EKD,EK4,DD4,K3,CAO,CC
115      CC = K3*CAO*(EKD-EK4)/DD4
116      RETURN
117      END
C*****
C
C      SUB DII
C
C      CALCULATION OF COE CONCENTRATION IN CASE II
C
C*****
C
118      SUBROUTINE DII(EKD,EK2,EK4,DD2,DD4,KD,K1,K3,K5,
$          T12,T34,CAO,CD)
119      REAL EKD,EK2,EK4,DD2,DD4,KD,K1,K3,K5,
$          T12,T34,CAO,CD
120      CD1 = (T12/DD2+T34/DD4+K5)*(1-EKD)/KD
121      CD2 = K1*(EK2-1)/DD2
122      CD3 = K3*(EK4-1)/DD4
123      CD = (CD1+CD2+CD3)*CAO
124      RETURN
125      END
C*****
C
C      SUB DIII
C
C      CALCULATION OF COE CONCENTRATION IN CASE III
C
C*****
C
126      SUBROUTINE DIII(EKD,EK2,DD2,KD,K2,K5,T12,CAO,CD)
127      REAL EKD,EK2,DD2,KD,K2,K5,T12,CAO,CD
128      XEK2 = K2*(EK2-1)
129      XEKD = KD*(EKD-1)
130      CD1 = T12*(XEK2-XEKD)/DD2
131      CD2 = K5*(EKD-1)/KD
132      CD = (CD1-CD2)*CAO
133      RETURN
134      END

```

RUN = 6

K = 0.0030000 K1 = 0.0006300 K2 = 0.0046000 K3 = 0.0000000
 K4 = 0.0000000 K5 = 0.0023700 K6 = 0.0001700

T(MIN)	1,5 COD	1,4 COD	COE	COA
60	0.8353	0.0301	0.1339	0.0007
120	0.6977	0.0480	0.2517	0.0027
180	0.5827	0.0574	0.3541	0.0058
240	0.4868	0.0611	0.4423	0.0099
300	0.4066	0.0610	0.5176	0.0148
360	0.3396	0.0585	0.5815	0.0204
420	0.2837	0.0547	0.6351	0.0266
480	0.2369	0.0500	0.6798	0.0333
540	0.1979	0.0451	0.7166	0.0404
600	0.1653	0.0402	0.7466	0.0479
660	0.1381	0.0355	0.7708	0.0556
720	0.1153	0.0311	0.7900	0.0636
780	0.0963	0.0270	0.8049	0.0717
840	0.0805	0.0234	0.8161	0.0800
900	0.0672	0.0202	0.8242	0.0884
960	0.0561	0.0173	0.8297	0.0968
1020	0.0469	0.0149	0.8330	0.1053
1080	0.0392	0.0127	0.8344	0.1138
1140	0.0327	0.0108	0.8342	0.1223
1200	0.0273	0.0092	0.8327	0.1308
1260	0.0228	0.0078	0.8301	0.1393
1320	0.0191	0.0066	0.8266	0.1477
1380	0.0159	0.0056	0.8223	0.1562
1440	0.0133	0.0047	0.8175	0.1645

RUN = 7

K = 0.0029000 K1 = 0.0008000 K2 = 0.0034800 K3 = 0.0000000
 K4 = 0.0000000 K5 = 0.0021000 K6 = 0.0003030

T(MIN)	1,5 COD	1,4 COD	COE	COA
60	0.8403	0.0396	0.1190	0.0011
120	0.7061	0.0655	0.2242	0.0042
180	0.5933	0.0811	0.3164	0.0092
240	0.4986	0.0894	0.3964	0.0157
300	0.4190	0.0923	0.4652	0.0235
360	0.3520	0.0915	0.5239	0.0325
420	0.2958	0.0882	0.5734	0.0425
480	0.2486	0.0833	0.6148	0.0533
540	0.2089	0.0775	0.6488	0.0648
600	0.1755	0.0712	0.6764	0.0769
660	0.1475	0.0647	0.6984	0.0894
720	0.1239	0.0584	0.7155	0.1022
780	0.1041	0.0523	0.7282	0.1154
840	0.0875	0.0466	0.7372	0.1287
900	0.0735	0.0412	0.7431	0.1422
960	0.0618	0.0364	0.7461	0.1557
1020	0.0519	0.0320	0.7468	0.1693
1080	0.0436	0.0280	0.7455	0.1828
1140	0.0367	0.0245	0.7425	0.1964
1200	0.0308	0.0213	0.7381	0.2098
1260	0.0259	0.0185	0.7324	0.2232
1320	0.0218	0.0161	0.7257	0.2365
1380	0.0183	0.0139	0.7183	0.2496
1440	0.0154	0.0120	0.7101	0.2626

RUN = 9

K = 0.0008500 K1 = 0.0003650 K2 = 0.0010180 K3 = 0.0000360
K4 = 0.0000000 K5 = 0.0010300 K6 = 0.0000000

T(MIN)	1,5 COD	1,4 COD	1,3 COD	COE
60	0.9190	0.0200	0.0020	0.0589
120	0.8469	0.0367	0.0039	0.1125
180	0.7823	0.0506	0.0055	0.1616
240	0.7241	0.0622	0.0069	0.2068
300	0.6716	0.0717	0.0083	0.2484
360	0.6240	0.0796	0.0095	0.2870
420	0.5806	0.0859	0.0106	0.3229
480	0.5411	0.0911	0.0115	0.3563
540	0.5049	0.0951	0.0125	0.3875
600	0.4717	0.0983	0.0133	0.4168
660	0.4412	0.1006	0.0141	0.4442
720	0.4130	0.1022	0.0148	0.4700
780	0.3871	0.1033	0.0154	0.4942
840	0.3630	0.1038	0.0160	0.5171
900	0.3408	0.1039	0.0166	0.5387
960	0.3201	0.1036	0.0171	0.5592
1020	0.3009	0.1030	0.0176	0.5785
1080	0.2831	0.1021	0.0180	0.5968
1140	0.2664	0.1009	0.0185	0.6142
1200	0.2509	0.0995	0.0188	0.6307
1260	0.2364	0.0980	0.0192	0.6464
1320	0.2229	0.0963	0.0196	0.6612
1380	0.2102	0.0945	0.0199	0.6754
1440	0.1983	0.0926	0.0202	0.6889
1500	0.1872	0.0906	0.0204	0.7017
1560	0.1768	0.0886	0.0207	0.7140
1620	0.1670	0.0864	0.0210	0.7256
1680	0.1578	0.0843	0.0212	0.7367
1740	0.1491	0.0821	0.0214	0.7473
1800	0.1410	0.0800	0.0216	0.7574
1860	0.1334	0.0778	0.0218	0.7671
1920	0.1262	0.0756	0.0220	0.7763
1980	0.1194	0.0734	0.0222	0.7851
2040	0.1130	0.0712	0.0223	0.7935
2100	0.1070	0.0691	0.0225	0.8015
2160	0.1013	0.0670	0.0226	0.8092
2220	0.0959	0.0649	0.0227	0.8165
2280	0.0908	0.0628	0.0229	0.8235
2340	0.0861	0.0608	0.0230	0.8302
2400	0.0815	0.0588	0.0231	0.8366
2460	0.0773	0.0568	0.0232	0.8427
2520	0.0732	0.0549	0.0233	0.8485
2580	0.0694	0.0531	0.0234	0.8541
2640	0.0658	0.0512	0.0235	0.8595
2700	0.0624	0.0494	0.0236	0.8646
2760	0.0592	0.0477	0.0237	0.8695
2820	0.0561	0.0460	0.0237	0.8741
2880	0.0532	0.0444	0.0238	0.8786
2940	0.0505	0.0428	0.0239	0.8829
3000	0.0479	0.0412	0.0240	0.8870
3060	0.0454	0.0397	0.0240	0.8909
3120	0.0431	0.0382	0.0241	0.8946
3180	0.0409	0.0368	0.0241	0.8982
3240	0.0388	0.0354	0.0242	0.9016
3300	0.0368	0.0341	0.0242	0.9049
3360	0.0350	0.0328	0.0243	0.9080
3420	0.0332	0.0315	0.0243	0.9110
3480	0.0315	0.0303	0.0244	0.9138
3540	0.0299	0.0291	0.0244	0.9166

RUN = 10

K = 0.0001020 K1 = 0.0000500 K2 = 0.0000400 K3 = 0.0000000
 K4 = 0.0000000 K5 = 0.0000540 K6 = 0.0000000

T(MIN)	1,5 COD	1,4 COD	COE
60	0.9938	0.0030	0.0032
120	0.9876	0.0059	0.0064
180	0.9815	0.0089	0.0096
240	0.9754	0.0118	0.0128
300	0.9694	0.0147	0.0159
360	0.9634	0.0175	0.0191
420	0.9574	0.0204	0.0222
480	0.9515	0.0232	0.0253
540	0.9457	0.0260	0.0283
600	0.9399	0.0287	0.0314
660	0.9341	0.0315	0.0344
720	0.9284	0.0342	0.0375
780	0.9227	0.0369	0.0405
840	0.9170	0.0395	0.0434
900	0.9114	0.0422	0.0464
960	0.9059	0.0448	0.0493
1020	0.9003	0.0474	0.0523
1080	0.8949	0.0500	0.0552
1140	0.8894	0.0525	0.0581
1200	0.8840	0.0551	0.0609
1260	0.8786	0.0576	0.0638
1320	0.8733	0.0601	0.0666
1380	0.8680	0.0625	0.0695
1440	0.8628	0.0650	0.0723
1500	0.8575	0.0674	0.0751
1560	0.8524	0.0698	0.0778
1620	0.8472	0.0722	0.0806
1680	0.8421	0.0746	0.0833
1740	0.8370	0.0769	0.0861
1800	0.8320	0.0792	0.0888

RUN = 11

K = 0.0002917 K1 = 0.0002190 K2 = 0.0006688 K3 = 0.0000420
K4 = 0.0000000 K5 = 0.0000727 K6 = 0.0000000

T(MIN)	1,5 COD	1,4 COD	1,3 COD	COE
60	0.9802	0.0127	0.0025	0.0046
120	0.9608	0.0247	0.0049	0.0095
180	0.9419	0.0359	0.0073	0.0149
240	0.9234	0.0464	0.0096	0.0206
300	0.9053	0.0562	0.0119	0.0266
360	0.8876	0.0654	0.0142	0.0328
420	0.8702	0.0740	0.0163	0.0394
480	0.8533	0.0820	0.0185	0.0462
540	0.8367	0.0895	0.0206	0.0532
600	0.8205	0.0965	0.0226	0.0604
660	0.8046	0.1030	0.0246	0.0679
720	0.7890	0.1090	0.0266	0.0754
780	0.7738	0.1145	0.0285	0.0832
840	0.7589	0.1197	0.0303	0.0911
900	0.7444	0.1244	0.0322	0.0991
960	0.7301	0.1288	0.0340	0.1072
1020	0.7161	0.1328	0.0357	0.1154
1080	0.7024	0.1365	0.0375	0.1236
1140	0.6890	0.1398	0.0391	0.1320
1200	0.6759	0.1429	0.0408	0.1404
1260	0.6631	0.1456	0.0424	0.1489
1320	0.6505	0.1481	0.0440	0.1574
1380	0.6382	0.1504	0.0455	0.1659
1440	0.6261	0.1524	0.0471	0.1745
1500	0.6143	0.1541	0.0485	0.1831
1560	0.6027	0.1557	0.0500	0.1916
1620	0.5913	0.1570	0.0514	0.2002
1680	0.5802	0.1581	0.0528	0.2088
1740	0.5693	0.1591	0.0542	0.2174
1800	0.5587	0.1599	0.0555	0.2259
1860	0.5482	0.1605	0.0569	0.2344
1920	0.5380	0.1610	0.0582	0.2429
1980	0.5279	0.1613	0.0594	0.2514
2040	0.5181	0.1615	0.0607	0.2598
2100	0.5084	0.1615	0.0619	0.2682
2160	0.4990	0.1615	0.0631	0.2765
2220	0.4897	0.1613	0.0642	0.2848
2280	0.4806	0.1610	0.0654	0.2930
2340	0.4717	0.1606	0.0665	0.3012
2400	0.4630	0.1601	0.0676	0.3093
2460	0.4544	0.1595	0.0687	0.3174
2520	0.4460	0.1589	0.0697	0.3254
2580	0.4378	0.1582	0.0708	0.3333
2640	0.4297	0.1573	0.0718	0.3411
2700	0.4218	0.1565	0.0728	0.3489
2760	0.4141	0.1555	0.0737	0.3566
2820	0.4065	0.1546	0.0747	0.3643
2880	0.3990	0.1535	0.0756	0.3718
2940	0.3917	0.1524	0.0766	0.3793
3000	0.3845	0.1513	0.0775	0.3867
3060	0.3775	0.1501	0.0783	0.3941
3120	0.3706	0.1489	0.0792	0.4013
3180	0.3638	0.1476	0.0801	0.4085
3240	0.3572	0.1463	0.0809	0.4156
3300	0.3507	0.1450	0.0817	0.4226
3360	0.3443	0.1436	0.0825	0.4295
3420	0.3380	0.1423	0.0833	0.4364

RUN = 27

K = 0.0030900 K1 = 0.0008900 K2 = 0.0035600 K3 = 0.0000000
 K4 = 0.0000000 K5 = 0.0022000 K6 = 0.0000780

T(MIN)	1,5 COD	1,4 COD	COE	COA
60	0.8308	0.0437	0.1252	0.0003
120	0.6902	0.0717	0.2370	0.0011
180	0.5734	0.0881	0.3360	0.0025
240	0.4764	0.0962	0.4232	0.0043
300	0.3957	0.0986	0.4993	0.0064
360	0.3288	0.0969	0.5654	0.0089
420	0.2731	0.0927	0.6225	0.0117
480	0.2269	0.0868	0.6716	0.0147
540	0.1885	0.0800	0.7135	0.0180
600	0.1566	0.0729	0.7491	0.0214
660	0.1301	0.0657	0.7792	0.0250
720	0.1081	0.0588	0.8044	0.0287
780	0.0898	0.0522	0.8255	0.0325
840	0.0746	0.0461	0.8429	0.0364
900	0.0620	0.0405	0.8571	0.0404
960	0.0515	0.0354	0.8687	0.0444
1020	0.0428	0.0308	0.8778	0.0485
1080	0.0355	0.0268	0.8850	0.0527
1140	0.0295	0.0232	0.8905	0.0568
1200	0.0245	0.0200	0.8945	0.0610
1260	0.0204	0.0172	0.8972	0.0652
1320	0.0169	0.0148	0.8989	0.0694
1380	0.0141	0.0127	0.8996	0.0736
1440	0.0117	0.0109	0.8996	0.0778
1500	0.0097	0.0093	0.8990	0.0820
1560	0.0081	0.0079	0.8978	0.0862
1620	0.0067	0.0068	0.8961	0.0904
1680	0.0056	0.0058	0.8941	0.0946
1740	0.0046	0.0049	0.8917	0.0988
1800	0.0038	0.0042	0.8891	0.1030
1860	0.0032	0.0035	0.8862	0.1071
1920	0.0027	0.0030	0.8831	0.1112
1980	0.0022	0.0025	0.8799	0.1154
2040	0.0018	0.0021	0.8766	0.1195
2100	0.0015	0.0018	0.8731	0.1236
2160	0.0013	0.0015	0.8696	0.1277
2220	0.0010	0.0013	0.8660	0.1317
2280	0.0009	0.0011	0.8623	0.1358
2340	0.0007	0.0009	0.8586	0.1398
2400	0.0006	0.0008	0.8548	0.1438
2460	0.0005	0.0006	0.8511	0.1478
2520	0.0004	0.0005	0.8473	0.1518

K values of each individual reaction step are fitted the experimental data by using Nonlinear Regression Analysis by Marquardt method.

The example of list of the program for 1,5 cyclooctadiene in run 27 is shown in the following page.


```

TITLE 'TEST';
DATA TEST;
    INPUT X Y @@;
    CARDS;
O .8494 60 .7861 120 .5441 180 .4575 240 .3654 300 .2919
360 .2474 420 .2058 480 .1728 540 .1486 600 .1298 660 .1122
720 .0992 780 .0902 840 .0826 900 .0750 960 .0697
1020 .0637 1080 .0578 1140 .0543 1200 .0521 1260 .0482
1320 .0433 1380 .0414 1440 .0400
1500 .0358 1560 .0313 1620 .0307 1680 .0298 1740 .0271
1800 .0266 1860 .02416
;
PROC NLIN BEST=10 PLOT METHOD=MARQUARDT;
    PARS BO=0 TO .002;
    MODEL Y=.8333*EXP(-BO*X);
    DER.BO = .8333*(-X)*EXP(-BO*X);
    OUTPUT OUT=B P=YHAT R=YRESID;
PROC PLOT DATA=B;
    PLOT Y*X='A' YHAT*X='P' /OVERLAY VPOS=25;
    PLOT YRESID*X/VREF=0 VPOS=25;
RUN;
//

```

TEST

NON-LINEAR LEAST SQUARES ITERATIVE PHASE

DEPENDENT VARIABLE: Y METHOD: MARQUARDT

ITERATION	B0	RESIDUAL SS
0	0	15.641286809600
1	0.0007278599	3.076624933024
2	0.0015472323	0.593393510142
3	0.0023707363	0.098226287524
4	0.0029125011	0.031338414446
5	0.0030817281	0.027708020384
6	0.0031057135	0.027646072131
7	0.0031080523	0.027645496250
8	0.0031082664	0.027645491432
9	0.0031082859	0.027645491392

CONVERGENCE CRITERION MET.

TEST

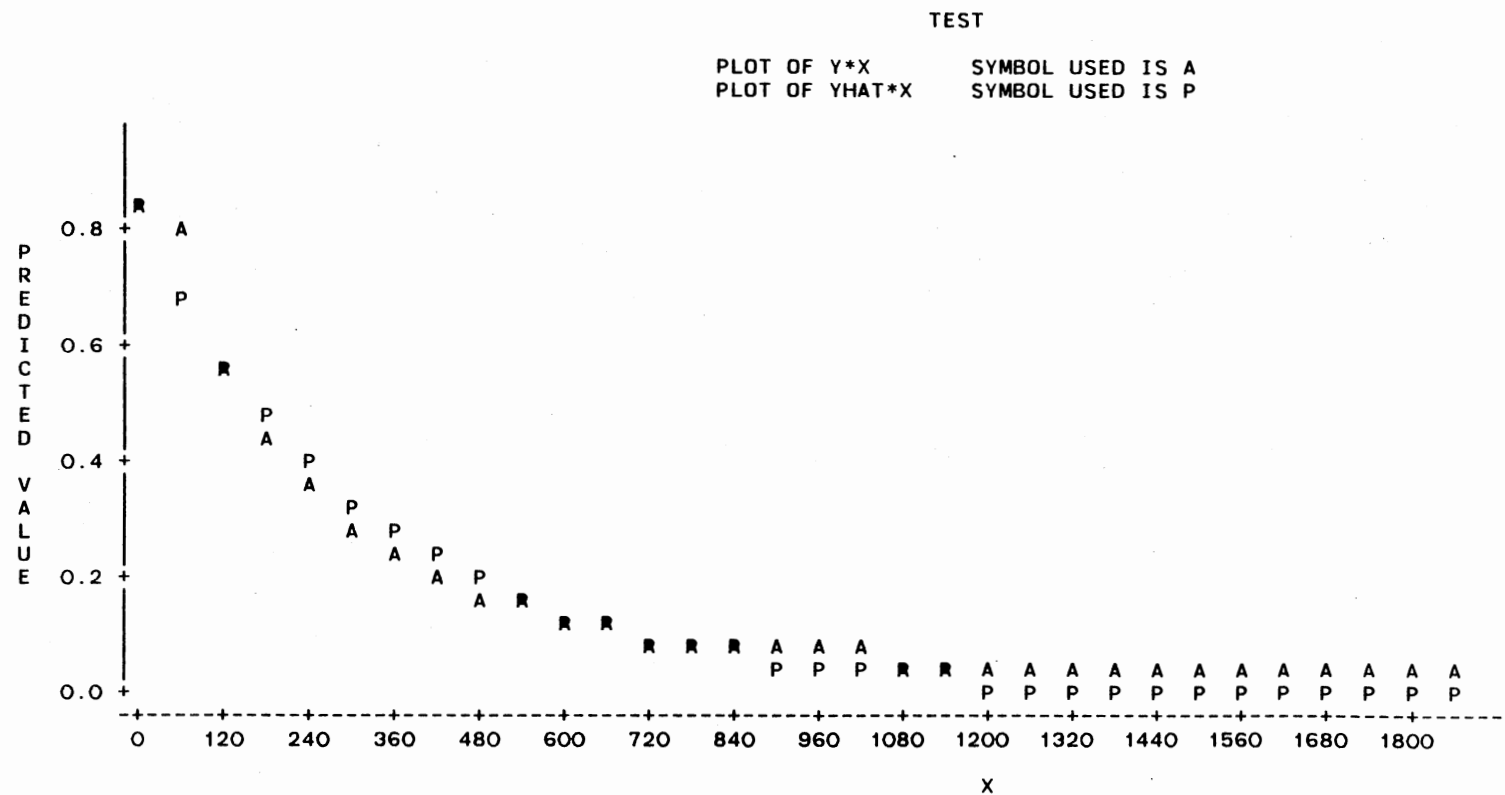
NON-LINEAR LEAST SQUARES SUMMARY STATISTICS DEPENDENT VARIABLE Y

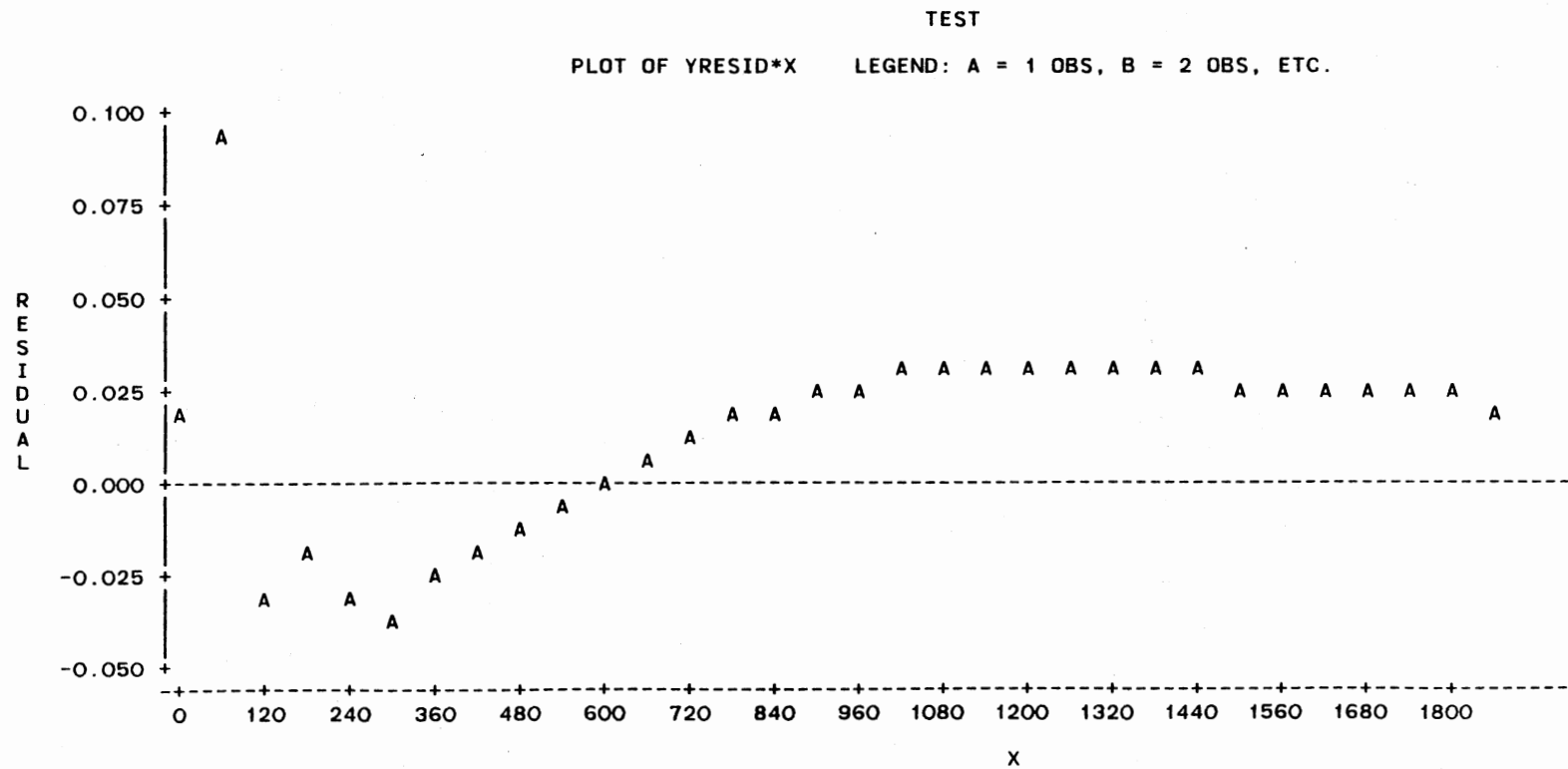
SOURCE	DF	SUM OF SQUARES	MEAN SQUARE
REGRESSION	1	2.2827745742	2.2827745742
RESIDUAL	31	0.0276454914	0.0008917900
UNCORRECTED TOTAL	32	2.3104200656	
(CORRECTED TOTAL)	31	1.4213222755	

PARAMETER	ESTIMATE	ASYMPTOTIC STD. ERROR	ASYMPTOTIC 95 % CONFIDENCE INTERVAL	
			LOWER	UPPER
B0	0.0031082859	.000096244071	0.00291199621	0.00330457563

ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS

CORR	B0
B0	1.0000





APPENDIX C

OTHER EXPERIMENTS IN THIS STUDY

OTHER EXPERIMENTS IN THIS STUDY

During this study, in addition to run 6, 7, 9, 10, 11, and 27, which are reported in Chapter III, a number of experiments were performed. The purposes and results of these experiments are presented briefly as follows:

Run 1 through 5 were made to select the appropriate conditions, such as suitable hydrogen pressure, an amount of catalyst, and stirring speed so that the course of the reaction could be followed in the convenient and accurate time frame. The results of these experiments showed that the reaction rate was independent of the stirring speed, especially in the range of 600 to 1000 rpm. The fact was also pointed out from a number of previous works with a similar catalyst by Dr. M. M. Johnson (personal communication).

In run 12 through 26, an effort was made to establish the reaction rate dependence on hydrogenation pressure. However, this attempt failed because the change of the hydrogen pressure measured in these runs could not be followed accurately, by using pressure gauge and equipment available in the laboratory.

Run 8 and 28 were duplicated to check the error in the experiments of run 6 and 7, respectively.

APPENDIX D
ERROR IN SAMPLE ANALYSIS

ERROR IN SAMPLE ANALYSIS

Liquid samples taken from a 300 ml Autoclave Engineer were used to determine the error in gas chromatographic analysis. Each sample was analyzed three times. In Table V through Table VII, the results are shown and reported as the weight percent of each compound in the reaction mixture. The error in the G. C. analysis varies from 0.1 to 3.8% depending on the concentration of the compound.

TABLE V
RESULTS OF GAS CHROMATOGRAPHIC ANALYSIS
FOR SAMPLE VI

	Weight Percent			
	1,5 COD	1,4 COD	COE	Cyclohexane
Injection 1	4.416	0.877	6.083	87.974
Injection 2	4.450	0.879	6.151	87.890
Injection 3	4.482	0.886	6.184	87.831
Average	4.449	0.881	6.139	87.898
Max. Error	0.033	0.005	0.056	0.076
Max. Error (%)	0.742	0.568	0.912	0.086

TABLE VI
RESULTS OF GAS CHROMATOGRAPHIC ANALYSIS
FOR SAMPLE XI

	Weight Percent			
	1,5 COD	1,4 COD	COE	Cyclohexane
Injection 1	1.752	0.442	8.878	88.262
Injection 2	1.783	0.443	8.921	88.112
Injection 3	1.791	0.447	9.047	88.072
Average	1.775	0.444	8.949	88.149
Max. Error	0.016	0.002	0.098	0.113
Max. Error (%)	0.901	0.450	1.095	0.128

TABLE VII
RESULTS OF GAS CHROMATOGRAPHIC ANALYSIS
FOR SAMPLE XVI

	Weight Percent				
	1,5 COD	1,4 COD	COE	COA	Cyclohexane
Injection 1	0.897	0.236	9.916	0.380	87.959
Injection 2	0.903	0.234	9.987	0.376	87.850
Injection 3	0.816	0.236	10.124	0.357	87.805
Average	0.905	0.235	10.009	0.371	87.871
Max. Error	0.019	0.016	0.002	0.098	0.113
Max. Error(%)	2.099	0.901	0.450	1.095	0.128

APPENDIX E

PRECISION OF SPECIFIC RATE CONSTANTS

PRECISION OF SPECIFIC RATE CONSTANTS

The rate constant of reaction individual step was calculated from data giving the state of the system at two different times.

The specific rate constant k_A , a first order reaction, will be given by (Benson, 1960).

$$k_A = \frac{1}{t_2 - t_1} \ln \frac{C_{A,1}}{C_{A,2}} \quad (E-1)$$

Assumed that the errors in measuring the four quantities $C_{A,1}$, $C_{A,2}$, t_1 , and t_2 are independent of each other; therefore, the error in the dependent k_A , can be calculated by

$$\begin{aligned} (\Delta k_A)^2 = & \left(\frac{\partial k_A}{\partial t_1} \right)^2 (\Delta t_1)^2 + \left(\frac{\partial k_A}{\partial t_2} \right)^2 (\Delta t_2)^2 + \left(\frac{\partial k_A}{\partial C_{A,1}} \right)^2 (\Delta C_{A,1})^2 \\ & + \left(\frac{\partial k_A}{\partial C_{A,2}} \right)^2 (\Delta C_{A,2})^2 \end{aligned} \quad (E-2)$$

Equation (E-2) can be rewritten in terms of relative errors $\Delta k_A/k_A$, $\Delta t_1/t_1$, etc. as follows:

$$\begin{aligned} \left(\frac{\Delta k_A}{k_A} \right)^2 = & \left(\frac{t_1}{k_A} \frac{\partial k_A}{\partial t_1} \right)^2 \left(\frac{\Delta t_1}{t_1} \right)^2 + \left(\frac{t_2}{k_A} \frac{\partial k_A}{\partial t_2} \right)^2 \left(\frac{\Delta t_2}{t_2} \right)^2 \\ & + \left(\frac{C_{A,1}}{k_A} \frac{\partial k_A}{\partial C_{A,1}} \right)^2 \left(\frac{\Delta C_{A,1}}{C_{A,1}} \right)^2 + \left(\frac{C_{A,2}}{k_A} \frac{\partial k_A}{\partial C_{A,2}} \right)^2 \left(\frac{\Delta C_{A,2}}{C_{A,2}} \right)^2 \end{aligned} \quad (E-3)$$

Equation (E-1) can be used to calculate the partial derivatives and then substituted into Equation (E-3), as follows:

$$\begin{aligned} \left(\frac{\Delta k_A}{k_A}\right)^2 &= \left(\frac{t_1}{t_2 - t_1}\right)^2 \left(\frac{\Delta t_1}{t_1}\right)^2 + \left(-\frac{t_2}{t_2 - t_1}\right)^2 \left(\frac{\Delta t_2}{t_2}\right)^2 \\ &+ \left(\frac{1}{\ln\left(\frac{C_{A,1}}{C_{A,2}}\right)}\right)^2 \left(\frac{\Delta C_{A,1}}{C_{A,1}}\right)^2 + \left(-\frac{1}{\ln\left(\frac{C_{A,1}}{C_{A,2}}\right)}\right)^2 \left(\frac{\Delta C_{A,2}}{C_{A,2}}\right)^2 \end{aligned} \quad (E-4)$$

In run 6, for example, $t_1 = 3600$ sec, $t_2 = 82800$ sec, $\Delta t_1 = \Delta t_2 = 1$ sec, $C_{A,1} = 1.0042$ mol/l, and $C_{A,2} = 0.025$ mol/l were selected to calculate the precision of specific rate constant, k' , of 1,5 COD. The relative error in measurement of 1,5 COD, $\Delta C_A/C_A$ is approximately 1.3% (from Appendix D.) On substituting these values in Equation (E-4) we find

$$\begin{aligned} \left(\frac{\Delta k_A}{k_A}\right) &= \pm (1.6 \times 10^{-10} + 1.459 \times 10^{-10} + 1.238 \times 10^{-5} + 1.238 \times 10^{-5})^{1/2} \\ &= \pm 0.00498 = \pm 0.498\% \end{aligned}$$

The error in specific rate constant is very small compared with the error in concentration measurement.

APPENDIX F

SULFUR MASS CONCENTRATION MEASUREMENT

SULFUR MASS CONCENTRATION MEASUREMENT

The concentration of sulfur compounds measured in this study was ppm, the mass of sulfur compounds in the solution mixture multiplied by a factor of 1,000,000; that is:

$$\text{ppm} = \frac{\text{mass of sulfur compound}}{\text{total mass of mixture}} (10^6)$$

as shown in the following example.

In run 6, 1.0 μl of thiophene, $\text{C}_4\text{H}_4\text{S}$, was added into the solution of 10.0 ml of 1,5 COD and 90.0 ml of cyclohexane.

The concentration of $\text{C}_4\text{H}_4\text{S}$ in ppm can be calculated as follows:

$$\text{Density of } \text{C}_4\text{H}_4\text{S} = 1.070$$

$$\text{Density of 1,5 COD} = 0.882$$

$$\text{Density of cyclohexane} = 0.779$$

therefore

$$\text{mass of 10.0 ml of 1,5 COD} = 0.882 \text{ gm/ml} \times 10 \text{ ml}$$

$$= 8.82 \text{ gm}$$

$$\text{mass of 90.0 ml of cyclohexane} = 0.779 \text{ gm/ml} \times 90 \text{ ml}$$

$$= 70.11 \text{ gm}$$

$$\text{mass of 1.0 } \mu\text{l of thiophene, } \text{C}_4\text{H}_4\text{S}, = 1.070 \text{ gm/ml} \times 1.0 \times 10^{-3} \text{ ml}$$

$$= 1.070 \times 10^{-3} \text{ gm}$$

The mass concentration of thiophene, $\text{C}_4\text{H}_4\text{S}$, in the solution, ppm,

$$\begin{aligned}
 &= \frac{\text{mass of thiophene, C}_4\text{H}_4\text{S}}{\text{mass of (thiophene, C}_4\text{H}_4\text{S, + 1,5 COD + cyclohexane)}} (10^6) \\
 &= \frac{1.070 \times 10^{-3} \text{ gm}}{(1.070 \times 10^{-3} + 8.82 + 70.11) \text{ gm}} \\
 &= 13.56 \text{ ppm}
 \end{aligned}$$

The other mass concentrations of sulfur compounds used in this study are shown in Table VIII.

TABLE VIII
AMOUNT AND MASS CONCENTRATION OF SULFUR COMPOUND

Sulfur compound	volume, μ l	mass concentration, ppm
Thiophene, C_4H_4S	1	13.6
	3	40.7
	6	81.3
Mercaptan, $C_{10}H_{21}SH$	1	10.7
	7.9	84.2

APPENDIX G

PROPRIETARY DATA OF HYDROGENATION OF BUTADIENE
IN C₄ STREAMS IN THE PRESENCE OF SULFUR

TABLE IX

Physical Properties of Pd Catalysts

Catalyst	Form	Composition	CBD, lb/ft ³	Surface Area, m ² /g	P.V., cm ³ /g (> 29 Å)	Pd Distribution
T2464	1/20" CDS	0.3% Pd balance Al ₂ O ₃	34.3	230	0.4 - 0.5	Increasing Penetration Depth
G68C	2.5 - 4mm spheres	0.3% Pd balance Al ₂ O ₃	46.8	110	0.5 - 0.6	↓
G68D	3/16" x 3/16" Tab.	0.5% Pd, 0.5% Cr balance Al ₂ O ₃	66.1	60	0.4 - 0.5	
G68A	3/16" x 1/8" Tab.	0.3% Pd balance Al ₂ O ₃	37.4	204	0.5 - 0.6	

TABLE X

**Hydrogenation Activity of Pd Catalysts for
Sulfur-free Feed**

LHSV, V/V/hr	33	Pressure, psig	190
T _{inlet} , °F	98	H ₂ /Butadiene (molar ratio)	2/1
Catalyst	Inlet BD (%)	Conversion (%)	
G68A	5.0	84.6	
G68D	5.0	93.1	
G68D	7.0	72.6	
G68C	5.0	99.6	
T2464	7.0	100.0	

TABLE XI

**Effect of 5 ppmw C₂H₅SH (2.6 ppmw S)
on Activity of G68C and T2464**

Catalyst	Sulfur Level	Inlet BD (%)	Conversion (%)
G68C	- 0 -	6.9	99.6
T2464	- 0 -	6.9	100.0
G68C	2.6 ppmw S	7.7	57.9
T2464	2.6 ppmw S	7.7	60.8

Note: H₂/BD had been lowered from 2/1 in Table IX to 1.5/1 to bring out differences in catalyst activity.

Comparison of Effects of CH_3SSCH_3 (DMS), $\text{C}_2\text{H}_5\text{SH}$,
and CH_3SCH_3 (DMS) on Hydrogenation Activity

Operation at more realistic process conditions and sulfur level.

Inlet temperature, °F	170
LHSV, V/V/hr	10
Pressure, psig	210
H_2 /BD	1.5/1
Inlet BD (mole %)	0.7 - 1.0
Inlet sulfur	20 ppmw sulfur

Figure 9. DMS

Figure 10. $\text{C}_2\text{H}_5\text{SH}$

Figure 11. DMS

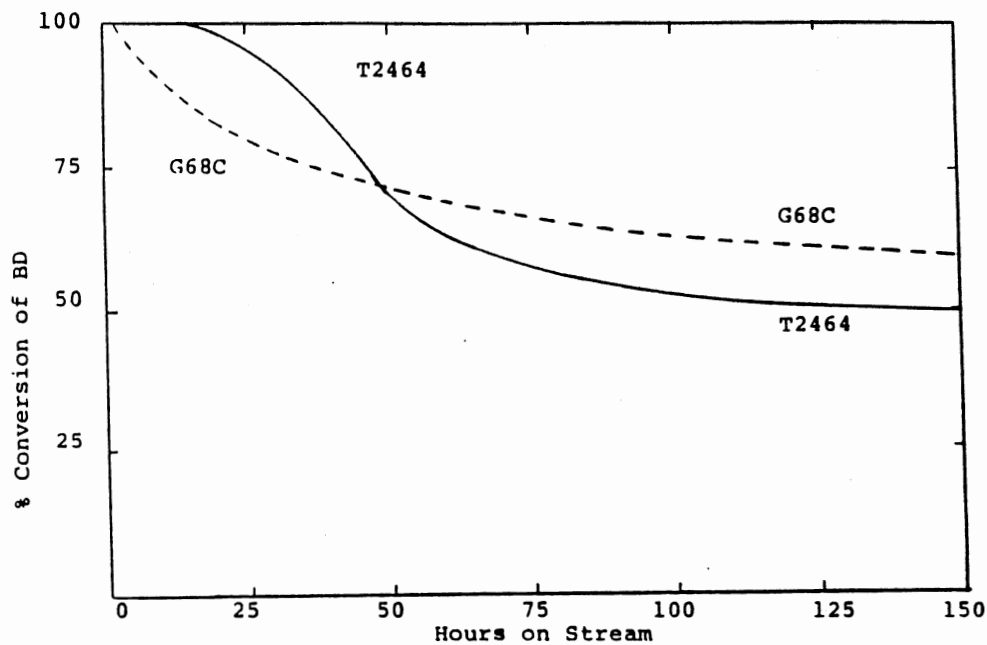


Figure 9. Life test for hydrogenation of BD in a C_4 stream containing 20 ppmw S as Dimethyl Disulfide.

Additional Test Conditions Suggested by Customers

TABLE XII

50 ppmw sulfur as C_2H_5SH

LHSV, V/V/hr	35	Pressure, psig	210
$T_{inlet}, ^\circ F$	160	H_2/BD (molar ratio)	2/1
Catalyst	Inlet BD (%)	Conversion (%)	Hours on Stream
G68C	0.66	4.1	6.0
T2464	0.66	7.0	6.0

Note that in addition to the large increase in temperature, a lower BD feedstock is being evaluated.

TABLE XIII

86 ppmw sulfur as Thiophene (C_4H_4S)

LHSV, V/V/hr	25	Pressure, psig	200
$T_{inlet}, ^\circ F$	154	H_2/BD (molar ratio)	3/1
Catalyst	Inlet BD (%)	Conversion (%)	
G68C	3.74	51.1	
G68D	3.74	65.0	

Unlike in Table X and XI, the catalysts of Table XII and XIII were still undergoing considerable deactivation. The conversions reported are only for a short period on stream.

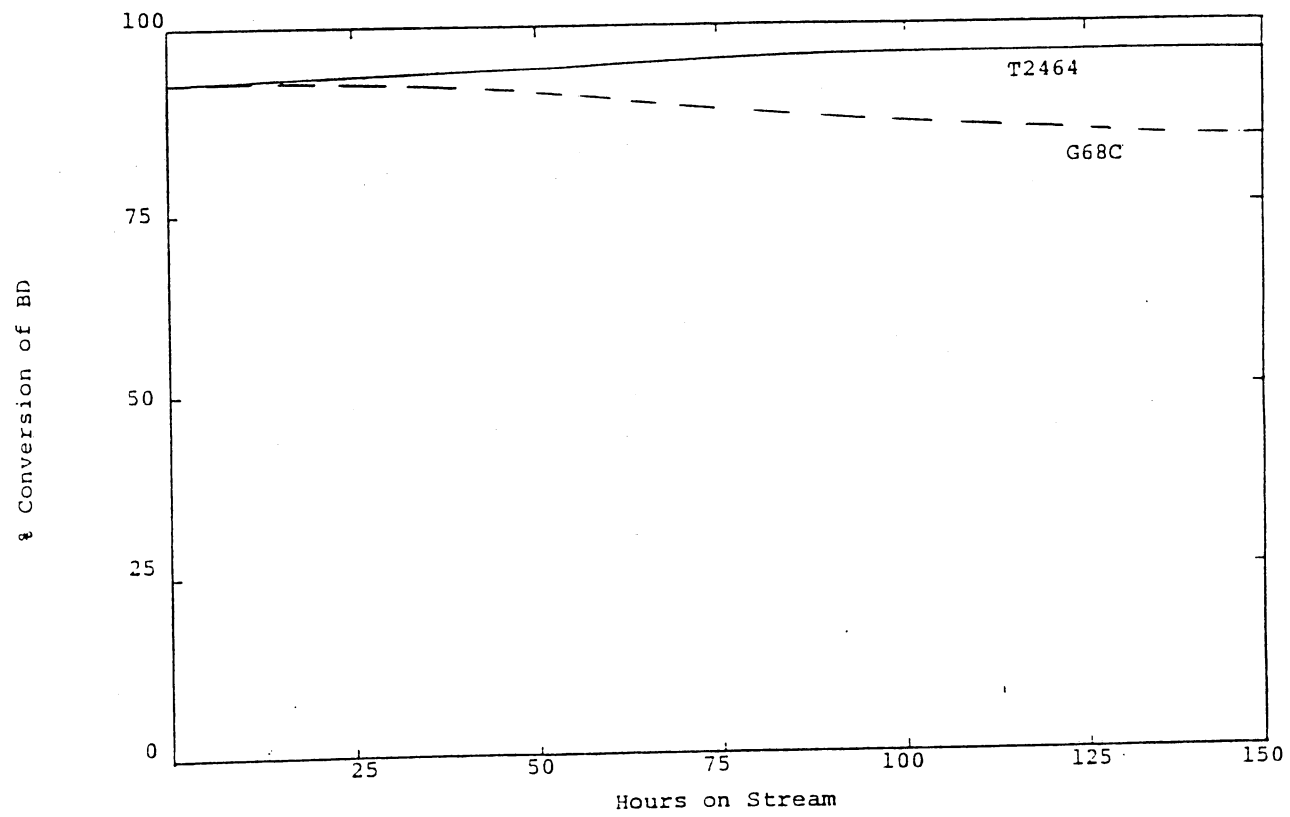


Figure 10. Life test for hydrogenation of BD in a C_4 stream containing 20 ppmw S as Ethyl Mercaptan.

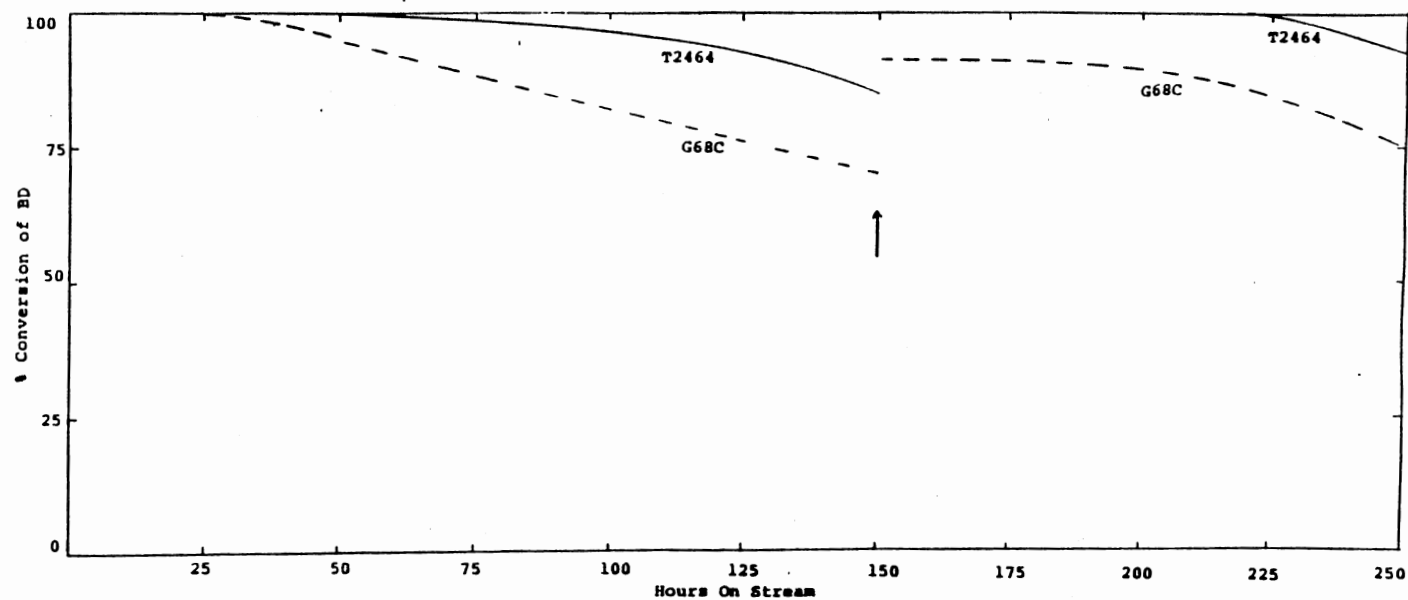


Figure 11. Life test for hydrogenation of BD in a C_4 stream containing 20 ppmw S as Dimethyl Sulfide. Test was interrupted at 150 HOS, and the reactor was locked in under the vapor pressure of liquid feed (25 psig) for 7 days. Note activity recovery.

Additional Approaches to Increasing Sulfur Resistance

1. One approach to increase the sulfur resistance of the Pd catalysts is to introduce "scavenger" metals. Pd catalysts prepared with Ni, Cu or W or various combinations thereof did not prove to extend the life of the catalyst.
2. The steady state activities observed in the tests for DMDS and C_2H_5SH could perhaps be improved by increasing the Pd content.
3. Preliminary studies indicate that higher P_{H_2} will improve activity substantially. The next set of studies will be carried out at 450 psig.

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VITA

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Master of Science

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